Binuclear Organometallic Compounds. Part VI.[1] Complexes containing Metal–Metal Bonds between Elements of Group IVA and Group IVB

By **B. M. Kingston** and **M. F. Lappert,*** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The isolation of stable complexes $(cp)_2M(Cl)M^1Ph_3$ (cp = π-C_5H_5; M = Zr or Hf; M^1 = Si or Ge) is described. Spectroscopic data and some M–Si cleavage reactions are reported. The complexes are of interest as d^0 complexes having metal–metal bonds and with the transition metal in a high (+4) oxidation state.

THIS paper describes compounds containing metal–metal bonds between elements of Group IVA and IVB, in which, clearly, π-contribution to such bonding is not possible. Preliminary accounts of this study have been published.[2] The crystal and molecular structure of one of these compounds, bis(π-cyclopentadienyl)chloro(triphenylsilyl)zirconium(IV) was described by Dr. K. W. Muir in Part IV.[3] While this work was in progress, communications dealing with similar topics have appeared.[4–6]

The chemistry of organometallic compounds having metal–metal bonds is a new field where progress has been rapid (see bibliography cited in Part I [7] and ref. 8). The interest derives *inter alia* from (*i*) a comparison with the corresponding σ-alkyl transition-metal complexes, (*ii*) the possibility of π-back-bonding from filled d_π-orbitals of the transition metal into empty *d*-orbitals of the Group IVB metal, and (iii) studies of hydrosilylation, a process of industrial importance. The compounds described here are significant because they are d^0 high-oxidation state (+4) complexes. Our synthetic procedure involved salt elimination according to equation (1) (M = Zr or Hf; M^1 = Si, Ge, or Sn; M^2 = Li or

$$(cp)_2MCl_2 + Ph_3M^1M^2 \longrightarrow (cp)_2M(Cl)M^1Ph_3 + M^2Cl \quad (1)$$

Na). Other attempted routes (see Experimental section) proved unsuccessful, as were attempts to prepare silylvanadium compounds.

Salt elimination according to equation (1) occurred readily at —50°, under an inert atmosphere, preferably argon (rather than nitrogen, *cf.* ref. 9), to give orange or yellow suspensions in tetrahydrofuran (THF). The latter was chosen as solvent since it is only slowly cleaved by the alkali-metal derivatives at ambient temperature.[10] At first, toluene–THF was used in order to precipitate the salts, but this was later found to be unnecessary. The metal–metal bonded complexes were difficult to purify since they are unstable in solution at room temperature (solutions slowly lighten in colour) and solubilities in organic solvents are low, being similar to those of the starting metallocene dichlorides $(cp)_2MCl_2$ (M = Zr or Hf) and of the compounds $Ph_6M^1_2$ (M^1 = Si, Ge, or Sn), the precursors of the Group IVB metal–alkali metal species. A similar difficulty was encountered in the synthesis of siloxytitanium compounds from $(cp)_2TiCl_2$ and the Ph_3SiO^- anion.[11] Attempts to replace both chloro-ligands of the Group IVA reactant did not give the expected bis-complex. This has also been observed in other [$(cp)_2MCl_2$–$OSiPh_3$ [11] and and $(cp)_2ZrCl_2$–EtMgBr [12]] systems.

---

[1] Part V, S. A. Keppie and M. F. Lappert, *J. Chem. Soc.* (*A*), 1971, 3216.

[2] D. J. Cardin, S. A. Keppie, B. M. Kingston, and M. F. Lappert, *Chem. Comm.*, 1967, 1035; B. M. Kingston and M. F. Lappert, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 371.

[3] Part IV, K. W. Muir, *J. Chem. Soc.* (*A*), 1971, 2663.

[4] R. S. P. Coutts and P. C. Wailes, *Chem. Comm.*, 1968, 260.

[5] E. Hengge and H. Zimmermann, *Angew. Chem. Internat. Edn.*, 1968, **7**, 142.

