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A facile synthetic route to (η^5-benzoylcyclopentadienyl)metal compounds

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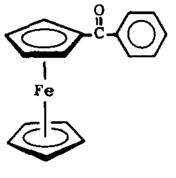
Abstract

A reaction between cyclopentadienylsodium and ethyl benzoate in refluxing THF produces (benzoylcyclopentadienyl)sodium (**4**) in 70–80% yield. Subsequent treatment of **4** in ethanol solution with thallium ethoxide affords (benzoylcyclopentadienyl)thallium (**3**) in nearly quantitative yield. Reactions of **3** with $Mn(CO)_5Br$, $Re(CO)_5Br$, $[Rh(CO)_2Cl]_2$ or $FeCl_2$ lead to the respective η^5-benzoylcyclopentadienyl derivatives of these metals, and demonstrate the utility of **3** in organometallic syntheses. Reactions of several of these organometallic ketones with cymantrenyllithium $[(\eta^5\text{-}C_5H_4Li)Mn(CO)_3]$ provide a useful new route to bimetallic compounds.

1. Introduction

Benzoylferrocene (**1**) and 1,1′-dibenzoylferrocene (**2**) have been known for many years, and are readily prepared by the Friedel–Crafts benzoylation of ferrocene [1–5]. The reactivity of these aromatic ketones under reduction conditions has been extensively studied, and a variety of novel mono- and bimolecular derivatives, including rearrangements products, have resulted [2–8]. η^5-Benzoylcyclopentadienyl derivatives of the related metalloaromatic compounds $(\eta^5\text{-}C_5H_5)_2M$ (M = Ru, Os) [9], $(\eta^5\text{-}C_5H_5)M(CO)_3$ (M = Mn, Tc, Re) [10–12] and $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$ [13] can also be prepared under Friedel–Crafts conditions in a similar manner, although their chemistry has been much less developed. In continuation of our studies on functionally substituted cyclopentadienyl-metal compounds [14–16], we now report a convenient new route to (η^5-benzoylcyclopentadienyl)metal compounds based on (benzoylcyclopentadienyl)thallium (**3**). The utility of these organometallic ketones in the formation of new bimetallic compounds is also described.



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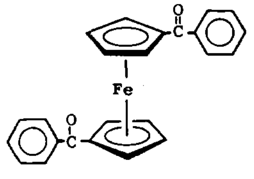

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2. Results and discussion

The synthesis, structure and reactivity of functionally substituted cyclopentadienyl-metal compounds [14,15] have been of considerable interest in our laboratories and elsewhere. We have recently demonstrated that cyclopentadienylthallium reagents containing formyl, acetyl, carbomethoxy or carboethoxy substituents are readily prepared from their sodium salts, and are also useful intermediates in the synthesis of corresponding functionalized transition metal compounds [16]. It was of subsequent interest to determine if this approach could also be extended to benzoylated derivatives.

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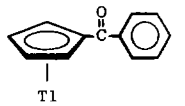

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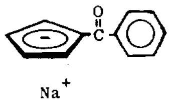
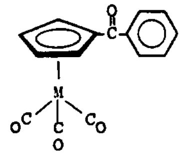


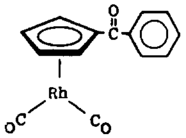
(4)

A reaction between cyclopentadienylsodium and ethyl benzoate in THF solution produced benzoylcyclopentadienylsodium (4) in 70–80% yield as a tan, slightly air-sensitive solid. A subsequent reaction with thallium ethoxide in ethanol solution afforded 3 in 92% yield. The product 3 was characterized by its ^1H and ^{13}C NMR spectra as well as by combustion analysis [17].

In order to determine the synthetic utility of 3 in the formation of transition metal analogs, we examined its reactivity with several transition metal halides. Reactions of 3 with $Mn(CO)_5Br$ and with $Re(CO)_5Br$ in benzene or toluene solution produced benzoylcymantrene (5) and its rhenium analog (6) in yields of 54% and 85%, respectively.

