

## BIS(CYCLOPENTADIENYLTHALLIUM)METHANE: A VERSATILE INTERMEDIATE FOR THE SYNTHESIS OF DINUCLEAR CYCLOPENTADIENYLMETAL CARBONYL COMPLEXES \*

THOMAS E. BITTERWOLF

*Department of Chemistry, United States Naval Academy, Annapolis, MD 21402 (U.S.A.)*

(Received March 7th, 1986)

### Summary

Bis(cyclopentadienylthallium)methane has been prepared from dicyclopentadienyl-methane and was shown to be a versatile starting material for the synthesis of a series of new dinuclear carbonylmetal complexes. Reactions of  $\text{CH}_2(\text{Cp-Tl})_2$  with carbonylhalometal complexes yielded  $\text{CH}_2[\text{CpMn}(\text{CO})_3]_2$ ,  $\text{CH}_2[\text{CpFe}(\text{CO})\text{Br}]_2$ ,  $\text{CH}_2[\text{CpRu}(\text{CO})_2\text{Cl}]_2$ ,  $\text{CH}_2[\text{CpRu}(\text{CO})_2]_2$ ,  $\text{CH}_2[\text{CpRh}(\text{CO})_2]_2$ ,  $\text{CH}_2[\text{CpRh}(\text{CO})]_2-\mu\text{-CO}$ , and  $\text{CH}_2[\text{CpIr}(\text{CO})_2]_2$ . Reduction of the iron and ruthenium halide derivatives was found to give the metal-metal bonded complexes, or the corresponding dianions depending on the time of reaction and the stoichiometry. The reaction of these dianions with methyl iodide to give the methyl derivatives is described. The facile decarbonylation of  $\text{CH}_2[\text{CpRh}(\text{CO})_2]_2$  and carbonylation of  $\text{CH}_2[\text{CpRh}(\text{CO})]_2-\mu\text{-CO}$  appears to be a consequence of the proximity of the two metal atoms. In contrast,  $\text{CH}_2[\text{CpIr}(\text{CO})_2]_2$  does not appear to form an analogous bridging compound under the reaction conditions. Complete spectral and physical data for the compounds are presented.

Dinuclear complexes in which two metal atoms are held in close proximity by one or more coupling ligands have considerable potential as vehicles for the study of metal-metal interactions and the interaction of ligands on adjacent metal atoms. In principle, one large class of these dinuclear compounds can be generated by coupling the cyclopentadienyl rings of cyclopentadienylmetal complexes either directly to form fulvalene derivatives or through alkyl or silyl linkages.

Several fulvalene derivatives have been reported by Smart [1,2] Vollhardt [3], Rausch [4] and their coworkers. Nelson and Wright [5] have examined the chemistry of dicyclopentadienyldimethylsilanecarbonyliron compounds in some detail. Tri-

\* Presented in part at the National Meeting of the American Chemical Society, Miami, FL, May 1985, INORG 277.

carbonyl manganese and -rhenium derivatives and a dicarbonyl cobalt derivative of dicyclopentadienyldimethylsilane were reported by Abel and Moorhouse [6], but no reactions of these compounds were examined. Werner, Scholz and Zolk [7] have reported the synthesis of several new carbonylrhodium, bis(trimethylphosphine)rhodium and mixed carbonyltrimethylphosphinerhodium derivatives of dicyclopentadienyldimethylsilane.

Several carbonylmetal derivatives of dicyclopentadienylmethane (**1**), have been reported. Cais and Feldkimmel [8] have prepared dicyclopentadienylmethane by reduction of dicyclopentadienyl ketone, but no analytical or spectral data were presented for the compound. The ketone was itself prepared by a Friedel-Crafts reaction of cymantrenylcarboxylic acid chloride with cymantrene. Bergman and Bryndza [9] have prepared bis(cyclopentadienylcobaltdicarbonyl)methane by the more general route of treating  $\text{Co}_2(\text{CO})_4$  with freshly prepared dicyclopentadienylmethane. Werner et al. [7] have reported the synthesis and molecular structure of  $\text{CH}_2[\text{CpRh}(\text{CO})]_2-\mu\text{-CO}$  as well as mixed carbonyltrimethylphosphine and bis(trimethylphosphine) complexes. These workers have described several reactions in which the basicity of the rhodium atom plays a significant role in the chemistry.

