Communication

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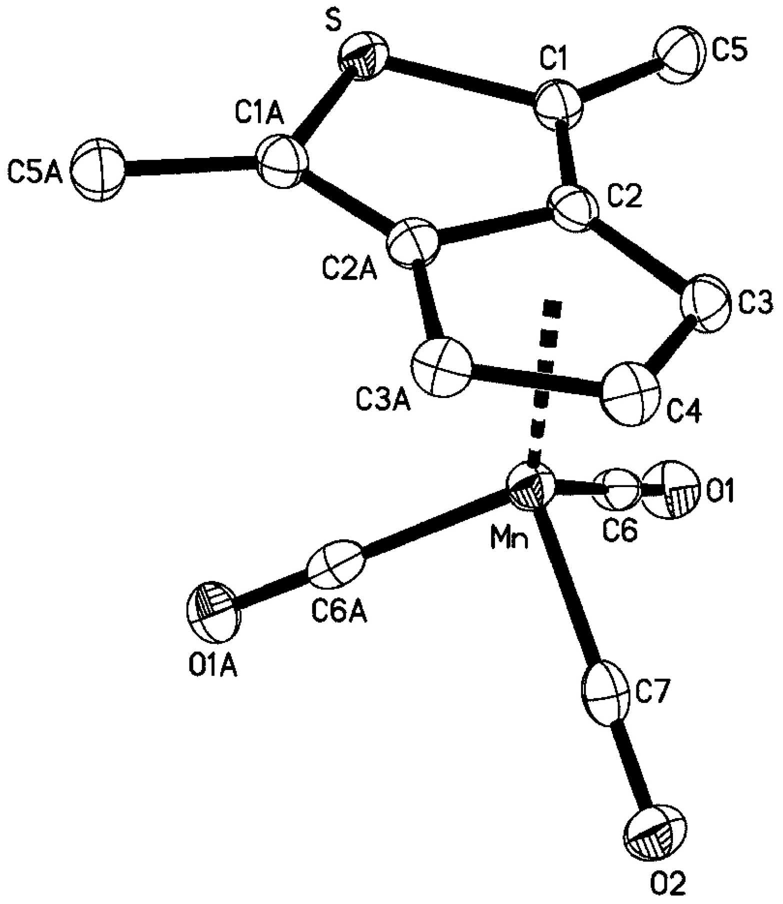

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Synthesis, Characterization, and Structure of Cyclopenta[*c*]thiophenes and Their Manganese Complexes

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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 antitumor properties.[1,2] Heterocycle-fused cyclopentadienyl, including cyclopenta[*c*]thienyl, zirconium complexes effectively catalyze the regiospecific 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*]thiophene[15] (2-thiapentalene) and its 1,3-dichloro,[15] 1,3-dimethyl,[16] and 1,3,5-trimethyl[6] 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 ^{1}H NMR resonances at δ 18−20. Thiation of 1,4-diketones to thiophenes by using H_2S,[23] P_4S_{10},[24] or 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide (Lawesson's reagent, LR)[25] is well precedented; 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 $[Mn_2(CO)_{10}]$ and an oxidatively coupled bis(4*H*-cyclopenta[*c*]thiophene).[17] In contrast, reactions of lithiated **2a** and **2c** with Me_3SnCl form isolable tin intermediates, $[SnMe_3(SC_7H_3\text{-}1,3\text{-}R_2)]$, which react smoothly with $[MnBr(CO)_5]$ to give $[Mn(\eta^5\text{-}SC_7H_3\text{-}1,3\text{-}R_2)(CO)_3]$ (**3a**, R = Me, 94%; **3c**, R = Ph, 90%).