[6] H. M. J. C. Creemers, F. Verbeek, and J. G. Noltes, *J. Organometallic Chem.*, 1968, **15**, 125.

[7] D. J. Cardin, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc.* (*A*), 1970, 2594.

[8] E. H. Brooks and R. J. Cross, *Organometallic Chem. Rev.* (*A*), 1970, **6**, 227.

[9] M. E. Vol'pin, V. B. Shur, R. V. Kudryavtsev, and L. A. Prodayko, *Chem. Comm.*, 1968, 1038.

[10] D. Wittenberg and H. Gilman, *Quart. Rev.*, 1959, **13**, 116.

[11] J. S. Skelcey, Ph.D. Thesis, Michigan State University, 1961.

[12] H. Sinn and G. Oppermann, *Angew. Chem. Internat. Edn.*, 1966, **5**, 962.

For the preparation of the lithium derivatives Ph_3M^1-Li (M = Si or Ge), the use of high purity lithium (*i.e.* >98%) was avoided. A trace of the more electropositive sodium apparently assists the cleavage of the dimetal compound $Ph_6M^1_2$. Using $Ph_6M^1_2$ and 98% Li, reaction was immediate, and this procedure was preferred (*cf.* ref. 13) to that using Ph_3MCl as a source of Ph_3MLi.

Hengge and Zimmermann claim to have synthesised $Ti(SiPh_3)_4$ and $(cp)_2Ti(SiPh_3)_2$;[5] however, their data for $Ti(SiPh_3)_4$ correspond closely with those reported for the siloxy-analogue $Ti(OSiPh_3)_4$.[14]

TABLE 1

Complexes having metal–metal bonds between elements of Groups IVA (oxidation state, +4) and IVB

Compound	Colour	^{1}H n.m.r.[a] cp	Me	Ph[b]	M.p.	Reference
$(cp)_2Zr(Cl)SiPh_3$	Orange	3·71		2·56	180s[c]	This study
$(cp)_2Hf(Cl)SiPh_3$	Yellow	3·76		2·55	180s	This study
$(cp)_2Zr(Cl)GePh_3$	Orange	3·57		2·55	190s	This study
$(cp)_2Hf(Cl)GePh_3$	Yellow	3·64		2·55	200s	This study
$(cp)_2Zr(Cl)SnPh_3$	Orange	3·53		2·55		This study
$(cp)_2Hf(Cl)SnPh_3$	Yellow	3·48		2·55		This study
$(cp)_2Zr(Cl)SnMe_3$	White	3·62	9·63		105s	This study
$Ti(SiPh_3)_4$	Yellow				395—400d	5
$Ti(SnPh_3)_4$	Ochre				130	6
$Zr(SnPh_3)_4$	Yellow				70—73	6
$(cp)_2Ti(SiPh_3)_2$	Yellow				280s	5
$(cp)_2Ti(SnPh_3)_2$	Green	3·33		2·90	80d	4
$(cp)_2Ti(Cl)GePh_3$	Green	3·85		2·70	193—196d	4
$(cp)_2Ti(Cl)SnPh_3$	Green	3·75		2·68	177—180d	4
$(MeO)_2Ti(SnPh_3)_2$	Yellow				260	6

[a] τ-Values obtained in THF (this study) or $CDCl_3$ (ref. 4) solutions. [b] Approximate centre of a multiplet. [c] In °C, the symbol 's' denotes sublimation temperature at *ca.* 10^{-3} mmHg, d = decomposition.

