Metal–metal Bonds between Elements of Groups IVA and IVB

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A RECENT report[1] of the isolation of an organosilyl derivative of zirconium has prompted us to report the preparation of several compounds containing bonds between Ti^{III}, Ti^{IV}, or Zr^{IV} and Sn^{IV} or Ge^{IV}.

The transition-metal derivative, cp_2TiCl, cp_2TiCl_2, or cp_2ZrCl_2 ($cp = \pi\text{-}C_5H_5$) in tetrahydrofuran (THF) solution was mixed with a stoicheiometric amount of $NaSnPh_3$ or $LiGePh_3$ in the same solvent under argon at acetone–dry ice temperature, and the mixture was then allowed to warm to room temperature. After removal of inorganic salts the products shown in the Table were isolated. All were handled in an inert atmosphere although the derivatives of Ti^{IV} and Zr^{IV} are probably sensitive only to moisture. Compounds were characterized by determination of total ash, and the ratio of integrated ^1H n.m.r. peaks.

The Ti^{III} derivatives were isolated as solvates, the fourth co-ordination position on the titanium being occupied by THF, the presence of which was shown by a band in the i.r. spectrum (KBr disc) at 1040 cm.$^{-1}$. The variation with temperature of the magnetic susceptibilities of the Ti^{III} compounds shows no evidence of spin–spin interaction; a Curie–Weiss law is followed, there being one unpaired electron per Ti atom.

Surprisingly the Ti^{IV} derivatives are green in colour, but their diamagnetism, satisfactory chlorine analyses, and the positions of their CH bending (⊥) bands in the i.r. spectrum (*ca.* 825 cm.$^{-1}$) are good confirmation of the presence of Ti^{IV}. Several attempted preparations of $cp_2Ti\cdot(GePh_3)_2$ gave only a burgundy-coloured product, the nature of which has yet to be established. The lead derivative $cp_2ClTi\cdot PbPh_3$ could be formed as a bright green solution in tetrahydrofuran at low temperatures, but deposition of lead occurred rapidly at room temperature.

Two Zr^{IV} compounds have been prepared similarly and have been isolated as pale yellow

TABLE

Characterization of metal–metal bonded compounds

(M = Ti or Zr, M′ = Sn or Ge)

Compound	Colour	M.p.	^{1}H n.m.r. (δ values in $CDCl_3$)
	M^{III}–M′ *Derivatives*		
$cp_2Ti{\cdot}SnPh_3$, THF	Emerald-green	80°[a]	b
$cp_2Ti{\cdot}GePh_3$, THF	Emerald-green	110°[a]	b
	M^{IV}–M′ *Derivatives*		
$cp_2ClTi{\cdot}SnPh_3$	Dark green	177—180°[a]	7·32,[c] 6·25
$cp_2ClTi{\cdot}GePh_3$	Dark green	193—196°[a]	7·30,[c] 6·15
	M′–M^{IV}–M′ *Derivatives*		
$cp_2Ti(SnPh_3)_2$	Green	80°[a]	7·10,[c] 6·77

[a] Decomposition.

[b] Paramagnetic, with one unpaired electron per Ti atom. In $CDCl_3$ solution these compounds abstract Cl· and show the spectrum of $cp_2ClTi{\cdot}M'Ph_3$.

[c] Ph protons; this peak is a singlet in pure compounds.

solids, but they have not yet been obtained completely pure. Their ^{1}H n.m.r. spectra in $CDCl_3$ are consistent with their formulation as $cp_2ClZr{\cdot}SnPh_3$ (δ 7·32, 6·32) and $cp_2ClZr{\cdot}GePh_3$ (δ 7·40, 6·15).

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[1] D. J. Cardin, S. A. Keppie, B. M. Kingston, and M. F. Lappert, *Chem. Comm.*, 1967, 1035.