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# Formation and synthetic utility of formyl-, acetyl-, carbomethoxy-, and carboethoxy-cyclopentadienylthallium

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## Abstract

Formyl- (**1**), acetyl- (**2**), carbomethoxy- (**3**) and carboethoxycyclopentadienylthallium (**4**) have been prepared in high yields from reactions of the corresponding functionally substituted cyclopentadienylsodium salts with thallium ethoxide in ethanol solution. Products **1–4** so produced are readily isolated as air-stable solids, and have been characterized by their $^1$H and $^{13}$C NMR spectra. Reactions of **1–4** with $Mn(CO)_5Br$, $Re(CO)_5Br$ or $[Rh(CO)_2Cl]_2$ provide convenient routes to the respective functionally substituted cyclopentadienyl derivatives of manganese, rhenium or rhodium, and demonstrate the utility of **1–4** in organometallic syntheses.

## Introduction

The synthesis, structure and reactivity of functionally substituted cyclopentadienyl-metal compounds [1] have been of considerable interest in our laboratories and elsewhere. Substituted cyclopentadienylthallium reagents are especially useful in this regard, and we have recently described the formation and reactivity of benzyl- and phenylcyclopentadienylthallium [2]. Binuclear analogs such as fulvalenedithallium [3,4] and bis(cyclopentadienylthallium)methane [5] have been prepared in an analogous manner, and their synthetic utility has been investigated.

As part of our ongoing program for the development of functionalized cyclopentadienylthallium reagents, we report here on convenient, high-yield routes to formyl- (**1**), acetyl- (**2**), carbomethoxy- (**3**) and carboethoxycyclopentadienylthallium (**4**). The synthetic utility of **1–4** in the formation of functionally substituted

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cyclopentadienyl derivatives of manganese, rhenium and rhodium is also described. Independent of our studies, Arthurs and coworkers have recently reported related syntheses of **1** and **2**, and have used **2** as an intermediate in the preparation of $(\eta^2\text{-}C_2H_4)_2(\eta^5\text{-}C_5H_4COCH_3)M$ (M = Rh, Ir) complexes [6].

## Results and discussion

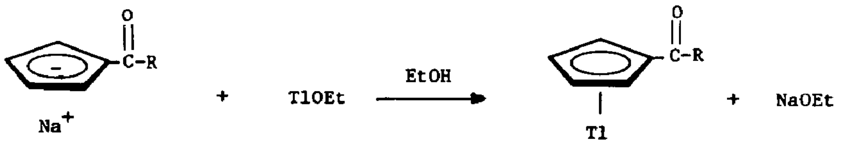
Cyclopentadienylthallium and its substituted derivatives are frequently prepared by metalation of the appropriate cyclopentadiene with thallium ethoxide in a suitable solvent [7]. We have subsequently found that reactions of functionally substituted cyclopentadienylsodium salts, themselves useful as intermediates in organometallic syntheses [1,8], with thallium ethoxide in ethanol provide a valuable route to the corresponding functionally substituted cyclopentadienylthallium derivatives.

These metathesis reactions proceed in high yield, and the products **1–4** so produced are readily isolated as air-stable solids. They have been characterized by means of their $^1H$ and $^{13}C$ NMR spectra and by combustion analyses.

In order to ascertain the synthetic utility of these organothallium compounds, we have examined their reactivities with both bromopentacarbonylmanganese and -rhenium. Reactions of **3** and **4** with $Mn(CO)_5Br$ produced the corresponding carboalkoxy compounds (**5**, **6**) in yields of 76% and 48%, respectively, whereas a reaction between **4** and $Re(CO)_5Br$ afforded the rhenium analog (**7**) in 56% yield.

Analogous reactions between $M(CO)_5Br$ (M = Mn, Re) and **1** or **2** likewise produced the corresponding formyl and acetyl derivatives in generally high yields: **8** (85%), **9** (82%), **10** (41%), and **11** (85%). A number of these functionally substituted cymantrene compounds and their rhenium analogs have been previously prepared starting with the parent systems $(\eta^5\text{-}C_5H_5)M(CO)_3$ (M = Mn, Re) (see Experimental section). The present route, utilizing the organothallium reagents **1–4**, thus represents a convenient alternative procedure.