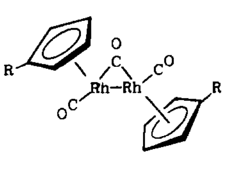


(5) M = Mn (6) M = Re

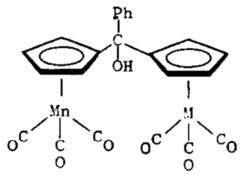


(7)

In a similar manner, (η^5-benzoylcyclopentadienyl)dicarbonylrhodium (7) was formed in 43% yield from a reaction between 3 and $[Rh(CO)_2Cl]_2$. Chromatographic separation of the reaction products also produced small amounts of a red solid, which on the basis of its IR and ^1H NMR spectra is believed to be bis-(η^5-benzoylcyclopentadienyl)tricarbonyldirhodium (8), as well as several polynuclear derivatives. Products of this type have previously been observed from reactions of substituted cyclopentadienylthallium compounds and $[Rh(CO)_2Cl]_2$ [16,18]. A reaction between $FeCl_2$ and 2 equiv. of 3 likewise afforded 1,1'-dibenzoylferrocene 2 in quantitative yield.



(8) R = benzoyl



(9) M = Mn (10) M = Re

It was also of interest to determine if benzoyl derivatives such as 5–7 could serve as intermediates in the formation of bimetallic compounds. Cymantrenyllithium [19–21] was readily prepared from cymantrene, n-butyllithium and TMEDA in THF solution at −78°C. Subsequent addition of either 5 or 6 followed by hydrolysis and normal workup produced dicymantrenylphenylcarbinol (9) as well as cymantrenylcyrhentrenylphenylcarbinol (10) in yields of 77% and 90%, respectively. These initial results suggest that reactions between acylcyclopentadienyl-metal compounds and organometallic lithium intermediates may provide a useful alternative route to both homo- and heterobimetallic systems. Additional studies along these lines are under current investigation in our laboratories.

3. Experimental section

All reactions were conducted under an atmosphere of nitrogen using Schlenk and glove box techniques. The purified nitrogen was prepared by passage through a heated copper (BTS) catalyst column, through a tube of phosphorus pentoxide, and finally through a tube of molecular sieves. Benzene, toluene, hexane and tetrahydrofuran (THF) were distilled under argon from sodium–potassium alloy. Dichloromethane was distilled from calcium hydride under argon. Absolute ethanol was used without further purification. Propionitrile was distilled from phosphorus pentoxide. $Mn(CO)_5Br$ [22], $Re(CO)_5Br$ [22] and $[Rh(CO)_2Cl]_2$ [23] were prepared by literature methods. Thallium ethoxide was either prepared by a literature method [24] or purchased from Aldrich Chemical Co. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was purchased from Aldrich and was dried and distilled from calcium hydride before use. Cymantrene [$CpMn(CO)_3$] was obtained as a generous gift from Ethyl Corporation. NMR spectra were obtained on Bruker/IBM NR-80 or Varian XL-200 spectrometers. IR spectra were obtained on Perkin-Elmer 1310 or Digilab Qualimatic FTIR spectrometers. Mass spectra were recorded on a Hewlett Packard VG 7070-HS GC/MS instrument using electron impact ionization. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA. (Note: thallium and its compounds are extraordinarily toxic and must be handled with appropriate safety measures.)

3.1. *(Benzoylcyclopentadienyl)sodium (4)*

Cyclopentadienylsodium was prepared from sodium sand (2.14 g, 0.093 mol), freshly cracked cyclopentadiene (9.0 ml, 7.2 g, 0.109 mol), and 30 ml of THF under a nitrogen atmosphere. After stirring overnight, a light-purple clear solution was obtained. Ethyl benzoate (13.97 g, 0.093 mol) was added dropwise, producing a light-brown turbid solution. The reaction mixture was heated at reflux with stirring overnight, *ca.* one-half the THF was removed under reduced pressure, and 100 ml of hexane was added. After stirring overnight, the resulting precipitate was filtered under nitrogen on a frit and dried under a high vacuum to produce 17.70 g of a yellow-tan solid. Assuming the product to be a mono-THF solvate [25], $Na[C_5H_4C(O)C_6H_5](THF)$ was obtained in 72% yield. An additional 2.17 g of product (total yield = 81%) could be obtained by concentrating the filtrate from the first crop to *ca.* one-third volume, addition of excess hexane, and drying. The product **4** can be handled in air for short periods of time, but slowly decomposes upon extended exposure.

