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Preliminary communication

THE SYNTHESIS AND REACTIONS OF FULVALENEDITHALLIUM*

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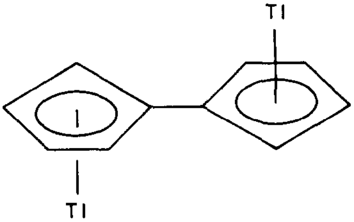
Summary

The reaction of dihydrofulvalene with TlOEt in Et_2O/hexane has given n fulvalenedithallium as an air-sensitive but thermally stable solid. This has been used in preparations of fulvalene complexes of Co, Rh, Ir, Ti, Mn and Re.

The construction of organometallic systems possessing two metals connected by ligand bridges, but not necessarily directly bonded, has been of considerable interest in recent years, in connection with probing potential electronic and chemical interactions between the metal centers [1, 2]. Fulvalene-bimetallic compounds, first described by us in 1969 [3], represent an excellent approach to such systems. However, synthetic methods thus far developed for forming the fulvalene ligand either involve numerous steps or the preparation of the fulvalene reagent immediately prior to use [4]. Our interest in combining the utility of the fulvalene dianion [5] with the mildness and reactivity of cyclopentadienylthallium compounds [6] led us to investigate the preparation of a dithallium derivative of fulvalene. We now wish to report the synthesis of fulvalenedithallium as an isolable solid and its reactions to form fulvalene complexes of cobalt, rhodium, iridium, titanium, manganese and rhenium.

The reaction of an ethyl ether/hexane solution of dihydrofulvalene with thal-



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*Dedicated to Professor Erwin Weiss on the occasion of his 60th birthday.

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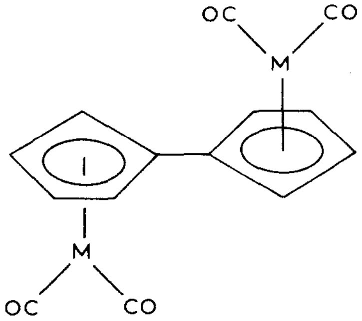
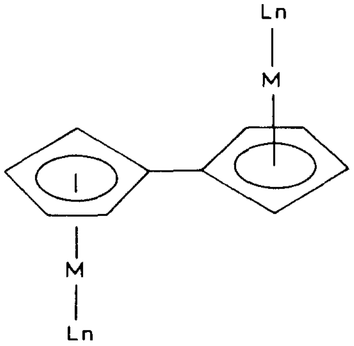
lium ethoxide affords chocolate brown fulvalenedithallium (**1**) as an air sensitive solid in 87—100% yield [7]. Compound **1** thus prepared is thermally stable at room temperature, but is best stored under argon at −20°C for prolonged periods.

Reactions of **1** with $[Rh(CO)_2Cl]_2$ [9], $[Ir(CO)_3Cl]_n$ [10], $[Rh(C_2H_4)_2Cl]_2$ [11], $[Rh(COT)Cl]_2$ [12] and $[Rh(COD)Cl]_2$ [13] in THF produce the new fulvalene-bimetallic compounds **2**—**6** in high yields [14] (COD = cyclooctadiene, COT = cyclooctatetraene).



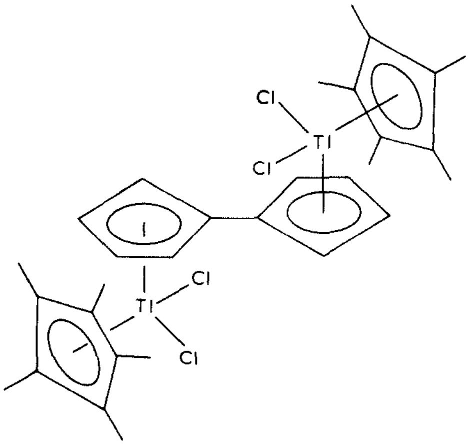
(**2** : M = Rh ;
3 : M = Ir ;
10:M = Co)



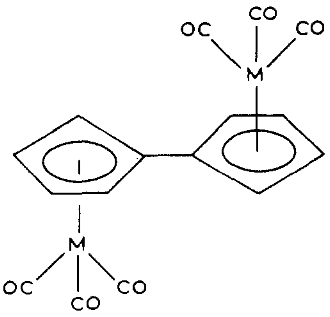
(**4** :M = Rh, Ln = $(C_2H_4)_2$;
5 :M = Rh, Ln = COT ;
6 :M = Rh, Ln = 1,5-COD ;
11:M = Co, Ln = COT)

Compound **1** has also proven useful in the formation of fulvalene derivatives of the early transition metals. For example, **1** reacts with $C_5Me_5TiCl_3$ [15] in refluxing benzene to form the novel dititanium complex **7** in 57% yield [16].

