# THE SYNTHESIS AND REACTIVITY OF SOME $\mu$ -PHTHALOYL AND $\mu$ -PHENYLENE COMPLEXES

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(Received 24 September 1990; accepted 5 December 1990)

**Abstract**—The binuclear  $\mu$ -phthaloyl compounds 1,4-C<sub>6</sub>H<sub>4</sub>(COM)<sub>2</sub>, where M = Re(CO)<sub>5</sub>, Mn(CO)<sub>5</sub>,  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>,  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>, Rh(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> or Co(CO)<sub>3</sub>(PPh<sub>3</sub>), have been prepared and converted to the  $\mu$ -phenylene compounds 1,4-C<sub>6</sub>H<sub>4</sub>M<sub>2</sub>, where M = Re(CO)<sub>5</sub>. Mn(CO)<sub>5</sub> or  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>. The reactions of the  $\mu$ -phthaloyl compounds with halogens, reducing agents and PPh<sub>3</sub> are reported, as are the reactions of the  $\mu$ -phenylene complexes with CO, synthesis gas, SO<sub>2</sub>, halogens and tertiary phosphines.

Mononuclear aryl complexes L<sub>n</sub>M-Ar are well known. These complexes can be models for metal aryl species in catalytic reactions which give monofunctional aryl products, ArX.<sup>1</sup> Difunctional aryl compounds such as the phthalic acids C<sub>6</sub>H<sub>4</sub>  $(COOH)_2$  are of great commercial importance.<sup>2</sup> Potential precursors of 1,4-C<sub>6</sub>H<sub>4</sub>X<sub>2</sub> compounds in a catalytic cycle would be the binuclear  $\mu$ -phenylene or  $\mu$ -phthaloyl complexes 1,4-C<sub>6</sub>H<sub>4</sub>(ML<sub>n</sub>)<sub>2</sub> or 1,4- $C_6H_4(COML_n)_2$ . When we started our investigations, very few binuclear compounds of these types were known. The compounds where  $ML_n = Mn(CO)_5$  or Re(CO)\_5 had been briefly mentioned,<sup>3</sup> as had 1,4-C<sub>6</sub>H<sub>4</sub>(Cp\*<sub>2</sub>Lu)<sub>2</sub> (Cp\* =  $\eta^{5}$ - $C_5Me_5$ ).<sup>4</sup> The compound 1,4- $C_6H_4[Ni(PPh_3)_2Br]_2$ is known<sup>5</sup> and  $1,4-C_6H_4$ [Fe(porphyrin)]<sub>2</sub> has recently been reported.<sup>6</sup> While our work was in progress, Hunter and co-workers reported some  $\mu$ phthaloyl and  $\mu$ -phenylene complexes<sup>7-10</sup> which we had independently prepared. We now report some examples of these complexes, some new data on previously prepared compounds, as well as the results of some reactivity studies on these compounds.

# **EXPERIMENTAL**

All reactions were performed under an atmosphere of high purity nitrogen using standard Schlenk tube techniques. Solvents were purified by standard procedures. The compounds  $Mn_2(CO)_{10}$ ,

 $\operatorname{Re}_2(\operatorname{CO})_{10}$ ,  $[\operatorname{CpFe}(\operatorname{CO})_2]_2$ ,  $[\operatorname{CpMo}(\operatorname{CO})_3]_2$  and  $Co_2(CO)_8$  were purchased from Strem; K-Selectride (potassium tri-sec-butylborohydride) was purchased from Aldrich. These and other reagents were used as received. The compounds  $RhCl(PPh_3)_3^{11}$ and  $[Co(CO)_3(PPh_3)]_2^{12}$  were prepared by standard procedures. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer and NMR spectra on either a Varian XL 100 or VXR 200 or a Bruker WH 90 instrument. Tetramethylsilane was used as an internal standard ( $\delta 0.00$  ppm) for NMR spectra. Mass spectra were recorded on a V.G. Micromass 16 F spectrometer operating at 70 eV and using an accelerating voltage of 4 kV. Melting points were determined on a Reichert Thermovar hotstage microscope. Microanalyses were performed in the microanalytical laboratory at the University of Cape Town. Photochemical reactions were carried out in a Hanovia photochemical reactor (125 W) and high pressure reactions in a 250 cm<sup>3</sup> Berghoff autoclave.

