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Ruthenocene 1,2-Dicarboxylic Acid, Carboxylic Anhydride, and Acid Chloride: A Facile Route to Metallocene-Fused Acenequinones

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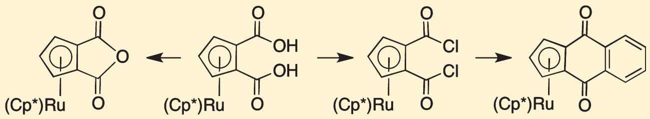
Supporting Information

ABSTRACT: The dehydration of 1′,2′,3′,4′,5′-pentamethylruthenocene-1,2-dicarboxylic acid with acetic anhydride gives 1′,2′,3′,4′,5′-pentamethylruthenocene-1,2-dicarboxylic anhydride, the first crystallographically characterized, metallocene-fused carboxylic anhydride. Treatment of the diacid with oxalyl chloride/DMF produces its 1,2-diacyl chloride, which is an excellent precursor for $AlCl_3$-promoted double Friedel−Crafts acylation reactions with a variety of arenes, including benzene, toluene, *o*-xylene, *p*-dimethoxybenzene, and ferrocene. X-ray structural determinations of an acenequinone and a unique ferrocene/ruthenocene-fused benzoquinone show distortions attributed to strong electron donation from pentamethylruthenocene.



Polycyclic aromatic hydrocarbons are benchmark semiconducting materials for organic field-effect transistors,[1] light-emitting diodes,[2] and photovoltaic cells.[3,4] Our long-term interest[5−11] in transition metal complexes of low-band-gap η^5-cyclopenta[*c*]thienyl monomers and polymers led us to consider polyacenes with terminal cyclopentadienyl metal groups, which are unknown except for simple η^5-indenyl complexes and a few benz[*f*]indenyl complexes of zirconium[12] and ruthenium.[13] We report here a route to metallocene-fused acenequinones, potential precursors for the desired acenes.

1,2-Dicarbophenoxycyclopentadienylsodium (**1**),[14] conveniently prepared by a single-step reaction of cyclopentadienylsodium with phenyl chloroformate,[11] forms with higher 1,2-selectivity than alkyl chloroformates, making **1** the preferred precursor for metallocene-1,2-dicarboxylates. Transmetalation of $[Ru(\mu_3\text{-}Cl)(Cp^*)]_4$[15] with **1** gives diester **2** in 78% yield (Scheme 1). Saponification of the diester[16] gives diacid **3** in 95% yield. Dehydration of **3** with refluxing acetic anhydride produces 1′,2′,3′,4′,5′-pentamethylruthenocene-1,2-dicarboxylic anhydride (**4**) in 84% yield. Two strong carbonyl infrared stretching frequencies at 1820 and 1764 cm^{-1} support the formation of a cyclic anhydride. The anhydride is surprisingly stable to water, surviving an aqueous workup. The only previous metallocene-fused carboxylic anhydride is 1,2-ferrocenedicarboxylic anhydride, prepared in very low yields by *N*,*N*′-dicyclohexylcarbodiimide (DCC) dehydration of 1,2-ferrocenedicarboxylic acid,[17,18] but properties (e.g., light sensitivity) reported by two groups are not entirely consistent. In contrast, DCC treatment of **3** gives a stable *N*,*N*′-dicyclohexyl-*N*-ruthenocenoylurea rather than the expected anhydride. Compounds **3** and **4** were characterized by their spectroscopic properties and X-ray structural determinations (*vide infra*).

Organic carboxylic anhydrides react with electron-rich aromatics under Friedel−Crafts conditions to give acenequinones.[19−24] However, our attempts to diacylate 1,4-dimethoxybenzene with **4** in molten $NaCl/AlCl_3$ resulted in the formation of an intractable mixture containing a small amount of a monoacylation product.

