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Formation and synthetic utility of benzyl- and phenyl-cyclopentadienylthallium

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Abstract

Benzyl- and phenyl-cyclopentadiene have been shown to react with thallium ethoxide in ethanol to give the corresponding benzyl- and phenyl-cyclopentadienylthallium compounds in excellent yield. These reagents are air stable for brief periods, have extended shelf-lives, and have been shown to be superior starting materials for the synthesis of a variety of cyclopentadienylmetal complexes.

Introduction

Cyclopentadienylthallium (**1**) has proved to be an exceptionally useful intermediate in organometallic and organic syntheses since it is readily prepared in high yield, can be conveniently stored and handled (in air), and is very reactive with most metal halides and many organic substrates [1,2]. Substituted derivatives of **1** might also be expected to serve as versatile synthetic intermediates, and recent studies in our laboratories and elsewhere have led to $(C_5H_4X)Tl$ (X = Cl, Br, I) [1], $(C_5H_4PR_2)Tl$ (R = Me, Ph) [2–4], $(C_5H_4CO_2Me)Tl$ [5,6], $(C_5H_4CN)Tl$ [6,7], $(C_5Me_5)Tl$ [8,9], $(C_5H_4SR)Tl$ (R = Me, Ph, *p*-Tol), $C_6H_3(NO_2)_2$-2,4] [10], $(C_5H_4CF_3)Tl$ [11], $(C_5H_4SiMe_3)Tl$ [12], $[C_5H_3(SiMe_3)_2\text{-}1,3]Tl$ [12], as well as the binuclear reagents fulvalenedithallium [13], bis(cyclopentadienylthallium)methane [14] and bis(cyclopentadienylthallium)dimethylsilane [15].

For many purposes, such as the formation of heterobinuclear complexes, it would be useful to have available a general route to cyclopentadienylmetal compounds that contain benzyl or phenyl substituents on the cyclopentadienyl ring. Benzylcyclopentadienyllithium [16-21] and -sodium [22,23] as well as phenylcyclopentadienyl-

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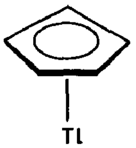
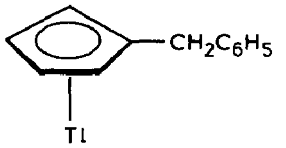
sodium [24] have been previously mentioned in the literature, but details concerning their formation, properties, and general reactivity are unfortunately lacking. *Meta*- and *para*-fluorophenylcyclopentadienyl salts of lithium, sodium, potassium and thallium as well as thallium and potassium salts of $C_5H_4CH(Me)Ph$ were reported in conjunction with an investigation of the metal-to-ring bonding in these compounds [25–27]. As part of our ongoing program for the development of functionalized cyclopentadienylthallium reagents, we report here on convenient, high-yield routes to benzylcyclopentadienylthallium (**2**) and phenylcyclopentadienylthallium (**3**), as well as reactions of these new reagents that demonstrate their synthetic utility in organometallic chemistry. **2** has been previously prepared by an alternate route and has been used in the preparation of tris(benzylcyclopentadienyl)chlorouranium [28].



(**1**)



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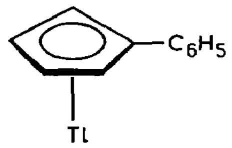

(**3**)

Results and discussion

A mixture of isomers of benzylcyclopentadiene is readily prepared by reaction of sodium cyclopentadienide with benzyl bromide followed by solvent removal and distillation of the colorless oil. Similar preparations have been reported by Raymond [28] and Wrighton [29]. Although this compound rapidly polymerizes at room temperature, it can be stored at $-78\,^{\circ}C$ for periods in excess of several weeks. Reaction of benzylcyclopentadiene with thallium ethoxide in ethanol yields benzylcyclopentadienylthallium (**2**) as an off-white solid in quantitative yield.