We have also investigated the utility of **1–4** in the synthesis of functionally substituted ($\eta^5$-cyclopentadienyl)dicarbonylrhodium compounds, since these were required in current $^{103}Rh$ NMR studies [9]. Reactions of **1** or **2** with $[Rh(CO)_2Cl]_2$ afforded excellent yields (83–92%) of the respective formyl (**12**) or acetyl (**13**)

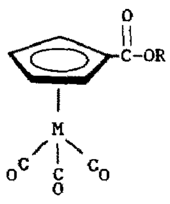


**1** R = H

**2** R = $CH_3$

**3** R = $OCH_3$

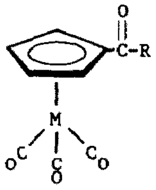
**4** R = $OCH_2CH_3$



5 M = Mn, R = $CH_3$

6 M = Mn, R = $CH_2CH_3$

7 M = Re, R = $CH_2CH_3$



8 M = Mn, R = H

9 M = Mn, R = $CH_3$

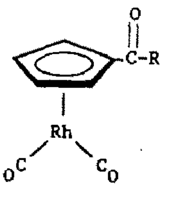
10 M = Re, R = H

11 M = Re, R = $CH_3$

analogs, whereas similar reactions of **3** or **4** with $[Rh(CO)_2Cl]_2$ gave the ester derivatives (**14**, **15**) in yields of 79% and 43%, respectively. In reactions leading to **13** and **15**, very small amounts of additional products were obtained, and were identified as binuclear compounds of the type $(CpR)_2Rh_2(CO)_3$ by means of spectral methods. We have previously reported the preparations of **12** and **13** via the corresponding functionally substituted cyclopentadienylsodium intermediates [10], but the present method produces **12** and **13** in substantially improved yields.

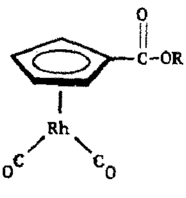
In our hands, the organothallium compounds **1**–**4** have been found to generally give high and reproducible yields of the corresponding cyclopentadienyl metal complexes without the storage and handling problems associated with the corresponding organosodium salts. With careful handling of the starting materials and waste products, the toxicity concerns associated with the use of thallium compounds can be responsibly addressed. In comparison with the sodium salts, there appear to be fewer side reactions with the thallium analogs due to their slightly lower ionic character.

It seems likely that organothallium compounds **1**–**4** should find considerable utility in the formation of functionally substituted cyclopentadienyl derivatives of other metals, in addition to those described above. Additional studies along these lines as well as reactions of **8**–**13** leading to heterobimetallic compounds are in progress and will be reported later.



12 R = H

13 R = $CH_3$



14 R = $CH_3$

15 R = $CH_2CH_3$

## Experimental

### General

All operations were conducted under a nitrogen atmosphere using standard Schlenk techniques. Nitrogen was deoxygenated with activated BTS catalyst and dried with $P_2O_5$ and molecular sieves. Benzene, toluene and hexane were purified by distillation from Na/K alloy under argon. Tetrahydrofuran (THF) and diethyl ether were predried over sodium wire and then distilled under argon from Na/K alloy. Dichloromethane was distilled from calcium hydride under argon. Benzonitrile was distilled from $P_2O_5$, whereas absolute ethanol was used without further purification. $Mn(CO)_5Br$ [11], $Re(CO)_5Br$ [11], $[Rh(CO)_2Cl]_2$ [12], and $TlOC_2H_5$ [13] were prepared by literature procedures. $Na(C_5H_4CO_2C_2H_5)$ [8,14], $Na(C_5H_4CO_2CH_3)$ [8,14], $Na(C_5H_4C(O)CH_3)$ [8,15] and $Na(C_5H_4CHO)$ [8,16] were synthesized by literature methods, employing 40% sodium dispersion instead of sodium sand. They were assumed to be formed as mono · THF solvates [15].

