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Preliminary communication

METAL—METAL BOND ENERGIES IN GROUP IVB—TRANSITION METAL CARBONYL DERIVATIVES AS MEASURED BY MASS SPECTROSCOPY

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Summary

Bond-dissociation energies D(M^1—M^2) have been calculated from appearance potential data for the complexes $Me_3M^1M^2(CO)_x$ (M^1 = Si, Ge, or Sn; M^2 = Co, $x = 4$ or M^2 = Re, $x = 5$) and indicate that there is strong intermetallic bonding in these compounds, especially for $Me_3SnRe(CO)_5$, for which D(Sn—Re) is 3.7 eV (ca. 360 kJ mol^{-1}).

Recently we reported an examination of the vibrational and mass spectroscopic properties of the metal—metal bonded complexes $Me_3M^1Mn(CO)_5$ (M^1 = Si, Ge, or Sn) incorporating calculation of bond-dissociation energies D(M^1—Mn) from ionization energy data [1]. Here we give a preliminary account of analogous results for corresponding tetracarbonylcobalt and pentacarbonylrhenium derivatives, which suggest for the latter the existence of a remarkably strong metal—metal interaction, especially in the case of the tin—rhenium bond.

The three cobalt complexes $Me_3M^1Co(CO)_4$ were obtained as reported previously [2]. Trimethylsilyl- and trimethylgermyl-pentacarbonylrhenium derivatives, which have not been isolated before, are colourless solids for which experimental and analytical data are given in Table 1; the tin analogue was synthesized as detailed elsewhere [3].

Calculation of bond-dissociation energies D(M^1—M^2) from appearance potential (AP) measurements as discussed earlier [1] gave the following values: (eV, ± 0.1) Me_3Ge—$Co(CO)_4$, 3.2; Me_3Sn—$Co(CO)_4$, 2.8; Me_3Si—$Re(CO)_5$, 3.1; Me_3Ge—$Re(CO)_5$, 3.2; and Me_3Sn—$Re(CO)_5$, 3.7. These results compare with D(M^1—Mn) near 2.5 eV for $Me_3M^1Mn(CO)_5$ [1]; and D(Ge—M^2), D(Sn—M^2) respectively in the ranges 2.03-2.81 and 2.32-3.28 eV (M^2 = Cr, Mo, or W) for the complexes $Me_3M^1M^2(\pi\text{-}C_5H_5)(CO)_3$ determined by Lappert et al. [4]. As reported by MacDiarmid and co-workers [5], an accurate datum for $Me_3SiCo(CO)_4$ could not be obtained owing to its low thermal stability.

These data confirm earlier evidence [1, 3-5] for strong intermetallic bond-

TABLE 1

PENTACARBONYLRHENIUM COMPLEXES

Compound	M.p. (°C)	Analysis Found (calcd.)		$\nu(CO)$ [a]	$\nu(M—M)$ [b]	$\tau(CH_3)$ [c]
		C	H			
$Me_3SiRe(CO)_5$ [d]	51-52	24.42 (24.05)	2.49 (2.25)	2110 2010	297	9.73
$Me_3GeRe(CO)_5$ [e]	53-55	21.44 (21.64)	1.82 (2.04)	2014	175	9.70

[a] IR vapour phase. [b] Raman, solid. [c] Cyclohexane solution, relative to $CHCl_3$ τ 2.75 from $SiMe_4$ [d] From $Re_2(CO)_{10}$ + excess Me_3SiH, 120°C, 12 days ca. 10% yield [e] From $Re(CO)_5^-$ + $GeMe_3Br$ in THF: 50% yield.

ing between Group IVB elements and transition metals. In particular, the D(Sn—Re) value of 3.7 eV (ca. 360 kJ mol^{-1}) appears to be the highest such bond energy yet recorded, substantially exceeding D(Sn—Sn) in $Me_3SnSnMe_3$ (260 kJ mol^{-1}) [6] and D(Re—Re) in $(CO)_5ReRe(CO)_5$ (214 kJ mol^{-1}) [7]. Accordingly, the 70 eV mass spectrum of $Me_3SnRe(CO)_5$ shows a striking predominance (95%) of ion-current carried by fragments in which the metal—metal bond nominally remains intact, and the energy of the ν(Sn—Re) stretching mode (151 cm^{-1}, Raman) leads to a significantly higher approximate force-constant [1, 8] than that calculated for the manganese analogue. A basis for rationalization of strong Sn—M bonding, particularly with M a third-row transition element has already been offered in terms of Mössbauer, ^{1}H NMR and structural data [9] and in relation to relative orbital overlap [4] including contributions from d_π—d_π-bonding effects.

More generally, the present data lend further credence to an increase [1, 4] in $D(M^1—M^2)$ (M^1 = Si, Ge, or Sn) both with M^2 further to the right in the transition series or further down a transition-metal sub-group.

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