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Synthetic Approaches to Organometallic Complexes for Electronics Applications

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Organic semiconductor chemistry has the potential for low start-up cost production of electronic devices such as transistors, sensors and organic solar panels.¹ However, there are a number of problems with classic organic semiconductors (e.g. polyacenes such as pentacene), including poor solubility and low stability. One of many possible workarounds to these problems is to synthesize organic acenes coordinated with metals (e.g., iron, manganese or ruthenium) to help improve solubility and stability as well as introduce enhanced electrical properties (smaller band gap), redox potentials (electrochemical switches) and new optical properties (electrochromism).

Figure 1: Synthesis of $[\text{Mn}(\text{CO})_3\{\eta^5\text{-C}_9\text{H}_3\text{-1,4-(4\text{-Tol})}_2\text{-2,3-(CO}_2\text{Me)}_2\}]$

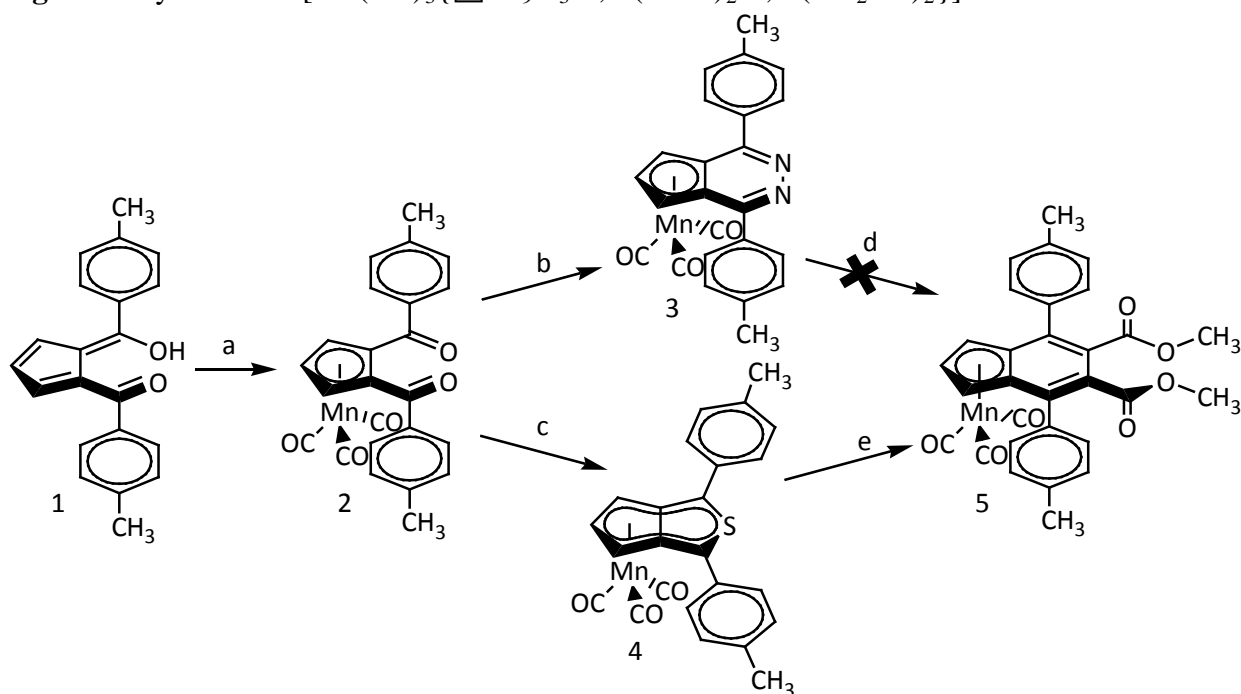


Figure 1: a. 1) Ti_2SO_4 , THF, 3 M KOH, H_2O , 3 h RT, 40%; 2) $\text{MnBr}(\text{CO})_5$, THF, 20 h reflux, 85%; b. N_2H_4 , MeOH, H_2O , 5 h reflux, 88%; c. P_4S_{10} , NaHCO_3 , CS_2 , 2 h reflux, 68%; d. Toluene, DMAD, 3 h reflux, 0%; e. Benzene, DMAD, 3 h reflux, 48%.