The new d^0 complexes and appropriate data are shown in Table 1 together with results of others.[4-6] It will be noticed that these compounds have appreciable thermal stability. Earlier it had been suggested that the stability of transition metal–Group IVB metal compounds decreases from right to left in a transition series and with increasing oxidation state of the transition metal.[15] Prior to our preliminary report[2] of the complex $(cp)_2Zr(Cl)SiPh_3$, a d^0 Zr^{IV} system, no compounds containing metal–metal bonds between elements of Group IVA and Group IVB were known (apart from dubious patent claims).[16] Of the silicon–transition metal derivatives, only one, $(cp)(CO)_3MoSiCl_3$,[17] had previously been obtained from the early d^0–d^4 transition elements and none in an oxidation state as high as (+4). The complexes $(cp)_2Zr(Cl)MPh_3$ (M = Ge or Sn) were independently synthesised by Coutts and Wailes.[4]

The compounds $(cp)_2M(Cl)M^1Ph_3$ (M = Zr or Hf; M^1 = Si or Ge) were characterised by analyses, identification of parent ions in the mass spectra, other spectroscopic data, some M–M^1 cleavage reactions, and, for M = Zr and M^1 = Si, by an *X*-ray single-crystal analysis.[3]

The mass spectra are simple and similar to each other; prominent ions are shown in Table 2. Parent ions are of low abundance, and the only other ions containing M–M^1 bonds are $(cp)_2MM^{1+}$, also of low intensity; by contrast the spectra of the complexes $(cp)M(CO)_3M^1Me_3$ (M = Cr, Mo, W; M^1 = Si, Ge, or Sn) show that a high proportion of the ion current is carried by ions containing metal–metal bonds.[18] The ion Ph_3M^{1+} is invariably the base peak, and the presence of the odd-electron ion $PhM^{1+\cdot}$ in appreciable intensity is an unusual feature. Migration of C_5H_5 from the transition metal to the Main Group metal to give the rearrangement ion $(cp)M^{1+\cdot}$ is a feature also of other compounds having metal–metal bonds.[18,19]

TABLE 2

Abundance of major fragments * in the mass spectra of $(cp)_2M(Cl)M^1Ph_3$

Ion	M–M^1 Zr–Si	Zr–Ge	Hf–Si	Hf–Ge
$(cp)_2ClM{-}M^1Ph_3{}^{+\cdot}$	4	2	3	3
$(cp)_2M{-}M^{1+}$		1	1	1
$cp_2M^{+\cdot}$	10	6	1	1
cpM^+	2	2		
cp_2ClM^+	6	7	7	13
$cpClM^{+\cdot}$	2	5		
Ph_3M^{1+}	57	57	58	51
$Ph_2M^{1+\cdot}$	11	9	17	18
PhM^{1+}	7	9	1	12
$(cp)M^{1+}$	1	2	2	1

* Relative ion abundances are given as percentage of the total yield of ions.

The ^{1}H n.m.r. spectra of the compounds $(cp)_2M(Cl)$-M^1Ph_3 (M = Zr or Hf; M^1 = Si or Ge) all show a single

---

[13] H. Gilman, D. J. Peterson, and D. Wittenberg, *Chem. and Ind.*, 1958, 1479; M. V. George, D. J. Peterson, and H. Gilman, *J. Amer. Chem. Soc.*, 1960, **82**, 403.

[14] F. Schindler and H. Schmidbaur, *Angew. Chem. Internat. Edn.*, 1967, **6**, 683, and references therein.

[15] H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 1401.

[16] U.S.P. 4,069,445/1962.

[17] W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1969, **89**, 2773.

[18] Part III, D. J. Cardin, S. A. Keppie, M. F. Lappert, M. R. Litzow, and T. R. Spalding, *J. Chem. Soc.* (*A*), 1971, 2262.

[19] *Cf.* D. B. Chambers, F. Glockling, and J. R. C. Light, *Quart. Rev.*, 1968, **22**, 317.

sharp peak *ca.* τ 3·5 assigned to the cyclopentadienyl protons (indicating an equivalence of both groups of ring protons), and a multiplet centred *ca.* τ 2·5 assigned to the Ph group protons. The chemical shifts associated with the protons of the (cp) ligand follow a distinct pattern Si > Ge > Sn which is the reverse of that expected on electronegativity grounds; a similar situation has been noted in the parent metallocene dihalide series.[20]

Far-i.r. spectra were recorded with a view to locating $\nu(M-M^1)$ but this proved impracticable owing to interference from absorptions due to the aromatic rings in the region of interest (250—350 cm^{-1}); this was confirmed by recording the spectra of $Ph_6M^1_2$.