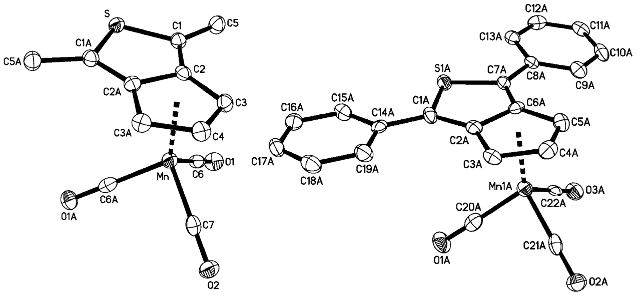

Figure 1. Thermal ellipsoid plots of the molecular structures of $[Mn(\eta^5\text{-}SC_7H_3\text{-}1,3\text{-}Me_2)(CO)_3]$ (**3a**, left) and $[Mn(\eta^5\text{-}SC_7H_3\text{-}1,3\text{-}Ph_2)(CO)_3]$ (**3c**, right). Hydrogen atoms are omitted for clarity.

These new cyclopenta[*c*]thienyl complexes were characterized spectroscopically[27] 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 $[Mn\{\eta^5\text{-}1,2\text{-}C_5H_3(COR)_2\}(CO)_3]$ (**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 $[Mn\{\eta^5\text{-}1,2\text{-}C_5H_3(COR)_2\}(CO)_3]$ (**5c**−**e**,**h**) with $P_4S_{10}/NaHCO_3$ in refluxing CS_2 give $[Mn(\eta^5\text{-}SC_7H_3\text{-}1,3\text{-}R_2)(CO)_3]$ (**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 $P_4S_{10}/NaHCO_3$ give deeply colored solutions, but we have not been

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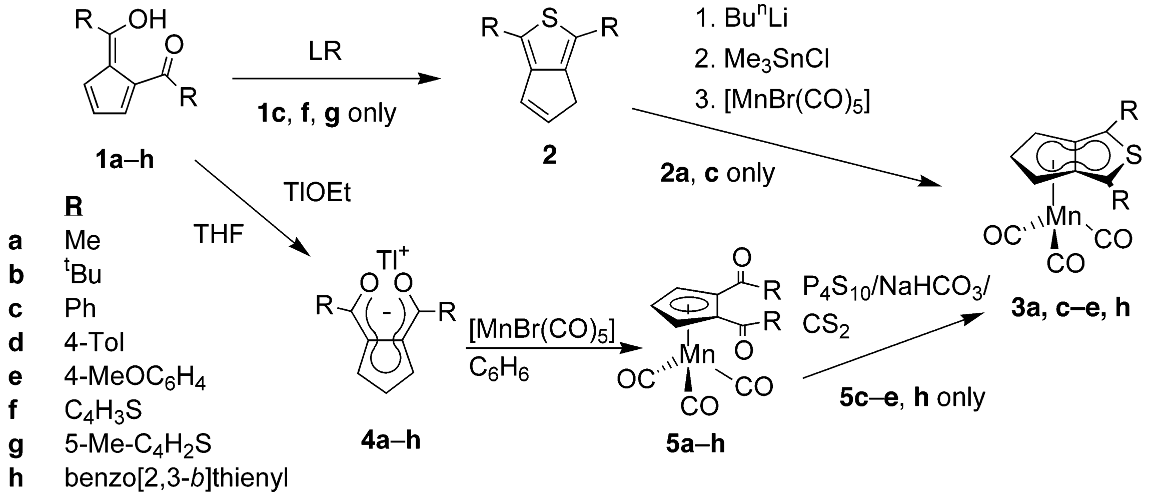
Scheme 1. Synthesis of 1,3-Diaryl-4*H*-cyclopenta[*c*]thiophenes and Their Manganese Complexes



