

Synthesis, Characterization, and Structure of Cyclopenta[*c*]thiophenes and Their Manganese Complexes

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Cyclopenta[*c*]thiophenes (**2**, Scheme 1) and η^5 -cyclopenta[*c*]thienyl complexes are useful in a broad range of applications. For example, several cyclopenta[*c*]thiophenes exhibit significant anti-tumor properties.^{1,2} Heterocycle-fused cyclopentadienyl, including cyclopenta[*c*]thienyl, zirconium complexes effectively catalyze the regioselective polymerization of 1-alkenes.^{3–6} We have a long-term interest^{7–10} in the electronic properties of organometallic analogues of the low-band-gap polymer poly(benzo[3,4-*c*]thiophene) (polyisothianaphthene)^{11–14} that incorporate η^5 -cyclopenta[*c*]thienyl monomers.

4*H*-Cyclopenta[*c*]thiophene¹⁵ (2-thiapentalene) and its 1,3-dichloro,¹⁵ 1,3-dimethyl,¹⁶ and 1,3,5-trimethyl⁶ derivatives have been prepared from 2,5-disubstituted thiophenes via multistep conversions that include low-yielding halomethylation and malonic ester steps. Even with an optimized^{17,18} synthesis of 1,3-dimethyl-5-oxo-5,6-dihydro-4*H*-cyclopenta[*c*]thiophene,¹⁹ scaling up the preparation of **2a** is difficult. All of these methods involve closure of a cyclopentadienyl ring on the [3,4-*c*] edge of a thiophene. The alternative approach, closure of a thiophene ring on a cyclopentadiene, has not been used to prepare cyclopenta[*c*]thiophenes. We report here a convenient, versatile preparation of several cyclopenta[*c*]thiophenes and cyclopenta[*c*]thienyl complexes.

1,2-Diacylcyclopentadienes are easily prepared by reactions of acyl halides with cyclopentadienyllithium.^{7,8,17,18,20–22} The compounds exist as 2-acyl-6-hydroxyfulvenes (Scheme 1, **1a–h**), shown by enolic ¹H NMR resonances at δ 18–20. Thiation of 1,4-diketones to thiophenes by using H₂S,²³ P₄S₁₀,²⁴ or 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide (Lawesson's reagent, LR)²⁵ is well preceded; for example, treatment of 1,2-dithienoylbenzene with LR gives 1,3-di(2-thienyl)benzo[*c*]thiophene in 83% yield.²⁶ Accordingly, treatment of 1,2-diaroylcyclopentadienes **1c**, **1f**, and **1g** with LR in refluxing toluene produces 1,3-diaryl-4*H*-cyclopenta[*c*]thiophenes (**2c**, 22%; **2f**, 15%; **2g**, 8%). Despite the modest yields, this two-step synthesis leads to cyclopenta[*c*]thiophenes with aryl substituents that would interfere with the electrophilic substitution steps of previous syntheses. Unfortunately, the LR method fails for 1,2-diacylcyclopentadienes with aliphatic acyls, including **1a,b**.

Two logical approaches to η^5 -cyclopenta[*c*]thienyl complexes are to attach a preformed cyclopenta[*c*]thienyl group to a metal center or to attach a suitable precursor ligand to a metal center, followed by closure of the thiophene ring. Using the first approach, 4*H*-cyclopenta[*c*]thienyl anions are too strongly reducing to undergo substitution reactions with metal halides. For example, lithiated **2a** reacts with [MnBr(CO)₅] to give mainly [Mn₂(CO)₁₀] and an

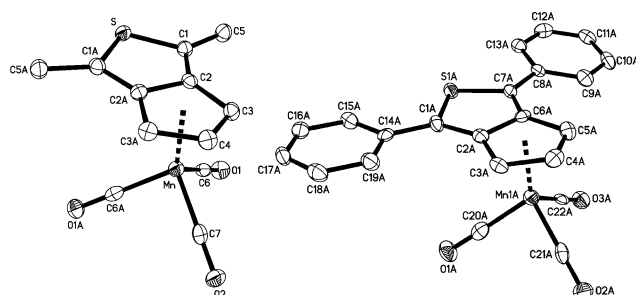


Figure 1. Thermal ellipsoid plots of the molecular structures of [Mn(η^5 -SC₇H₃-1,3-Me₂)(CO)₃] (**3a**, left) and [Mn(η^5 -SC₇H₃-1,3-Ph₂)(CO)₃] (**3c**, right). Hydrogen atoms are omitted for clarity.

oxidatively coupled bis(4*H*-cyclopenta[*c*]thiophene).¹⁷ In contrast, reactions of lithiated **2a** and **2c** with Me₃SnCl form isolable tin intermediates, [SnMe₃(SC₇H₃-1,3-R₂)], which react smoothly with [MnBr(CO)₅] to give [Mn(η^5 -SC₇H₃-1,3-R₂)(CO)₃] (**3a**, R = Me, 94%; **3c**, R = Ph, 90%).

