

# Evaluation of Heteroleptic Pt(II) $\beta$ -Diketonate Complexes as Precatalysts for the Photoactivated Curing of Silicone Resins

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## Supporting Information

### 1. General

All manipulations of air and moisture sensitive compounds were carried out using standard Schlenk techniques or in a glove box under an atmosphere of argon or dinitrogen. NMR spectra were recorded at 25°C on a Bruker Avance spectrometer working at 300 MHz (300.1 MHz for <sup>1</sup>H, 75.5 MHz for <sup>13</sup>C and 121.5 MHz for <sup>31</sup>P); chemical shifts ( $\delta$ ) are reported in units of ppm relative to the residual solvent signals and to external 85% H<sub>3</sub>PO<sub>4</sub> (for <sup>31</sup>P). UV-Vis analyses were carried out on a Varian CARY 100 Bio spectrophotometer. ESI-MS analyses were performed using a LCQ-Duo (Thermo-Finnigan) operating in positive ion mode. Instrumental parameters: capillary voltage 10 V, spray voltage 4.5 kV; capillary temperature 200 °C; mass scan range from 150 to 2000 amu; N<sub>2</sub> was used as sheath gas; the He pressure inside the trap was kept constant. The pressure directly read by an ion gauge (in the absence of the N<sub>2</sub> stream) was  $1.33 \times 10^{-5}$  Torr. Sample solutions were prepared by dissolving the compounds in acetonitrile. Sample solutions were directly infused into the ESI source by a syringe pump at 8  $\mu$ L/min flow rate. Elemental analyses were carried out by the microanalytical laboratory of Chemical Sciences Department (University of Padova) with a Fisons EA 1108 CHNS-O apparatus.

### 2. Preparation of [PtCl<sub>2</sub>(DMSO)<sub>2</sub>] [1]

The reagent was prepared by dissolving 0.3083 g (0.743 mmol) K<sub>2</sub>PtCl<sub>4</sub> in 10 ml water under air. 0.20 ml (2.8 mmol) DMSO were then added and the resulting solution was left to stand overnight. The product crystallized from the reaction solution as yellow needles, which were filtered off, washed with water and dried under air (199.0 mg, yield 63%). The product was used without further characterization.

### 3. Preparation of complex 1 [2]

A solution containing 0.10 ml (0.969 mmol) acetylacetone, 0.0265 g (0.472 mmol) KOH and 5 ml water was added dropwise to a suspension of 0.2041 g (0.483 mmol) [PtCl<sub>2</sub>(DMSO)<sub>2</sub>] in 10 ml water. The initially pale yellow suspension turned with time into a brighter yellow solution. After ca. 1 h

stirring a fluffy precipitate started to form. The greenish-yellow precipitate was separated by filtration after 24 h reaction time and dried in an oven at 60°C for 15 minutes. Yield 44.8 mg (23%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 5.60 (s, 1H, Cy-H/acac), 3.49 (s, 6H,  $J_{\text{H-Pt}}=24$  Hz,  $\text{CH}_3/\text{DMSO}$ ), 2.09 (s, 3H,  $\text{CH}_3/\text{acac}$ ), 2.06 (s, 3H,  $\text{CH}_3/\text{acac}$ ). Elemental analysis calcd. for  $\text{C}_7\text{H}_{13}\text{ClO}_3\text{PtS}$  (407.79 g/mol): C 20,62%, H 3,21%, S 7,89%; found C 20,41%, H 2,95%, S 7,21%.

#### 4. Preparation of complex 2 [2]

A solution containing 0.24 mL (2.3 mmol) acetylacetone and 0.0744 g (1.33 mmol) KOH in 3.5 mL MeOH was added dropwise to a suspension of 0.1990 g (0.471 mmol)  $[\text{PtCl}_2(\text{DMSO})_2]$  in 13 mL MeOH. The resulting mixture was stirred at room temperature for 24 h, after which the solvent was evaporated to dryness, yielding a yellow solid. The solid residue was then stirred together with 8 mL chloroform for 20 minutes. The resulting mixture was filtered and the filtrate was again evaporated to dryness. The resulting solid was then stirred together with 5 mL diethylether for 1 h. The residual solid was filtered off and dried in air. Yield 123.9 mg (56%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 5.58 (s, 1H, Cy-H/O,O'-acac), 4.84 (s, 1H, Cy-H/ $\gamma$ -acac,  $J_{\text{H-Pt}} = 122$  Hz), 3.35 (s, 6H,  $J_{\text{H-Pt}} = 24$  Hz,  $\text{CH}_3/\text{DMSO}$ ), 2.33 (s, 6H,  $\text{CH}_3/\gamma$ -acac), 2.05 (s, 3H,  $\text{CH}_3/\text{O},\text{O}'\text{-acac}$ ), 1.99 (s, 3H,  $\text{CH}_3/\text{O},\text{O}'\text{-acac}$ ). Elemental analysis calcd. for  $\text{C}_{12}\text{H}_{20}\text{O}_5\text{PtS}$  (471.41 g/mol): C 30.57%, H 4.28%, S 6.80%; found C 30.33%, H 4.55%, S 7.01%.