In this paper, we shall describe the synthesis of bis(cyclopentadienylthallium)methane (**2**) which has proved to be a versatile reagent for the preparation of several new dinuclear complexes of **1**, including derivatives of Mn, Fe, Ru, Rh, and Ir. The syntheses and spectral properties of these derivatives are also described.

TABLE 1

ANALYTICAL DATA AND MELTING POINTS FOR DICYCLOPENTADIENYLMETHANE DERIVATIVES

Compound	Analysis (Found (calcd.)(%))		M.p. (°C)
	C	H	
<b>2</b>	24.33 (23.98)	1.92 (1.83)	165-170 dec
<b>3</b>	34.02 (34.22)	1.96 (1.90)	92-94 dec
<b>4</b>	49.40 (49.18)	2.99 (2.73)	250 dec
<b>6</b>	-	-	oil
<b>7</b>	40.48 (39.47)	2.35 (2.19)	218-219 dec
<b>8</b>	34.14 (34.16)	1.93 (1.90)	161-162
<b>10</b>	-	-	oil
<b>11</b>	48.61 (48.57)	2.57 (2.38)	112-113
<b>12</b>	-	-	oil
<b>13</b>	38.69 (38.89)	2.35 (2.32)	185 dec
<b>14</b>	-	-	oil

In subsequent publications, we shall describe the use of dicyclopentadienylmethane and its sodium salt in the synthesis of iron and Group 6 carbonyl compounds, respectively.

## Results and discussion

The reaction of cyclopentadienylthallium with carbonylmetal halides is a convenient route for the preparation of a variety of cyclopentadienyl carbonylmetal complexes. Cymantrene- and cyclopentadienyl-dicarbonylrhodium are easily prepared by reaction of cyclopentadienylthallium with  $\text{BrMn}(\text{CO})_5$  and  $[\text{ClRh}(\text{CO})_2]_2$ , respectively [10,11]. Blackmoor et al. [12], have reported that cyclopentadienylthallium reacts with  $[\text{Cl}_2\text{Ru}(\text{CO})_3]_2$  to give cyclopentadienyldicarbonylruthenium chloride and a trace of the cyclopentadienyldicarbonylruthenium dimer. We have found that cyclopentadienylthallium reacts with  $\text{Br}_2\text{Fe}(\text{CO})_4$  to give cyclopentadienyldicarbonyliron bromide in fair yields [3].

Dicyclopentadienylmethane (**1**) is prepared by the method of Shaltegger [14] as modified by Bergman and Bryndza [9]. Reaction of **1** with thallium(I) ethoxide in

TABLE 2

IR SPECTRAL DATA FOR DICYCLOPENTADIENYLMETHANE COMPLEXES IN  $\text{CH}_2\text{Cl}_2$  ( $\text{cm}^{-1}$ )

Compound	Terminal	Bridging
3	2049, 2005	
4	1996, 1947	1778
6	2004, 1946	
7	2055, 2005	
8	2014, 1961, 1942	1780 (w)
10	2074, 1951	
11	2022, 1941	
12	2034, 1982	
13	2017, 1971	1817
14	2032, 1957	

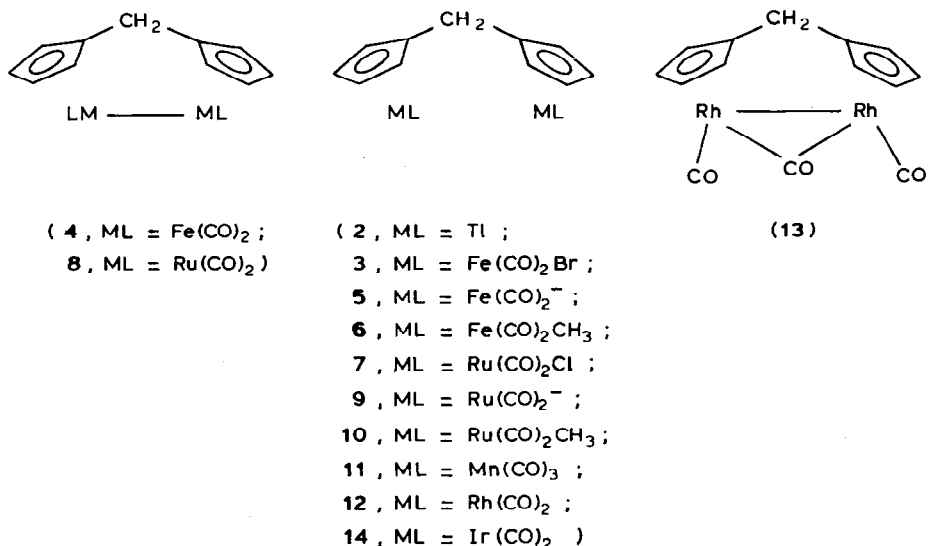
TABLE 3

$^1\text{H}$  NMR SPECTRAL DATA (in ppm relative to TMS)