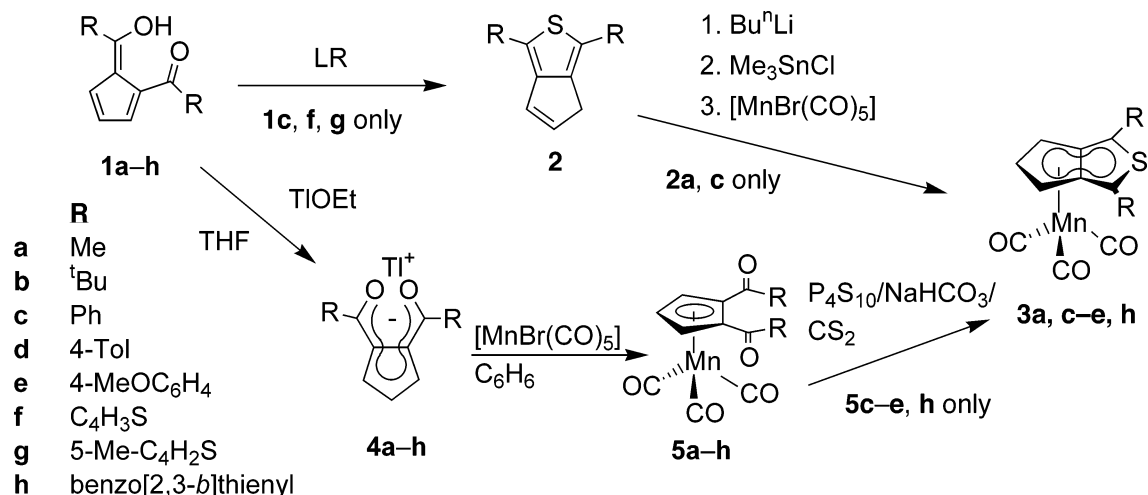
These new cyclopenta[*c*]thienyl complexes were characterized spectroscopically²⁷ and crystallographically.²⁸ Plots of the molecular structures of **3a** and **3c** are shown in Figure 1. The cyclopenta[*c*]thienyl ligands are planar to within 0.021(2) Å for **3a** and 0.026(3) and 0.025(3) Å for the two independent molecules of **3c**. Similar to η^5 -indenyl complexes, the manganese atom is displaced away from the ring-fusion bond of the cyclopenta[*c*]thienyl ligand (average Mn–C distances: 2.255(2) Å to fused vs 2.123(3) Å to nonfused carbons for **3a**; 2.249(4) Å to fused vs 2.123(4) Å to nonfused carbons for **3c**), reflecting the low π -bond order for the ring-fusion carbon in a cyclopenta[*c*]thienyl anion.²⁹ The phenyl substituents of **3c** are slightly out of coplanarity with the cyclopenta[*c*]thienyl system, tilted by 11.48(7), 4.14(6), 19.7(1), and 14.19(9)° and twisted by torsion angles of 3.4(7), 10.1(7), 13.4(7), and 18.7(7)° for the two independent molecules of **3c**.

A second approach to an η^5 -cyclopenta[*c*]thienyl complex entails coordination of a 1,2-diacylcyclopentadienyl ligand (**1**) followed by closure of the thiophene ring. Coordination of 1,2-diacylcyclopentadienyl to [Mn(CO)₃] is accomplished by deprotonation of **1a–h** with thallium(I) ethoxide in THF to give thallium reagents **4a–h**, followed by reaction with [MnBr(CO)₅] to give diacyl complexes [Mn{ η^5 -1,2-C₅H₃(COR)₂}(CO)₃] (**5a–h**) in high yield. Reactions of **5a–h** with Lawesson's reagent do not cleanly close the acyl groups to thiophenes, but the method used by Kursanov^{30,31} to convert monoacyl cymantrenes to thiones works well. Reactions of [Mn{ η^5 -1,2-C₅H₃(COR)₂}(CO)₃] (**5c–e,h**) with P₄S₁₀/NaHCO₃ in refluxing CS₂ give [Mn(η^5 -SC₇H₃-1,3-R₂)(CO)₃] (**3c**, 35%; **3d**, 33%; **3e**, 21%; **3h**, 33%). The procedure efficiently gives η^5 -cyclopenta[*c*]thienyl complexes, but unfortunately, it is so far limited to aromatic acyl groups. Reactions of aliphatic (**5a,b**) or simple thienyl (**5f,g**) η^5 -1,2-diacylcyclopentadienyl complexes with P₄S₁₀/NaHCO₃ give deeply colored solutions, but we have not been

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Scheme 1. Synthesis of 1,3-Diaryl-4*H*-cyclopenta[*c*]thiophenes and Their Manganese Complexes

able to isolate η^5 -cyclopenta[*c*]thienyl products, even **3a** that is clearly stable.