Preparative column chromatography was conducted using neutral alumina that had been dried in an oven for several days. Analytical high pressure liquid chromatography was conducted with a Gow/Mac HPLC unit using a 15 cm silica column. $^1H$ NMR spectra were obtained on Varian A-60, Bruker/IBM NR-80, or Bruker/IBM NR-300 spectrometers. $^{13}C$ NMR spectra were obtained on Varian XL-300 or Bruker/IBM NR-300 spectrometers. Infrared spectra were recorded on Perkin Elmer 1310 or Digilab Qualimatic FTIR spectrometers. Mass spectrometry was carried out by Dr. Gary Knerr using both electron impact and chemical ionization modes on a VG 7070-HS GC/MS using direct ionization. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA, or by Desert Analytics, Tucson, AZ.

**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.

### *(Carboethoxycyclopentadienyl)thallium (4)*

Into a 100-ml nitrogen-flushed Schlenk flask were added $Na(C_5H_4CO_2C_2H_5)$ (THF) (3.87 g, 17 mmol), 75 ml of 100% ethanol and a stir bar. With stirring, thallium ethoxide (1.7 ml, 25 mmol) was added dropwise via a syringe. After stirring for 30 min, the supernatant solution was decanted and the solid product was washed twice each with ethanol, diethyl ether, and hexane. The product was obtained as an air-stable tan powder in quantitative yield (5.80 g), m.p. (vacuum) 152–160 °C, m.p. (air) 143°C (dec) (lit. m.p. 80–82°C [17]). (Found: C, 28.28; H, 2.55. $C_8H_9O_2Tl$ calcd.: C, 28.14; H, 2.66%). $^1H$ NMR ($Me_2SO$-$d_6$) $\delta$ 6.22 (t, 2 H, H (2,5)), 5.63 (t, 2 H, H(3,4)), 4.01 (q, 2 H, $J$ 7.08 Hz, $CH_2$), 1.19 (t, 3 H, $J$ 7.08 Hz, $CH_3$). $^{13}C$ NMR ($Me_2SO$-$d_6$) $\delta$ 165.56 (C=O), 112.27 (C(1)), 111.87 (C(2,5)), 110.06 (C(3,4)), 57.27 ($CH_2$), 14.74 ($CH_3$). IR (KBr) 1645 (s), 1468 (s), 1441 (m), 1366 (m), 1345 (w), 1301 (s), 1167 (w), 1127 (s), 1046 (w), 745 (s) $cm^{-1}$.

### *(Carbomethoxycyclopentadienyl)thallium (3)*

A solution of 1.76 g (8.1 mmol) of $Na(C_5H_4CO_2CH_3)$(THF) in 40 ml of 100% ethanol was treated with 0.60 ml (8.5 mmol) of thallium ethoxide. After separation, washing and drying, the product was obtained as an air-stable tan solid in 93% yield

(2.47 g), m.p. (vacuum) 179–192° C, m.p. (air) 144° C (dec) (lit. m.p. 140–142° C (dec) [18], m.p. 136–140° C (dec) [14], m.p. 136–139° C [19]). $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 6.24 (t, 2 H, H(2,5)), 5.65 (t, 2 H, H(3,4)), 3.52 (s, 3 H, $CH_3$). $^{13}$C NMR ($Me_2SO$-$d_6$) $\delta$ 165.94 (C=O), 111.71 (C(2,5)), 109.98 (C(3,4)), 49.24 ($CH_3$). IR (KBr) 1653 (s), 1477 (s), 1457 (m), 1364 (m), 1348 (m), 1311 (s), 1190 (m), 1137 (s), 1047 (m), 746 (s) $cm^{-1}$.

