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Synthetic Approaches to Manganese-Complexed Acenes for Electronics Applications

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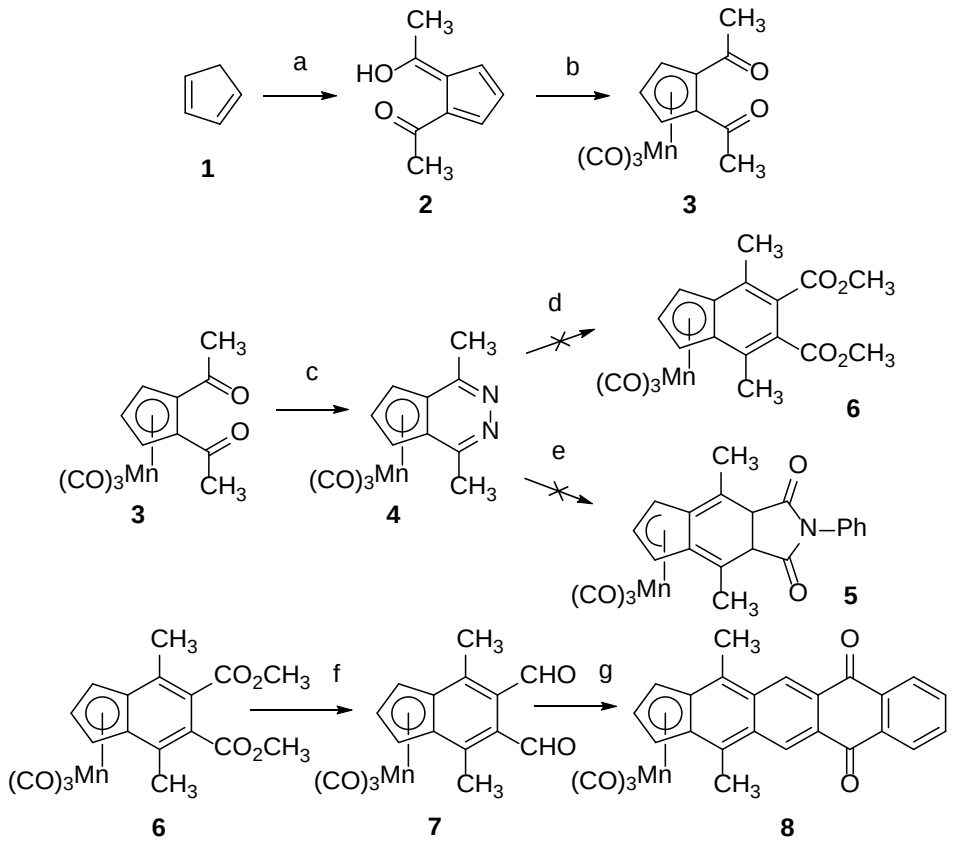
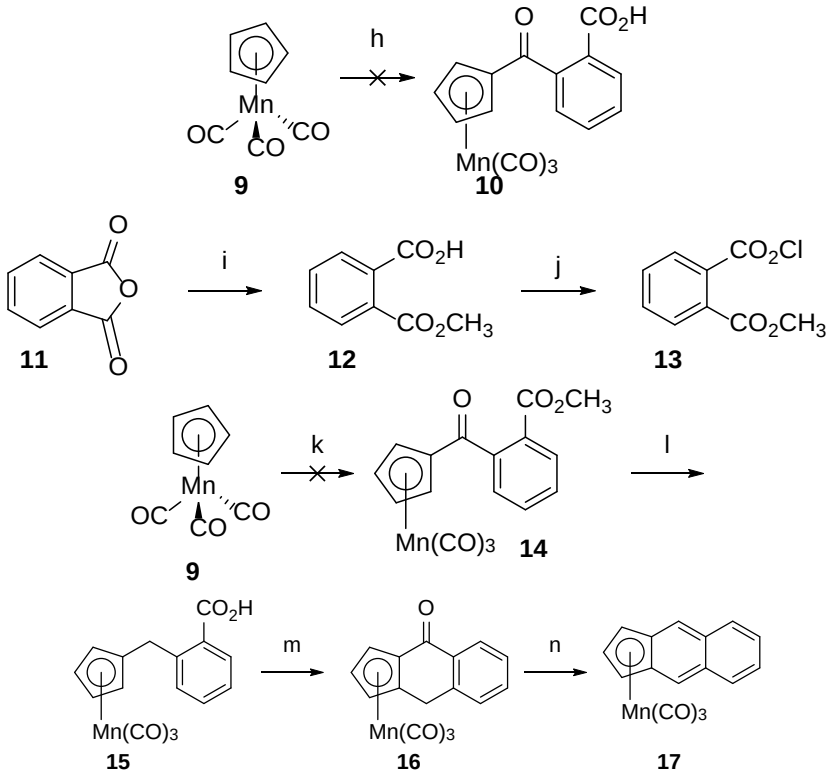
Organic chemistry has the potential for a low start-up cost for the production of electronic devices such as transistors, sensors and solar cells. Unfortunately, there are a number of problems with classic organic semiconductors, (e.g., polyacenes such as pentacene) including poor solubility and low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