Treatment of **3** with oxalyl chloride/DMF led to its 1,2-diacyl chloride (**5**) in 50% isolated yield. Complex **5** is stable under dry conditions, but is more efficiently generated *in situ* to acylate arenes, including benzene, toluene, *o*-xylene, *p*-dimethoxybenzene, and ferrocene (Scheme 1), giving acenequinone complexes **6a**−**e** (42−58%) and **7** (36%). Complex **7** contains an unusual μ-[(1,2,3,3a,8a-η:4a,5,6,7,7a-η)-4,8-dihydro-4,8-dioxo-*s*-indacene-1,4a(1*H*)-diyl] bridging two different metals, precedented only by a pair of symmetrical diruthenium compounds.[25] Whereas toluene gives a single product (**6b**), ^1H NMR shows that *o*-xylene gives two isomers (**6c**,**d**) in a 1:1 ratio, implying that the arene undergoes electrophilic substitution first *para* to an activating substituent, followed by an indiscriminate second acylation. Dimethoxyacenequinone **6e** undergoes facile demethylation with anhydrous $AlCl_3$ to give dihydroxyquinone complex **9**, with a H-bonded phenolic ^1H NMR resonance at 12.93 ppm. The reduction of **6b** with $LiAlH_4$ gave a single (by ^1H and ^{13}C NMR) diol complex (**8**, 68%), presumably the *syn* isomer resulting from nucleophilic hydride addition to the side of the acenequinone ligand *opposite* the large Cp* group.

X-ray crystal structures of **3**, **4**, **6a**, and **7** (Figure 1) all exhibit typical ruthenocene geometry with nearly linear (Cp centroid)−Ru−(Cp* centroid) angles ranging from 177.38(13)° (**3**) to 175.60(6)° (**7**). In all structures the Ru atom is situated *closer* to the two ring-fusion carbons than to the other three carbons of the Cp ring, with the Ru−C shift ranging from 0.026(3) Å in **3** to 0.099(16) Å in **7**. Similar asymmetry was observed in $[(Ru(Cp^*))_2\{\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5H_3(CO)_2C_5H_3\}]$,[25] $[Ru(\eta^5\text{-}C_5H_4COMe)(Cp^*)]$,[26] and $[Ru\{\eta^5\text{-}1,2\text{-}C_5H_3(COPh)_2\}(Cp^*)]$.[12] Curiously,

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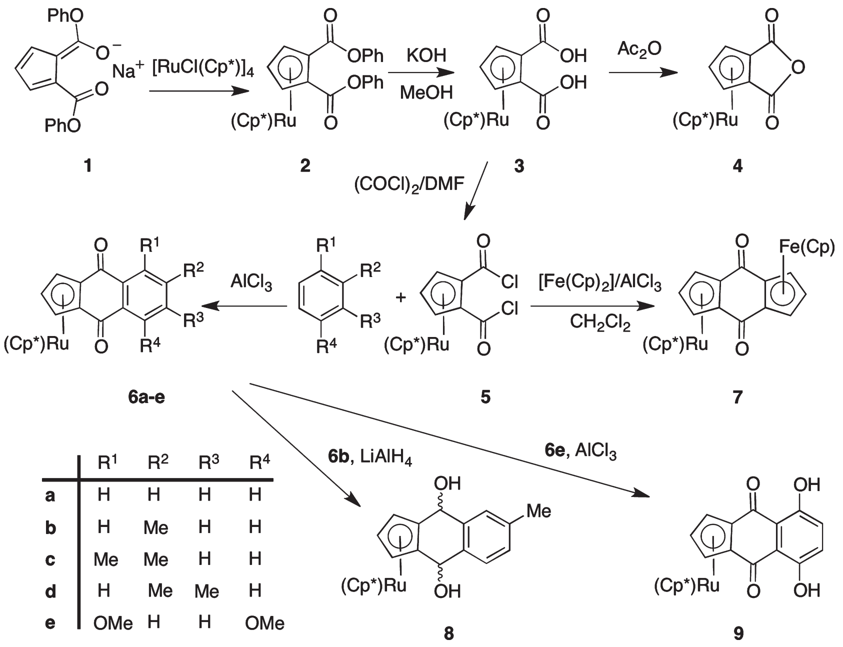
Scheme 1. Synthesis of Pentamethylruthenocene-1,2-dicarboxylic Acid and Its Derivatives