### *(Acetylcyclopentadienyl)thallium (2)*

A solution of 6.56 g (32.5 mmol) of $Na(C_5H_4C(O)CH_3)(THF)$ in 75 ml of 100% ethanol was treated with 2.2 ml (31 mmol) of thallium ethoxide. After separation, washing and drying, the product was obtained as an air-stable tan powder in 79% yield (7.64 g). An attempt was made to obtain an analytically pure product by recrystallization from benzonitrile followed by washing with cold acetonitrile, cold diethyl ether, and drying (m.p. (vacuum) 222–223° C, m.p. (air) 118° C (dec.) (lit. m.p. 145° C [6]). (Found: C, 32.05; H, 2.30. $C_7H_7OTl$ calcd.: C, 26.99; H, 2.26%). $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 6.24 (t, 2 H, H(2,5)), 5.68 (t, 2 H, H(3,4)), 2.11 (s, 3 H, $CH_3$). $^{13}$C NMR ($Me_2SO$-$d_6$) $\delta$ 189.61 (C=O), 124.88 (C(1)), 112.11 (C(2,5)), 111.64 (C(3,4)), 26.43 ($CH_3$). IR (KBr) 1595 (s), 1551 (s), 1474 (s), 1353 (s), 1338 (s), 1110 (m), 1056 (m), 1036 (m), 1018 (m), 892 (m), 743 (s), 644 (m) $cm^{-1}$.

### *(Formylcyclopentadienyl)thallium (1)*

A solution of 4.15 g (22.1 mmol) of $Na(C_5H_4CHO)(THF)$ in 75 ml of 100% ethanol was treated with 2.5 ml (35 mmol) of thallium ethoxide. After separation, washing and drying, the product was obtained as a moderately air-stable tan powder in quantitative yield (6.56 g). An analytical sample was prepared by recrystallization from benzonitrile followed by washing twice each with 5 ml of cold acetonitrile, 5 ml of cold diethyl ether and drying (m.p. (vacuum) 163–170° C, m.p. (air) 144° C (dec.), lit. m.p. 150–152° C [6]. (Found: C, 25.23; H, 1.83. $C_6H_5OTl$ calcd.: C, 24.23, H. 1.69%). $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 9.58 (minor peak), 9.16 (s, 1 H, CHO), 6.20 (t, 2 H, H(2.5)), 5.78 (t, 2 H, H(3,4)). $^{13}$C NMR ($Me_2SO$-$d_6$) $\delta$ 180.8, 166.7, 125.8, 113.3. IR (KBr) 1600 (s), 1560 (s), 1467 (m), 1388 (w), 1324 (s), 1281 (m), 1033 (m), 738 (s), 609 (m) $cm^{-1}$.

### *($\eta^5$-Carboethoxycyclopentadienyl)tricarbonylmanganese (6)*

$Mn(CO)_5Br$ (0.951 g, 3.46 mmol) was placed in a nitrogen-flushed 100 ml Schlenk flask together with 50 ml of benzene and a stir bar. To the flask was subsequently added (carboethoxycyclopentadienyl)thallium (1.212 g, 3.55 mmol). A condenser and oil bubbler were attached and the mixture was stirred at reflux for 4 days. 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 high vacuum to yield a yellow oil (0.458 g, 48%). Purification on an alumina column eluting with hexane gave an analytically pure product (0.447 g, 47%). (Found: C, 47.81; H, 3.40. $C_{11}H_9MnO_5$ calcd.: C, 47.85; H, 3.28%). $^1$H NMR ($CDCl_3$) $\delta$ 5.42 (s, 2 H, H(2,5)), 4.76 (s, 2 H, H(3,4)), 4.24 (q, 2 H, $J$ 7.05 Hz, $CH_2$), 1.29 (t, 3 H, $J$ 7.05 Hz, $CH_3$). $^{13}$C NMR ($CDCl_3$) $\delta$ 223.08 (Mn–CO), 165.06 (C=O), 87.27 (C(2,5)), 84.85 (C(1)), 83.10 (C(3,4)), 61.10 ($CH_2$), 14.12 ($CH_3$). IR ($CH_2Cl_2$) 2031 (s), 1948 (s), 1720 (m) $cm^{-1}$. MS $m/e$ 276 $(M)^+$, 249 $(M-CO)^+$, 231 $(M-OC_2H_5)^+$, 220 $(M-2CO)^+$, 192 $(M-3CO)^+$.