3.2. *(Benzoylcyclopentadienyl)thallium* (**3**)

Into a nitrogen-flushed Schlenk tube were added $Na[C_5H_4C(O)C_6H_5](THF)$ (17.7 g, 0.067 mol), 180 ml of 100% ethanol and a stir bar. With stirring, thallium ethoxide (4.59 ml, 16.2 g, 0.065 mol) was added dropwise via a syringe. After stirring for 3.5 h, the product was collected in air in a Buchner funnel and was washed with two 20-ml portions of ethanol and two 20-ml portions of hexane. After drying, the product was obtained as an air-stable brown powder (23.0 g, 92%). An analytically pure sample was obtained by recrystallization from propionitrile and drying in a high vacuum; m.p. (vac. or air) 205–206°C. Anal. Found: C, 38.70; H, 2.52. $C_{12}H_9OTl$ calc.: C, 38.58; H, 2.43%. ^1H NMR (Me_2SO-d_6): δ 7.64 (m, 2H, *o*-Ph); 7.36 (m, 3H, *m*-,*p*-Ph); 6.28 (t, 2H, $H_{2,5}$); 5.81 (t, 2H, $H_{3,4}$). ^{13}C NMR (Me_2SO-d_6): δ 187.34 (C=O); 142.93, 128.74, 128.00, 127.09 (Ph); 122.93 (C_1); 114.22 ($C_{2,5}$); 112.22 ($C_{3,4}$). IR (KBr): 1596m, 1581m, 1552s, 1465s, 1348s, 1056s, 1046s, 856s, 764s, 730s cm^{-1}.

3.3. *(η^5-Benzoylcyclopentadienyl)tricarbonylmanganese* (**5**)

$Mn(CO)_5Br$ (1.046 g, 3.80 mmol) was added to a nitrogen-flushed, 100-ml Schlenk flask together with 50 ml of benzene and a stir bar. To the flask was subsequently added (benzoylcyclopentadienyl)thallium (1.435 g, 3.84 mmol). A condenser and oil bubbler were attached and the mixture was stirred at reflux for 24 h. The TlBr was removed by filtration in air through a Buchner funnel packed with filter paper and Celite. The filtrate was concentrated via a rotary evaporator followed by drying in a high vacuum to yield a red solid. The product was purified on an alumina column, eluting with hexane, to produce 0.64 g (54%) of a yellow solid, m.p. 70–72°C (lit. m.p. 69–70°C; 73.5–74.5°C [10,11]). Anal. Found: C, 58.24; H, 2.88. $C_{15}H_9MnO_4$ calc.: C, 58.46; H, 2.94%. ^1H NMR ($CDCl_3$): δ 7.75 (d, 2H, *o*-Ph); 7.50 (m, 3H, *m*-,*p*-Ph); 5.48 (s, 2H, $H_{2,5}$); 4.89 (s, 2H, $H_{3,4}$). ^{13}C NMR ($CDCl_3$): δ 222.84 (C=O); 192.2 (C=O); 137.83, 132.47, 128.54, 128.06 (Ph); 88.11 ($C_{2,5}$); 83.71 ($C_{3,4}$). IR (CH_2Cl_2): 2031s, 1951s, 1655m cm^{-1}. MS: *m/e* 308 (M^+), 281 $(M-CO)^+$, 253 $(M-2\ CO)^+$, 224 $(M-3\ CO)^+$.