The crystal and molecular structure of $(cp)_2Zr(Cl)SiPh_3$ were discussed in Part IV;[3] the molecule is essentially tetrahedral around Zr, and the feature of interest is the exceptionally long Zr–Si distance [>0·3 Å longer than in any other silicon–transition metal (Mn^{II}, Fe^{IV}, Co^{I}, Rh^{III}, or Pt^{II}) compounds]. A paper has recently appeared[21] which permits the following comparisons (Table 3) to be made of M–C and M–Si bond lengths; ideally the C and Si compounds of each pair should be exactly matched, but such data are not at present available. It is clear that the difference, Δ, of M–Si and M–C bond lengths is far greater for the d^0 (Zr^{IV}) complexes than the d^6 (Rh^{III}) or d^8 (Pt^{II}), and for d^0 approximates to the difference in covalent radii (C, 0·77; Si, 1·17 Å). It is reasonable to infer that (*i*) the M–Si bond is weak in d^0 complexes (as is consistent with the mass spectral data), and (*ii*) that in the d^6 and d^8 complexes metal–silicon π-bonding is likely.

TABLE 3

Some M–Si and M–C bond distances (Å)

Bond	M =	Zr^{IV}	Rh^{III}	Pt^{II}
M–Si		2·81 [a]	2·20 [b]	2·29 [c]
M–C		2·27 [d]	2·08 [e]	2·08 [f]
Δ		0·54	0·12	0·21

[a] In $cp_2Zr(Cl)SiPh_3$, K. W. Muir, *J. Chem. Soc.* (*A*), 1971, 2663. [b] In $[Cl_3SiRh(H)(Cl)(PPh_3)_2]$, K. W. Muir and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 440. [c] In *trans*-$[Ph_2MeSiPt(Cl)(PMe_2Ph)_2]$, P. M. Harrison and R. Mason, unpublished results; P. M. Harrison, Ph.D. Thesis, University of Sheffield, 1968. [d] In $Zr(CH_2Ph)_4$, G. R. Davies, J. A. Jarvis, B. T. Kilbourn, and A. J. P. Pioli, *Chem. Comm.*, 1971, 677. [e] In $[MeRhI_2(PPh_3)_2]$, P. G. H. Troughton and A. C. Skapski, *Chem. Comm.*, 1968, 575. [f] In *trans*-$[Me_3SiCH_2Pt(Cl)(PMe_2Ph)_2]$, B. Jovanović, Lj. Manojlović-Muir, and K. W. Muir, unpublished results.

Two cleavage reactions were demonstrated. Reaction with hydrogen chloride [equation (2)] was straightforward, but with hydrogen bromide [equation (3)] was somewhat more complex.

$$(cp)_2Zr(Cl)SiPh_3 + HCl \longrightarrow (cp)_2ZrCl_2 + Ph_3SiH \quad (2)$$

$$(cp)_2Hf(Cl)SiPh_3 + HBr \longrightarrow (cp)_2Hf(Br)Cl + (cp)_2HfBr_2 + Ph_3SiH \quad (3)$$

The mixed halogeno-compound $(cp)_2Hf(Br)Cl$ is known to redistribute to give an essentially statistical distribution of the three species $(cp)_2HfCl_2$, $(cp)_2HfBr_2$, and $(cp)_2Hf(Br)Cl$ at equilibrium.[20] The fact that the bischloro-complex was not observed in our cleavage experiment must be due to hydrogen bromide (here in excess) acting as a brominating agent by an exchange mechanism. The Zr–Si bond was also quantitatively cleaved by $CDCl_3$ within 24 h to yield $(cp)_2ZrCl_2$ as shown by ^1H n.m.r.