Phenylcyclopentadiene can be readily prepared by reaction of phenylmagnesium bromide with 2-cyclopentenone to give phenylcyclopentenol which dehydrates upon vacuum distillation to produce a mixture of isomers of phenylcyclopentadiene as a waxy solid. Wahren and his coworkers have reported the synthesis of several substituted phenylcyclopentadienes by reaction of cyclopentadienylcopper tributylphosphine with substituted iodobenzenes [30,31]. Phenylcyclopentadiene is moderately stable to polymerization at room temperature, but it is best stored at $0\,^{\circ}C$ for extended periods.

Reaction of the phenylcyclopentadiene mixture with thallium ethoxide in ethanol gives phenylcyclopentadienylthallium (**3**) as a yellow solid in quantitative yield.

^1H NMR spectra of **2** and **3** in DMSO-d_6 contained AA′BB′ resonances for the cyclopentadienyl protons and characteristic benzyl and phenyl resonances. Both compounds gave good elemental analyses.

The reactions of cyclopentadienylthallium reagents and metal halides, metal carbonyl halides, and cyclopentadienylmetal halides to yield new cyclopentadienylmetal complexes is well established [1,14,32–35]. Reactions of compounds **2** and **3** with several metal reagents were examined to demonstrate the usefulness of these compounds as starting materials in organometallic synthesis. These reactions are summarized in Table 1. Reaction of **2** and **3** with bromopentacarbonylmanganese

Table 1

Summary of reactions

$RCpTl + X_nML \rightarrow RCpML$		
Bz	$BrMn(CO)_5$	$BzCpMn(CO)_3$
Bz	$BrRe(CO)_5$	$BzCpRe(CO)_3$
Ph	$BrMn(CO)_5$	$PhCpMn(CO)_3$
Bz	$FeCl_2$	$(BzCp)_2Fe$
Bz	$TiCl_4$	$(BzCp)_2TiCl_2$
Bz	$CpTiCl_3$	$(BzCp)CpTiCl_2$
Ph	$CpTiCl_3$	$(PhCp)CpTiCl_2$
Bz	$[Cl_2Ru(CO)_3]_2$	$[BzCpRu(CO)_2]_2$
		$BzCpRu(CO)_2Cl$
Ph	$[Cl_2Ru(CO)_3]_2$	$[PhCpRu(CO)_2]_2$
		$PhCpRu(CO)_2Cl$
Bz	$[ClRh(CO)_2]_2$	$BzCpRh(CO)_2$
		$(BzCp)_2Rh_2(CO)_3$
		$[BzCpRh(CO)]_3$
Ph	$[ClRh(CO)_2]_2$	$PhCpRh(CO)_2$
		$(PhCp)_2Rh_2(CO)_3$
		$[PhCpRh(CO)]_3$
Bz	"$ICo(CO)_4$"	$BzCpCo(CO)_2$

yielded the known benzyl- [36] and phenyl-cymantrene [36] derivatives in good yield. Similarly, benzylcyclopentadienyltricarbonylrhenium is recovered from the reaction of **2** and bromopentacarbonylrhenium. **2** reacts with $FeCl_2$ and $TiCl_4$ to give 1,1'-dibenzylferrocene [37] and 1,1'-dibenzyltitanocene dichloride, respectively.

Asymmetric titanocene dichloride compounds in which only one cyclopentadienyl ring is substituted can be prepared by reaction of **2** and **3** with cyclopentadienyltitanium trichloride. Reaction of **2** and **3** with $[Cl_2Ru(CO)_3]_2$ gives both the $[RCpRu(CO)_2]_2$ and $RCpRu(CO)_2Cl$ derivatives. Reaction of **2** with $[ClRh(CO)_2]_2$ gave a mixture of products from which the benzylcyclopentadienyldicarbonylrhodium and its dimer and trimer decarbonylation products could be isolated. Reaction of **3** with $[ClRh(CO)_2]_2$ gave a similar mixture from which phenylcyclopentadienyldicarbonylrhodium was isolated as a dark red crystalline solid. The dinuclear rhodium derivative of **3** was isolated as a dark red oil which could not be fully freed of solvent.