The main purpose of this research is to find practical methods to produce such organometallic complexes as well as to characterize these compounds using a number of different spectroscopic techniques including IR spectra, ^{1}H-NMR, ^{13}C-NMR and X-ray crystallography. If the target compounds are synthesized, they will be examined in electrochemical studies for optoelectronic applications.



Scheme 1: *a. THF, Na, Cp, acetyl chloride; b. 1. TlOEt, Et_2O, 2. $MnBr(CO)_5$, THF or C_6H_6 c. MeOH, N_2H_4, 90 min, reflux, >95%; d. DMAD, benzene or DCM, reflux or RT, 0%; e. N-phenylmaleimide, hydroquinone, benzene, RT, days, 0%; f. full reduction followed by partial oxidation; e. double aldol condensation*

Two possible approaches to manganese-complexed acenes have been explored. The first approach involves double aldol condensations of manganese-complexed indenyl dialdehydes. Previous work explored this approach through Diels-Alder cycloaddition of dimethyl acetylenedicarboxylate (DMAD) with manganese-complexed thiophenes prepared from 1,2-C_5H_3(C-4-TolOH)(CO-4-Tol).[1] Our current approach attempts Diels-Alder cycloaddition of pyridazine **4** with DMAD to prepare the indenyl diester **6** and N-phenylmaleimide to test the reactivity of **4** towards dienophiles. These reactions typically yielded many products, but compounds **5** and **6** could not be isolated or characterized. Reduction and subsequent partial oxidation of the indenyl diester should yield **7**, an indenyl dialdehyde. An aldol condensation of **7** with 1,4-naphthalenediol should yield the highly desirable complex **8**, a manganese-complexed "pentacenequinone". If possible, aromatization of **8** may yield a manganese-complexed acene, which may have desirable electronic properties. The first approach is outlined in Scheme 1.



Scheme 2: *h. n-BuLi, phthalic anhydride, attempted in Et_2O, hexanes and THF, -78 ^oC i. MeOH reflux, 5 h, 100%; j. $SOCl_2$, DMF, toluene, reflux at 95 ^oC, 100%; k.* ***13****, $AlCl_3$, CS_2, Et_2O, reflux, 4 d; l. ester saponification followed by full ketone reduction; m. cyclization; n. aromatization.*

A second approach to organometallic acenes is through Friedel-Crafts reaction of metallocenes with the phthalic mixed acyl chloride/ester (**13**). The resulting product then can be reduced and cyclized to build the correct carbon framework. An attempt at aromatization should form the desired organometallic acene. This approach is outlined in Scheme 2. Unfortunately, previous work on the aromatization of similar ferrocenequinones resulted in dimerized products.[2] Due to the electron deficiency of manganese (compared to iron), aromatization may be more viable in cymantrene-fused acene/napthoquinones and anthrones. Reaction *k* was attempted by modifying literature conditions for the corresponding reaction with ferrocene.[3] A second attempt was made by modifying literature conditions for similar Friedel-Crafts

reactions with cymantrene.[4,5] An alternative direct approach to the acid form of **13** (**10**) was attempted with phthalic anhydride and *n*-butyllithium, but yielded only the butylated phthalic anhydride.