An attempt to synthesise $Hg(Cl)SiPh_3$ by the reaction of $(cp)_2Zr(Cl)SiPh_3$ with $HgCl_2$ proved unsuccessful; $(cp)_2ZrCl_2$, Ph_3SiCl, and Hg were isolated. $Hg(SiPh_3)_2$ has been prepared as a very light-sensitive solid unstable in THF.[22]

EXPERIMENTAL

Rigorous precautions were taken to exclude moisture and air in experiments aimed at isolating complexes containing metal–metal bonds and manipulations were carried out in an argon atmosphere. Solvents were dried by conventional techniques and THF, the solvent most commonly used, was stored permanently under an argon atmosphere and was distilled from the potassium benzophenone ketyl complex immediately prior to use.

^1H N.m.r. spectra were recorded on a Varian A60 spectrometer. Mass spectra were obtained on an A.E.I. MS9 instrument by Dr. T. R. Spalding. Low frequency i.r. data (40—400 cm^{-1}) were obtained using an R.I.I.C. FS620 Michelson interferometer.

Alkali-metal derivatives of Group IVB elements and their precursors were synthesised by reported procedures,[23] as were Me_6Sn_2,[24] Me_3SnBr,[24] Ph_3SiH,[25] Me_3SiF,[26] $(cp)_2HfCl_2$,[20] and $(cp)_2ZrF_2$.[20] Other compounds used in this study were either purchased [$GeCl_4$, SnX_4 (X = Cl, Br), $HfCl_4$, $(cp)_2MCl_2$ (M = Ti, Zr, or V), Li] or supplied by colleagues [Me_6Si_2, $Zr(NMe_2)_4$, $(cp)_2Zr(NMe_2)_2$, and $(C_6F_5)_2PhSiH$].

All of the complexes were unstable in solution and were purified by sublimation. However, extensive decomposition occurred near the sublimation temperatures, and the process was extremely slow. It was, therefore, impracticable to purify the products in large quantities. Yields are estimated from ^1H n.m.r. spectra of the crude products and are based on consumption of the Group IVA metallocene dichloride. Other data, including elemental analyses, were collected on sublimed samples. Attempts to measure molecular weights isopiestically in benzene were unsuccessful.

---

[20] P. M. Druce, B. M. Kingston, M. F. Lappert, T. R. Spalding, and R. C. Srivastava, *J. Chem. Soc.* (*A*), 1969, 2106.

[21] G. R. Davies, J. A. Jarvis, B. T. Kilbourn, and A. J. P. Pioli, *Chem. Comm.*, 1971, 677.

[22] R. A. Jackson, *Chem. Comm.*, 1966, 827.

[23] H. Gilman and G. D. Lichtenwalter, *J. Amer. Chem. Soc.*, 1958, **80**, 608; C. Tamborski, F. L. Ford, W. L. Lehn, G. J. Moore, and E. J. Soloski, *J. Org. Chem.*, 1962, **27**, 619; W. L. Wells and T. L. Brown, *J. Organometallic Chem.*, 1968, **11**, 271; D. Blake, G. E. Coates, and J. M. Tate, *J. Chem. Soc.*, 1961, 618.

[24] H. C. Clark and C. J. Willis, *J. Amer. Chem. Soc.*, 1960, **82**, 1888.

[25] H. Gilman and H. W. Melvin, *J. Amer. Chem. Soc.*, 1949, **71**, 4050.

[26] M. G. Voronkov, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 1957, 517.