Reaction of **2** with $Co(CO)_xI$ (from I_2 and $Co_2(CO)_8$) gave benzylcyclopentadienylcobaltdicarbonyl as a red-orange oil. This compound was very air sensitive in solution, and in one instance a sample of this compound appeared to be oxidized to the known benzoylcyclopentadienyldicarbonylcobalt [38] on storage. Despite repeated attempts at purification elemental analysis of this compound was only fair.

With the possible exception of the benzylcyclopentadienyldicarbonylcobalt derivative described above, all compounds were air stable. The spectral and physical properties of the benzyl and phenyl compounds paralleled their cyclopentadienyl analogs. All compounds, with the exception of bis(phenylcyclopentadienyl)tricarbonyldirhodium and benzylcyclopentadienyldicarbonylcobalt noted above, gave good analyses or compared favorably to previously reported spectral and physical properties.

Throughout these studies HPLC has been used to examine reaction mixtures and to evaluate the purity of recovered materials. We have found that most cyclopentadienylcarbonylmetal compounds chromatograph smoothly and reproducibly on a 25 cm column employing 10 μm silica gel using 3/7 THF/petroleum ether as an eluant. The eluant mixture is deoxygenated by passing a steady stream of helium through the storage bottle. Although reactions with the silica gel usually preclude analysis of dicyclopentadienyltitanium dichloride derivatives, compounds in which there is only a single metal–halide bond (such as cyclopentadienyldicarbonylruthenium chloride and its derivatives) chromograph with no apparent problems.

Further examinations of the chemistry of these compounds will be concerned with the formation of heterodinuclear complexes by reaction of the benzyl- and phenyl-cyclopentadienyl complexes with tris(acetonitrile)tricarbonylchromium and related arene complexing agents and with the formation of derivatives by carbonyl or halide substitutions.

Experimental

General

All operations were carried out under a nitrogen atmosphere using standard Schlenk, vacuum or dry box techniques except where specified. Nitrogen was deoxygenated with activated BTS catalyst and dried with molecular sieves and P_2O_5. Diethyl ether and tetrahydrofuran (THF) were predried over sodium wire and distilled under nitrogen from sodium-benzophenone ketyl. Pentane, hexane, dichloromethane, benzene and toluene were dried and distilled under argon from calcium hydride. Alumina (CAMAG, neutral grade) was predried while mixing on a rotary evaporator attached to a vacuum pump for 2 h. The alumina was subsequently deactivated with argon-saturated water (5% by weight) and stored under argon until use. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, MA or Galbraith Laboratories of Knoxville, TN. Thallium ethoxide was either purchased from Aldrich Chemical Co. or prepared from thallium metal as described by Fieser and Fieser [39]. $Co_2(CO)_8$, $BrMn(CO)_5$, and $Re_2(CO)_{10}$ were purchased from Strem Chemicals. Sodium dispersion (40% in mineral spirits) was purchased from Aldrich. Cyclopentenone [40], $[Cl_2Ru(CO)_3]_2$ [41], $[ClRh(CO)_2]_2$ [42], and $C_5H_5TiCl_3$ [43] were prepared by literature methods. $Re(CO)_5Br$ was prepared in quantitative yield from $Re_2(CO)_{10}$ using a procedure analogous to that used for $Mn(CO)_5Br$.

IR spectra were recorded in dichloromethane solution using a Perkin–Elmer Model 1750 FTIR Spectrometer. ^1H NMR spectra were recorded on a Varian Associates FT 80 A NMR Spectrometer operating at 79.542 MHz with tetramethylsilane (TMS) as a reference standard. HPLC analysis of reaction mixtures and of purified compounds were conducted using a Gow-Mac HPLC with a 25 cm Alltech silica gel column and 3/7 THF/petroleum ehter as an eluant.

Note. Thallium and its compounds are extraordinarily toxic and must be handled with appropriate safety precautions. Gloves should always be worn when handling these materials.