Future work on this project will attempt to optimize Friedel-Crafts reaction of cymantrene with **13** or find other routes to compound **10** or **14**. Compound **14** can be converted to **10** by hydrolysis of the ester. Compounds **10** will then be reduced to **15**. Compound **15** will be cyclized and the aromatization of **16** can be attempted following the routes attempted in the corresponding ferrocene complex in previous work in the group.[1]

Experimental

General: All reagents, catalysts, and solvents were obtained from commercial sources and used without further purification unless otherwise noted. Reaction flasks were nitrogen purged or flushed by evacuating oven-baked glassware to less than 300 μmHg and refilling with dry nitrogen gas at least three times. Solvents for reactions were dried over sodium wire with benzophenone and distilled, except for CH_2Cl_2, which was dried over calcium hydride and distilled. CS_2 and DMAD were dried over activated molecular sieves and distilled. Solution ^{1}H NMR spectra were collected on a Bruker 400 MHz instrument with $CDCl_3$, DMSO-d_6 or C_6D_6 as solvent. Chemical shifts are reported in ppm relative to residual solvent peaks (δ = 7.26, 7.16 or 2.50 ppm, respectively). All IR spectra were collected on a germanium crystal ATR Nicolet iS10 FT-IR spectrometer.

Synthesis of 1,2-$C_5H_3(CCH_3OH)(COCH_3)$ (2). A sodium cyclopentadiene solution is prepared by adding excess (15 mL, 11.79 g, 0.178 mol, 66.1 g/mol, 0.786 g/mL) freshly cracked cyclopentadiene monomer in four batches to a nitrogen-flushed 250 mL side arm flask, equipped with a magnetic stir bar and containing very dry THF (150 mL) and sodium wire (3.775 g, 164.2 mmol, 22.99 g/mol), with slow stirring (to reduce sodium wire clumping) and at 0 ^{o}C over an ice bath (to slow cyclopentadiene dimerization) until all the sodium wire dissolves (about 1 h if the sodium wire does not clump). Over ice, acetyl chloride (7.76 mL, 8.47 g, 109 mmol, 78.49 g/mol, 1.104 g/mL) is added dropwise for 15 min to the clear sodium cyclopentadienide solution, which immediately becomes red. The reaction is vigorously stirred for 2 more h.

The contents of the flask are emptied into a 250 mL separatory funnel and washed with a hydrochloric acid solution (3 M, 50 mL). A white precipitate forms immediately, but then quickly dissolves after shaking. The dark red organic phase is collected and the yellow aqueous phase is washed three times with 15 mL portions of ethyl ether (or until the aqueous phase becomes colorless). The organic phases are combined, dried with magnesium sulfate and sodium bicarbonate and solvent evacuated with a rotovap and then Schlenk-line vacuum at 300 μmHg. The dark red liquid is then distilled at 0.9–1.3 mmHg, with the desired compound collected as a light yellow liquid at 60-80 ^{o}C (4.2 g, crude yield of 41%). The compound should be kept dry, cool and in a dark location (otherwise visible decomposition occurs within hours). **^{1}H NMR (400 MHz, $CDCl_3$, ppm):** δ 2.55 (s, 6H, Me), 6.40 (t, 1H, ^{3}J = 3.4 Hz, CHC*H*CH), 7.33 (d, 2H, ^{3}J = 3.4 Hz, C*H*CHC*H*), 18.14 (s, 1H, OH)

Synthesis of [Tl{1,2-$C_5H_3(COCH_3)_2$}] (thallium salt of 2). The fulvene from the previous step is dried under a flow of nitrogen with magnesium sulfate and extracted, via cannula, with freshly distilled THF (120 mL) into a dry, nitrogen-flushed 250 mL Schlenk flask containing a magnetic stir bar and capped with a septum. From a tared syringe, thallium ethoxide (1.35 g, 5.41 mmol, 249.44 g/mol) is added dropwise with the immediate formation of a white precipitate (appears yellow in solution). The reaction mixture is vigorously stirred for 2 more h and passed through a fine frit. The filtrand is washed with cold ethyl ether to yield the thallium salt of fulvene as a fine, cream-colored powder (1.82 g, 95% based on thallium ethoxide). Excess unreacted fulvene is immediately recovered via rotovap and Schlenk-line vacuum and then stored to prevent decomposition. The salt can be stored for months without significant

decomposition. **^{1}H NMR (400 MHz, DMSO-d_6, ppm):** δ 2.27 (s, 6H, Me), 5.60 (t, 1H, ^{3}J = 3.3 Hz, CHC*H*CH), 6.40 (d, 2H, ^{3}J = 3.3 Hz, C*H*CHC*H*)

Synthesis of [Mn(CO)$_3${η^5-1,2-$C_5H_3(COCH_3)_2$}] (3). To a dry, nitrogen-flushed 125 mL Schlenk flask equipped with a magnetic stir bar and a reflux condenser, the thallium fulvene salt (250 mg, 0.707 mmol, 353.55 g/mol) and $MnBr(CO)_5$ (195 mg, 0.709 mmol, 274.89 g/mol) are added and degassed via Schlenk-line vacuum. Freshly distilled benzene (45 mL) is added to the mixture, stirred and refluxed for 13 h (the reaction can also be run with THF and a 16 h reaction time with similar yields). The reaction is observed to undergo three color changes: light yellow, to light orange, to a white precipitate/light yellow color.