Compound	$\text{C}_5\text{H}_4$	$\text{CH}_2$	$\text{CH}_3$	Solvent
3	4.36 (s)	3.15 (s)		<i>a</i>
4	4.50, 4.36 ( $\text{A}^2\text{B}^2$ )	1.71 (s)		<i>a</i>
6	3.95 (s)	2.51 (s)	0.27 (s)	<i>b</i>
7	5.68, 5.48 ( $\text{A}^2\text{B}^2$ )	3.25 (s)		<i>c</i>
8	5.31, 4.90 ( $\text{A}^2\text{B}^2$ )	3.65 (s)		<i>a</i>
10	5.17, 5.08 ( $\text{A}^2\text{B}^2$ )	3.13 (s)	0.30 (s)	<i>a</i>
11	4.68 (s)	3.21 (s)		<i>a</i>
12	4.94, 4.82 ( $\text{A}^2\text{B}^2$ )	2.77 (s)		<i>a</i>
13	5.76, 5.46 ( $\text{A}^2\text{B}^2$ )	3.55 (s)		<i>a</i>
14	5.52, 5.43 ( $\text{A}^2\text{B}^2$ )	3.00 (s)		<i>a</i>

*a*  $\text{CDCl}_3$ , *b* Benzene- $d_6$ , *c* Acetone- $d_6$ .

ethanol gives high yields of bis(cyclopentadienylthallium)methane (**2**) as a yellow-orange powder. Reaction of **2** with carbonylmethyl halides such as  $\text{Br}_2\text{Fe}(\text{CO})_4$ ,  $[\text{Cl}_2\text{Ru}(\text{CO})_3]_2$ ,  $\text{BrMn}(\text{CO})_5$ ,  $[\text{ClRh}(\text{CO})_2]_2$  and  $[\text{ClIr}(\text{CO})_3]_x$  in refluxing benzene of hexane results in the formation of the corresponding dinuclear carbonyl complexes in poor to excellent yield as described in the Experimental Section. Physical, analytical and spectral features of these compounds are summarized in Tables 1–3.



$\text{CH}_2[\text{CpFe}(\text{CO})_2\text{Br}]_2$  (**3**) is recovered as a red, air-stable solid. Treatment of this material with sodium-potassium alloy in THF gives mixtures of  $\text{CH}_2[\text{CpFe}(\text{CO})_2]_2(\text{Fe}-\text{Fe})$  (**4**) and its related dianion, **5**. **5** can also be generated by treatment of **4** with sodium-potassium alloy. **4** can also be prepared directly by treatment of **1** with  $\text{Fe}(\text{CO})_5$  in refluxing xylene/THF similar to the procedures developed by Nelson and Wright [5]. **4** has been shown to react smoothly with bromine to generate **3**.

IR spectra of **5** in THF show a set of carbonyl stretching frequencies at 1867, 1789 and  $1771\text{ cm}^{-1}$  which correspond remarkably well to those reported at 1868, 1792 and  $1772\text{ cm}^{-1}$  by Ellis and Flom [15] for the  $\text{CpFe}(\text{CO})_2^-$  anion generated by sodium-potassium alloy in THF. **5** reacts with methyl iodide to form **6** which corresponds closely to the analogous  $\text{CpFe}(\text{CO})_2\text{CH}_3$  reported by Davison, McCleverty and Wilkinson [16].

Reaction of  $[\text{Cl}_2\text{Ru}(\text{CO})_3]_2$  with **2** gives both  $\text{CH}_2[\text{CpRu}(\text{CO})_2\text{Cl}]_2$  (**7**) and  $\text{CH}_3[\text{CpRu}(\text{CO})_2]_2(\text{Ru}-\text{Ru})$  (**8**). By analogy with  $[\text{CpRu}(\text{CO})_2]_2$  [11], **8** reacts with HCl,  $\text{CHCl}_3$  and oxygen in ethanol to give **7** as a pale-yellow solid. Reaction of **7** with sodium-potassium alloy in THF forms mixtures of **8** and its dianion **9**, as found for **3**. Reaction of **9** with methyl iodide gives the dimethyl derivative **10** whose spectral properties are similar to those of  $\text{CpRu}(\text{CO})_2\text{CH}_3$  [16].

