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A facile one-pot synthesis of [(COD)Pt(CH_3)$_2$]

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A novel one-pot synthesis of dimethyl(1,5-cyclooctadiene)platinum(II), i.e. [(COD)Pt(CH_3)$_2$] (complex 1), was developed in 92% yield using platinum acetylacetonate, 1,5-cyclooctadiene and trimethylaluminium. Complex 1 was fully characterized by ^{1}H and ^{13}C NMR, mass spectrometry, cell dimensions and elemental analysis. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: complex synthesis; dimethyl(1,5-cyclooctadiene) platinum(II)

INTRODUCTION

The synthesis of dimethyl(1,5-cyclooctadiene)platinum(II), i.e. [(COD)Pt(CH_3)$_2$], was first reported by Doyle *et al.* in 1963[1] and its molecular structure determined by single-crystal X-ray diffraction is shown in Fig. 1.[2] It has been used as a valuable precursor for numerous platinum complexes by replacing 1,5-cyclooctadiene (COD) with L, where L = phosphine, isocyanide, amine, bipyridyl, trialkylarsine or trialkylstibane.[3] Doyle's preparation comprised two steps: [(COD)PtI_2] was synthesized from K_2PtCl_6 with a yield of 56%; and [(COD)PtI_2] was transformed into [(COD)Pt(CH_3)$_2$] via a Grignard reaction with a yield of 71%. Clark and Manzer[4] tried to improve the yield by preparing [(COD)PtCl_2] from K_2PtCl_4 and subsequently displacing the chloride anions with iodine almost quantitatively. In a third step, [(COD)Pt(CH_3)$_2$] was obtained by metathesis of [(COD)PtI_2] with CH_3Li in 87% yield. However, Pringle *et al.*[5] reported poor yields (<20%) using this three-step procedure, and hence developed another two-step synthesis of [(COD)Pt(CH_3)$_2$]. With K_2PtCl_4 as the starting material a yield of 63–67% was obtained, whereas [PtCl_2(SMe_2)$_2$)$_2$] gave yields up to 90%. However, all these preparative approaches were found to be troublesome. As reported in a preliminary communication,[6] the formation of [(COD)Pt(CH_3)$_2$] was identified via mass spectrometry during decomposition of intermediate complex **2** in the presence of COD (see Scheme 1). Here, we report a facile, high-yield one-pot synthesis of [(COD)Pt(CH_3)$_2$] via the addition of COD at the beginning of the reaction (see Scheme 2).

EXPERIMENTAL

Synthesis of the material

Commercially available Pt(acac)$_2$ and Al(CH_3)$_3$ were used without further purification. 1,5-Cyclooctadiene (COD) and toluene were dried carefully and saturated with argon prior to use. All preparations were carried out in dried solvents under an argon atmosphere using Schlenk techniques.

A 2.0 g amount of Pt(acac)$_2$ (5.08 mmol) in 150 ml of toluene was mixed with 0.69 ml of COD (5.59 mmol) in 40 ml of toluene, and then 50 ml of Al(CH_3)$_3$ (1.9 ml, 15.2 mmol) solution in toluene was added dropwise within 1 h under stirring. Stirring was continued for a further 24 h at room temperature. The resulting yellow solution was concentrated to ~10 ml *in vacuo* (1×10^{-2} mbar), slowly cooled down to −30 °C and kept at the same temperature overnight to yield colourless crystals. The supernatant was collected and inspected using transmission electron microscopy (TEM). The crystals were washed with 2 × 5 ml of *n*-pentane at −30 °C and further dried *in vacuo* (1×10^{-2} mbar). Yield: 1.2 g of off-white crystals (**1**) (92%). Anal. calc. for $C_{10}H_{18}Pt$: C, 36.03; H, 5.44; Pt, 58.52. Found: C, 36.10; H, 5.41; Pt, 58.35.

Recrystallization of **1** from dichloromethane at −40 °C yielded a colourless crystal. Found: C, 35.98; H, 5.37; Pt, 58.41

Complex **1** can be obtained almost quantitatively if those parts left in the supernatant during crystallization and washing are recovered.