Synthesis of benzylcyclopentadiene

Sodium cyclopentadienide was prepared by the reaction of 40% sodium dispersion in mineral spirits with cyclopentadiene in THF solution. Typically, 23.0 g (0.40

mole Na) of 40% sodium dispersion was placed in a 500 ml, 3-neck flask outfitted with a spin bar, condenser and vacuum/nitrogen inlet. The flask was evacuated for 10 min at 1–10 mmHg to degas the sodium dispersion. Nitrogen was backflushed into the flask and 250 ml of dry, degassed THF added. A 100-ml dropping funnel was placed on the flask and 35–40 ml of freshly distilled cyclopentadiene added at a rate sufficient to maintain boiling. (Alternately, the flask can be immersed in ice water and the rate of cyclopentadiene addition substantially increased.) After addition of the cyclopentadiene, the solution was heated to 50 °C for 1 h to ensure completion. After this period the solution was clear and slightly pink.

Benzyl chloride, 60 g (0.47 mole) was added over about 5 min to the warm THF solution. The mixture was stirred for 2 h at 50–55 °C then cooled to room temperature. About 25 ml of cold water was added to the solution and the resulting mixture swirled until a solid white precipitate of sodium chloride formed. The solution was filtered through Celite, dried with magnesium sulfate and refiltered to remove the drying agent. The solvents were removed from the solution using a rotary evaporator. After most of the solvent had been removed the oil was placed under high vacuum at room temperature for 0.5 h to remove residual traces of solvent and unreacted cyclopentadiene.

The oil which remained after removal of the solvent was distilled under vacuum. The product began to distill at about 60 °C (0.1 mmHg) and was collected in a dry ice chilled trap. Material collected prior to this was discarded. Distillation was continued with the temperature slowly rising to about 85 °C. The colorless distillate is stable in the freezer overnight or indefinitely at −78 °C. Yield: 40–60%.

Synthesis of benzylcyclopentadienylthallium (2)

Benzylcyclopentadiene, 3.88 g (25 mmol), was taken up in 100 ml of ethanol in a 250-ml single-neck flask outfitted with a spin bar and equipped with a septum. The flask was flushed with nitrogen using syringe techniques. Thallium ethoxide, 7.0 g (29 mmol), was added slowly to the stirred ethanol solution by syringe. A white precipitate formed immediately. When all of the thallium ethoxide had been added, the solution was stirred for 30 min. The solution was then decanted from the solid and the solid was washed twice with ethanol and subsequently with ether and pentane. Filtration gave a shiny grey-white solid in quantitative yield. This solid is relatively air-stable, but does darken on exposure to light. ^{1}H NMR: (DMSO-d_6) 7.28 (5H, broad singlet) 5.76 and 5.60 (4H, AA′BB′ pair), 3.70 (2H, s). Found: C, 39.79; H, 2.97. $C_{12}H_{11}Tl$ calcd.: C. 40.07; H, 3.08%.

Synthesis of phenylcyclopentadiene

Cyclopentenone, 10.0 g (0.12 mol) was placed in a 250-ml, three-necked flask equipped with a mechanical stirrer, addition funnel and nitrogen inlet. Ethyl ether, 100 ml, was added and the flask immersed in a salt-ice bath. Phenylmagnesium bromide (prepared from 18.7 g of bromobenzene and 4.9 g of magnesium turnings) in ethyl ether was slowly added to the 2-cyclopentenone solution so that the temperature of the reaction mixture remained below 0 °C. A pink precipitate formed rapidly upon addition of the Grignard reagent. After all of the Grignard reagent was added, the mixture was stirred for an additional 1.5 h to ensure complete reaction. The resulting pink suspension was poured into 300 ml of ice cold concentrated aqueous ammonia saturated with ammonium chloride. The organic layer was separated and the aqueous layer extracted with three 100-ml portions of ethyl ether. The ether extracts were combined and dried over magnesium sulfate. After removal of the magnesium sulfate by filtration, the ethyl ether was removed using a rotary evaporator and the remaining oil was transferred to a 25 ml distilling flask equipped with a spin bar, and distillation head. To prevent crystallization of the product in the distillation, it was necessary to wrap the distilling head with heating tape. The product was vacuum distilled 70–100 ° C (0.1 mmHg) to give a white, waxy solid. Yield: 50–80%.