Reaction of **2** with  $\text{BrMn}(\text{CO})_5$  in refluxing benzene gives  $\text{CH}_2[\text{CpMn}(\text{CO})_3]_2$  (**11**) in good yield. We have reproduced the synthesis reported by Cais and Feldkimmel [8] and confirmed that the compound obtained by reduction of dicymantrenyl ketone is identical to compound **11** prepared by our technique.

Reaction of **2** with  $[\text{CpRh}(\text{CO})_2]_2$  in pentane gives  $\text{CH}_2[\text{CpRh}(\text{CO})_2]_2$  (**12**) as a dark brown oil in excellent yield. When **12** is heated in refluxing benzene, it readily loses carbon monoxide to give  $\text{CH}_2[\text{CpRh}(\text{CO})]_2-\mu\text{-CO}$  (**13**), which is isolated as a dark red polycrystalline solid. **13** in benzene at room temperature reacts with carbon monoxide at 50 psi to regenerate **12**. The ease with which **12** loses carbon monoxide to give the bridged carbonyl derivative differs sharply from the behavior of cyclopentadienyldicarbonylrhodium. Decarbonylation of this latter compound to form the bridged carbonyl dimer requires either photolysis [17] or reaction with a decarbonylating agent such as trimethylamineoxide [18]. Apparently the decarbonylation reaction of **12** is greatly accelerated by the immediate proximity of the two metal atoms. The rhodium compounds **12** and **13** have an extensive chemistry which will be described in subsequent publications.

Reaction of **2** with  $[\text{CpIr}(\text{CO})_3]_x$  in benzene gives **14** as a red-brown oil. Unlike the analogous rhodium compound, **14** does not appear to lose carbon monoxide to form a bridged carbonyl species. Additional work is proceeding on both the thermal and photochemical decarbonylation of **14**.

### Spectral studies

The carbonyl stretching regions of the infrared spectra of compounds **3**–**14** are presented in Table 2. The relative positions of these absorption bands are entirely consistent with values previously reported for the analogous cyclopentadienyl compounds.

IR spectra of **4** are characterized by strong bands in the terminal and bridging carbonyl regions. The positions of these bands are almost identical to those reported by Cotton and Yagupsky [19] for the *cis* isomer of the bis(cyclopentadienyldicarbonyliron) dimer.

The IR spectra of **8** in a variety of solvents (See Supplemental Data) show strong terminal carbonyl absorptions, but only weak absorptions in the region associated with bridging carbonyls. Similarly, Vollhardt and Weidman [2] have reported only the terminal stretching absorptions of the analogous fulvalenebis(dicarbonylruthenium)(*Ru*–*Ru*) derivative. It appears that the bridging carbonyl absorptions are weak or missing for that compound as well. Cotton and Yagupsky [19] have explained the fluxional behavior of the carbonyl groups in bis(cyclopentadienyldicarbonylruthenium)(*Ru*–*Ru*) by assuming that there is a dynamic equilibrium between the bridged and nonbridged forms of the compound. Fischer et al. [20] found that the bridged form predominates at low temperatures, but that the two forms are in about equal concentrations at room temperature. Apparently the

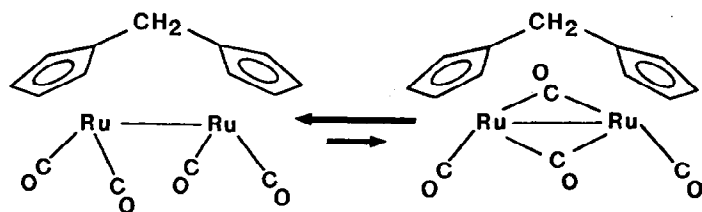


Fig. 1. Probable equilibrium between terminal and bridged isomers of **8**.

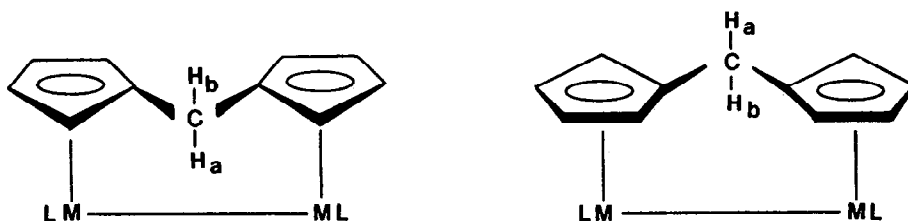


Fig. 2. Conformational forms associated with methylene proton averaging.

geometric constraints imposed by tying the rings together in both **8** and its fulvalene analog shift the equilibrium illustrated in Fig. 1 so that the nonbridged form is favored.