# $\mu$ -Phthaloyl complexes

# Preparation of $1,4-C_6H_4[COCpMo(CO)_3]_2(1)$

A solution of Na[CpMo(CO)<sub>3</sub>] (2.04 mmol) was added to a solution of  $1,4-C_6H_4(COCl)_2$  (0.21 g, 1.02 mmol) in THF (2 cm<sup>3</sup>) at  $-78^{\circ}C$ . The reaction mixture was then stirred at  $-78^{\circ}C$  for 30 min and then allowed to warm up to room temperature over 30 min. The solvent was removed to give a brown residue which was extracted with CH<sub>2</sub>Cl<sub>2</sub>

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(50 cm<sup>3</sup>) and filtered. The filtrate was evaporated, resulting in an orange-red residue which was dissolved in benzene and chromatographed on an alumina column. A red band was eluted with benzene which gave [CpMo(CO)<sub>3</sub>]<sub>2</sub> (78%). An orange band was eluted with 20% CH<sub>2</sub>Cl<sub>2</sub>/benzene which produced an orange-yellow solid on evaporation. The solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane to yield the required product. The yield, m.p.,

to yield the required product. The yield, m.p., elemental analysis and spectral data for this and other new complexes are given in Table 1. The compounds  $1,4-C_6H_4(COM)_2$  [where M = Mn(CO)<sub>5</sub> (2) or CpFe(CO)<sub>2</sub> (3)] were prepared in a similar way, as has been described by Hunter

# Preparation of $1,4-C_6H_4[CORe(CO)_5]_2$ (4)

A solution of the sodium salt Na[Re(CO)<sub>5</sub>] (2 mmol) in THF (30 cm<sup>3</sup>) was added dropwise to a solution of 1,4-terephthaloyl dichloride (1 mmol) in THF (5 cm<sup>3</sup>) with rapid stirring. The reaction mixture was stirred for 3 h after which the solvent was removed and the residue triturated with water ( $4 \times 30$  cm<sup>3</sup>). The solid product was filtered off, washed with diethyl ether ( $5 \times 30$  cm<sup>3</sup>) and dried *in vacuo*.

# Preparation of $1,4-C_6H_4[COCo(CO)_3(PPh_3)]_2$ (5)

The compound  $[Co(CO)_3(PPh_3)]_2$  (0.50 g, 0.62 mmol) as a suspension in THF (20 cm<sup>3</sup>) was stirred

Compound number	Yield (%)	Melting point (°C)	Microanalysis" (%)		$\frac{\text{IR } \nu(\text{CO})^b}{(\text{cm}^{-1})}$		NMR <sup>c</sup>	$\delta$ (ppm)	
1	7	131–138	C H	46.0 2.2	(46.3) (2.3)	2024 m 1607 m	1938 s	7.44 5.54	$(4H, C_6H_4)$ $(10H, C_5H_5)$
4	44	210–218	C H	27.8 0.7	(27.6) (0.5)	2133 w 2018 sh 1976 vs	2060 m 2002 s 1566 m		e
5	23	204–212	C H	63.3 3.8	(63.7) (3.6)	2051 w 1966 s	1983 s 1622 m	7.72 7.44	(4H, C <sub>6</sub> H <sub>4</sub> ) (30H, C <sub>6</sub> H <sub>5</sub> )
6	74	206–211	C H	62.5 4.6	(62.9) (4.2)	1701 m	1665 w <sup>d</sup>		e
7	56	210–215	С Н	26.5 0.70	(26.4) (0.55)	2128 w 2020 s	1986 sh	7.26 183.4 181.5 134.3 146.1	(4H, $C_6H_4$ ) <sup>f</sup> (CO) (CO) (Re—C of $C_6H_4$ ) (other C of $C_6H_4$ )
10	18	166–173	C H	32.0 0.68	(32.3) (0.68)	2137 m 2051 s	2985 w 2022 m		e
11	33	198–210	C H	22.0 0.49	(22.4) (0.47)	2158 w	2045 vs		e
12	77	174–181	C H	42.7 2.4	(43.0) (2.5)	2054 s	2011 vs	7.38 5.10	$(s, 4H, C_6H_4)$ (s, 10H, C <sub>5</sub> H <sub>5</sub> )
13	65	161–164	C H	58.5 3.8	(59.1) (4.0)	2065 m 1969 vs	1988 s 1946 s	7.38 6.90 1.67	(m, 20H, $C_6H_5$ ) (s, 4H, $C_6H_4$ ) (d, 6H, $J = 9$ Hz)
15	11	98-107	C H	72.5 4.8	(72.2) (4.9)	1913 s		7.34 6.54 4.36	(m, 30H, C <sub>6</sub> H <sub>5</sub> ) (s, 4H, C <sub>6</sub> H <sub>4</sub> ) (d, 10H, C <sub>5</sub> H <sub>5</sub> )