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, $[\mathrm{Mn}(\eta^5\text{-}\mathrm{SC_7H_3}\text{-}1,3\text{-}\mathrm{R_2})(\mathrm{CO})_3]$ (**3a**,**c**; R = Me, Ph), are prepared in high yield by ligand substitution reactions of $[\mathrm{MnBr(CO)_5}]$ with $[\mathrm{SnMe_3(SC_7H_3}\text{-}1,3\text{-}\mathrm{R_2})]$. Alternatively, thiation with $\mathrm{P_4S_{10}/NaHCO_3}$ converts $[\mathrm{Mn}\{\eta^5\text{-}1,2\text{-}\mathrm{C_5H_3(COR)_2}\}(\mathrm{CO})_3]$ (**5c**−**e**,**h**) to $[\mathrm{Mn}(\eta^5\text{-}\mathrm{SC_7H_3}\text{-}1,3\text{-}\mathrm{R_2})(\mathrm{CO})_3]$ (**3c**−**e**,**h**; R = Ph, 4-tolyl, 4-MeOC$_6$H$_4$, benzo[2,3-*b*-]thienyl).

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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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(27) Selected spectroscopic data: (**3a**) ^{1}H NMR (200 MHz, C$_6$D$_6$, ppm) δ 4.66 (t, 1H, CHC*H*CH, $^3J_{\mathrm{HH}} = 2.6$ Hz), 4.48 (d, 2H, C*H*CHC*H*, $^3J_{\mathrm{HH}} = 2.6$ Hz), 2.07 (s, 3H, Me). ^{13}C NMR (100 MHz, (CD$_3$)$_2$CO, ppm) δ 225.74 (b, CO), 123.20 (s, CH$_3$*C*SC), 116.53 (s, CH*C*CS), 96.47 (dt, CH*C*HCH, $^1J_{\mathrm{CH}} = 176.07$ Hz, $^2J_{\mathrm{CH}} = 5.89$ Hz), 63.72 (dt, *C*HCH*C*H, $^1J_{\mathrm{CH}} = 182.71$ Hz, $^2J_{\mathrm{CH}} = 5.89$ Hz), 13.29 (q, Me, $^1J_{\mathrm{CH}} = 129.66$ Hz). IR (KBr, cm^{-1}) 2011, 1917 (CO). (**3c**) ^{1}H NMR (200 MHz, CDCl$_3$, ppm) δ 5.47 (t, $^3J_{\mathrm{HH}} = 2.6$ Hz, 1H, CHC*H*CH), 5.51 (d, $^3J_{\mathrm{HH}} = 2.6$ Hz, 2H, C*H*CHC*H*), 7.28−7.34 (m, 2H, H_{para}), 7.41−7.48 (m, 4H, H_{meta}), 7.67−7.70 (m, 4H, H_{ortho}). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$, ppm) δ 64.4 (*C*HCH*C*H), 96.6 (CH*C*HCH), 113.0, 125.5, 127.4, 128.9, 129.3, 133.7 (Ar), 224.0 (*C*O). IR (KBr, cm^{-1}) 2008, 1926 (CO), 1603 (C═C). See Supporting Information for full data on all new compounds.
(28) Selected crystallographic data: (**3a**) C$_{12}$H$_9$MnO$_3$S, monoclinic, $P2_1/m$, $a = 6.4450(3)$ Å, $b = 9.0870(4)$ Å, $c = 9.9650(6)$ Å, b = 96.7940(19)°, $V = 579.51(5)$ Å^3, $Z = 2$, $\theta = 2.06$ to 27.46°, 4030 reflections (1414 unique), 8$\underline{6}$ params, $R1 = 0.0320$, $wR2 = 0.0716$. (**3c**) C$_{22}$H$_{13}$MnO$_3$S, triclinic, $P\bar{1}$, $a = 11.1210(2)$ Å, $b = 13.2140(2)$ Å, $c = 13.3160(3)$ Å, $\alpha = 66.5710(9)$°, $\beta = 85.0370(9)$°, $\gamma = 76.7720(9)$°, $V = 1747.83(6)$ Å^3, $Z = 4$, $\theta = 1.67$ to 25.00°, 12 168 reflections (6164 unique), 487 params, $R1 = 0.0552$, $wR2 = 0.1156$. See Supporting Information for full details.
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