Cymantrene $[\text{Mn}(\text{CO})_3\{\eta^5\text{-C}_5\text{H}_5\}]$ and its derivatives are well studied and can be easily synthesized via thallium mediated transmetalation of fulvenes and manganese pentacarbonyl bromide.² Compound 1, a fulvene, can be easily synthesized from sodium cyclopentadiene and p-toluoyl chloride (54% yield), upon which reaction with thallium sulfate in THF/KOH selectively forms the insoluble thallium salt of compound 1 (40% yield), which can be easily isolated. (In this case, extensive purification of compound 1 does not increase the yield between the two steps)³ A reaction of compound 2 with phosphorus pentasulfide offers a facile, high

yielding (up to 68%) synthesis of compound 4, a thiophene.³ Diels-Alder of compound 3 with dimethyl acetylenedicarboxylate (DMAD) yields compound 5, an indenyl diester, with 48% yield.

Similar to the corresponding ruthenium complex, compound 4 (a pyridazine), can be synthesized from compound 2 upon refluxing in methanol and hydrazine hydrate with a high yield (88%).^{4,5} This method is preferred to the thiophene because of its higher yield, increased stability and conservative use of toxic reagents. Occasionally (especially in scales larger than 200 mg of compound 2), unreacted hydrazine ignites the reaction after the evacuation of solvent. Treatment with small amounts of water (5 mL) and limited exposure to air shortly after solvent evacuation can help alleviate this problem. Diels-Alder with analogous organic pyridazines and DMAD tend to require harsh conditions and long reaction times.⁶ Diels-Alder with compound 4 and DMAD tends to yield the demetallated analogue of compound 4 [1,2-C₅H₃(C-4-Tol)₂N₂H], compound 2 and intractable dark red oil. Further optimization of these reaction conditions may be required. Reduction and subsequent partial oxidation of the indenyl diester (compound 5) should yield compound 6, an indenyl dialdehyde. An aldol condensation of compound 6 with 1,4-naphthalenediol should yield the highly desirable compound 7, a manganese-complexed “pentacenequinone”. If possible, aromatization of compound 7 may yield a manganese-complexed acene, which may have desirable electronic properties.

Figure 2: Extension sequence for cymantrene-terminated acenequinones

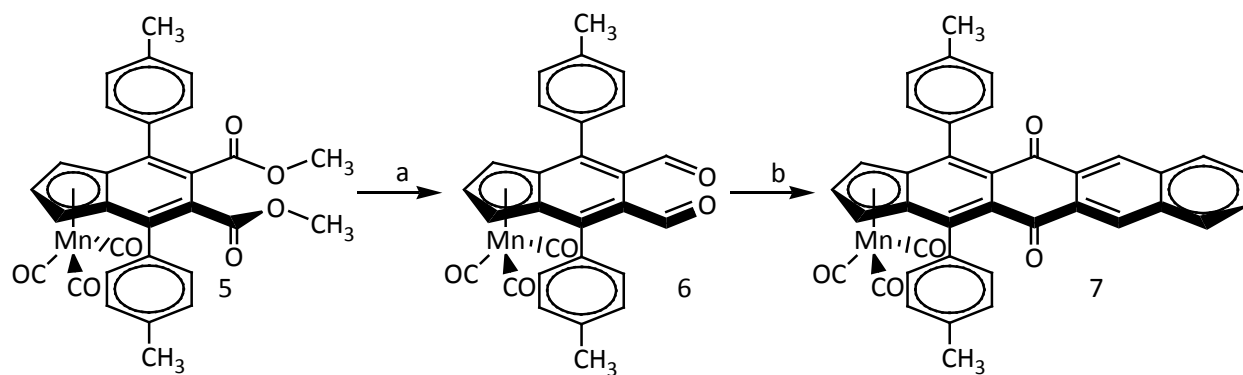


Figure 2: a. partial reduction, or full reduction with partial oxidation; b. aldol condensation with 1,4-naphthalenediol