### ($\eta^5$-Carbomethoxycyclopentadienyl)tricarbonylmanganese (5)

A solution of $Mn(CO)_5Br$ (1.020 g, 3.71 mmol) and (carbomethoxycyclopentadienyl)thallium (1.218 g, 3.72 mmol) in 50 ml of toluene was stirred at reflux under nitrogen for 30 h. Filtration and removal of the solvent produced a yellow solid (0.74 g, 76%). Chromatography on alumina using hexane elution removed unreacted $Mn(CO)_5Br$. Elution with 20% $CH_2Cl_2$ in hexane afforded a yellow solid (0.34 g, 35%). Sublimation at 25°C/0.1 torr yielded large yellow crystals, mp 46-49°C (lit. m.p. 53°C [20]). $^1H$ NMR ($CDCl_3$) $\delta$ 5.43 (s, 2 H, H(2,5)), 4.77 (s, 2 H, H(3,4)), 3.79 (s, 3 H, $OCH_3$). (At 60 MHz, the cyclopentadienyl resonances are observed as apparent triplets). $^{13}C$ NMR ($CDCl_3$) $\delta$ 222.98 (Mn–CO), 165.64 (C=O), 87.26 (C(2,5)), 84.59 (C(1)), 83.18 (C(3,4)), 52.15 ($OCH_3$). IR ($CH_2Cl_2$) 2022 (s), 1940 (s), 1720 (s), 1471 (M), 1427 (w), 1372 (m), 1288 (s), 1190 (m), 1143 (s) $cm^{-1}$. MS $m/e$ 262 $(M)^+$, 231 $(M-OCH_3)^+$, 206 $(M-2CO)^+$, 178 $(M-3CO)^+$.

### ($\eta^5$-Acetylcyclopentadienyl)tricarbonylmanganese (9)

A solution of $Mn(CO_5Br$ (0.995 g, 3.62 mmol) and (acetylcyclopentadienyl)thallium (1.127 g, 3.62 mmol) in 50 ml of toluene was stirred at reflux under nitrogen for 100 h. Filtration and removal of the solvent produced an orange solid. The product was purified on an alumina column using 1 : 1 toluene-hexane as the eluent to give a yellow solid (0.73 g, 82%). Sublimation at 25°C/0.1 torr yielded yellow needles, m.p. ($N_2$) 40–42°C (lit m.p. 39.5–42°C [21–23]. $^1H$ NMR ($CDCl_3$) $\delta$ 5.40 (s, 2 H, H(2,5)), 4.83 (s, 2 H, H(3,4)), 2.30 (s, 3 H, $CH_3$). (At 90 MHz, the cyclopentadienyl resonances appeared as apparent triplets). $^{13}C$ NMR ($CDCl_3$) $\delta$ 222.79 (Mn–CO), 194.84 (C=O), 91.88 (C(1)), 86.84 (C(2,5)), 83.66 (C(3,4)), 26.69 ($CH_3$). IR ($CH_2Cl_2$) 2031 (s), 1950 (s), 1685 (m) $cm^{-1}$.