Preparation of Chlorobis(π-cyclopentadienyl)(triphenylsilyl)zirconium(IV).—A solution of triphenylsilyl-lithium [from hexaphenyldisilane (6·4 g, 1·0 mol) and lithium (0·6 g, 7·0 g atom)] in THF (100 ml) was added dropwise (2 h) to a stirred suspension of dichlorobis(π-cyclopentadienyl)zirconium(IV) (7·0 g, 1·9 mol) in THF (100 ml) at −50°. After further stirring (1 h), THF was removed *in vacuo* to leave an orange solid, which was stirred with light petroleum (b.p. 40—60°; 50 ml) and then filtered. The orange residue (90%) was dried *in vacuo* and then sublimed to give orange, amorphous *chlorobis(π-cyclopentadienyl)(triphenylsilyl)zirconium*(IV) (Found: C, 63·4; H, 4·9; Cl, 7·3; Si, 5·1. $C_{28}H_{25}ClSiZr$ requires C, 65·1; H, 5·4; Cl, 6·9; Si, 5·4%).

Preparation of Chlorobis(π-cyclopentadienyl)(triphenylgermyl)zirconium(IV).—The above procedure was applied with only slight modifications. Triphenylgermyl-lithium [from hexaphenyldigermane (2·0 g, 1·0 mol) and lithium (0·3 g, 13·2 g-atom)] in THF (30 ml) was added to dichlorobis(π-cyclopentadienyl)zirconium(IV) (1·8 g, 1·9 mol) in THF (10 ml) at −20°. After removal of solvent, trituration with light petroleum, and filtration, the residual orange solid (74%) was sublimed to afford *chlorobis(π-cyclopentadienyl)(triphenylgermyl)zirconium*(IV) (Found: C, 59·1; H, 4·5. $C_{28}H_{25}ClGeZr$ requires C, 59·9; H, 4·5%).

Reaction of Dichlorobis(π-cyclopentadienyl)zirconium(IV) *with Triphenylstannylsodium*.— Triphenylstannylsodium [from bromotriphenylstannane (2·9 g, 1·0 mol), sodium (0·3 g, 2·0 g-atom) and naphthalene (1·7 g, 2·0 mol)] in 1,2-dimethoxyethane (50 ml) and dichlorobis(π-cyclopentadienyl)zirconium(IV) (1·9 g, 1·0 mol) were stirred (1·5 h) at −78°. The mixture was warmed to 25° and the solvent was removed from the deep orange solution. The usual work-up procedure gave a pale-orange powder (31%), the ^1H n.m.r. spectrum of which was consistent with the formula $(cp)_2Zr(Cl)SnPh_3$. Attempted sublimation below 220° (10^{-3} mmHg) led to extensive decomposition.

Similarly, the reaction of triphenylstannylsodium (1·0 mol) with dichlorobis(π-cyclopentadienyl)hafnium(IV) (1·0 mol) gave a pale-yellow solid (50%) which could not be further purified.

Preparation of Chlorobis(π-cyclopentadienyl)(triphenylsilyl)hafnium(IV).—As in the zirconium experiment, triphenylsilyl-lithium [from hexaphenyldisilane (1·7 g, 1·0 mol) and lithium (0·2 g, 8·8 g-atom)] in THF (35 ml) was added dropwise (1·5 h) to a stirred THF solution (10 ml) of dichlorobis(π-cyclopentadienyl)hafnium(IV) (2·5 g, 2·0 mol) at −40°. The mixture was further stirred (1·5 h) as it warmed to 25° and the solvent was then removed *in vacuo*. The yellow solid compound (83%) was sublimed to yield bright-yellow *chlorobis(π-cyclopentadienyl)(triphenylsilyl)hafnium*(IV) (Found: C, 55·7; H, 4·0; Cl, 6·1; Si, 4·7. $C_{28}H_{25}ClHfSi$ requires C, 55·7; H, 4·2; Cl, 5·9; Si, 4·7%).