The  $^1\text{H}$  NMR spectra of the neutral compounds are summarized in Table 3. In all cases the protons of the methylene linkage between the rings give rise to a singlet resonance at room temperature. For those compounds without a direct metal-metal linkage the environment of the methylene protons is expected to be averaged by the free rotation of the cyclopentadienyl moieties. For the remaining compounds in which the metal atoms are coupled, one would expect the methylene protons to occupy magnetically distinct regions and hence give rise to an AB quartet. This is, in fact, observed for several derivatives of these dinuclear compounds, but not for the simple carbonyl derivatives reported here. It seems likely that compounds **4**, **8**, and **13** undergo a rapid rearrangement which flips the methylene group from side to side as illustrated in Fig. 2. A preliminary study of the variable temperature  $^{13}\text{C}$  NMR spectra of **13** supports this proposal. It has been found that the resonances of the four nonbridgehead ring carbons merge into a broad singlet at room temperature, but are clearly resolved into four resonances at  $-50^\circ\text{C}$  [21].

Mass spectra of compounds **4**, **8**, **11**, **12**, **13**, and **14** have been recorded (See Supplemental Data). In all cases, the compounds show a sequential loss of carbon monoxide. For all cases, except **12** and **14**, a molecular ion is observed.

## Experimental

Dicyclopentadienylmethane was prepared by the method of Bryndza [9b]. Thallium ethoxide was prepared from thallium metal as described by Fieser and Fieser [22]. Sodium-potassium alloy [15],  $\text{Br}_2\text{Fe}(\text{CO})_4$  [23],  $[\text{Cl}_2\text{Ru}(\text{CO})_3]_2$  [24], and  $[\text{ClRh}(\text{CO})_3]_2$  [25] were prepared by literature methods.  $\text{BrMn}(\text{CO})_5$  and  $[\text{ClIr}(\text{CO})_3]_x$  were purchased from Strem. All reactions and purification steps were conducted under nitrogen in solvents which were freshly distilled under nitrogen from sodium ketyl (benzene) or calcium hydride (THF).

Infrared spectra were recorded on a Perkin-Elmer Model 1750 FT-IR.  $^1\text{H}$  NMR spectra were recorded on a Varian Associates FT 80A NMR spectrometer operating at 79.542 MHz. Mass spectra were recorded on a Finnigan Model 4610 Mass Spectrometer operating in the electron impact mode. Routine reaction product analyses were conducted using a Gow-Mac HPLC with a silica gel column and 3/7 THF/petroleum ether as an eluant. Elemental analyses were conducted by Galbraith Laboratories, Inc. of Knoxville, TN. Analysis of bis(cyclopentadienylthallium)-methane was conducted by the Microanalytical Laboratory of The University of Massachusetts.

*Synthesis of  $CH_2(CpTi)_2$  (2)*

$CH_2Cp_2$  (**1**) is prepared by the method of Bryndza [9b] and is used immediately after its distillation. In a typical reaction, involving 23 g of 40% sodium dispersion and excess freshly distilled cyclopentadiene about 8 g of **1** is recovered.

**1** (8.00 g, 55.5 mmol), is placed in a 250 ml round bottom flask equipped with a stir bar. Ethanol (80 ml) is added and the flask is fitted with a rubber septum and flushed with nitrogen using syringe techniques. Thallium ethoxide (29.9 g, 120 mmol), is transferred to the flask by syringe and is added dropwise to the stirred solution of **1**. (*Note*: Thallium ethoxide is highly toxic and should only be handled with gloves and appropriate protective clothing!) A cloudy precipitate forms almost immediately. After addition of all of the thallium ethoxide, the yellow suspension is stirred at room temperature for another hour. It is frequently necessary to break up the product with a spatula in order to achieve uniform mixing.

The yellow precipitate is collected on a glass frit and washed with several portions of ethyl ether and pentane. The resulting powder is transferred to a Schlenk storage flask which is sealed, evacuated, then back flushed with nitrogen. Typical yields are 18 g (60%). Samples stored under nitrogen in the cold appear to be indefinitely stable. Prolonged exposure to air causes darkening of the compound. Slightly darkened material may be used without serious affect on yields.