Table 1. Data for  $\mu$ -phthaloyl and  $\mu$ -phenylene compounds

<sup>a</sup> Calculated values in parentheses.

<sup>d</sup> Nujol mull.

 $^{f}$ CD<sub>2</sub>Cl<sub>2</sub>.

and Szigety.9

 $<sup>{}^{</sup>b}$  CH<sub>2</sub>Cl<sub>2</sub> solution unless otherwise stated; s = strong, m = medium, w = weak.

<sup>&</sup>lt;sup>c</sup>CDCl<sub>3</sub> solution unless otherwise stated.

<sup>&</sup>lt;sup>e</sup> Not recorded due to insolubility of sample.

with a sodium amalgam (0.1 g Na in  $2 \text{ cm}^3 \text{ Hg}$ ) for 18 h. The resulting green solution of Na[Co  $(CO)_3(PPh_3)$ ] (1.24 mmol) was added to a solution of  $1,4-C_6H_4(COCl)_2$  (0.13 g, 0.62 mmol) in THF  $(2 \text{ cm}^3)$  and the mixture stirred for 18 h at room temperature. The solvent was removed leaving a green residue which was extracted with  $CH_2Cl_2$  (60 cm<sup>3</sup>) and filtered. The volume of the filtrate was reduced to  $ca \ 10 \ cm^3$  and chromatographed on a Florisil column. A pale yellow band containing 1,4- $C_6H_4(COCl)_2$  and  $1,4-C_6H_4(COOH)_2$  was eluted initially using CH<sub>2</sub>Cl<sub>2</sub>. A bright yellow band was then eluted with  $CH_2Cl_2$ /ethanol (1:1) which gave a solid on evaporation. This was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane to give microcrystals of the product. The same compound is obtained, in lower yield, from the reaction of  $Na[Co(CO)_4]$  with 1,4- $C_6H_4(COCl)_2$  followed by the addition of PPh<sub>3</sub> to the reaction mixture.

### Preparation of $1,4-C_6H_4[CORhCl_2(PPh_3)_2]_2$ (6)

To a solution of RhCl(PPh<sub>3</sub>)<sub>3</sub> (0.50 g, 0.54 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) was added a solution of 1,4-C<sub>6</sub>H<sub>4</sub>(COCl)<sub>2</sub> (0.055 g, 0.27 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 cm<sup>3</sup>) and the reaction mixture was stirred for 6.5 h at room temperature. During this time, the solution changed colour from red to yellow and a fine precipitate formed. Hexane (100 cm<sup>3</sup>) was added and the resulting precipitate was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub> (4×10 cm<sup>3</sup>) to give the product as yellow microcrystals. IR (Nujol):  $\nu$ (RhCl) 356 and 324 cm<sup>-1</sup>.

#### $\mu$ -Phenylene complexes

# Preparation of $1,4-C_6H_4[Re(CO)_5]_2$ (7)

The compound 3 (0.050 g, 0.064 mmol), as a suspension in methyl isobutyl ketone (5 cm<sup>3</sup>), was refluxed for 35 min then filtered hot. The solvent was reduced and the resulting mixture cooled to  $-15^{\circ}$ C to give the product as white microcrystals.

