Metal-Metal Bond Formation: Trimethylsilyl- and Trimethylgermyl-platinum(II) Complexes

By F. GLOCKLING and K. A. HOOTON (Department of Chemistry, The University, Durham)

The methods available for establishing metalmetal bonds between organo-derivatives of the Group IV elements and transition metals of Groups VIII and I are restricted to reactions illustrated by,1,2

cis- or
$$trans$$
-(Et₃P)₂PtCl₂ + 2Ph₃GeLi \rightarrow
cis- and $trans$ -(Et₃P)₂Pt(GePh₃)₂.

More versatile procedures are available for those transition metals which form reactive alkali-metal derivatives [such as Mn(CO)₅Na³ and C₅H₅Fe (CO), Na4] or reactive hydrides.5

For comparative reactivity and spectroscopic studies we required a method of forming Me₃M-Pt and Me_3M-Au bonds (M = Si, Ge) where the alkali-metal derivatives, Me₃MLi or Me₃MK are, as yet, unknown. We find that bistrimethylsilylmercury^{6,7} and bistrimethylgermylmercury are convenient sources of Me₃Si- and Me₃Ge-groups for the preparation of trimethylsilyl and trimethylgermyl complexes of platinum(II). Equimolar ratios of cis-bistriethylphosphineplatinum(II) chloride and (Me₃Si)₂Hg give an almost quantitative yield of the complex (I).

The use of 2 mols of bistrimethylsilylmercury failed to substitute both Pt-Cl bonds, and the resulting deep green reaction mixtures afforded only low yields of (I). Bistrimethylgermylmercury,

$$cis-(Et_{3}P)_{2}PtCl_{2} + (Me_{3}Si)_{2}Hg \xrightarrow{C_{6}H_{6}}$$

$$Me_{3}Si\cdot Pt(Cl)(PEt_{3})_{2} + Me_{3}SiCl + Hg$$
(I)

a yellow sublimable, air-sensitive solid, prepared from bromotrimethylgermane and sodium amalgam, reacts similarly with cis-(Et₃P)₂PtCl₂ to give $Me_3Ge \cdot Pt(Cl)(PEt_3)_2$ (II).

Both (I) and (II) are low-melting (48° and 35° respectively) pale yellow crystalline solids, and their proton magnetic resonance spectra indicate a trans-configuration of groups in solution. Spinspin coupling between the Me₃M protons and the $^{195}\mathrm{Pt}$ nucleus ($I=\frac{1}{2},\,34\%$ abundant) was observed with $J(^{1}H^{-195}Pt) = 24.6$ and 20.0 c./sec. for (I) and (II) respectively. Among the reactions of these complexes which have been studied, that with water provides the greatest contrast; whereas the trimethylgermyl complex (II) is stable in aqueous diglyme, the trimethylsilyl complex (I) is hydrolysed too rapidly for its rate to be followed by

- F. Glockling and K. A. Hooton, J. Chem. Soc., 1962, 2658.
 R. J. Cross and F. Glockling, J. Chem. Soc., 1965, 5422.
 R. D. Gorsich, J. Amer. Chem. Soc., 1962, 84, 2486.
 T. S. Piper, D. Lemal, and G. Wilkinson, Naturwiss., 1965, 43, 129.

- J. Lewis and S. B. Wild, J. Chem. Soc. (A), 1966, 69.
 E. Wiberg, O. Stecher, H. J. Andrascheck, L. Kreuzbichler, and E. Staude, Angew Chem. Internat. Edn., 1963, 2,
 - ⁷ R. W. Bott and C. Eaborn, private communication.