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UTILIZATION OF HEXAMETHYLDITIN IN THE SYNTHESIS OF ORGANOTIN–TRANSITIONAL METAL COMPLEXES

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SUMMARY

Hexamethylditin is shown to be a good reagent for the direct formation of organotin–transitional metal bonded complexes. The formation of Sn–Mn, Sn–Re, Sn–Mo, Sn–W, Sn–Fe, Sn–Co and Sn–Ni bonded organometallic compounds is reported.

INTRODUCTION

The methods for the formation of tin-transitional metal bonds in organometallic complexes usually involve the utilization of the halide, or the hydride or the anion of the transitional metal system[1-3]. Many of these reagents involve preparation from a metal–metal bonded dimeric system, as for example in (1).

$$(CO)_5MnMn(CO)_5 \xrightarrow{2\ Na} Na^+Mn(CO)_5 \xrightarrow{Me_3SnCl} Me_3SnMn(CO)_5 \qquad (1$$

Recently hexamethylditin has been reported to react directly with triruthenium dodecacarbonyl[4] and with tetrakis(triphenylphosphine)platinum[5] to give species with tin–ruthenium and tin–platinum bonds respectively. This prompts us to report our own synthetic studies utilizing hexamethylditin.

RESULTS AND DISCUSSION

Dicobalt octacarbonyl, dimanganese dodecacarbonyl and dirhenium dodecacarbonyl all react with hexamethylditin according to eqns. (1), (2) and (3) respectively.

$$Co_2(CO)_8 + Mn_3SnSnMe_3 \rightarrow 2\ Me_3SnCo(CO)_4 \qquad (1)$$

$$Mn_2(CO)_{10} + Me_3SnSnMe_3 \rightarrow 2\ Me_3SnMn(CO)_5 \qquad (2)$$

$$Re_2(CO)_{10} + Me_3SnSnMe_3 \rightarrow 2\ Me_3SnRe(CO)_5 \qquad (3)$$

A considerable variation in ease of reaction is notable, and effects the yield considerably. Thus hexamethylditin and dicobalt octacarbonyl undergo reaction at 20° and after 10 h an 85% yield of (trimethylstannyl)cobalt tetracarbonyl may be isolated. In contrast, however, dimanganese dodecacarbonyl and hexamethylditin react only at around 140°; and after 10 h a yield of 45% of (trimethylstannyl)manganese pentacarbonyl was obtained. It seems likely that the lower yield is due both to a slower reaction rate, and to a slow decomposition of the product under these conditions. The stronger rhenium–rhenium bond in dirhenium dodecacarbonyl requires even more forcing conditions and a yield of only 10% is obtained for reaction (3) after 48 h at 180°.

Eqns. (4), (5) and (6) illustrate similar types of reaction with various dimeric cyclopentadienyl metal carbonyls. Here also a marked variation in ease of reaction and yield are observable. The greatest ease of reaction and high yield appear to be associated with those metal–metal bonded carbonyls which also possess bridging carbonyl groups. It is interesting to recall that insertion reactions of main group metals into transitional metal–metal bonds are also most easily carried out when bridging carbonyls are present[6].

$$[(\pi\text{-}C_5H_5)Ni(CO)]_2 + Me_3SnSnMe_3 \rightarrow 2\,(\pi\text{-}C_5H_5)Ni(CO)SnMe_3 \quad (4)$$

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + Me_3SnSnMe_3 \rightarrow 2\,(\pi\text{-}C_5H_5)Fe(CO)_2SnMe_3 \quad (5)$$

$$[(\pi\text{-}C_5H_5)M(CO)_3]_2 + Me_3SnSnMe_3 \rightarrow 2\,(\pi\text{-}C_5H_5)M(CO)_3SnMe_3 \quad (6)$$

(M = Mo and W)

The formation of $(\pi\text{-}C_5H_5)Ni(CO)SnMe_3$ by this method in good yield (66%) is especially useful in that it can be utilized as an intermediate for futher synthetic steps; and may be used as a substitute for reactions requiring the $[(\pi\text{-}C_5H_5)Ni(CO)]^-$ anion, which is somewhat inaccessible[7].

It is possible that these reactions involve the fission of the transitional metal–metal bond and formation of free radicals. It would therefore appear possible that free radicals such as $Mn(CO)_5$, $Re(CO)_5$, $(\pi\text{-}C_5H_5)Fe(CO)_2$ etc. are formed under quite mild reaction conditions.

EXPERIMENTAL

The variability of reaction rate and product stability was such that no generalized reaction condition could be formulated, and each synthesis required particular circumstances. All reactions were carried out under nitrogen. Figures in parentheses after IR frequencies refer to the relative intensities of the carbonyl bands with the strong band given a value (10).

(Trimethylstannyl)cobalttetracarbonyl

Dicobalt octacarbonyl (3.42 g, 1 mol.) and hexamethylditin (3.28 g, 1 mol.) were stirred in pentane (25 ml) to 10 h at ~25°. Solvent was removed at 25°/10 mm, and the product sublimed onto a probe at −78° to afford (trimethylstannyl)cobalt tetracarbonyl (5.5 g, 82%) as pale grey crystals, m.p. 72–74° (lit.[8] 73–75°). (Found: C, 24.9; H, 2.8. $C_7H_9CoO_4Sn$ calcd.: C, 25.1; H, 2.7%.) IR carbonyl bands at 2081 (7½), 2021 (7), 1939 (10) and 1999 (10) cm^{-1}. $\tau(CH_3)$ 9.37.

Both hexane and diethyl ether are suitable solvents for this reaction.