The compound  $1,4-C_6H_4[Mn(CO)_5]_2$  (8) was prepared in 74% yield by refluxing the corresponding  $\mu$ -phthaloyl compound in toluene and  $1,4-C_6H_4[CpFe(CO)_2]_2$  (9) was obtained in 26% yield on UV irradiation of a toluene solution of the  $\mu$ phthaloyl compound 4; the data obtained for the manganese and iron compounds agreed well with that reported by Hunter and Szigety.<sup>9</sup>

# Reactions of the $\mu$ -phthaloyl compounds

# (a) With halogens

 $1,4-C_6H_4[COMnCO)_5]_2$  (2) with Br<sub>2</sub> or I<sub>2</sub>. A suspension of 2 (0.19 mmol) in THF (7 cm<sup>3</sup>) was

stirred at room temperature for *ca* 70 h with the halogen (0.76 mmol). Unreacted starting material (48%) was filtered off and  $1,4-C_6H_4(COOH)_2$  (48%) and Mn(CO)<sub>5</sub>X [where X = Br (44%), I (32%)] were isolated from the filtrate and identified by their IR spectra.

1,4-C<sub>6</sub>H<sub>4</sub>[COCpFe(CO)<sub>2</sub>]<sub>2</sub> (3) with Br<sub>2</sub> or I<sub>2</sub>. In a similar way, 4 (0.21 mmol) was reacted with the halogen (0.42 mmol) in THF (7 cm<sup>3</sup>) for 20 min to give 1,4-C<sub>6</sub>H<sub>4</sub>(COOH)<sub>2</sub> (94%) and CpFe(CO)<sub>2</sub>X [where X = Br (85%), I (77%)], the latter compounds were identified by IR and <sup>1</sup>H NMR.

1,4-C<sub>6</sub>H<sub>4</sub>[CORe(CO)<sub>5</sub>]<sub>2</sub> (4) with Br<sub>2</sub> or I<sub>2</sub>. In a similar way, 3 (0.13 mmol) was reacted with the halogen (0.26 mmol) in THF (7 cm<sup>3</sup>) for 2 h to give 1,4-C<sub>6</sub>H<sub>4</sub>(COOH)<sub>2</sub> (83%) and Re(CO)<sub>5</sub>X [where X = Br (74%), I (69%)].

#### (b) With tertiary phosphines

1,4-C<sub>6</sub>H<sub>4</sub>[COCpFe(CO)<sub>2</sub>]<sub>2</sub> (3) with PPh<sub>3</sub>. A mixture of **4** (0.41 mmol) and PPh<sub>3</sub> (0.82 mmol) in toluene (200 cm<sup>3</sup>) was irradiated in a photochemical reactor for 4 h. The solvent was removed and a benzene solution of the residue was chromatographed on an alumina column. An orange band was eluted with benzene which, after evaporation and recrystallization gave 1,4-C<sub>6</sub>H<sub>4</sub>[CpFe(CO) (PPh<sub>3</sub>)]<sub>2</sub> (**15**) as orange microcrystals. Elution with CH<sub>2</sub>Cl<sub>2</sub>/benzene (1:9) gave **9** (6%).

#### (c) With reducing agents

1,4-C<sub>6</sub>H<sub>4</sub>[COMn(CO)<sub>5</sub>]<sub>2</sub> (2) with K-Selectride. K-Selectride (0.76 cm<sup>3</sup> of a 1 M THF) solution was added to a suspension of 2 (0.38 mmol) in THF (5 cm<sup>3</sup>) at  $-78^{\circ}$ C. The reaction mixture immediately changed colour from yellow to orange and the IR showed new bands at 1886 and 1557 cm<sup>-1</sup> which are assigned to Mn(CO)<sub>5</sub><sup>-</sup> and an unstable formyl complex. The only product isolated after work-up of the reaction mixture was Mn<sub>2</sub>(CO)<sub>10</sub> (61%).

