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REACTION OF HEXAMETHYLDITIN WITH DICOBALT OCTACARBONYL

A NEW COBALT-CATALYZED DISPROPORTIONATION OF HEXAMETHYLDITIN INTO TETRAMETHYLTIN AND DIMETHYLSTANNYLENE

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Summary

Hexamethylditin is known to react with dicobalt octacarbonyl in diethyl ether or pentane solution to give trimethyltincobalt tetracarbonyl as the sole product. As reported below in stronger coordinating solvents like THF the reaction is accompanied by a novel type of reaction, viz. a rapid dicobalt octacarbonyl-catalyzed disproportionation of hexamethylditin to give tetramethyltin and dimethylstannylene.

Introduction

We previously observed that Group IV metal—metal bonded compounds, R_6M_2 and $R'_6M'_2$, disproportionate rapidly under polar conditions to give the asymmetric di-metal compounds $R_3MM'R'_3$ (R, R' = alkyl; M, M' = Ge, Sn). These disproportionations are equilibrium reactions and the equilibrium constants for a series of such reactions have been determined [2-4]. During the course of our studies Abel and Moorhouse [1] reported that the reaction of hexamethylditin with bi-nuclear transition metal compounds such as $Co_2(CO)_8$, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, which offers a suitable route to the corresponding trimethyltin transition metal derivatives (eqn. 1).

$$Me_6Sn_2 + M_2(CO)_n \rightarrow 2\ Me_3SnM(CO)_{n/2} \qquad (1)$$

M = Co, n = 8; 10 h at 20°, 85%
M = Mn, n = 10; 10 h at 140°, 45%
M = Re, n = 10; 48 h at 180°, 10%

In order to determine whether the latter type of reactions also involve a distinct equilibrium, the reaction of hexamethylditin with dicobalt octacarbonyl was studied in greater detail. A new catalytic effect discovered in the course of this study forms the subject of this paper.

Results and discussion

In diethyl ether solution hexamethylditin reacts rapidly with dicobalt octacarbonyl to give trimethyltincobalt tetracarbonyl as the sole product (eqn. 2).

$$Me_6Sn_2 + Co_2(CO)_8 \rightarrow 2\ Me_3SnCo(CO)_4 \quad (2)$$

According to PMR spectroscopy, after 3 h at room temperature the reaction has proceeded about 65%, and is complete after 24 h*. In THF solution, however, in addition to trimethyltincobalt tetracarbonyl (I) considerable amounts of tetramethyltin (II) and dimethyltinbis(cobalt tetracarbonyl) (III) are formed as well. Thus, as determined by PMR spectroscopy, the average of three different runs of the reaction of 1 mole of Me_6Sn_2 with 1 mole of $Co_2(CO)_8$ in THF gave 1.0 mole of I, 0.5 mole of II and 0.3 mole of III. A solid was deposited in the brown reaction mixtures.

$$Me_6Sn_2 + Co_2(CO)_8 \xrightarrow{THF} \approx 1.0\ \underset{(I)}{Me_3SnCo(CO)_4} + \approx 0.5\ \underset{(II)}{Me_4Sn} + \approx 0.3\ \underset{(III)}{Me_2Sn[Co(CO)_4]_2} \quad (3)$$

The formation of II and III might be explained by a disproportionation of trimethyltincobalt tetracarbonyl (I), according to eqn. 4, analogous to the disproportionation reaction reported by George [5] for $Me_3SnMo(CO)_2$-(π-C_5H_5)(Ph_3P) at 200° and by Clark et al. [6] for $Me_3SnMn(CO)_5$ at 130°. However, compound I, prepared in diethyl ether, according to eqn. 2, appeared to be completely stable in THF solution for more than nine days at room temperature both as such and in the presence of hexamethylditin or dicobalt octacarbonyl. The reverse reaction also could not be induced.

$$2\ Me_3SnCo(CO)_4 \overset{THF}{\not\rightleftharpoons} Me_4Sn + Me_2Sn[Co(CO)_4]_2 \quad (4)$$

Furthermore, reaction of one mole of hexamethylditin with a catalytic amount (10%) of dicobalt octacarbonyl in THF gave over 90% of tetramethyltin, < 10% of I and a brownish, insoluble solid.

These results point to a 1,2-methyl shift in hexamethylditin catalyzed by dicobalt octacarbonyl, according to eqn. 5.

$$Me_3SnSnMe_3 \xrightarrow{0.1\ Co_2(CO)_8} Me_4Sn + [Me_2Sn] \quad (5)$$

Reaction 5 also proceeds readily in acetonitrile and in acetone solution (> 90% Me_4Sn within 24 h at 20°). The reaction proceeds much more slowly

* The reaction was also found to be effective for the preparation of $Et_3SnCo(CO)_4$ (from Et_6Sn_2) and $Et_2ClSnCo(CO)_4$ (from $Et_2ClSnSnClEt_2$) (see Experimental).

in diethyl ether (27% Me_4Sn after 20 h, 95% Me_4Sn after 168 h at 20°), and does not take place at all in apolar solvents such as pentane or benzene.