### ($\eta^5$-Formylcyclopentadienyl)tricarbonylmanganese (8)

A solution of $Mn(CO)_5Br$ (1.014 g, 3.69 mmol) and (formylcyclopentadienyl)thallium (1.1103 g, 3.71 mmol) in 50 ml of toluene was stirred at reflux under nitrogen for 4 days. Filtration and removal of the solvent produced an orange solid. The product was purified by chromatography on alumina using 1 : 1 toluene-hexane as the eluent to yield a yellow solid (0.73 g, 85%). Sublimation at 25°C/0.1 torr afforded yellow crystals, m.p. 77–78°C (lit. m.p. 74–75°C [21]). $^1H$ NMR ($CDCl_3$) $\delta$ 9.58 (s, 1 H, CHO), 5.44 (s, 2 H, H(2,5)), 4.91 (s, 2 H, H(3,4)). $^{13}C$ NMR ($CDCl_3$) $\delta$ 222.23, (Mn–CO), 186.72 (C=O), 91.34 (C(1)), 86.85 (C(2,5)), 84.21 (C(3,4)), 91.34 (C(1)), 86.85 (C(2,5)), 84.21 (C(3,4)). IR ($CH_2Cl_2$) 2028 (s), 1948 (s), 1688 (m) $cm^{-1}$.

### ($\eta^5$-Carboethoxycyclopentadienyl)tricarbonylrhenium (7)

A solution of $Re(CO)_5Br$ (1.038 g, 2.555 mmol) and (carboethoxycyclopentadienyl)thallium (0.872 g, 2.55 mmol) in 50 ml of benzene was stirred at reflux under nitrogen for 25 h. Filtration and removal of the solvent produced a light yellow oil. Purification on an alumina column eluting with hexane yielded an analytically pure product (0.581 g, 56%). (Found: C, 32.60; H, 2.20. $C_{11}H_9O_5Re$ calcd.: C, 32.43; H, 2.23%). $^1H$ NMR ($CDCl_3$) $\delta$ 5.99 (t, 2 H, H(2,5)), 5.35 (t, 2 H, H(3,4)), 4.25 (q, 2 H, $J$ 7.12 Hz, $CH_2$), 1.29 (t, 3 H, $J$ 7.12 Hz, $CH_3$). $^{13}C$ NMR ($CDCl_3$) $\delta$ 191.97 (Re–CO), 163.56 (C=O), 88.79 (C(2,5)), 85.11 (C(3,4)), 84.43 (C(1)), 61.33 ($CH_2$), 14.03 ($CH_3$). IR ($CH_2Cl_2$) 2031 (s), 1939 (s), 1722 (m) $cm^{-1}$. MS $m/e$ 408 $(M)^+$, 380 $(M-CO)^+$, 363 $(M-OC_2H_5)^+$, 352 $(M-2CO)^+$, 324 $(M-3CO)^+$.

### *($\eta^5$-Acetylcyclopentadienyl)tricarbonylrhenium (11)*

A solution of $Re(CO)_5Br$ (0.285 g, 0.701 mmol) and (acetylcyclopentadienyl)thallium (0.222 g, 0.713 mmol) in 25 ml of benzene was stirred at reflux under nitrogen for 24 h. Filtration and removal of the solvent produced an off-white solid. The product was purified on an alumina column, using 1 : 1 $CH_2Cl_2$-heptane as the eluent, to yield a white solid (0.224 g, 85%), m.p. 78–80 °C (lit. m.p. 78 °C [22]). (Found: C, 31.96; H, 1.88. $C_{10}H_7O_4Re$ calcd.: C, 31.83; H, 1.87%). $^1H$ NMR ($CDCl_3$) $\delta$ 5.96 (t, 2 H, H(2,5)), 5.38 (t, 2 H, H(3,4)), 2.32 (s, 3 H, $CH_3$). $^{13}C$ NMR ($CDCl_3$) $\delta$ 191.64 (Re–CO), 96.40 (C(1)), 87.97 (C(2,5)), 85.17 (C(3,4)), 26.42 ($CH_3$). IR ($CH_2Cl_2$) 2032 (s), 1939 (s), 1688 (m) $cm^{-1}$. MS $m/e$ 378 $(M)^+$, 350 $(M-CO)^+$, 322 $(M-2CO)^+$, 294 $(M-3CO)^+$.