1,4-C<sub>6</sub>H<sub>4</sub>[COCpFe(CO)<sub>2</sub>]<sub>2</sub> (3) with K-Selectride or LiAlH<sub>4</sub>. Similarly, the reaction of 4 with K-Selectride gave [CpFe(CO)<sub>2</sub>]<sub>2</sub> (65%), whereas the corresponding reaction with LiAlH<sub>4</sub> gave [CpFe(CO)<sub>2</sub>]<sub>2</sub> (67%) and starting material (29%).

1,4-C<sub>6</sub>H<sub>4</sub>[COMn(CO)<sub>5</sub>]<sub>2</sub> (2) with LiBEt<sub>3</sub>H. The reaction was carried out in THF at room temperature and monitored by IR. New bands were observed at 1880 and 1560 cm<sup>-1</sup> but the only product isolated was  $Mn_2(CO)_{10}$  (54%).

1,4-C<sub>6</sub>H<sub>4</sub>(COM)<sub>2</sub> [M = Mn(CO)<sub>5</sub> CpFe(CO)<sub>2</sub> or Re(CO)<sub>5</sub>] with BH<sub>3</sub> · THF. No reaction of these  $\mu$ phthaloyl compounds was observed with BH<sub>3</sub> · THF at room temperature in THF.

# Reactions of µ-phenylene compounds

# (a) With CO

1,4-C<sub>6</sub>H<sub>4</sub>[Mn(CO)<sub>5</sub>]<sub>2</sub> (8) with CO. The autoclave was charged with 8 (0.11 mmol), THF (10 cm<sup>3</sup>) and CO (30 atm). The mixture was then stirred at room temperature for 22 h, after which time the autoclave was vented and the solvent removed under reduced pressure from the reaction solution to give a white solid. The solid was washed with ether and identified as 2 (84%).

 $1,4-C_6H_4M_2$  with CO. Similarly, reaction of  $1,4-C_6H_4[Re(CO)_5]_2$  (7) with CO (30 atm) on stirring at room temperature for 48 h gave 3 (20%) and unreacted starting material. Compound 9 showed no reaction with CO under these conditions.

#### (b) With synthesis gas

1,4-C<sub>6</sub>H<sub>4</sub>[Mn(CO)<sub>5</sub>]<sub>2</sub> (8) with CO/H<sub>2</sub> (1:1). The autoclave was charged with 8 (0.21 mmol), THF (10 cm<sup>3</sup>) and CO/H<sub>2</sub> (1:1) (40 atm) and the mixture heated at 70°C for 3.5 h. The autoclave was cooled and the gases vented. The resulting yellow solution was filtered and the solvent removed under reduced pressure. Addition of hexane gave a white solid which was filtered off and identified as 1,4-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>OH)<sub>2</sub> (69%) by <sup>1</sup>H NMR, IR and mass spectra. The solvent was removed from the yellow filtrate to give Mn<sub>2</sub>(CO)<sub>10</sub> (71%).

1,4-C<sub>6</sub>H<sub>4</sub>M<sub>2</sub> with CO/H<sub>2</sub> (1:1), where M = Re(CO)<sub>5</sub> or CpFe(CO)<sub>2</sub>. Under similar conditions to the above, 7 gave a mixture of products containing unreacted starting material, 3, 1,4-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>OH)<sub>2</sub> and an unidentified aldehyde species, which could not be separated. Similarly, 9, after 8 h, gave unreacted starting material (58%) and [CpFe(CO)<sub>2</sub>]<sub>2</sub> (37%).

# (c) With $SO_2$

1,4-C<sub>6</sub>H<sub>4</sub>[Re(CO)<sub>5</sub>]<sub>2</sub> (7) with SO<sub>2</sub>. A Carius tube was charged with 7 (0.07 mmol) and liquid SO<sub>2</sub> (10 cm<sup>3</sup>) was condensed onto the solid and the tube was sealed with its Teflon tap. The tube was then treated at 80°C for 48 h. The SO<sub>2</sub> was evaporated to give a cream coloured residue which was extracted with CH<sub>2</sub>Cl<sub>2</sub>, filtered and the solvent removed. The resulting solid was recrystallized from hot CHCl<sub>3</sub>/hexane to give 1,4-C<sub>6</sub>H<sub>4</sub>[SO<sub>2</sub>Re(CO)<sub>5</sub>]<sub>2</sub> (11) as a white microcrystalline solid; IR (Nujol):  $\nu$ (SO) 1186s, 1048s cm<sup>-1</sup>.