Synthesis of [Mn(CO)₃{ η -1,2-C₅H₃(C-4-Tol)₂N₂}] (Compound 3)

Eighty-five percent hydrazine hydrate (15 drops) is added to a solution of compound 2 (105.3 mg) in methanol (40 mL, ACS grade) in a 125 mL nitrogen flushed Schlenk flask equipped with a condenser and a magnetic stir bar. The reaction is allowed to reflux and vigorously stir for 3 hours. Monitoring by TLC also shows the formation of small amounts of 1,2-C₅H₃(C-4-Tol)₂N₂H.

The workup consists of careful evacuation of solvent and water, followed by the addition of 5 mL distilled water to help prevent ignition from any unreacted hydrazine. The resulting precipitate is filtered and chromatographed in silica with a 2:3 mixture of ethyl acetate to hexanes. The second fraction is collected and solvent evacuated to yield $[\text{Mn}(\text{CO})_3\{\text{C}_9\text{H}_3\text{-1,2-C}_5\text{H}_3(\text{C-4-Tol})_2\text{N}_2\}]$ (92.8 mg, 88% yield, m.p. 218-220 °C, decomposed), in the form of yellow needle crystals.

^1H NMR (400 MHz, C_6D_6 , ppm): δ 2.135 (s, 6H, Me), 4.244 (t, 1H, $^3\text{J} = 2.8$ Hz, CHCHCH), 4.731 (d, 2H, $^3\text{J} = 2.8$ Hz, CHCHCH), 7.096 (d, 4H, $^3\text{J} = 7.6$ Hz, Ar), 7.982 (d, 4H, $^3\text{J} = 8.4$ Hz, Ar)

Synthesis of $[\text{Mn}(\text{CO})_3\{\text{C}_9\text{H}_3\text{-1,4-(4-Tol)}_2\text{-2,3-(CO}_2\text{Me)}_2\}]$ (Compound 5)

Via cannula, a dry, nitrogen flushed solution of compound 4 (50 mg in 30 mL benzene, distilled) is transferred to a dry, nitrogen flushed 125 mL Schlenk flask mounted with a condenser and a magnetic stir bar, to which distilled and dry DMAD (1 mL) is added to via syringe. The reaction is allowed to reflux for 3 hours, during which the reaction color slowly proceeds to yellow. Monitoring the reaction by TLC also shows the formation of compound 2.

The reaction mixture solvent is then evacuated without heating and allowed to sit under a 150 μmHg vacuum at room temperature for 1 hour, during which unreacted DMAD is partially removed (or seen to reflux). The brown oil is then transferred onto a densely packed silica column in hexanes and allowed to elute with a gradient of hexane to 1:1 mixture of diethyl ether and hexane, which effectively removes unreacted DMAD. The second visible (pale yellow) fraction is then collected, solvent evacuated, and triturated with cold pentane to yield a pale yellow powder (29.9 mg, 48% yield, m.p. 54-56 °C).

^1H NMR (400 MHz, C_6D_6 , ppm): δ 2.025 (s, 6H, Me), 3.110 (s, 6H, Me), 3.885 (t, 1H, $^3\text{J} = 2.4$ Hz, CHCHCH) 4.483 (d, 2H, $^3\text{J} = 2.4$ Hz, CHCHCH), 7.506 (d, 4H, $^3\text{J} = 8.0$ Hz, Ar), 6.941 (d, 4H, $^3\text{J} = 7.6$ Hz, Ar)

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