	R1	R2	R3	R4
a	H	H	H	H
b	H	Me	H	H
c	Me	Me	H	H
d	H	Me	Me	H
e	OMe	H	H	OMe

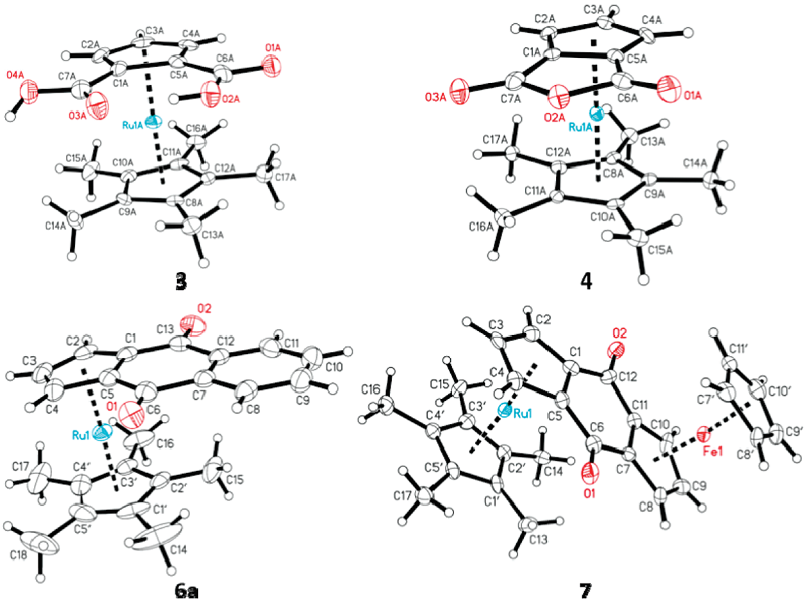


Figure 1. Thermal ellipsoid plots of the molecular structures of [Ru{η^5-$C_5H_3(CO_2H)$-1,2}(Cp*)] (**3**), [Ru{η^5-$C_5H_3(CO)_2O$-1,2}(Cp*)] (**4**), [Ru{η^5-$C_5H_3(CO)_2C_6H_4$}(Cp*)] (**6a**), and [Ru(Cp*){μ_2-η^5:η^5-1,2-$C_5H_3(CO)_2$-1,2-C_5H_3)}Fe(Cp)] (**7**).

the Fe atom in **7** shows a classic indenyl effect,[27−30] shifting 0.082(16) Å *away from* the two ring-fusion carbon atoms. In **6a**, the Cp−CO bonds, C1−C13 and C5−C6, are 0.044(4) Å shorter than the Ph−CO bonds, C12−C13 and C6−C7. Although the disubstituted cyclopentadienyl ligands of **3**, **4**, **6a**, and **7** are nearly planar, there are some subtle deviations. The two carboxylic acid moieties of **3** lie in the cyclopentadienyl plane (interplanar angles 3.2−4.4°), held together by a network of intra- and intermolecular hydrogen bonds with carboxylate O−H−O distances ranging from 2.532(4) to 2.592(4) Å and a methanol oxygen atom 2.859(5) Å from O3A. The cyclopentadienyl anhydride ring of **4** is essentially planar, with angles of 3.2° and 5.3° between the Cp (C1−C5) and anhydride (C1, C5−C7,

Chart 1. Structural Distortions in Compounds 6a and 7

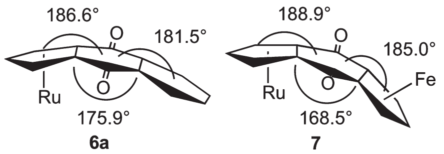
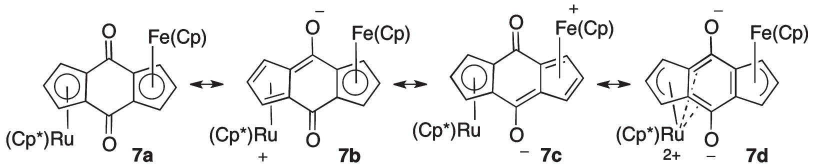


Chart 2. Resonance Description of Compound 7



O1−O3) planes in two independent molecules. The bending of the quinone ligands of **6a** and **7** is illustrated in Chart 1. In both complexes, the quinone portion of the ligand is inclined slightly *toward* [Ru(Cp*)], but in **7** the quinone is inclined slightly *away from* [Fe(Cp)]. Much of the bending is due to a slight folding of the quinone ring along the O−C−C−O axis, by 4.1° in **6a** and 11.5° in **7**.

We suggest that the structural distortions are due to the stronger electron-donor character of [Ru(Cp*)] compared to [Fe(Cp)]. In both **6** and **7**, electron-rich [Ru(Cp*)] shifts *toward* the electron-withdrawing carbonyl substituents, while in **7** relatively electron-deficient [Fe(Cp)] shifts *away from* the carbonyls. Donation of electron density from [Ru(Cp*)] to the carbonyls in **6** and **7** results in a decreased carbonyl stretching frequency from 1660 cm^{-1} for 9,10-anthraquinone to 1650 cm^{-1} for **6** and 1643 cm^{-1} for **7**. The lower C═O bond order is rationalized by the resonance forms **7b**−**d** in Chart 2.