 $1,4-C_6H_4[Mn(CO)_5]_2$  (8) with SO<sub>2</sub>. Similarly, this reaction was carried out with 8 (0.21 mmol) and

SO<sub>2</sub> (10 cm<sup>3</sup>) at 80°C for 60 h, after which time the SO<sub>2</sub> was allowed to evaporate. The pale yellow residue was extracted with ethanol (3 × 20 cm<sup>3</sup>), filtered and the solvent removed. The resulting solid was washed with CH<sub>2</sub>Cl<sub>2</sub> (4 × 10 cm<sup>3</sup>) to give 1,4-C<sub>6</sub>H<sub>4</sub>[SO<sub>2</sub>Mn(CO)<sub>5</sub>]<sub>2</sub> (10) as a yellow microcrystalline solid; IR (Nujol):  $\nu$ (SO) 1190s, 1030m cm<sup>-1</sup>.

1,4-C<sub>6</sub>H<sub>4</sub>[CpFe(CO)<sub>2</sub>]<sub>2</sub> (9) with SO<sub>2</sub>. Similarly, a Carius tube was charged with 9 (0.07 mmol) and liquid SO<sub>2</sub> (10 cm<sup>3</sup>). The mixture was then stirred at room temperature for 38 h. The excess SO<sub>2</sub> was evaporated and the resulting residue recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane to give 1,4-C<sub>6</sub>H<sub>4</sub>[SO<sub>2</sub>CpFe (CO)<sub>2</sub>]<sub>2</sub> (12) as a yellow solid; IR (Nujol):  $\nu$ (SO) 1193m, 1045m cm<sup>-1</sup>.

# (d) With halogens

1,4-C<sub>6</sub>H<sub>4</sub>[CpFe(CO)<sub>2</sub>]<sub>2</sub> (9) with Br<sub>2</sub> or I<sub>2</sub>. A solution of 9 (0.23 mmol) in THF (12 cm<sup>3</sup>) was treated with Br<sub>2</sub> (0.46 mmol) and the brown mixture stirred for 30 min at room temperature. The solvent was removed leaving a red-brown residue. This was taken up in CH<sub>2</sub>Cl<sub>2</sub> and chromatographed on an alumina column. Elution with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:9) resulted in 1,4-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub> (84%). Elution with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1) gave CpFe(CO)<sub>2</sub>Br (82%).

Similarly, the reaction of 9 with  $I_2$  gave 1,4- $C_6H_4I_2$  (60%) and CpFe(CO)<sub>2</sub>I (62%).

 $1,4-C_6H_4[Re(CO)_5]_2$  (7) with Br<sub>2</sub>. A similar reaction with 7 (0.28 mmol) in THF (12 cm<sup>3</sup>) gave 1,4- $C_6H_4Br_2$  (76%) and Re(CO)<sub>5</sub>Br (81%).

#### (e) With tertiary phosphines

1,4-C<sub>6</sub>H<sub>4</sub>[Mn(CO)<sub>5</sub>]<sub>2</sub> (8) with PMePh<sub>2</sub>. A solution of 8 (0.13 mmol) and PMePh<sub>2</sub> (0.26 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) was treated with Me<sub>3</sub>NO·2H<sub>2</sub>O (0.26 mmol) and the solution stirred at room temperature until no starting material remained, as judged by the IR spectrum. The solution was concentrated and chromatographed on an alumina column. Elution with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1) gave a yellow solid from which 1,4-C<sub>6</sub>H<sub>4</sub>[Mn(CO)<sub>4</sub> (PMePh<sub>2</sub>)]<sub>2</sub> (13) was isolated. A similar reaction of 7 with PPh<sub>3</sub> gave 1,4-C<sub>6</sub>H<sub>4</sub>[Mn(CO)<sub>4</sub>(PPh<sub>3</sub>)]<sub>2</sub> (14) (76%).