Trace amounts of CpTi resulting from the incomplete purification of **1** can be removed from **2** by extraction with DMSO. **2** is almost totally insoluble in DMSO while CpTi is moderately soluble. Residual DMSO may be removed from **2** by washing with ethyl ether and pentane as described above. (*Note*: DMSO solutions of CpTi must be handled with extreme care to prevent accidental poisoning.)

*Synthesis of  $CH_2[CpFe(CO)_2Br]_2$  (3)*

**2** (2.50 g, 4.53 mmol) is placed into a nitrogen-flushed, 250 ml flask equipped with a stir bar. THF (100 ml) is added to the flask and freshly prepared  $Br_2Fe(CO)_4$  (3.26 g, 10 mmol), is added slowly. The reaction is rapid and vigorously evolves carbon monoxide. After addition is complete, the suspension is stirred for 4 h, then filtered through Celite. The filtrate is stripped of THF and the resulting solid is taken up in 7/3 petroleum ether/benzene and chromatographed on a silica gel column using the same solvent as an eluant. A yellow foreband is eluted from the column followed by a dark red band. Removal of the solvent from the red band gives 1.5 g of **3** (Yield 63%). Analytical samples were prepared by recrystallization from methylene chloride/pentane.

Attempts to scale up this reaction have been uniformly unsuccessful.

*Reaction of 3 with sodium-potassium alloy. Synthesis of  $CH_2[CpFe(CO)_2]_2$  (4) and  $CH_2[CpFe(CO)_2CH_3]_2$  (6)*

**3** (0.5 g, 0.90 mmol) is placed in a 100 ml Schlenk flask which is outfitted with a spin bar, and the flask is evacuated and backflushed with nitrogen. THF (50 ml) is added to the flask to give a bright red solution. Sodium-potassium alloy, 0.4 ml, is added to the flask by syringe, and the mixture is vigorously stirred. After 3 h, the reaction mixture is transferred by cannuli to a Schlenk filter flask and filtered into a Schlenk reaction flask. Addition of methyl iodide (1.5 ml) to the solution gives a fine suspension of potassium iodide. After 1 h, the solution is stripped and the resulting residue is taken up in 90/10 petroleum ether/THF and eluted on a  $30 \times 2$

cm silica gel column. A yellow band is eluted which was shown by IR and  $^1\text{H}$  NMR to be **6**. Further elution with 1/1 petroleum ether/THF removed a red band which was stripped to give a red crystalline solid. Spectral and analytical data show this compound to be **4**.

Yields of **6** can be optimized by permitting the reduction of **3** to proceed overnight at which time most of the **4** produced is converted to the dianion, **5**. Alternately, **4** can be used as a starting material.

#### *Reaction of 4 with bromine*

**4** (0.20 g, 0.55 mmol) is taken up in 30 ml of  $\text{CHCl}_3$  and 86 mg (0.55 mmol) of  $\text{Br}_2$  in 5 ml of  $\text{CHCl}_3$  is added dropwise at room temperature. IR and HPLC analysis of the reaction product confirmed the complete conversion of **4** to **3**.

#### *Synthesis of $\text{CH}_2[\text{CpRu}(\text{CO})_2\text{Cl}]_2$ (**7**) and $\text{CH}_2[\text{CpRu}(\text{CO})_2]_2$ (**8**)*

**2** (5.00 g, 9.09 mmol) and  $[\text{Cl}_2\text{Ru}(\text{CO})_3]_2$ , 4.73 g (9.09 mmol), are placed into a 100 ml Schlenk reaction flask outfitted with a spin bar. The flask is evacuated and backflushed with nitrogen. Benzene (50 ml) is added to the flask and the suspension refluxed for 10 h. The reaction mixture is filtered through Celite and the benzene removed. The resulting oil is taken up in methylene chloride and chromatographed on a  $2 \times 20$  cm alumina column with methylene chloride as an eluant. A light yellow band is eluted which yields 0.44 g (10.6% yield) of **7** upon removal of solvent. Analytical samples were prepared by recrystallization from methylene chloride/pentane solutions. Further elution of the column with acetone gives 0.23 g (4.8% yield) of **8** which can be recrystallized from acetone/water. A small additional quantity of **8** can be recovered by extraction of the Celite filtered residue with acetone followed by chromatography on alumina.