The precipitate (thallium bromide) is filtered through a thick pad of celite, washed with ethyl ether and the solvent in the filtrate is evacuated via rotovap and Schlenk-line vacuum at 300 μmHg at room temperature. The red semi-solid is triturated with cold pentane to yield the diketone as a light yellow solid (179 mg, 88%). Further purification is possible with chromatographic techniques (using silica gel, eluted with 1:5 ethyl ether:hexanes). The compound may remain liquid when containing small amounts of impurities. Slow crystallization will occur with pressures less than 300 μmHg. **^{1}H NMR (400 MHz, C_6D_6, ppm):** δ 1.97 (s, 6H, Me), 3.56 (t, 1H, ^{3}J = 2.8 Hz, CHC*H*CH), 4.34 (d, 2H, ^{3}J = 2.8 Hz, C*H*CHC*H*)

Synthesis of [Mn(CO)$_3${η^5-1,2-$C_5H_3(CCH_3)_2N_2$}] (4). The diketone (105 mg, 0.364 mmol, 288.13 g/mol) and ACS grade methanol (50 mL) are added to a nitrogen-flushed Schlenk flask equipped with a magnetic stir bar and reflux condenser. An excess of hydrazine hydrate (85%, 20 drops) is added to the reaction mixture, stirred and refluxed for 90 min (or when all the diketone has reacted) while being monitored by TLC. The reaction mixture takes on a slightly lighter yellow color during the process.

The solvent is carefully evacuated on the rotovap until less than 1 mL of the methanol/hydrazine mixture remains. The reaction is then quenched with water without exposure to air. Immediately, a bright yellow precipitate forms. This precipitate may be filtered with slight loss of yield and air dried. Alternatively, the precipitate may be extracted with ethyl ether, dried with magnesium sulfate and solvent evacuated with rotovap and Schlenk-line vacuum to yield a light yellow/orange solid (103 mg, 99%). Impurities can be removed with chromatographic techniques (on silica gel, eluted with EtOAc). The pyridazine decomposes slowly when kept in air in solution, but can be stored as a solid. **^{1}H NMR (400 MHz, C_6D_6, ppm):** δ 2.344 (s, 6H, Me), 4.013 (s, 3H, C*H*C*H*C*H*)

Attempted synthesis of [Mn(CO)$_3${η^3-C_9H_5-1,4-$(CH_3)_2$-2,3-$(CO)_2NC_6H_5$}] (5)
General procedure: Compound **4** (1 equiv.) and N-phenylmaleimide (1.1 equiv, 173.17 g/mol) was added to a dry, nitrogen-flushed Schlenk flask that was equipped with a magnetic stir bar and reflux condenser. Freshly distilled solvent (20-40 mL for 50-100 mg of **3**) was added to the reaction flask and the reaction was vigorously stirred/refluxed and monitored by TLC until sufficient product is formed or all starting material has been consumed.

Attempt 1: Used compound **4** (79.3 mg, 0.28 mmol, 284.15 g/mol), N-phenylmaleimide (105 mg, 0.606 mmol, 173.17 g/mol), hydroquinone (30 mg) and 40 mL freshly distilled benzene as solvent. The same conditions as above were used. The reaction vessel is wrapped with aluminum foil and stirred at room temperature for 48 h. The reaction progress is monitored by TLC as the reaction color changes from yellow to green. TLC indicates the formation of a blue product. Chromatography on a column of silica (eluted with Et_2O) yields a blue powder (less than 8.2 mg) which appears to be NMR silent. The starting material is recovered (76 mg, 95%).

Test reactions with similar conditions indicate that **4** does not react with hydroquinone, nor does hydroquinone react with N-phenylmaleimide at these conditions. Reaction in a non-N_2-flushed flask also yields the blue compound, therefore this is likely an oxidation product.