Preparation of Chlorobis(π-cyclopentadienyl)(triphenylgermyl)hafnium(IV).—Similarly, the reaction of triphenylgermyl-lithium [from hexaphenyldigermane (2·0 g, 1·0 mol) and lithium (0·2 g, 8·8 g-atom)] with dichlorobis(π-cyclopentadienyl)hafnium(IV) (2·5 g, 2·0 mol) in THF (40 ml) afforded a yellow powder (66%) which gave on sublimation bright-yellow *chlorobis(π-cyclopentadienyl)(triphenylgermyl)hafnium*(IV) (Found: C, 52·1; H, 3·9. $C_{28}H_{25}ClGeHf$ requires C, 51·9; H, 3·9%).

Preparation of Chlorobis(π-cyclopentadienyl)(trimethylstannyl)zirconium(IV).—A solution of trimethylstannyl-lithium [from chlorotrimethylstannane (3·8 g, 1·0 mol) and lithium (1·5 g, 11·4 g-atom)] in THF was prepared and analysed. An aliquot (20 ml, 1·0 mol) was added dropwise (2 h) to a stirred solution of dichlorobis(π-cyclopentadienyl)-zirconium(IV) (2·9 g, 1·0 mol) in THF (20 ml) below −20°. The solvent was removed *in vacuo* and the brown residue was pumped dry. Sublimation afforded a white crystalline compound, the spectra [^1H n.m.r. (τ values in THF: 3·62, 9·63), i.r., and mass] of which indicated the formation of chlorobis(π-cyclopentadienyl)(trimethylstannyl)zirconium(IV) (1·7 g, 41·0%), which was not, however, separable from an impurity by either resublimation or recrystallisation.

Some Unsuccessful Syntheses.—A mixture of triphenylsilane (10·4 g, 4·0 mol) and tetrakis(dimethylamido)-zirconium(IV) (2·7 g, 1·0 mol) in light petroleum (b.p. 40—60°, 75 ml) was heated under reflux (14 h). Volatile material was trapped (−78°) and transferred to an excess of standard acid. Back titration showed that no dimethylamine had been evolved.

Triphenylsilane (1·5 g, 1·8 mol) and bis(π-cyclopentadienyl)bis(dimethylamido)zirconium(IV) (1·0 g, 1·0 mol) were heated initially at 60° (10 h) and finally at 125° (3 days). The silane was not consumed, but the amido-reactant slowly decomposed with the evolution of base (equivalent to 54·5 ml of 0·05M H_2SO_4). Similarly (75°, 3 days; 100°, 1 day), using bis(pentafluorophenyl)phenylsilane (2·0 mol) and bis(π-cyclopentadienyl)bis(dimethylamido)zirconium(IV) (1·0 mol) gave the same result.

A mixture of triphenylsilane (1·7 g, 1·0 mol), dichlorobis(π-cyclopentadienyl)zirconium(IV) (2·0 g, 1·0 mol), and triethylamine (0·7 g, 1·0 ml, 1·0 mol) was stirred (14 h) in refluxing benzene (25 ml). After cooling, the solvent was decanted from well-formed crystals of the zirconocene dichloride (1·7 g, 85·0%). Solvent removal *in vacuo* gave a viscous oil (1·9 g) which was crystallised from methanol. The white crystals so obtained were shown (m.p. and i.r.) to be unchanged triphenylsilane (1·4 g, 82·3%).

Fluorotrimethylsilane (0·8 g, 1·9 mol) and hexamethyldistannane (1·6 g, 1·0 mol) were mixed in diethyl ether (15 ml) under nitrogen, and the solution was heated under reflux (16 h). Volatile material was removed to leave a colourless liquid identified (g.l.c. and i.r.) as hexamethyldistannane (1·6 g, 100%).

A dark green, air-sensitive powder resulted from stirring triphenylsilyl-lithium (1 mol) and dichlorobis(π-cyclopentadienyl) vanadium(IV) (1 mol) in THF at 78°. Attempted sublimation (140°, 10^{-3} mmHg) caused immediate decomposition. The ^1H n.m.r. spectrum of the crude product was very broad and the e.s.r. spectrum, though inconclusive, indicated the presence of a d^1 system different from the starting dichloride.