#### *Reduction of 7. Synthesis of $\text{CH}_2[\text{CpRu}(\text{CO})_2\text{CH}_3]_2$ (**10**)*

**7** (0.50 g, 0.95 mmol) is treated with sodium-potassium alloy in THF as described for **3** above. IR monitoring of the reaction solution showed the gradual formation of **8** followed by its decline as the dianion, **9**, was formed. After 20 h, the solution was filtered and 1.0 g of methyl iodide was added. After 1 h, the cloudy solution was filtered and the solvent removed. Chromatography of the resulting oil on a  $1 \times 10$  cm alumina column with 3/1 petroleum ether/methylene chloride as an eluant yielded a single yellow band which gave 70 mg of **10** (15% yield) upon solvent removal.

#### *Chlorination of 8*

**8** (0.50 g, 1.1 mmol) is added to a mixture consisting of 35 ml of ethanol, 7.0 ml of chloroform and 1.1 ml of concentrated hydrochloric acid in a 100 ml Schlenk flask equipped with a stir bar. Oxygen is bubbled through the stirred solution using a fritted bubbler. After 1 h, the reaction mixture is stripped and the residue is taken up into chloroform and dried with magnesium sulfate. After removal of the drying agent, the solution is stripped to give **7** in quantitative yield.

#### *Synthesis of $\text{CH}_2[\text{CpMn}(\text{CO})_3]_2$ (**11**)*

**2** (4.5 g, 8.2 mmol) and  $\text{BrMn}(\text{CO})_5$  (5.00 g, 18.2 mmol), are refluxed in benzene as described for the synthesis of **7** and **8**. Filtration of the reaction mixture followed



by removal of the solvent gave a light orange crystalline solid. Recrystallization from methylene chloride/pentane gives 1.30 g of **11** (43.6% yield).

*Synthesis of  $CH_2[CpRh(CO)_2]_2$  (**12**) and  $CH_2[CpRh(CO)]_2-\mu-CO$  (**13**)*

**2** (4.23 g, 7.7 mmol) and  $[ClRh(CO)_2]_2$  (3.00 g, 7.7 mmol) are taken up in hexane and refluxed for 4.5 h. The solution is filtered through Celite and stripped. The resulting oil is chromatographed on a  $1 \times 20$  cm alumina column using petroleum ether as an eluant. About 0.74 g of **12** is recovered as a brown oil after removal of the solvent (21% yield).

Extraction of the Celite residue with methylene chloride gives a red solution which is stripped to give a red solid. Recrystallization of the solid from methylene chloride/pentane gives 2.12 g of **13** (64% yield).

A similar reaction in benzene gave **12** as the predominant product. Extended reactions in either solvent yield **13** as the exclusive product.

*Carbonylation and decarbonylation reactions of **12** and **13***

A sample of **12** was taken up in benzene and refluxed. IR analysis of the solution over a period of hours showed the growth of new carbonyl stretching bands due to **13**.

A sample of **13** was taken up in benzene and transferred to a nitrogen flushed high pressure reaction bomb. The bomb was pressurized with 50 psi of carbon monoxide and left overnight at room temperature. IR analysis of the recovered solution showed it to be mostly **12** with only traces of **13** remaining.

*Synthesis of  $CH_2[CpIr(CO)_2]_2$  (**14**)*

**2** (0.44 g, 0.80 mmol) and 0.55 g (1.60 mmol)  $[ClIr(CO)_3]_x$  are taken up in 50 ml of benzene and refluxed overnight. After cooling, the red-brown reaction mixture is filtered through Celite and stripped of benzene. The resulting residue is taken up in methylene chloride and chromatographed on a  $1 \times 20$  cm alumina column using methylene chloride as an eluant. A yellow band is eluted with yields 0.24 g (23% yield) of **14** as a yellow-brown oil. A purple band of unknown composition was also observed to move slowly on the column. An insufficient quantity of this purple compound was available for detailed examination.

**Acknowledgements**

We wish to thank the Research Corporation for their support of this research, and the Johnson–Matthey Co. for their generous gift of rhodium and iridium chloride. We wish to acknowledge the advice and assistance of Professor William Geiger of the University of Vermont, and Professor Marvin Rausch of the University of Massachusetts. Mass spectra were recorded by Miss Patti Matson of the University of Vermont.