Attempt 2: The same conditions were used as in attempt 1. The reaction was more carefully N_2 purged and monitored by TLC to yield yellow product in replacement of the blue band (R_f is close to but less than R_f for N-phenylmaleimide). Isolation of the product with column workup yielded < 10 mg of yellow semi-solid. ^{1}H NMR analysis leads to the conclusion that this may be a demetallated decomposition product (no peaks in the Cp-proton region).

Attempted synthesis 4: [Mn(CO)$_3${η^5-C$_9$H$_3$-1,4-(CH$_3$)$_2$-2,3-(CO$_2$CH$_3$)$_2$}] (5)

General procedure: The pyridazine (**3** ,1 equiv., 284.15 g/mol) is dissolved in the selected solvent (15-30 mL) in inert conditions in a 50 mL round bottom flask capped with a septum and transferred via cannula to a dry, aluminum foil wrapped, nitrogen-flushed Schlenk flask equipped with a magnetic stir bar and reflux condenser. The cannula and round bottom flask are washed with the selected solvent (10 mL) again to recover all of the pyridazine. To the stirred solution, with a backflow of nitrogen, an excess of DMAD (8 equivalents) is added. The mixture is refluxed until all starting material has been consumed (monitored by TLC, eluted with pure EtOAc, Et_2O or a mixture with hexanes can be used depending on which band needs to be eluted).

The reaction mixture is cooled and solvent evacuated. The oily mixture is then chromatographed on a column of silica (giving a multiple bands that alternate in red and yellow color) with EtOAc to yield multiple fractions of red to yellow oil, which are triturated with cold pentane to yield crude semi-solid material. ^{1}H NMR of each fraction is often too broad to interpret or contains many complex peaks in the Cp and ester regions of the spectrum. The desired product does not appear to be present. All reaction conditions attempted gave the same result.

Reaction conditions attempted

Solvent	Temperature	Duration
Benzene	Reflux	1 h
Benzene	RT	18 h to 3 d
Hexanes	Reflux	1 h
Hexanes	RT	18 h

Attempted Synthesis of [Mn(CO)$_3${η^5-1-C$_5$H$_3$(CO-2-C$_6$H$_4$CO$_2$H)}] (10). A solution of cymantrene (200 mg, 0.98 mmol, 204 g/mol) is dissolved in 20 mL of very dry THF in a dry, nitrogen-flushed 125 mL Schlenk flask capped with a septum. The solution is cooled to -77 ^{o}C using a dry ice/acetone bath and *n*-BuLi (1 mL, 0.98 mmol, pretitrated at 0.98 M in hexanes) is added dropwise to the solution. The reaction mixture is stirred for one h and gives a light brown color. A previously prepared solution of phthalic anhydride (163 mg, 1.1 mmol, 148.12 g/mol) in very dry THF (5 mL) is added dropwise via cannula. After five h the solution is dark red.

The reaction mixture is quenched with ice water and a dilute HCl solution. The solvent is evacuated to yield a light yellow powder. Aqueous extraction is attempted in Et_2O but has no phase separation. Chromatography on silica gel with an elution gradient from hexanes to EtOAc/MeOH yields full recovery of cymantrene and the phthalic mixed acid/butyl ester. [are you sure about the ester?] This reaction was initially attempted with dry hexanes as the solvent with the same result.

Synthesis of 1-(CO_2H)-2-(CO_2CH_3)-C_6H_4 (12). Phthalic anhydride (2.02 g, 13.6 mmol, 148.12 g/mol) is added to Na_2SO_4-dried reagent grade MeOH (50 mL) in a dry Schlenk flask equipped with a magnetic stir bar and reflux condenser. The reaction is stirred and refluxed for 5 h. The MeOH is removed via rotovap to yield a tan liquid. The liquid is dissolved in 30 mL of $CHCl_3$ and cooled to -20 ^oC for 20 min. The few small white crystals are filtered away and the $CHCl_3$ is removed from the mother liquor via rotovap. Crystals form slowly from the resulting oil to yield **14** (2.30 g, 94%). **^{1}H NMR (400 MHz, $CDCl_3$, ppm):** δ 3.914 (s, 3H, Me), 7.643-7.581 (m, 2H), 7.766-7.719 (m, 1H), 7.851-7.807 (m, 1H)