Analyses

The ^{1}H and ^{13}C NMR measurements were carried out on a Bruker AMX-300 spectrometer at 25 °C. Chemical shifts of ^{1}H and ^{13}C spectra were calibrated according to the deuterated solvent signals and converted to the TMS scale. Elemental analysis was performed at H. Kolbe Microanalysis

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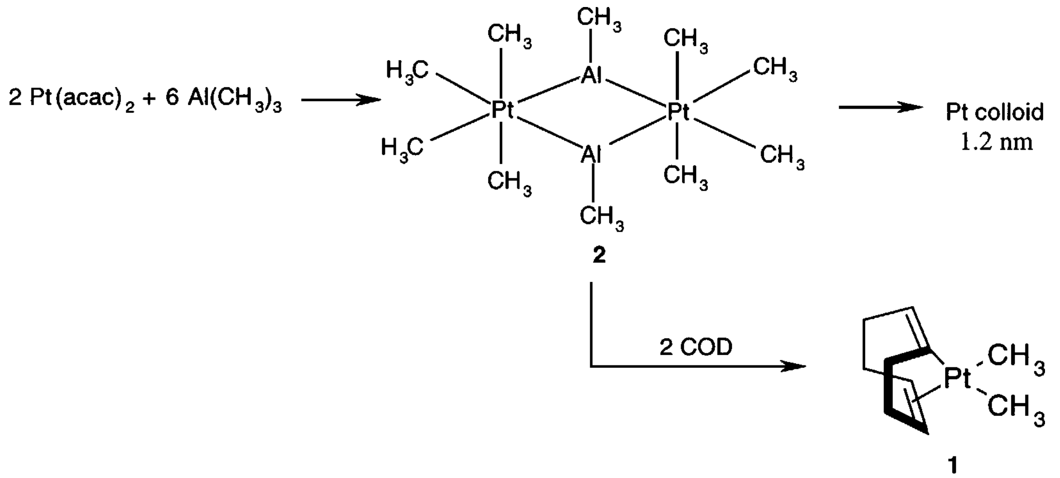


Scheme 1.

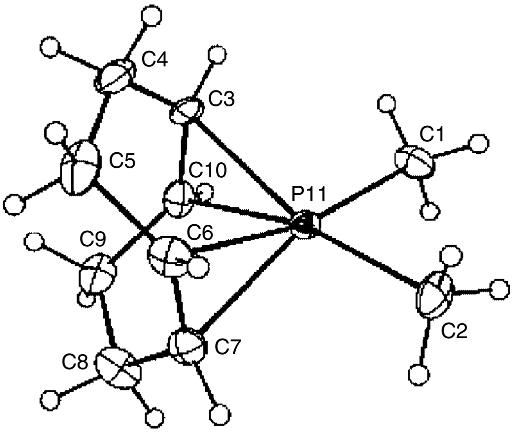


Figure 1. An ORTEP diagram of [(COD)Pt(CH$_3$)$_2$][2].

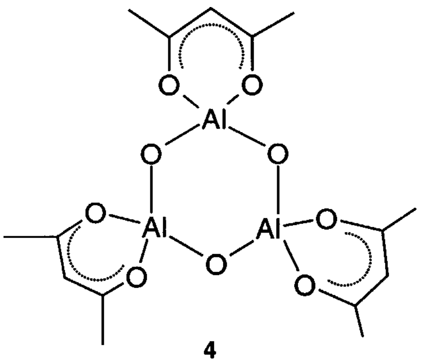
$$\mathrm{Pt(acac)_2 + COD + 2\ Al(CH_3)_3 \longrightarrow (COD)Pt(CH_3)_2 + 2\ \underset{\mathbf{3}}{(acac)Al(CH_3)_2}}$$

Scheme 2.

Laboratory, Muelheim an der Ruhr, Germany. Mass spectrometric analyses were performed on a Finnigan MAT 8400 mass spectrometer The cell dimensions of recrystallized complex **1** were determined from data collected on a Bruker Kappa-CCD diffractometer equipped with Mo Ka radiation and a low-temperature apparatus (100 K). Transmission electron microscopy measurements were performed using a Hitachi H 7500 instrument operated at an accelerating voltage of 100 kV.