Synthesis of phenylcyclopentadienylthallium (3)

Phenylcyclopentadiene, 3.5 g (25 mmol), was dissolved in 100 ml of ethanol in a 250-ml single-neck flask equipped with a spinbar and sealed with a septum. The flask was flushed with nitrogen using syringe techniques. Thallium ethoxide, 7.0 g (29 mmol), was added slowly by syringe to the stirred reaction mixture. A pale yellow precipitate formed immediately. After addition of all of the thallium ethoxide the solution was stirred for 1 h and then rapidly filtered through a medium porosity glass frit. The solid was washed with ethanol, ethyl ether and hexane and dried under vacuum. The resulting yellow compound is stable to brief exposure to air but is best stored under nitrogen in the cold. Exposure to light results in darkening but does not seem to affect yields in subsequent reactions. Yield: 80–90%. ^{1}H NMR: (DMSO-d_6) 7.49–6.89 (5H, complex multiplet), 6.29 and 5.74 (4H, AA'BB' pair). Found: C, 37.99, H, 2.40. $C_{11}H_9Tl$ calcd. C, 38.23; H, 2.63%.

Synthesis of benzylcymantrene

In a nitrogen filled Schlenk flask were placed **2**, 0.539 g (1.5 mmol), and 50 ml of benzene. Bromomanganesepentacarbonyl, 0.412 g (1.5 mmol) was added and the mixture stirred for 24 h. The reaction mixture was filtered through a Celite plug. Removal of the solvent yielded 0.61 g of a yellow oily residue. An analytical sample was obtained by distillation, b.p. 75 ° C/0.05 mmHg) (lit. b.p. 80 ° C/0.2 mmHg; m.p. 38 ° C [36]). IR: (diethyl ether) 2050(w), 2020(s), 1935(s) cm^{-1}. NMR: (CDCl$_3$) 7.27 (s, phenyl), 4.64 (s, Cp), 3.57 (s, CH$_2$). Found: C, 60.92; H, 3.74. $C_{15}H_{11}O_3Mn$ calcd for: C, 61.24; H, 3.57%.

Synthesis of phenylcymantrene

Phenylcymantrene was prepared from **3**, 8.5 g (25 mmol), and bromopentacarbonylmanganese, 6.74 g (25 mmol), by a procedure analogous to that described above for benzylcymantrene. After removal of solvent the yellow oil was chromatographed on alumina using 10% dichloromethane in petroleum ether as an eluant. A single yellow band eluted from the column and solvent was removed to give 5.0 g of phenylcymantrene as a yellow solid, m.p. 36–37 ° C (lit. b.p. 65–70 ° C/0.3 mmHg. [36]. Yield 73%.

Synthesis of benzylcyclopentadienyltricarbonylrhenium

Reaction of **2**, 2.12 g (6.17 mmol), and bromopentacarbonylrhenium, 2.0 g (4.93 mmol), in refluxing benzene overnight gave, after solvent removal, an orange semi-solid. This material was taken up in 20% dichloromethane in petroleum ether and chromatographed on an alumina column to produce a single orange band. Removal of solvent from this band left 1.5 g of a yellow oil which crystallized upon standing to give a yellow solid, m.p. 51.5–52.0 °C. Yield 71%. IR: (CH_2Cl_2) 2022(s), 1924(s) cm^{-1}. NMR: ($CDCl_3$) 7.26 (s, phenyl), 5.22 (s, Cp), 3.72 (s, CH_2). Found: C, 42.70; H, 2.70; O, 11.46. $C_{15}H_{11}O_3Re$ calcd.: C, 42.35; H, 2.61; O, 11.28%.