### *($\eta^5$-Formylcyclopentadienyl)tricarbonylrhenium (10)*

A solution of $Re(CO)_5Br$ (2.00 g, 4.93 mmol) and (formylcyclopentadienyl)thallium (1.60 g, 5.39 mmol) in 50 ml of benzene was stirred at reflux under nitrogen for 16 h. Filtration and removal of the solvent produced a red solid. The product was purified by recrystallization from heptane-$CH_2Cl_2$. (0.742 g, 41%), m.p. 90–91 °C (lit. m.p. 91–91.5 °C [23]). $^1H$ NMR ($CDCl_3$) $\delta$ 9.58 (s, 1 H, CHO), 6.01 (s, 2 H, H(2,5)), 5.47 (s, 2 H, H(3,4)). $^{13}C$ NMR ($CDCl_3$) $\delta$ 190.85 (Re–CO), 183.56 (C=O), 96.38 (C(1)), 87.91 (C(2,5)), 85.57 (C(3,4)). IR ($CH_2Cl_2$) 2039 (s), 1943 (s), 1695 (m) $cm^{-1}$.

### *($\eta^5$-Carboethoxycyclopentadienyl)dicarbonylrhodium (15)*

$[Rh(CO)_2Cl]_2$ (1.006 g, 2.59 mmol) was heated at reflux with stirring with (carboethoxycyclopentadienyl)thallium (1.786 g, 5.23 mmol) in 50 ml of benzene under nitrogen for 18 h. Filtration and removal of the solvent afforded a dark red oil. The product was purified by chromatography on an alumina column, eluting with hexane, to yield an analytically pure red oil (0.666 g, 43%). (Found: C, 40.63; H, 3.06. $C_{10}H_9O_4Rh$ calcd.: C, 40.57; H, 3.06%). $^1H$ NMR ($CDCl_3$) $\delta$ 5.88 (m, 2 H, H(2,5)), 5.56 (m, 2 H, H(3,4)), 4.19 (dq, 3 H, $J$(H–H) 7.10 Hz, $J$(H–Rh) 1.25 Hz, $CH_2$), 1.26 (dt, 3 H, $J$(H–H) 7.10 Hz, $J$(H–Rh) 1.25 Hz, $CH_3$). $^{13}C$ NMR ($CDCl_3$) $\delta$ 188.85 (Rh–CO), 163.22 (C=O) 98.60 (C(1)), 91.06 (C(2,5)), 87.96 (C(3,4)), 60.54 ($CH_2$), 14.04 ($CH_3$). IR ($CH_2Cl_2$) 2054 (s), 1991 (s), 1708 (m) $cm^{-1}$. MS $m/e$ 296 $(M)^+$, 268 $(M-CO)^+$, 251 $(M-OC_2H_5)^+$, 240 $(M-2CO)^+$.

Further elution with 30% $CH_2Cl_2$ in hexane resulted in a red band which produced a dark red solid upon removal of the solvent. Spectral data indicates that this product is a binuclear complex, ($\mu^2$-carbonyl)bis[($\eta^5$-carboethoxycyclopentadienyl)carbonylrhodium] (8 mg, 0.5%). $^1H$ NMR ($CDCl_3$) $\delta$ 5.95 (m, H(2,5)), 5.60 (m, H(3,4)), 4.25 (q, $J$ 7.11 Hz, $CH_2$), 1.31 (t, $J$ 7.11 Hz, $CH_3$). $^{13}C$ NMR ($CDCl_3$)(major peaks) $\delta$ 92.72, 91.14, 60.79, 53.40, 14.23. IR ($CH_2Cl_2$) 2055 (w), 2030 (w), 1996 (s), 1945 (w), 1835 (w), 1712 (s) $cm^{-1}$.