1,4-C<sub>6</sub>H<sub>4</sub>[CpFe(CO)<sub>2</sub>]<sub>2</sub> (9) with PPh<sub>3</sub>. Compound 9 (0.23 mmol) and PPh<sub>3</sub> (0.46 mmol) in benzene (150 cm<sup>3</sup>) was irradiated for 2 h. The solution was concentrated, chromatographed on an alumina column and eluted with benzene to give 1,4-C<sub>6</sub>H<sub>4</sub>[CpFe(CO)(PPh<sub>3</sub>)]<sub>2</sub> (15) (11%).

#### DISCUSSION

The  $\mu$ -phthaloyl compounds of molybdenum, manganese, rhenium, iron and cobalt were prepared by the following route acterization data obtained for compounds 8 and 9 agreed well with that reported by Hunter and Szigety.<sup>9</sup> An attempt to synthesize 9 from Na[CpFe(CO)<sub>2</sub>] and 1,4-C<sub>6</sub>H<sub>4</sub>I<sub>2</sub> in refluxing THF



5  $M = Co(CO)_3(PPh_3)$ 

The rhodium complex, 1,4-C<sub>6</sub>H<sub>4</sub>[CORhCl<sub>2</sub>  $(PPh_3)_2_2$  (6), was prepared by the oxidative addition reaction of RhCl(PPh<sub>3</sub>)<sub>3</sub> to 1,4-C<sub>6</sub>H<sub>4</sub>(COCl)<sub>2</sub>. Characterization data for the new  $\mu$ -phthaloyl compounds are given in Table 1. Data for compounds 2 and 3 have recently been reported by Hunter and Szigety.9 Like the manganese and iron compounds (2 and 3) the rhenium and rhodium compounds (4 and 6) are air-stable in contrast to the molybdenum and cobalt compounds (1 and 5). With the exception of the cobalt compound, all the  $\mu$ -phthaloyl compounds are rather insoluble. The v(CO) bands in the IR spectra for 1, 2 and 4 are in similar positions to those reported for the respective mononuclear analogues CpMo(CO)<sub>3</sub>(COPh)<sup>13</sup> and  $M(CO)_{s}(COPh)$  (where M = Mn or Re).<sup>14</sup> The IR spectrum of 6 is similar to that reported for  $RhCl_2(PPh_3)_2(COR)$ ,<sup>15</sup> suggesting that the PPh<sub>3</sub> groups in both compounds may be trans to each other.

The  $\mu$ -phenylene compounds of manganese, rhenium and iron were prepared by decarbonylation of the  $\mu$ -phthaloyl precursors: gave  $1,4-C_6H_4I[CpFe(CO)_2]$  in 4% yield. We were not able to efficiently decarbonylate compounds 1, 5 and 6 to give  $\mu$ -phenylene products.

Mass spectra of the  $\mu$ -phthaloyl compounds 2–4 did not show parent ions and the highest mass peaks we observed correspond to  $[M - 2CO]^+$ ; in fact, the spectra are identical to those of the corresponding  $\mu$ -phenylene complexes 7–9.

As reported by Hunter and Szigety,<sup>9</sup> we observe parent ions in the mass spectra for compounds 7– 9. We have also identified the main fragmentation pathways for these compounds which can be summarized as follows:

For compound 8:

- (1) Loss of 10 CO's from parent to give  $M_2(C_6H_4)$
- (2) Loss of  $M(CO)_5$  from parent then 5 CO's

For compound 7:

- (1) and (2) above but also
- (3) Loss of  $C_6H_4$  from parent followed by 10 CO's



3  $M = CpFe(CO)_2$ 

We obtained the rhenium and manganese compounds (7 and 8) by refluxing the appropriate  $\mu$ phthaloyl compounds in toluene or methyl isobutyl ketone. For compound 9, decarbonylation was effected by either UV irradiation or chemical decarbonylation using RhCl(PPh<sub>3</sub>)<sub>3</sub>. The char-

For compound 9:

- Loss of 4 CO's from parent to give Cp<sub>2</sub>Fe<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)
- (2) Loss of  $CpFe(CO)_2$  from parent then 2 CO's.

# Reactivity of the $\mu$ -phthaloyl complexes

Most of the reactions outlined below were carried out on the  $\mu$ -phthaloyl compounds (2-4).