Synthesis of 1-(CO_2Cl)-2-(CO_2CH_3)-C_6H_4 (13). The phthalic mixed ester/acid **12** (2.30 g, 12.8 mmol, 180.16 g/mol) is added to a stirred solution of $SOCl_2$ (1.9 mL, 3.05 g, 25.6 mmol, 118.97 g/mol) in dry toluene (12 mL) with DMF (6 drops) in a dry, nitrogen-flushed Schlenk flask equipped with a reflux condenser. The reaction is placed into a pre-heated 95 ^oC oil bath and stirred for 1 h. The solvent is then evacuated at 10-20 μmHg to yield **13** quantitatively as tan oil. Compound **13** should be pure enough for further reactions. Purity can be confirmed by ^{1}H NMR. **^{1}H NMR (400 MHz, $CDCl_3$, ppm):** δ 3.895 (s, 3H, Me), 7.592-7.518 (m, 2H), 7.666-7.648 (m, 1H), 7.901-7.883 (m, 1H)

Attempted Synthesis of [$Mn(CO)_3${η^5-1-C_5H_3(CO-2-$C_6H_4CO_2CH_3$)}] (14)

Attempt 1: A solution of the acyl chloride **13** (388 mg, 1.96 mmol, 198.6 g/mol) is prepared in 5 mL of freshly distilled CS_2 in a dry, nitrogen-flushed flask capped with a septum. A solution of $AlCl_3$ in Et_2O is prepared by equipping a dry 25 mL sidearm flask with a solid addition sidearm containing freshly sublimed $AlCl_3$ (261 mg, 1.96 mmol, 133.3 g/mol). Et_2O is added through the gas inlet and frozen with liquid nitrogen and placed under vacuum. The flask is purged with dry nitrogen gas as the Et_2O melts (to degas the Et_2O and prevent the Et_2O from condensing in the solid addition sidearm). The $AlCl_3$ is added slowly to the cold Et_2O (the reaction is very exothermic).

To a solution of cymantrene (200 mg, 0.98 mmol, 204 g/mol) in dry Et_2O in a 125 mL Schlenk flask the acyl chloride/CS_2 solution is added via cannula dropwise. The reaction mixture is heated to reflux and the $AlCl_3$/Et_2O solution is added dropwise over the course of 2 min via cannula. Immediately an oily brown precipitate is observed. After 24 h of reflux, a second batch of $AlCl_3$, as prepared previously, is added.

The reaction mixture is poured over ice in a separatory funnel, with the immediate formation of white precipitate. The reaction flask is washed with Et_2O, which is also added to the separatory funnel. The aqueous phase is acidified with concentrated hydrochloric acid to a pH of approximately 2. The mixture is vigorously shaken and the organic phase is separated and kept. Three more extractions (and shaking) with Et_2O (10 mL) are done or until the aqueous phase is colorless. The organic phases are combined and dried with anhydrous $MgSO_4$. The organic phase is filtered and the solvent evacuated via rotovap to yield red oil. The red oil is chromatographed on silica with a gradient from hexanes to DCM to EtOAc to yield recovered cymantrene (139 mg, 70 % recovery), phthalic acid, the mixed acid/ester **12** and intractable dark red oil that was not characterized.

Attempt 2: A solution of cymantrene (200 mg, 0.98 mmol, 204 g/mol) and the acyl chloride **13** (195 mg, 0.98 mmol, 198.6 g/mol) is prepared in dry CH_2Cl_2 in a dry, nitrogen-flushed Schlenk flask equipped with solid addition sidearm containing freshly sublimed $AlCl_3$ (668 mg, 5.02 mmol, 133.3 g/mol). The reaction mixture is cooled to 0 ^oC in an ice bath and half of the $AlCl_3$ is added slowly over the course of 15 min. The reaction mixture is allowed to warm to room temperature and is stirred for 2 d, when the rest of the $AlCl_3$ is added at 0 ^oC in one batch. The reaction mixture is a dark red color. The reaction is allowed to stir for 3 more d and is monitored by TLC for the disappearance of cymantrene.

The workup is the same as in attempt 1. Chromatography yields cymantrene (25 mg, 13 % recovery), an unknown yellow compound (44 mg), phthalic acid and the mixed acid/ester **12**. The intractable red

material was not washed out of the column. The unknown yellow compound appears to be a mixture of two compounds that are inseparable by chromatography and appears consistently in repeated trials of this procedure. The unknown compound does contain metal carbonyl functionality (visible in the IR spectra) and characteristic Cp protons for monosubstituted cymantrene in the ^{1}H NMR spectra, but is missing the expected aromatic protons. A possible structure for the unknown has not been solved.

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