3.4. *(η^5-Benzoylcyclopentadienyl)tricarbonylrhenium* (**6**)

A solution of $Re(CO)_5Br$ (0.913 g, 2.25 mmol) and (benzoylcyclopentadienyl)thallium (0.840 g, 2.25 mmol) in 50 ml of toluene was stirred at reflux under nitrogen for 25 h. Filtration and removal of the solvent produced a tan solid (0.840 g, 85%). The product was purified by recrystallization from ethanol/water to yield off-white crystals (0.470 g), m.p. (air) 101.5–103°C (lit. m.p. 101°C [12]). Anal. Found: C, 40.83; H, 2.10. $C_{15}H_9O_4Re$ calc.: C, 41.00; H, 2.06%. ^1H NMR ($CDCl_3$): δ 7.9–7.3 (m, 5H, Ph); 6.04 (t, 2H, $H_{2,5}$); 5.45 (t, 2H, $H_{3,4}$). IR (CH_2Cl_2): 2035s, sh, 1940vs, b, 1653m cm^{-1}.

3.5. *1,1'-Dibenzoylferrocene* (**2**)

Anhydrous ferrous chloride (0.597 g, 4.71 mmol) and (benzoylcyclopentadienyl)thallium (3.517 g, 9.40 mmol) were heated at reflux in 50 ml of THF under nitrogen for 3 days. The reaction mixture was filtered through a Buchner funnel packed with Celite. The filtrate was concentrated by means of a rotary evaporator and subsequently dried under a high vacuum to yield a dark purple oil (1.85 g, 99%). The product was crystallized from ethanol/water to produce 1,1'-dibenzoylferrocene, m.p. 99–101°C (lit. m.p. 105–106°C [2]). The spectral properties of the product were identical to those of an authentic sample.

3.6. *(η^5-Benzoylcyclopentadienyl)dicarbonylrhodium* (**7**)

$[Rh(CO)_2Cl]_2$ (1.273 g, 3.27 mmol) was heated at reflux with stirring with (benzoylcyclopentadienyl)thallium (2.480 g, 6.64 mmol) in 50 ml of benzene under nitrogen for 18 h. The solvent was removed under a high vacuum and the residue was chromatographed on a silica column. Elution with dichloromethane/hexane (1 : 1) produced a yellow band which upon removal of the solvent yielded a yellow solid (0.94 g, 43%). Further elution removed a red band that was isolated as an oil (0.47 g). The initial yellow product was further purified by recrystallization from dichloromethane/hexane and subsequently by vacuum sublimation (50–60°C, 0.1 Torr), m.p. 63–63.5°C. Anal. Found: 51.45; H, 2.84. $C_{14}H_9O_3Rh$ calc.: C, 51.25; H, 2.76%. ^1H NMR ($CDCl_3$): δ 7.90–7.78 (m, 2H, *o*-Ph); 7.52–

7.36 (m, 3H, *m*-,*p*-Ph); 5.51 (t, 2H, $H_{2,5}$); 5.66 (dt, 3H, *J*(H–Rh) = 0.91 Hz, $H_{3,4}$). IR (CH_2Cl_2): 2060s, 1990s, 1635m cm^{-1}.

The red oil was further purified on a second silica column. Elution with dichloromethane/hexane (7:3) produced a red solid upon removal of the solvent. Spectra data indicated that this is the binuclear complex bis-(η^5-benzoylcyclopentadienyl)tricarbonyldirhodium (**8**). ^1H NMR ($CDCl_3$): δ 7.96–7.84 (m, 2H, *o*-Ph); 7.50–7.40 (m, 3H, *m*-,*p*-Ph); 6.02 (t, 2H, $H_{2,5}$); 5.69 (t, 2H, $H_{3,4}$). IR (CH_2Cl_2): 2040s, 2000s, 1835m, 1640m cm^{-1}.