**References**

- 1 J.C. Smart and C.J. Curtis, *Inorg. Chem.*, 16 (1977) 1788.
- 2 J.C. Smart and C.J. Curtis, *Inorg. Chem.*, 17 (1978) 3290.
- 3 (a) K.P.C. Vollhardt and T.W. Weidman, *J. Am. Chem. Soc.*, 105 (1983) 1676; (b) *Organometallics*, 3 (1984) 82; (c) J.S. Drage and K.P.C. Vollhardt, *Organometallics*, 4 (1985) 191.

- 4 (a) M.D. Rausch, R.F. Kovar and C.S. Kraihanzel, *J. Am. Chem. Soc.*, 91 (1969) 1259; (b) R.F. Kovar and M.D. Rausch, *J. Org. Chem.*, 38 (1973) 1918.
- 5 (a) G.O. Nelson and M.E. Wright, *J. Organomet. Chem.*, 206 (1981) C21; (b) M.M. Harris, J.D. Atwood, M.E. Wright and G.O. Nelson, *Inorg. Chem.*, 21 (1982) 2117; (c) G.O. Nelson and M.E. Wright, *J. Organomet. Chem.*, 239 (1982) 353; (d) *idem*, *Organometallics*, 1 (1982) 565; (e) M.E. Wright, T.M. Mezza, G.O. Nelson, N.R. Armstrong, V.W. Day and M.R. Thompson, *Organometallics*, 2 (1983) 1711.
- 6 E.W. Abel and S. Moorhouse, *J. Organomet. Chem.*, 29 (1971) 227.
- 7 H. Werner, H.J. Scholz and R. Zolk, *Chem. Ber.*, 118 (1985) 4531.
- 8 M. Cais and M. Feldkimmel, *Tetrahedron Lett.*, (1961) 440.
- 9 (a) H.E. Bryndza and R.G. Bergman, *J. Am. Chem. Soc.*, 101 (1979) 4766; (b) H.E. Bryndza, Ph.D. Dissertation, Univ., California, Berkeley, 1981.
- 10 A.N. Nesmeyanov, K.N. Anisimov and N.E. Kolobova, *Izv. Akad. Nauk, SSSR Ser. Khim.*, (1964) 2220.
- 11 (a) K. Bittler and E.O. Fischer, *Z. Naturforsch.*, 166 (1961) 225; (b) J. Knight and M.J. Mays, *J. Chem. Soc. A*, (1970) 654.
- 12 T. Blackmore, J.D. Cotton, M.I. Bruce, and F.G.A. Stone, *J. Chem. Soc., Dalton*, (1968) 2931.
- 13 T.E. Bitterwolf and T. Fritz, unpublished results, 1984.
- 14 H. Shaltegger, M. Neuenschwander, and D. Meuche, *Helv. Chim. Acta*, 48 (1965) 955.
- 15 J.E. Ellis and E.A. Flom, *J. Organomet. Chem.*, 99 (1975) 263.
- 16 A. Davison, J.A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, (1963) 1133.
- 17 (a) O.S. Mills and J.P. Nice, *J. Organomet. Chem.*, 10 (1967) 337; (b) J. Evans, B.F.G. Johnson, J. Lewis, and J.R. Norton, *J. Chem. Soc., Chem. Commun.*, (1973) 79; (c) R. Hill and S.A.R. Knox, *J. Chem. Soc., Dalton*, (1975) 2622.
- 18 R.J. Lawson and J.R. Shapley, *J. Am. Chem. Soc.*, 98 (1976) 7433.
- 19 F.A. Cotton and G. Yagupsky, *Inorg. Chem.*, 6 (1967) 15.
- 20 (a) R.D. Fischer, A. Vogler and K. Noack, *J. Organomet. Chem.*, 7 (1967) 135; (b) K. Noack, *ibid.*, 7 (1967) 151.
- 21 T.E. Bitterwolf and B.V. Johnson, unpublished results, 1985.
- 22 M. Fieser and L.F. Fieser, *Reagents for Organic Synthesis*, vol 2, Wiley-Intersciences, New York, 1969, p. 407.
- 23 (a) I.A. Cohen and F. Basolo, *J. Inorg. Nucl. Chem.*, 28 (1966) 511. (b) W. Heiber and G. Bader, *Z. Anorg. Allg. Chem.*, 190 (1930) 193.
- 24 D.H. Gibson, W.-L. Hsu, A.L. Steinmetz, and B.V. Johnson, *J. Organomet. Chem.*, 208 (1981) 89.
- 25 J.A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 8 (1966) 211.