### *($\eta^5$-Carbomethoxycyclopentadienyl)dicarbonylrhodium (14)*

A mixture of $[Rh(CO)_2Cl]_2$ (0.20 g, 0.51 mmol), (carbomethoxycyclopentadienyl)thallium (0.34 g, 1.04 mmol) and 75 ml of THF was stirred under $N_2$ at 25 °C for 24 h. The solvent was removed and the residue taken up in diethyl ether and chromatographed on a silica gel column. Elution with 2 : 1 ether-hexane developed a single band which when collected and removed afforded 0.22 g (79%) of the desired product. An analytical sample was obtained by distillation at 50 °C/$10^{-2}$ torr. (Found: C, 38.07; H, 2.46. $C_9H_7O_4Rh$ calcd.: C, 38.32, H, 2.51%). $^1$H NMR (acetone-$d_6$) $\delta$ 6.10 (m, 2 H, H(2,5)), 5.90 (m, 2 H, H(3,4)), 3.80 (s, 3 H, $CH_3$). IR (neat) 2020 (s), 1975 (s), 1715 (s), 1480 (s), 1430 (s) 1370 (s), 1270 (s), 1190 (m), 1130 (s), 1060 (m), 1025 (w), 1010 (w), 965 (m), 900 (w), 800 (m), 780 (w), 700 (m) cm$^{-1}$.

### *($\eta^5$-Acetylcyclopentadienyl)dicarbonylrhodium (13)*

A mixture of $[Rh(CO)_2Cl]_2$ (1.00 g, 2.57 mmol), (acetylcyclopentadienyl)thallium (1.76 g, 5.65 mmol) and 50 ml of benzene was stirred at reflux under $N_2$ for 18 h. Filtration and removal of the solvent produced an oil. The latter was purified on an alumina column, eluting with 15/85 $CH_2Cl_2$-hexane, to yield a red oil (1.26 g, 92%). $^1$H NMR ($C_6D_6$) $\delta$ 5.32 (m, 2 H, H(2,5)), 4.89 (m, 2 H, H(3,4)), 1.90 (s, 3 H, $CH_3$). $^{13}$C NMR ($C_6D_6$) $\delta$ 189.47 (Rh–CO), 107.2 (C(1)), 91.48 (C(2,5)), 86.46 (C(3,4)), 25.61 ($CH_3$). IR ($CH_2Cl_2$) 2055 (s), 1992 (s), 1667 (m) cm$^{-1}$.

Continued elution produced another band which was detectable by spectroscopy. Spectral data indicates that this product is a binuclear complex, ($\mu^2$-carbonyl)bis[($\eta^5$-acetylcyclopentadienyl)carbonylrhodium]. $^1$H NMR ($C_6D_6$) $\delta$ 5.56 (m, H(2,5)), 5.00 (m, H(3,4)), 2.06 (s, $CH_3$). $^{13}$C NMR ($C_6D_6$) $\delta$ 200.38 (t, *J*(C–Rh) 42.6 Hz, Rh–CO), 190.45 (s, C=O), 105.6 (s, C(1)), 93.06 (s, C(2,5)), 90.29 (s, C(3,4)), 26.00 (s, $CH_3$). IR ($CH_2Cl_2$) 2033 (m), 1999 (s), 1833 (m), 1669 (m) cm$^{-1}$.

### *($\eta^5$-Formylcyclopentadienyl)dicarbonylrhodium (12)*

$[Rh(CO)_2Cl]_2$ (2.00 g, 5.14 mmol) was stirred at reflux under $N_2$ for 18 h in 60 ml of benzene with (formylcyclopentadienyl)thallium (3.36 g, 11.3 mmol). Filtration and removal of the solvent gave a red oil. The product was purified on an alumina column, using 1 : 1 $CH_2Cl_2$-hexane as the eluent, to yield a red oil (2.16 g, 83%). $^1$H NMR ($CDCl_3$) $\delta$ 9.25 (s, 1 H, CHO), 5.16 (m, 2 H, H(2,5)), 4.85 (m, 2 H, H(3,4)). $^{13}$C NMR ($CDCl_3$) $\delta$ 188.7 (Rh–CO), 181.1 (C=O), 107.8 (C(1)), 92.4 (C(2,5)), 86.2 (C(3,4)). IR ($CH_2Cl_2$) 2059 (s), 1997 (s), 1680 (m), 1663 (m) cm$^{-1}$.

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