In the reaction between stoichiometric amounts of Me_6Sn_2 and $Co_2(CO)_8$ in coordinating solvents such as THF the two competitive reactions 2 and 5 appear to take place. The rate of reaction 5 decreases with decreasing basicity of the solvent, $k_{THF} > k_{Et_2O} > k_{pentane}$ (no reaction), so that in apolar solvents reaction 2 occurs nearly exclusively. The formation of $Me_2Sn[Co(CO)_4]_2$ (III) may thus be explained by insertion of the dimethylstannylene intermediate into the cobalt—cobalt bond of dicobalt octacarbonyl, analogous to the insertion of $SnCl_2$ into the cobalt—cobalt bond reported by Bonati et al. [7].

$$[Me_2Sn] + Co_2(CO)_8 \rightarrow (CO)_4CoSnMe_2Co(CO)_4 \qquad (6)$$

Attempts to trap the dimethylstannylene (eqn. 5) with methyl iodide or with diphenyl disulphide [8], failed. Careful bromination of the resulting insoluble organotin residue and subsequent PMR and GLC analysis demonstrated the presence of Me_3SnBr, Me_2SnBr_2 and $MeSnBr_3$, indicating that the dimethylstannylene had polymerized to form a polytin product with a branched structure.

In order to gather some information on the mechanism of this new type of reaction several compounds were screened for catalytic activity in reaction (5). No catalytic activity was observed for trimethyltincobalt tetracarbonyl, sodiumcobalt tetracarbonyl, cobalt dibromide, cobalt bis(acetylacetonate), methylmagnesium bromide or metallic lithium. Iodocobalt tetracarbonyl, prepared by cleavage of dicobalt octacarbonyl with iodine [9], was an effective catalyst (90% of Me_4Sn after 24 h at 20°). Apparently $Co(CO)_4^+$, rather than Co^{2+} or $Co(CO)_4^-$ species are involved in the catalysis mechanism.

In a recent paper by Seyferth and Spohn [10], dealing with the reaction of alkylmercury halides with dicobalt octacarbonyl in THF, a dissociation of $Co_2(CO)_8$ into cationic and anionic species is postulated (eqn. 7). The $Co_2(CO)_8$

$$Co_2(CO)_8 + THF \rightarrow Co(CO)_4^+ \cdot THF + Co(CO)_4^- \qquad (7)$$

catalyzed disproportionation of hexamethylditin (reaction 5) could thus be explained in terms of reactions 8-10.

$$Co(CO)_4^+ \cdot THF + Me_3SnSnMe_3 + Co(CO)_4^- \rightarrow Me_3SnSnMe_2Co(CO)_4 + MeCo(CO)_4 + THF \qquad (8)$$

$$Me_3SnSnMe_2Co(CO)_4 \rightarrow Me_3SnCo(CO)_4 + [Me_2Sn] \qquad (9)$$

$$Me_3SnCo(CO)_4 + MeCo(CO)_4 \xrightarrow{THF} Me_4Sn + Co(CO)_4^+ \cdot THF + Co(CO)_4^- \qquad (10)$$

The rate-determining step will be reaction 8, viz. an electrophilic attack of cobalt at carbon [cf. 11, 12]. The resulting pentamethylditincobalt tetracarbonyl will undergo a rapid 1,2-shift of the cobalt tetracarbonyl group (eqn. 9), in a similar way as observed with functionally-substituted ditins such as chloropentaethylditin and 1,2-dichlorotetraethylditin [13, 14]. The intermediate formation of the thermally rather unstable methylcobalt tetracarbonyl is supported by the observation that reaction between equimolar amounts of $Me_3SnCo(CO)_4$, $Co_2(CO)_8$ and MeI gives rise to the formation of about 10% of Me_4Sn after 24 h at 20°, no $Me_2Sn[Co(CO)_4]_2$ being detectable.

Attempts to bring about reaction 5 with other ditins, such as hexaethylditin, and with hexaethyldigermane, failed at room temperature. This may be explained by the rapidly decreasing rate of electrophilic substitution at carbon in th order Me ≫ Et > Pr [11, 12] and R_4Sn ≫ R_4Ge [12]. Under more forcing conditions (7 h at 60°) with hexaethylditin some 10% decrease of ditin was observed, but no tetraethyltin could be detected by GLC. Presumably at elevated temperatures deethylation does take place, but the thermally very unstable ethylcobalt tetracarbonyl decomposes instantaneously.

Dimanganese decacarbonyl is also effective as a catalyst in reaction 5, but less so than dicobalt octacarbonyl: after 20 h at 20° in THF solution only abou 32% of tetramethyltin was observed (GLC).

