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Improved Syntheses of $[PtMe_2(1,5\text{-}COD)]$

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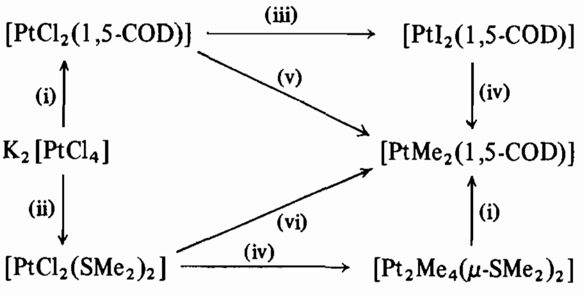
The complex $[PtMe_2(1,5\text{-}COD)]$ (**1**), (1,5-COD = 1,5-cyclooctadiene) is a useful starting material for the synthesis of $[PtMe_2L_2]$ where $L = PR_3$ [1–3], RNC [1], amine [1], bipyridyl [1], AsR_3 [1, 3] or SbR_3 [3]. The best reported [1] synthesis of **1** is in three steps from $K_2[PtCl_4]$, the final step of which is the metathesis of $[PtI_2(1,5\text{-}COD)]$ with MeLi to give **1** in 87% yield. However, in our hands this route often gave poor yields (<20%) and/or deposited platinum metal. We have thus developed two, simple, two-step syntheses of **1** that give reliable yields of 70–90%. (Scheme 1.)



Scheme 1. (i) 1,5-COD; (ii) SMe_2; (iii) NaI; (iv) MeLi; (v) $LiCuMe_2$; (vi) MeLi followed by 1,5-COD.

Treatment of $[PtCl_2(1,5\text{-}COD)]$ with two equivalents of lithium dimethyl cuprate in diethyl ether gives **1** in 70–75% yield. Using one equivalent of dimethyl cuprate gave low (<30%) yields of **1** and attempts to use heterocuprates (e.g. Li[MeCuCN] or Li[MeCuC≡CPh]) did not give the desired product.

We found that 1,5-COD displaces SMe_2 from $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ to give **1** in 78% yield. More conveniently **1** can be prepared in 90% yield from $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ generated *in situ* from $[PtCl_2(SMe_2)_2]$ and MeLi.

Experimental

$[PtCl_2(1,5\text{-}COD)]$ [4], $[PtCl_2(SMe_2)_2]$ [5] and $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ [6] were prepared by literature methods. Copper iodide was freshly prepared [7] and dried at 100 °C for 12 h prior to use. Methyl lithium and 1,5-cyclooctadiene were used as supplied (Aldrich Chemical Co.). Diethylether was freshly distilled from sodium/benzophenone. The purity of product **1** was determined by ^1H NMR.

Preparation of $[PtMe_2(1,5\text{-}COD)]$ (1)

A. From $[PtCl_2(1,5\text{-}COD)]$

Copper(I) iodide (0.25 g, 1.31 mmol) was suspended in dry diethylether (5 ml) and cooled to −20 °C under nitrogen. MeLi (2.0 ml, 1.5 M in diethylether, 3.0 mmol) was added rapidly to give a yellow precipitate at first, followed by a clear pale yellow solution, to which was added $[PtCl_2(1,5\text{-}COD)]$ (0.25 g, 0.67 mmol). The dark suspension that formed was stirred and allowed to warm to room temperature over 30 min by which time the mixture was yellow–brown. The mixture was then cooled to −20 °C and hydrolysed with a few drops of water. The mixture was allowed to warm to room temperature, more water (10 ml) and diethylether (10 ml) was added and then stirred for a further 15 min. After filtration, the diethylether layer was separated, washed with water (10 ml) and then dried over Na_2CO_3. Evaporation of the diethylether gave the pure white solid product, 0.17 g, 77%. ^1H NMR: δ 4.76, $J(PtH)$ 39 Hz, 4H; δ 2.22, 8H; δ 0.67, $^2J(PtH)$ 83 Hz, 6H.

B. From $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$

1,5-COD (0.06 ml, 0.49 mmol) was added to a well stirred solution of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.11 g, 0.19 mmol) in dichloromethane (5 ml). After 75 min, the solution was evaporated under reduced pressure and light petroleum (boiling point (b.p.) 30–40 °C) (5 ml) added to induce formation of the white solid product, 0.10 g 78%.

C. From $[PtCl_2(SMe_2)_2]$

MeLi (1.9 ml, 1.5 M in diethylether, 2.85 mmol) was added dropwise to a stirred, cold (0 °C) suspension of $[PtCl_2(SMe_2)_2]$ (0.50 g, 1.28 mmol) in diethylether (30 ml) under nitrogen. After 5 min, further MeLi (1.0 ml, 1.5 M in diethylether, 1.50 mmol) was added and the mixture stirred and allowed to warm slowly to 20 °C. When no yellow colour remained and the solution became cloudy (~10 min), water (50 ml) was added followed by 1,5-COD (0.40 ml, 3.3 mmol). The mixture was stirred for 1 h and then the layers separated, the aqueous layer extracted with diethylether (3 × 20 ml) and the combined organic extracts dried over $MgSO_4$. After filtration and removal of the solvent

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under reduced pressure, the product was obtained as an off-white solid, 0.382 g, 90%.

This product was pure enough for further syntheses but if a pure white solid was desired then the above crude product could be extracted with light petroleum, b.p. 30–40 °C, the solution filtered through fine filter paper and the solvent then removed. Alternatively, the crude product can be dissolved in dichloromethane (10 ml) and the solution stirred with Florisil (0.5 g), filtered and then evaporated. Typical recovery of the product was 86%.

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