Synthesis of 1,1′-bis(benzylcyclopentadienyl)iron (1,1′-bis(benzyl)ferrocene)

2, 2.72 g (7.57 mmol), was added to a solution of anhydrous ferrous chloride, 0.48 g (7.57 mmol), in 200 ml of THF. The reaction mixture was refluxed for 24 h and the warm solution was filtered over an alumina plug in a fritted funnel. The solvent was removed under vacuum and the product was crystallized from benzene/pentane, m.p. 100–102 °C (lit. m.p. 105–106 °C [37]). Recovered 0.75 g, yield: 54%. NMR: ($CDCl_3$) 7.2 (phenyl), 4.04 (Cp), 3.66 (CH_2).

Synthesis of 1,1′-bis(benzylcyclopentadienyl)titanium dichloride

Titanium tetrachloride, 0.347 ml (3.2 mmol), was added to a stirred slurry of **2**, 1.80 g (5.0 mmol), in benzene and the mixture was refluxed for 16 h. The cooled solution was filtered over Celite and the solvent removed under vacuum. The red residue was crystallized from benzene/pentane, m.p. 151–154 °C. Recovered 0.85 g, yield, 80%. NMR: ($CDCl_3$) 7.2 (phenyl), 4.2 (CH_2, 4.1 (Cp). MS: m/e 425 (M^+), 390 (M^+), 390 ($M^+ - Cl$), 355 ($M^+ - 2Cl$). Found: C, 65.48; H, 4.92. $C_{24}H_{22}TiCl_2$ calcd.: C, 67.16; H, 5.17%.

Synthesis of (benzylcyclopentadienyl) (cyclopentadienyl)titanium dichloride

2, 3.0 g (8.33 mmol), and cyclopentadienyltitanium trichloride, 3.0 g (13.7 mmol), were added to 60 ml of benzene in a 100 ml flask. The suspension was refluxed under nitrogen for 3–4 hours during which time the benzene phase turned deep orange. After heating, the suspension was filtered through Celite and the filtrate was concentrated. Precipitation of solid began when the solution volume had been reduced to about 15 ml. The solution was cooled and the product collected by filtration. A second crop could be collected by adding pentane to the benzene filtrate. The product is a pink powder, m.p. 170 °C. Recovered 2.0 g, yield 71%. NMR: ($CDCl_3$) 7.25 (s, phenyl), 6.49 (s, Cp), 6.41 (m, benzyl-Cp), 4.10 (s, CH_2). MS: m/e 339 (M^+), 304 ($M^+ - Cl$), 269 ($M^+ - 2$ Cl). Found: C, 59.71; H, 5.06. $C_{17}H_{16}TiCl_2$ calcd.: C, 60.21; H, 4.76%.

Synthesis of (phenylcyclopentadienyl) (cyclopentadienyl)titanium dichloride

3, 4.0 g (11.5 mmol) and cyclopentadienyltitanium trichloride, 4.0 g (18.2 mmol), were reacted as described above for the benzyl analog. After filtration of the reaction mixture the solvent was removed to give a grey solid. Recovered 0.32 g, yield 8.2%. NMR: (acetone-d_6) 7.72 (m, 2H, phenyl), 7.33 (m, 3H, 7.15 (t, 2H, AA′BB′ phenyl-Cp), 6.72 (t, 2H, AA′BB′ phenyl-Cp), 6.53 (s, 5H, Cp). Found: C, 59.25; H, 4.37. $C_{16}H_{14}TiCl_2$ calcd.: C, 59.11; H, 4,34%.

Synthesis of bis(benzylcyclopentadienyldicarbonylruthenium) and benzylcyclopentadienyldicarbonylruthenium chloride