RESULTS AND DISCUSSION

Equivalent molar amounts of Pt(acac)$_2$ and COD reacted smoothly in toluene at room temperature after the injection of three equivalents of Al(CH$_3$)$_3$. The ^{1}H NMR spectra of the reaction mixture confirmed that >99% of the COD was coordinated to Pt after 8 h. Because the by-product [(acac)Al(CH$_3$)$_2$] (**3**) precipitates below −30 °C, the pure Pt complex **1** can be obtained by simple crystallization from the concentrated reaction mixture at −30 °C followed by washing with pentane. Using mass spectrometry compound **3** was evidenced as a by-product with a characteristic mass of m/z 141. Furthermore, the fragments with characteristic masses of m/z 255, 271 and 369 suggested the formation of by-product **4** (see Scheme 3), which had been identified when trimethylaluminium was used to reduce platinum acetylacetonate.[7]



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Scheme 3.

The purity of the as-prepared complex **1** was checked carefully by mass spectrometry, NMR and elemental analysis. Mass spectrometric analyses confirmed the molecular weight of **1** to be 333, and no impurities were observed. However, the yield did not exceed 80% and TEM investigation of the brown supernatant showed the presence of 1.2 nm Pt nanoparticles, which had been found earlier when platinum acetylacetonate was reduced by trimethylaluminium in the absence of COD.[6] Thus, it was an obvious step to improve

Table 1. The ^{1}H NMR data of complex **1**

	δ_H (ppm)			J(PtH) (Hz)		Relative intensity[a]		
Solvent	HC=CH	CH_2	$Pt(CH_3)$	HC=CH	$Pt(CH_3)$	CH=CH (4H)	CH_2 (8H)	$Pt(CH_3)$ (6H)
d_8-Toluene	4.53	1.80	1.12	40	83	3.9	8.1	6.0
$CDCl_3$	4.78	2.27	0.70	40	82	3.9	8.1	6.0
CD_2Cl_2	4.78	2.30	0.66	41	83	3.9	8.3	5.9
$CDCl_3$[b]	4.89	2.38	0.81	40	86	4.5	9.2	8.5

[a] Calculation of relative intensity was based on the assumption of 18 protons in the as-prepared complex **1**.
[b] Data from Ref. 1.

Table 2. The ^{13}C NMR data of complex **1**

	δ_C (ppm)			J(PtC) (Hz)	
Solvent	C3=C10, C6=C7	C4–C5, C8–C9	C1, C2	C3=C10, C6=C7	C1, C2
d_8-Toluene	98.2	30.0	6.0	55	783
$CDCl_3$	99.4	30.2	4.8	54	771
CD_2Cl_2	99.7	30.5	4.8	55	778
$CDCl_3$[a]	98.8	29.9	4.7		
CD_2Cl_2[a]	99.0	30.3	4.8		

[a] Data from Ref. 8

the yield by using excess COD to prevent the formation of colloidal Pt particles. In fact, the formation of colloidal Pt can be avoided completely via the utilization of excess COD and slow addition of $Al(CH_3)_3$, as described in the Experimental section.

As shown in Table 1, ^{1}H NMR confirms the literature data.[1] The ^{13}C NMR spectral results are given in Table 2, including the $^{13}C-^{195}Pt$ coupling constants. The ^{13}C chemical shifts found in complex **1** are in good agreement with those reported in the literature.[8] In addition, the crystallographic data of complex **1**, as shown in Table 3, are consistent with those published in the literature.[2,9, 10]

CONCLUSION

Complex $[(COD)Pt(CH_3)_2]$ is available from simple starting materials in a one-pot procedure and can be isolated in high purity with 92% yield. Very recently, we found this complex to be a valuable precursor for the preparation of colloidal Pt particles and heterogeneous catalysts. This work is still in progress.

Acknowledgements

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Table 3. Crystal data of complex **1**

		Literature data		
	Complex **1**	Ref. 2	Ref. 9	Ref. 10
Temperature (K)	100	235	150	173
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	8.1268	8.129	8.134	8.1705
b (Å)	18.0430	18.217	18.105	18.222
c (Å)	7.2758	7.339	7.3117	7.3452
β (°)	115.607	115.899	115.708	115.890
Crystal colour	Colourless	Colourless	Colourless	Colourless
Volume (Å^3)	962.07	977.7		983.8

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