In summary, 1,3-diaryl-4*H*-cyclopenta[*c*]thiophenes are efficiently prepared from 1,2-diaroylcyclopentadienes by use of Lawesson's reagent. η^5 -Cyclopenta[*c*]thienyl complexes, [Mn(η^5 -SC₇H₃-1,3-R₂)(CO)₃] (**3a,c**; R = Me, Ph), are prepared in high yield by ligand substitution reactions of [MnBr(CO)₅] with [SnMe₃(SC₇H₃-1,3-R₂)]. Alternatively, thiation with P₄S₁₀/NaHCO₃ converts [Mn(η^5 -1,2-C₅H₃(COR)₂)(CO)₃] (**5c-e,h**) to [Mn(η^5 -SC₇H₃-1,3-R₂)(CO)₃] (**3c-e,h**; R = Ph, 4-tolyl, 4-MeOC₆H₄, benzo[2,3-*b*]thienyl).

Acknowledgment. We thank the Research Corporation, the U.S. Department of Energy (DE-FG02-00ER45847), and the University of Kentucky Research Challenge Trust Fund for support.

Supporting Information Available: General procedures; syntheses and spectroscopic data for **1d-h**, **2c,f,g**, **3a,c-e,h**, **4a,b,d-h**, and **5a-h**; tables of crystallographic details, atomic coordinates and displacement parameters, bond distances, angles and crystallographic information files (CIF) for the structures of **3a** and **3c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Selected spectroscopic data: (**3a**) ¹H NMR (200 MHz, C₆D₆, ppm) δ 4.66 (t, 1H, CHCHCH, ³J_{HH} = 2.6 Hz), 4.48 (d, 2H, CHCHCH, ³J_{HH} = 2.6 Hz), 2.07 (s, 3H, Me). ¹³C NMR (100 MHz, (CD₃)₂CO, ppm) δ 225.74 (b, CO), 123.20 (s, CH₂CSC), 116.53 (s, CHCCS), 96.47 (dt, CHCHCH, ¹J_{CH} = 176.07 Hz, ²J_{CH} = 5.89 Hz), 63.72 (dt, CHCHCH, ¹J_{CH} = 182.71 Hz, ²J_{CH} = 5.89 Hz), 13.29 (q, Me, ¹J_{CH} = 129.66 Hz). IR (KBr, cm⁻¹) 2011, 1917 (CO). (**3c**) ¹H NMR (200 MHz, CDCl₃, ppm) δ 5.47 (t, ³J_{HH} = 2.6 Hz, 1H, CHCHCH), 5.51 (d, ³J_{HH} = 2.6 Hz, 2H, CHCHCH), 7.28–7.34 (m, 2H, H_{para}), 7.41–7.48 (m, 4H, H_{meta}), 7.67–7.70 (m, 4H, H_{ortho}). ¹³C{¹H} NMR (50 MHz, CDCl₃, ppm) δ 64.4 (CHCHCH), 96.6 (CHCHCH), 113.0, 125.5, 127.4, 128.9, 129.3, 133.7 (Ar), 224.0 (CO). IR (KBr, cm⁻¹) 2008, 1926 (CO), 1603 (C=C). See Supporting Information for full data on all new compounds.
- Selected crystallographic data: (**3a**) C₁₂H₉MnO₃S, monoclinic, P2₁/m, *a* = 6.4450(3) Å, *b* = 9.0870(4) Å, *c* = 9.9650(6) Å, β = 96.7940(19)°, *V* = 579.51(5) Å³, *Z* = 2, θ = 2.06 to 27.46°, 4030 reflections (1414 unique), 86 params, *R*₁ = 0.0320, *wR*₂ = 0.0716. (**3c**) C₂₂H₁₃MnO₃S, triclinic, P1, *a* = 11.1210(2) Å, *b* = 13.2140(2) Å, *c* = 13.3160(3) Å, α = 66.5710(9)°, β = 85.0370(9)°, γ = 76.7720(9)°, *V* = 1747.83(6) Å³, *Z* = 4, θ = 1.67 to 25.00°, 12 168 reflections (6164 unique), 487 params, *R*₁ = 0.0552, *wR*₂ = 0.1156. See Supporting Information for full details.
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JA054513N