A reverse salt elimination experiment, using sodium hexacarbonylvanadate(-1) and chloromethyldiphenylsilane also gave no characterised product.

Dichlorobis(π-cyclopentadienyl)titanium(IV) (2·5 g, 1·0 mol) and hexamethyldisilane (1·5 g, 1·0 mol) were stirred (18 h) in refluxing benzene (75 ml). No chlorotrimethylsilane was evolved. Removal of the volatile material *in vacuo* afforded crimson titanocene dichloride (2·3 g, 92·0%).

A quartz tube (100 × 7 mm) was evacuated and filled with difluorobis(π-cyclopentadienyl)zirconium(IV) (0·33 g, 1·0 mol) and hexamethyldistannane (0·85 g, 2·0 mol). The tube was suspended in cyclohexane vapour (b.p.

81·4°) during 10 h while illuminated by a u.v. lamp (Hanovia 500 W medium pressure mercury arc). The solid gradually darkened as a tin mirror formed, but much liquid still remained. The tube was opened under argon and volatile material removed *in vacuo* to a trap (−78°). The trap contents (0·84 g, 98·8%) were shown (g.l.c. and i.r.) to be pure hexamethyldistannane. Preliminary experiments involving the same reactants in (*a*) refluxing benzene (3 days) and (*b*) refluxing chloroform (3 days) also showed no reaction, the starting materials being recovered in practically quantitative yields.

Reaction of Chlorobis(π-cyclopentadienyl)(triphenylsilyl)-zirconium(IV) *with Hydrogen Chloride.*—Anhydrous hydrogen chloride (in excess) was bubbled through a suspension of the zirconium compound (0·80 g) in benzene (25 ml) at 25°. The orange colour faded during stirring (24 h). The solution was filtered, and the solvent removed from the filtrate *in vacuo* to leave a white crystalline product in an oily matrix. This residue was washed with benzene (5 ml) to remove the oil, and the benzene solution was filtered. The white crystalline residue (0·32 g) was shown (i.r.) to be dichlorobis(π-cyclopentadienyl)zirconium(IV), while the filtrate afforded triphenylsilane (0·43 g) (authentic spectra).

A similar experiment using the silylhafnium complex (1·0 g) and hydrogen bromide was carried out in a high vacuum system. It yielded, besides triphenylsilane, two $(cp)_2HfX_2$ derivatives, which were shown (i.r., ^1H n.m.r., and elemental analyses) to be dibromobis(π-cyclopentadienyl)hafnium(IV) and bromochlorobis(π-cyclopentadienyl)-hafnium(IV), in high yield.

Reaction of Chlorobis(π-cyclopentadienyl)triphenylsilyl-zirconium(IV) *with Mercury*(II) *Chloride.*—A solution of freshly sublimed mercury(II) chloride (0·7 g, 1·1 mol); in THF (5 ml) was added dropwise (1 h) to a stirred suspension of chlorobis(π-cyclopentadienyl)triphenylsilyl-zirconium(IV) (1·2 g, 1·0 mol) in THF (5 ml) at 25°. The solution darkened and mercury was deposited together with a cream solid. Replacement of THF by light petroleum (b.p. 40—60°) followed by filtration and evaporation yielded a white solid (0·5 g, 82·6%), identified (i.r.) as chlorotriphenylsilane. The hydrocarbon-insoluble material gave, on work up, dichlorobis(π-cyclopentadienyl)zirconium(IV) (0·6 g, 88·2%) and mercury.

We thank the S.R.C. and Midland Silicones Ltd., for financial support and the latter also for chlorosilanes, and Drs. K. W. Muir and T. R. Spalding for helpful discussions.

[1/1464 *Received, August* 16*th*, 1971]