#### 5. Preparation of complex 3 [3]

30.0 mg (0.114 mmol) triphenylphosphine were added under stirring to a solution containing 38.4 mg (0.094 mmol) complex 1 in 4 mL chloroform. The solution was stirred at room temperature for 45 minutes, after which the solution was concentrated and treated with diethylether to precipitate the product. The resulting pale yellow solid was filtered off and dried in air. Yield 35.5 mg (64%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.73 (m, 6H, Ph), 7.45 (m, 3H, Ph), 7.39 (m, 6H, Ph), 5.39 (s, 1H, Cy-H/O,O'-acac), 2.02 (s, 3H,  $\text{CH}_3/\text{O},\text{O}'\text{-acac}$ ), 1.47 (s, 3H,  $\text{CH}_3/\text{O},\text{O}'\text{-acac}$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ): 0.40 ( $J_{\text{P-Pt}} = 4195$  Hz). Elemental analysis calcd. for  $\text{C}_{23}\text{H}_{22}\text{ClO}_2\text{PPt}$  (591.89 g/mol): C 46.67%, H 3.75%; found C 46.99%, H 3.91%.

#### 6. Preparation of complex 4 [3]

15.0 mg (0.057 mmol) triphenylphosphine were added under stirring to a solution containing 25.7 mg (0.054 mmol) complex 2 in 3 mL chloroform. The solution was stirred at room temperature for 1 h, after which the solution was concentrated and treated with pentane. The product crystallized out of the resulting solution upon cooling in the freezer. Yield 6 mg (17%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.69 (m, 6H, Ph), 7.45 (m, 3H, Ph), 7.40 (m, 6H, Ph), 5.42 (s, 1H, Cy-H/O,O'-acac), 3.94 (ds, 1H,  $J_{\text{H-P}} = 6$  Hz,  $J_{\text{H-Pt}} = 110$  Hz, Cy-H/ $\gamma$ -acac), 2.13 (s, 6H,  $\text{CH}_3/\gamma$ -acac), 2.02 (s, 3H,  $\text{CH}_3/\text{O},\text{O}'\text{-acac}$ ), 1.47 (s, 3H,  $\text{CH}_3/\text{O},\text{O}'\text{-acac}$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ): 4.51 ( $J_{\text{P-Pt}} = 4492$  Hz). Elemental analysis calcd. for  $\text{C}_{23}\text{H}_{22}\text{ClO}_2\text{PPt}$  (655.55 g/mol): C 51.30%, H 4.46%; found C 51.11%, H 4.31%.

#### 7. Preparation of complexes 5 and 6 [4]

95.9 mg (0.244 mmol)  $\text{Pt}(\text{acac})_2$  were dissolved in 1 mL pyridine under an inert atmosphere and heated under stirring at 100-110°C for 1 h. The initially yellow solution turns darker and becomes orange. 3.5 mL octane were then added and the resulting precipitate was separated by centrifugation and washed with additional 3.5 mL aliquots of hexane. The resulting off-white solid

was then extracted with diethylether (5x3.5 ml). The residual solid is complex **6**; yield 13.1 mg (10%). The combined diethylether phases from the extraction were concentrated and complex **5** was precipitated upon addition of 3.5 ml n-octane. The solid was centrifuged, washed with additional n-octane and subsequently dried under vacuum. Yield 38.0 mg (33%).

Complex **5**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 8.70 (ds,  $J_{\text{H-H}} = 6$  Hz,  $J_{\text{H-Pt}} = 43$  Hz, 2H, pyr), 7.80 (t,  $J_{\text{H-H}} = 6$  Hz, 1H, pyr), 7.34 (t,  $J_{\text{H-H}} = 6$  Hz, 2H, pyr), 5.50 (s, 1H,  $\text{C}\gamma\text{-H/acac}$ ), 5.05 (s,  $J_{\text{H-Pt}} = 129$  Hz, 1H,  $\text{C}\gamma\text{-H}/\gamma\text{-acac}$ ), 2.24 (s, 6H,  $\text{CH}_3/\gamma\text{-acac}$ ), 1.96 (s, 3H,  $\text{CH}_3/\text{O,O}'\text{-acac}$ ), 1.87 (s, 3H,  $\text{CH}_3/\text{O,O}'\text{-acac}$ ). Elemental analysis calcd. for  $\text{C}_{15}\text{H}_{19}\text{NO}_4\text{Pt}$  (472.38 g/mol): C 38.14%, H 4.05%, N 2.97%; found C 38.42%, H 3.95%, N 3.01%.

Complex **6**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 8.45 (ds,  $J_{\text{H-H}} = 6$  Hz,  $J_{\text{H-Pt}} = 39$  Hz, 4H, pyr), 7.80 (t,  $J_{\text{H-H}} = 6$  Hz, 2H, pyr), 7.43 (t,  $J_{\text{H-H}} = 6$  Hz, 4H, pyr), 4.29 (ss,  $J_{\text{H-Pt}} = 102$  Hz, 2H,  $\text{C}\gamma\text{-H}/\gamma\text{-acac}$ ), 1.87 (s, 12H,  $\text{CH}_3/\gamma\text{-acac}$ ). Elemental analysis calcd. for  $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4\text{Pt}$  (551.47 g/mol): C 43.55%, H 4.39%, N 5.08%; found C 43.42%, H 4.21%, N 5.21%.

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