Continued elution of this column with dichloromethane/hexane (8:2) removed a green band that solidified upon removal of the solvent. ^1H NMR ($CDCl_3$): δ 7.78–7.66 (m, 2H, *o*-Ph); 7.53–7.37 (m, 3H, *m*-,*p*-Ph); 6.08 (t, 2H, $H_{2,5}$); 5.54 (t, 2H, $H_{3,4}$). IR (CH_2Cl_2): 1985s, 1785s, 1640s cm^{-1}. Dichloromethane (100%) eluted a yellow band that solidified to a brown solid upon removal of the solvent. ^1H NMR ($CDCl_3$): δ 7.93–7.81 (m, 2H, *o*-Ph); 7.55–7.46 (m, 3H, *m*-,*p*-Ph); 5.88 (t, 2H, $H_{2,5}$); 5.63 (t, 2H, $H_{3,4}$). IR (CH_2Cl_2): 1870, 1820, 1640 cm^{-1}. Further elution with 100% dichloromethane produced a very small purple band that yielded a trace amount of purple solid. IR (CH_2Cl_2): 1720, 1640 cm^{-1}.

3.7. *Dicymantrenylphenylcarbinol* (**9**)

THF (20 ml) was added to a nitrogen-purged 100-ml Schlenk flask containing cymantrene (0.391 g, 1.92 mmol) and a stir bar. The flask was fitted with a septum and then cooled in a dry ice/propanol bath to −78°C. TMEDA (0.30 ml, 1.9 mmol) and 2.5 M *n*-butyllithium in hexane (0.80 ml, 1.9 mmol) were then added via a syringe with stirring. After 40 min, benzoylcymantrene (0.586 g, 1.90 mmol) dissolved in 12 ml of THF was transferred to the Schlenk flask via a cannula, resulting in a red solution. The reaction mixture was allowed to stir and warm to room temperature for 15 h, after which time it was hydrolyzed with dilute hydrochloric acid in a 125-ml separatory funnel. After addition to the acid, the upper organic layer changed from red-brown to green. During subsequent washing with distilled water, the organic layer became yellow-orange. Removal of the THF in a high vacuum yielded a dark yellow solid (0.75 g, 77%). Recrystallization of the product from ethanol/water gave golden crystals of **9**, m.p. 177–180°C. Anal. Found: C, 54.29; H, 3.03. $C_{23}H_{14}O_7Mn_2$ calc.: C, 53.93; H, 2.76%. ^1H NMR ($CDCl_3$): δ 7.39 (m, 5H, Ph); 5.06 (t, 2H); 4.66 (m, 6H); 2.50 (s, 1H, OH). Deuterium exchange with D_2O eliminated the latter resonance.

3.8. *(η^5-Cymantrenylphenylhydroxymethylcyclopentadienyl)tricarbonylrhenium (cymantrenylcyrhentrenylphenylcarbinol)* (**10**)

Cymantrenyllithium was prepared as described above at −78°C from cymantrene (0.245 g, 1.20 mmol), TMEDA (0.18 ml, 1.2 mmol) and 1.6 M n-butyllithium in hexane (0.75 ml, 1.2 mmol) in 20 ml of THF. After 45 min, (η^5-benzoylcyclopentadienyl)tricarbonylrhenium (0.490 g, 1.12 mmol) dissolved in 20 ml of THF was transferred to the Schlenk flask via a cannula. The reaction mixture was allowed to stir and warm to room temperature for 20 h, after which time it was hydrolyzed with dilute hydrochloric acid. The organic layer was washed with distilled water, and the THF was removed in a high vacuum to produce a dark yellow oil (0.651 g, 90%). Purification was achieved by column chromatography on alumina packed in hexane. Elution with dichloromethane/hexane (3:7) produced a yellow band, which after removal of the solvent resulted in a yellow crystalline solid (0.648 g, 90%). An analytical sample was obtained by recrystallization from ethanol/water, m.p. 194–195°C. Anal. Found: C, 42.90; H, 2.21. $C_{23}H_{14}O_7MnRe$ calc.: C, 42.93; H, 2.19%. ^1H NMR ($CDCl_3$): δ 7.35 (m, 5H, Ph); 5.60 (m, 1H); 5.25 (m, 3H); 5.03 (m, 1H); 4.63 (m, 3H); 2.39 (s, 1H, OH).

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