2, 3.36 g (9.36 mmol), and $[Cl_2Ru(CO)_3]_2$, 2.0 g (3.92 mmol), and 6 ml of benzene were placed in a nitrogen-flushed 100-ml flask equipped with a spinbar, reflux condenser and nitrogen inlet. The reaction mixture was refluxed for 6 h. The suspension was filtered through Celite and the red filtrate concentrated using a rotary evaporator. The resulting red oil was taken up in 40% dichloromethane in petroleum ether and chromatographed on alumina. Two poorly resolved yellow bands were separated. Both bands gave red oils upon removal of solvent. HPLC analysis of both bands showed them to consist of four components in varying concentrations. Recrystallization of the first band from dichloromethane/heptane gave 0.30 g of benzylcyclopentadienyldicarbonylruthenium dimer as golden-yellow platelets, m.p. 162–164°C. Yield 6.1%. IR: (CH_2Cl_2) 2000(s), 1957(s), 1934(sh), 1804(sh), 1769(s) cm^{-1}. NMR: ($CDCl_3$) 7.25 (s, phenyl), 5.10 (s, Cp), 3.71 (s, CH_2). Found: C, 53.83; H, 3.60. $C_{28}H_{22}O_4Ru_2$ calcd.: C, 53.84; H, 3.55%. Recrystallization of the second band from dichloromethane/heptane gave 0.62 g of benzylcyclopentadienyldicarbonylruthenium chloride as yellow needles, m.p. 123–124°C. Yield 32%. IR: (CH_2Cl_2) 2052(s), 2001(s) cm^{-1}. NMR: ($CDCl_3$) 7.07 (s, phenyl), 4.34 (t, Cp), 3.94 (t, Cp), 3.32 (s, CH_2). Found: C, 48.17; H, 3.14. $C_{14}H_{11}O_2RuCl$ calcd.: C, 48.35; H, 3.19%. It was not possible to recover and purify the remaining two components.

Synthesis of bis(phenylcyclopentadienyldicarbonylruthenium and phenylcyclopentadienyldicarbonylruthenium chloride

3, 1.0 g (2.89 mmol), and $[Cl_2Ru(CO)_3]_2$, 0.37 g (1.45 mmol), were reacted in benzene as described for the benzyl derivative above. After filtration of the reaction mixture through Celite and removal of solvent, the remaining red oil was chromatographed on alumina using 50% dichloromethane in petroleum ether as an eluant. Two bands were recovered. Recrystallization of the first band from dichloromethane/heptane gave 86 mg of bis(phenylcyclopentadienyldicarbonylruthenium) as a yellow crystalline solid, m.p. 155–161°C. Yield 5%. IR: (CH_2Cl_2) 2001(s), 1959(s), 1936(sh), 1808(sh), 1775(s) cm^{-1}. NMR: ($CDCl_3$) 7.36 (s, phenyl), 5.49 (t, Cp), 5.18 (t, Cp). Found: C, 52.85; H, 3.25. $C_{26}H_{18}O_4Ru_2$ calcd.: C, 52.35; H, 3.02%. Recrystallization of the second band from dichloromethane/heptane gave 80 mg of phenylcyclopentadienyldicarbonylruthenium chloride as a yellow crystalline solid, m.p. 179–180°C. Yield 8.3%. IR: (CH_2Cl_2) 2054(s), 2003(s) cm^{-1}. NMR: ($CDCl_3$) 7.41 (s, phenyl), 5.75 (t, Cp), 5.45 (t, Cp). Found: C, 47.07; H, 2.67. $C_{13}H_9O_2RuCl$ calcd.: C, 46.79; H, 2.70%.