(Trimethylstannyl)manganesepentacarbonyl

Dimanganese dodecacarbonyl (3.90 g, 1 mol.) and hexamethylditin (3.28 g, 1 mol.) were heated together 140°/10 h without solvent. Slow sublimation of the product onto a probe kept at −80° yielded (trimethylstannyl)manganese pentacarbonyl (3.24 g, 45%) as colourless crystals, m.p. 27–28° (lit.[9] 26–27°). (Found: C, 27.1; H, 2.56. $C_8H_9MnO_5Sn$ calcd.: C, 26.8; H, 2.53%.) IR carbonyl bands at 2089(2), 1998(6), 1992(10) and 1958($\frac{1}{2}$). $\tau(CH_3)$ 9.53.

Similar yields are obtained using diglyme as a solvent; and the yield may be markedly improved by using a molar excess of hexamethylditin, though under the latter conditions it is difficult to remove last traces of hexamethylditin from the product.

(Trimethylstannyl)rhenium pentacarbonyl

Dirhenium dodecacarbonyl (3.27 g, 1 mol.) and hexamethylditin (3.28 g, 2 mols.) were heated (180–200°/18 h) in triglyme. After cooling, the mixture was poured into cold deaerated water. The precipitated product was redissolved in ether and the solution dried over magnesium sulphate and filtered. Removal of the ether left the crude material which was purified by sublimation to give (trimethylstannyl)rhenium pentacarbonyl (0.66 g, 10%), m.p. 57–58° (lit.[9] 51–58°). (Found: C, 20.0; H, 1.8. $C_8H_9O_5ReSn$ calcd.: C, 19.6; H, 1.9%.) IR carbonyl bands at 2110(1.3), 2004(10), and 1968($\frac{1}{2}$). $\tau(CH_3)$ 9.57.

(Trimethylstannyl)-π-cyclopentadienylnickel carbonyl

Bis(π-cyclopentadienylnickel carbonyl) (6.08 g, 1 mol.) and hexamethylditin (6.56 g, 2 mols.) were heated (72°/66 h) in hexane (60 ml). This reaction mixture was then chromatographed on florisil with hexane to afford initial traces of nickel tetracarbonyl and hexamethylditin followed by the product, which after removal of solvent at low pressure was distilled to afford trimethylstannyl-π-cyclopentadienylnickel carbonyl (8.36 g, 66%), 55–56°/0.008 mm, as a very air-sensitive orange red liquid with a particularly evil smell. The extremely air-sensitive nature of the liquid prevented satisfactory analytical data from being obtained, but the single sharp IR carbonyl band at 1999 cm^{-1}, and the constant boiling point of the distillate indicated a pure product. Analyses for carbon of ~30% instead of 34.3% were obtained presumably due to oxidation in transference.

Subsequent compounds eluted from the chromatography column were unreacted bis(π-cyclopentadienylnickelcarbonyl) (10% recovery) and tri-π-cyclopentadienyltrinickel dicarbonyl (6%).

(Trimethylstannyl)-π-cyclopentadienyliron dicarbonyl

Bis(π-cyclopentadienyliron dicarbonyl) (9.48 g, 1 mol.) and hexamethylditin (6.56 g, 1 mol.) were heated (7 h) under reflux in xylene (30 ml). Removal of xylene 20°/0.05 mm was followed by sublimation[10] of the residue at 70°/0.005 mm, onto a water cooled probe in a molecular still type apparatus. This procedure afforded (trimethylstannyl)-π-cyclopentadienyliron dicarbonyl (8.2 g, 60%). (Found: C, 35.5; H, 4.3. $C_{10}H_{14}FeO_2Sn$ calcd.: C, 35.2; H, 4.1%.) $\tau(CH_3)$ 9.55; $\tau(C_5H_5)$ 5.10 as an orange brown air-sensitive liquid.

(Trimethylstannyl)-π-cyclopentadienylmolybdenum tricarbonyl

Bis(π-cyclopentadienylmolybdenum tricarbonyl)(4.90 g, 1 mol.) and hexamethylditin (3.28 g, 1 mol.) were heated (14 h) in xylene under reflux conditions. Subsequent removal of solvent 20°/0.01 mm, and sublimation onto an ice cooled probe afforded white (trimethylstannyl)-π-cyclopentadienylmolybdenum tricarbonyl (1.62 g, 20%), m.p. 98–99° (lit.[11] 97–99°). (Found: C, 32.5; H, 3.8. $C_{11}H_{14}MoO_3Sn$ calcd.: C, 32.3; H, 3.5%.) IR carbonyl bands at 1996(9½), 1920(7), 1893(10). $\tau(CH_3)$ 9.56, $\tau(C_5H_5)$ 4.59.

The yield in this reaction is somewhat variable for reasons unknown to us. A somewhat higher yield is obtained on occasions with use of dyglime as solvent, and pouring the reaction mixture into deaerated water followed by filtration and sublimation.

(Trimethylstannyl)-π-cyclopentadienyltungsten tricarbonyl

Bis(π-cyclopentadienyltungsten tricarbonyl) (6.66 g, 1 mol.) and hexamethylditin (4.88 g, 1.5 mols.) were heated (40 h) under reflux conditions in light petroleum (180–200°). After filtration the product was separated by chromatography on florisil with pentane, and subsequent sublimation, to yield (trimethylstannyl)-π-cyclopentadienyltungsten tricarbonyl {10% based on $[\pi\text{-}C_5H_5W(CO)_3]_2$}, m.p. 118–120° (lit.[11] 119–120°). (Found: C, 26.3; H, 2.8. $C_{11}H_{14}O_3SnW$ calcd.: C, 26.6; H, 2.8%.) IR carbonyl bands at 1993(9½), 1915(7½), 1890(10). $\tau(CH_3)$ 9.42, $\tau(C_5H_5)$ 4.55 as pale yellow crystals.

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