Reactions of **1** with $BrMn(CO)_5$ [17] or $BrRe(CO)_5$ [17] in refluxing benzene produce compounds **8** and **9** in yields of 86 and 94%, respectively. These syntheses represent an improved route to the previously reported com-



(**7**)

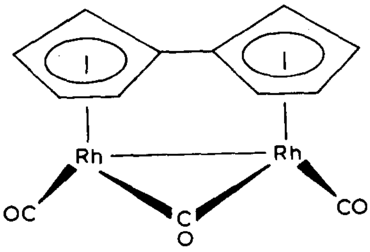


(**8**:M = Mn ;
9:M = Re)

pounds 8 [3, 18] and 9 [19], which were previously obtained in low overall yields by multi-step procedures.

Compound 1 likewise reacts with "ICo(CO)$_n$" [20] to afford the previously reported compound 10 [4, 21], although it is obtained in lower yield (52%) than by other methods [4]. Photolysis of 10 in the presence of excess COT gives the new complex 11 in fair yield [22].

(η^5:η^5-Fulvalene)tetracarbonyldirhodium (2) reacts with one equivalent of trimethylamine-*N*-oxide dihydrate in refluxing benzene to form the tricarbonyl complex 12 in 43% yield [23]. The infrared spectrum of 12 exhibits two terminal CO bands and one bridging CO band. The two terminal bands resulting from symmetric and asymmetric stretching indicate that the carbonyl ligands are *cis* to one another. This is in contrast to the parent compound $Cp_2Rh_2(CO)_3$ which exhibits only one terminal CO band [24] and whose molecular structure shows that the terminal carbonyls are *trans* to one another [25], thus eliminating the symmetrical CO stretch.



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Further studies are currently being undertaken to expand this chemistry to other metal systems and to study the electrochemistry and hydrogen activation abilities of these compounds.

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14 In a typical experiment, fulvalenedithallium (2.72 g, 5.07 mmol) and THF (150 ml) were added to an argon flushed 300 ml Schlenk flask. Dichlorotetracarbonyldirhodium (1.97 g, 5.07 mmol) was added and the solution was stirred at room temperature for 22 h. The solvent was removed and the residue was chromatographed on a 3 × 3 cm plug of alumina with pentane, producing an orange band. The solvent was removed to yield 1.64 g (72%) of **2** as orange-red crystals. An analytical sample was obtained by sublimation (90°C/10^{-3} Torr) followed by two recrystallizations from pentane, m.p. 99—101°C. Found: C, 37.56; H, 1.89. $C_{14}H_{10}O_4Rh_2$ calcd.: C, 37.70; H, 1.81%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm (multiplicity)): 5.71 (t); 5.42 (t); IR (THF): ν(CO) 2030, 1970 cm^{-1}; mass spectrum: *m/e* 446 (M^+). **3**: yellow crystals, 52%, m.p. 149—151°C (dec.); ^{1}H NMR ($CDCl_3$, 90 MHz): 5.69 (t), 5.47 (t); IR (THF): ν(CO) 2020, 1960 cm^{-1}; mass spectrum: *m/e* 622—626 (M^+). **4**: yellow needles, 73%, m.p. >145°C (dec.); ^{1}H NMR ($CDCl_3$, 300 MHz): 5.55 (d of t), 5.08 (t), 2.57 (m), 1.20 (m); mass spectrum: *m/e* 446 (M^+). **5**: golden yellow platelets, 75%, m.p. 261—264°C (dec.); ^{1}H NMR ($CDCl_3$, 300 MHz): 5.66 (s, 4H), 5.58 (t, 2H), 5.08 (t, 2H), 3.84 (s, 4H); mass spectrum: *m/e* 542 (M^+). **6**: golden yellow needles, 80%, m.p. 257—258°C (dec.), ^{1}H NMR ($CDCl_3$, 300 MHz): 5.38 (t, 2H), 4.99 (t, 2H), 3.64 (s, 4H), 2.16 (m, 4H), 1.88 (q, 4H); mass spectrum: *m/e* 550 (M^+).

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22 **11**: red brown powder, 32%, m.p. dec. >150°C; ^{1}H NMR ($CDCl_3$, 300 MHz): 5.46 (s, 4H), 5.24 (t, 2H), 4.39 (t, 2H), 3.18 (s, 4H); mass spectrum: *m/e* 454 (M^+).

23 **12**: dark red needles, 43%, m.p. >100°C (dec.); ^{1}H NMR ($CDCl_3$, 60 MHz): 5.91 (t), 5.25 (m); IR (THF): ν(CO) 2000, 1967, 1833 cm^{-1}; mass spectrum: *m/e* 418 (M^+).

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