Experimental

All reactions were performed in rigorously dried apparatus under dry, oxygen-free nitrogen. Unless otherwise indicated, the starting materials were prepared according to published procedures or purchased. All materials were purified under nitrogen before use.

Recording of the PMR spectra, GLC analyses and elemental analyses were carried out in the Department of Physical-Organic and Analytical Chemistry (Head: Dr. A. Mackor) of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands.

Reaction of Me_6Sn_2 with $Co_2(CO)_8$

(a). In diethyl ether. Me_6Sn_2 (1.75 g, 5.3 mmol) and $Co_2(CO)_8$ (1.82 g, 5.3 mmol) were dissolved in 12.5 ml of diethyl ether. According to PMR spectroscopy, after 3 h at room temperature about 65% of Me_6Sn_2 had been converted into $Me_3SnCo(CO)_4$, and the reaction was complete after 24 h. Evaporation of the solvent in vacuo and sublimation of the residue gave 2.7 g (76%) of $Me_3SnCo(CO)_4$, m.p. 68-70° (lit. [1] m.p. 72-74°).

A similar reaction of $Co_2(CO)_8$ with Et_6Sn_2 and with $Et_2ClSnSnClEt_2$, respectively, afforded the compounds:

$Et_3SnCo(CO)_4$, b.p. 67-68°/0.4 mm; n_D^{20} 1.5552; yield, 50%. (Found: C, 32.2; H, 4.3. Calcd.: C, 31.84; H, 4.01%.)

$Et_2ClSnCo(CO)_4$, b.p. 80-83°/0.6 mm; n_D^{20} 1.5790; yield, 50%. (Found: C, 24.5; H, 2.7; Cl, 8.9. Calcd.: C, 25.07; H, 2.63; Cl, 9.25%.)

(b). In THF; molar ratio $Me_6Sn_2/Co_2(CO)_8 = 1$. A PMR tube was charged with 0.4 ml of THF, 0.074 g (0.22 mmol) of $Co_2(CO)_8$, 45.5 μl (0.22 mmol) of Me_6Sn_2 and 15 μl of TMS (internal standard). PMR spectra were recorded after various times. After 1 h at room temperature about 75% of the Me_6Sn_2 [δ(Me—Sn) = 0.20 ppm] had been consumed to give $Me_3SnCo(CO)_4$ [δ(Me—Sn) = 0.65 ppm], Me_4Sn [δ(Me—Sn) = 0.07 ppm] and $Me_2Sn[Co(CO)_4]_2$ [δ(Me—Sn) = 1.13 ppm]. After 24 h the PMR spectrum showed the presence of $Me_3SnCo(CO)_4$ (I), Me_4Sn (II) and $Me_2Sn[Co(CO)_4]_2$ (III) in the molar ratio 1/0.42/0.24, and the Me_6Sn_2

had been consumed completely. A small amount of sediment had been deposited. Duplicate experiments gave an average molar ratio (after 24 h) of I/II/III = 1/0.5/0.3.

(c). In THF; molar ratio $Me_6Sn_2/Co_2(CO)_8$ = 10. A PMR tube was charged with 0.6 ml of THF, 6.4 mg (0.019 mmol) of $Co_2(CO)_8$, 40 μl (0.19 mmol) of Me_6Sn_2 and 40 μl of TMS. After 24 h at room temperature the PMR spectrum showed the presence of about 90% of Me_4Sn, together with about 10% of $Me_3SnCo(CO)_4$. GLC analysis confirmed the presence of Me_4Sn in high yield.

Similar experiments were carried out at room temperature in acetone-d_6 (> 90% of Me_4Sn after 24 h), in acetonitrile (10% of Me_4Sn after 1.5 h; > 90% of Me_4Sn after 24 h), in diethyl ether (27% of Me_4Sn after 20 h; 95% of Me_4Sn after 168 h), in pentane and in benzene (no reaction after 24 h).

Reaction of Me_6Sn_2 with 10 mole % of $ICo(CO)_4$

To a solution of 6.6 mg (0.019 mmol) of $Co_2(CO)_8$ in 0.5 ml of diethyl ether were added 0.019 mmol of iodine (260 μl of a diethyl ether solution containing 0.075 mmol/ml of iodine). After 5 min at 20° the solvent was evaporated in vacuo, the green solid residue was taken up in 1.0 ml of THF and 80 μl (125 mg, 0.19 mmol) of Me_6Sn_2 was added. A PMR spectrum recorded after 3 h at 20° showed the presence of a trace of Me_4Sn, and after 24 h about 90% of Me_4Sn was present, together with about 10% of Me_6Sn_2.

In a similar way the reaction between equimolar amounts of $Me_3SnCo(CO)_4$, $Co_2(CO)_8$ and MeI were carried out in THF.

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