In summary, 1′,2′,3′,4′,5′-pentamethylruthenocene-1,2-dicarboxylic acid and its derived carboxylic anhydride and acid chloride can be prepared simply in high yield, opening new avenues in organometallic Friedel−Crafts chemistry. The resulting benz[*f*]indenyl quinone complexes are potential precursors for organometallic polyacenes. Aromatization of the quinone ligands and extension of this chemistry to longer acene chains and other transition metals are in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Syntheses and data for **1**−**9**; tables of crystallographic details, atomic coordinates, displacement parameters, bond distances, and angles; and CIFs for **3**, **4**, **6a**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Mas-Torrent, M.; Rovira, C. *Chem. Soc. Rev.* **2008**, *37*, 827–838.
(2) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028–5048.
(3) Hains, A. W.; Liang, Z.; Woodhouse, M. A.; Gregg, B. A. *Chem. Rev.* **2010**, *110*, 6689–6735.
(4) Li, C.; Liu, M.; Pschirer, N. G.; Baumgarten, M.; Müllen, K. *Chem. Rev.* **2010**, *110*, 6817–6855.
(5) Blankenbuehler, M. T.; Selegue, J. P. *J. Organomet. Chem.* **2002**, *642*, 268–274.
(6) Eaton, D. L.; Selegue, J. P.; Anthony, J. E.; Patrick, B. O. *Heterocycles* **2002**, *57*, 2373–2381.
(7) Selegue, J. P.; Swarat, K. A. *J. Am. Chem. Soc.* **2002**, *115*, 6448–6449.
(8) Snyder, C. A.; Selegue, J. P.; Dosunmu, E.; Tice, N. C.; Parkin, S. *J. Org. Chem.* **2003**, *68*, 7455–7459.
(9) Snyder, C. A.; Selegue, J. P.; Tice, N. C.; Wallace, C. E.; Blankenbuehler, M. T.; Parkin, S.; Allen, K. D. E.; Beck, R. T. *J. Am. Chem. Soc.* **2005**, *127*, 15010–15011.
(10) Wallace, C. E.; Selegue, J. P.; Carrillo, A. *Organometallics* **1998**, *17*, 3390–3393.
(11) Tice, N. C.; Parkin, S.; Selegue, J. P. *J. Organomet. Chem.* **2007**, *692*, 791–800.
(12) Kim, D. H.; Lee, J. A.; Lee, B. Y.; Chung, Y. K. *J. Organomet. Chem.* **2005**, *690*, 1822–1828.
(13) Zhao, X.; Luo, X.; Li, B.; Song, H.; Xu, S.; Wang, B. *Eur. Polym. J.* **2008**, *144*, 3264–3270.
(14) Busetto, L.; Cassani, M. C.; Zanotti, V.; Albano, V. G.; Sabatino, P. *Organometallics* **2001**, *20*, 282–288.
(15) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698–1719.
(16) Khurana, J. M.; Chauhan, S.; Bansal, G. *Monatsh. Chem.* **2004**, *135*, 83–87.
(17) Roling, P. V.; Rausch, M. D. *J. Org. Chem.* **1974**, *39*, 1420–1424.
(18) Richards, J. H.; Curphey, T. J. *Chem. Ind. (London)* **1956**, 1456.
(19) Kende, A. S.; Tsay, Y.-G.; Mills, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 1967–1969.
(20) Paulsen, H.; Luettke, W. *Chem. Ber.* **1979**, *112*, 2907–2912.
(21) Ishizumi, K.; Ohashi, N.; Tanno, N. *J. Org. Chem.* **1987**, *52*, 4477–4485.
(22) Mitscher, L. A.; Gill, H.; Filippi, J. A.; Wolgemuth, R. L. *J. Med. Chem.* **1986**, *29*, 1277–1281.
(23) Wong, C. M.; Gordon, P. M.; Chen, A. G.; Lam, H. Y. P. *Can. J. Chem.* **1987**, *65*, 1375–9.
(24) Tang, M. L.; Oh, J. H.; Reichardt, A. D.; Bao, Z. *J. Am. Chem. Soc.* **2009**, *131*, 3733–3740.
(25) Sato, M.; Suzuki, M.; Okoshi, M.; Kurasina, M.; Watanabe, M. *J. Organomet. Chem.* **2002**, *648*, 72–80.
(26) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 6130–6135.
(27) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307–318.
(28) Lobanova, I. A.; Zdanovich, V. I. *Russ. Chem. Rev.* **1988**, *57*, 967–980.
(29) Basolo, F. *New J. Chem.* **1994**, *18*, 19–24.
(30) Calhorda, M. J.; Romão, C. C.; Veiros, L. F. *Chem.—Eur. J.* **2002**, *8*, 868–875.