Synthesis of benzylcyclopentadienyldicarbonylrhodium

2, 4.4 g (13.0 mmol), and $[ClRh(CO)_2]_2$, 2.0 g (5.14 mmol), were reacted in benzene as described above for the preparation of bis(benzylcyclopentadienyldicarbonyl)rhodium. After filtration and removal of the benzene solvent the resulting red oil was chromatographed on alumina using petroleum ether as an initial eluant. Petroleum ether eluted a single yellow band which was stripped of solvent to give benzylcyclopentadienyldicarbonylrhodium as an orange oil. IR: (CH_2Cl_2) 2040 (s), 1974(s) cm^{-1}. NMR: ($CDCl_3$) 7.26 (s, phenyl), 5.37 (t, Cp), 5.32 (t, Cp), 3.65 (s, CH_2). Found: C, 54.12; H, 3.84. $C_{14}H_{11}O_2Rh$ calcd.: C, 53.50; H, 3.50%. Continued elution of the column with 15% dichloromethane in petroleum ether gave a red band which was stripped of solvent to give bis(benzylcyclopentadienyl)tricarbonyldirhodium as a dark red-brown oil. IR: (CH_2Cl_2) 2040(s), 1977(s), 1808(s). NMR ($CDCl_3$) 7.27 (s, phenyl), 5.33 (s, Cp), 3.66 (s, CH_2). Found: C, 54.38; H, 4.09. $C_{27}H_{22}O_3Rh_2$ calcd.: C, 54.00; H, 3.67%. Further elution of the column with 30% dichloromethane in petroleum ether eluted an olive drab band followed by a purple band. The olive drab band was stripped of solvent to give tris(benzylcyclopentadienyl)tricarbonyltrirhodium as a green solid, m.p. 145–146 ° C. IR: (CH_2Cl_2) 1844(s), 1790(s) cm^{-1}. NMR: ($CDCl_3$) 7.24 (s, phenyl), 5.39 (s, Cp), 3.48 (s, CH_2). Found: C, 54.31; H, 4.06. $C_{39}H_{33}O_3Rh_3$ calcd.: C, 54.55; H, 3.85%. The purple band yielded a small amount of purple product. IR: (CH_2Cl_2) 1845(s), 1786(s), 1699(s) cm^{-1}. Although insufficient material was available for full characterization, it is likely that the purple material is a tetrameric benzylcyclopentadienylrhodium derivative.

Synthesis of phenylcyclopentadienyldicarbonylrhodium

As described above for the benzyl derivative, **3**, 3.40 g (9.86 mmol), and $[ClRh(CO)_2]_2$, 2.0 g (5.14 mmol), were reacted in refluxing benzene. The residue after filtration and solvent removal was chromatographed on an alumina column using petroleum ether as an eluant. A yellow band was recovered which gave 1.84 g of phenylcyclopentadienylrhodium dicarbonyl as a deep red solid, m.p. 61–63 ° C. Yield 60%. IR: (CH_2Cl_2) 2040(s), 1979(s) cm^{-1}. NMR: ($CDCl_3$) 7.49–7.22 (m, phenyl), 5.90 (t, Cp), 5.52 (t, Cp). Found: C, 52.34; H, 3.27; O, 10.61. $C_{13}H_9O_2Rh$ calcd.: C, 52.02; H, 3.02; O, 10.66%. Continued elution with 20% dichloromethane in petroleum ether gave a dark red band which gave bis(phenylcyclopentadienyl)tricarbonyldirhodium as a deep red oil upon solvent removal. IR: (CH_2Cl_2) 1981(s), 1815(s) cm^{-1}. NMR: ($CDCl_3$) 7.15 (s, phenyl), 5.54 (t, Cp), 5.07 (t, Cp). Repeated attempts to crystallize this material failed to give a solid. All samples of this material were shown by HPLC to contain trimeric and tetrameric impurities so no analytical sample was available.

Synthesis of benzylcyclopentadienyldicarbonylcobalt

To a nitrogen flushed Schlenk flask were added $Co_2(CO)_8$, 0.75 g, (2.19 mmol), and THF (50 ml). Iodine, 0.56 g (2.20 mmol), was added slowly with stirring. After 1.5 h the green solution was transferred via cannula to a stirred slurry of **2**, 1.54 g (4.28 mmol), in 150 ml of THF contained in a 300 ml Schlenk flask at room temperature. The reaction mixture was stirred for 48 h, filtered through a Celite plug, the solvent removed and the residue was chromatographed on an alumina column. Elution with pentane yielded a red band. Removal of the solvent gave 0.3 g of benzylcyclopentadienylcobalt dicarbonyl as a red oil. Yield: 26%. IR: (pentane) 2030(s), 1965(s) cm^{-1}. NMR: ($CDCl_3$) 7.25 (phenyl), 4.95 (Cp), 3.55 (CH_2). MS: m/e 270 M^+. Found: C, 66.44; H, 5.65. $C_{14}H_{11}O_2Co$ calcd.: C, 62.24; H, 4.10%.

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