# (a) Reactivity of the $\mu$ -phthaloyl complexes 2–4 with halogens

Although there are many reports of electrophilic cleavage of transition metal–carbon bonds of alkyl compounds, there are few reports of similar reactions of metal aroyl compounds and none that we are aware of on binuclear  $\mu$ -phthaloyl compounds.<sup>1</sup> We have investigated the reactions of the  $\mu$ phthaloyl compounds of manganese, rhenium and iron with Br<sub>2</sub> and I<sub>2</sub> in THF at room temperature. In each case the metal halide and terephthalic acid were produced

$$1,4-C_6H_4(COM)_2 + 2X_2 \longrightarrow 2M-X$$
$$+ [1,4-C_6H_4(COX)_2] \longrightarrow 1,4-C_6H_4(COOH)_2$$
Not observed

[where  $M = Mn(CO)_5$ ,  $Re(CO)_5$  or  $CpFe(CO)_2$ ; X = Br or I]; the terephthalic acid may result from hydrolysis of aroyl halide intermediates.

Even though the same type of products were obtained for the three complexes  $1,4-C_6H_4(COM)_2$ , the rates of the reactions were significantly different and followed the order CpFe(CO)<sub>2</sub> > Re(CO)<sub>5</sub> > Mn(CO)<sub>5</sub>. This may be explained on the basis that metal-carbon bond cleavage is an electrophilic process. This is borne out by the reactivity order following decreasing electron density on the metal and that the reactions with iodine appear slower than those with bromine.

(b) The reaction of  $1,4-C_6H_4[COCpFe(CO)_2]_2$  with PPh<sub>3</sub>

Substitution of CO by PPh<sub>3</sub> is difficult in this complex since no reaction of compound **3** with PPh<sub>3</sub> occurred after refluxing in xylene for 3 days. UV irradiation in toluene for 4 h produced a 9% yield of the substituted phenylene complex, viz. 1,4- $C_6H_4$ [CpFe(CO)(PPh<sub>3</sub>)]<sub>2</sub> (**15**).

# (c) Reactions of $\mu$ -phthaloyl complexes with reducing agents

Attempts to reduce the aroyl CO groups in compounds 2 and 3 were made using K-Selectride, LiAlH<sub>4</sub>, LiBEt<sub>3</sub>H or BH<sub>3</sub> · THF as reducing agents. Compounds 2 and 3 reacted with K-Selectride to give anionic intermediates, however, no new products could be isolated. Reaction of 3 with LiAlH<sub>4</sub> was slow and  $[CpFe(CO)_2]_2$  was the only product identified, whereas  $[Mn(CO)_5]^-$  was the only product identified from the reaction of 2 with LiBEt<sub>3</sub>H. No reactions of 2–4 with BH<sub>3</sub> · THF were observed.

#### *Reactivity of the* $\mu$ *-phenylene complexes*

# (a) With CO

Compound 8 gave 85% conversion to the  $\mu$ phthaloyl compound 2 after 22 h with CO (30 atm) in THF. There was no reaction of 8 with CO (1 atm) after 48 h. Compound 8 undergoes CO insertion much less readily than its mononuclear analogue Mn(CO)<sub>3</sub>Ph.<sup>16</sup> The rhenium compound is less readily carbonylated than the manganese complex and only 20% of the  $\mu$ -phthaloyl compound 4 was isolated after 48 h reaction time with CO (30 atm) at room temperature. The iron complex 9 showed no CO insertion under similar conditions.

#### (b) With synthesis gas $(CO/H_2, 1:1)$

The reaction of  $1,4-C_6H_4[Mn(CO)_5]_2$  (8) gave  $1,4-C_6H_4(CH_2OH)_2$  as the only isolable organic product and  $Mn_2(CO)_{10}$ . The reaction appears to be similar to that reported for  $(CO)_5Mn(CH_2)_4$   $Mn(CO)_5$  with synthesis gas.<sup>17</sup> In both these cases, the reaction with synthesis gas leads, via initial CO insertion, to a diol. No evidence for any further carbon chain growth is observed. This may be a general result in catalytic reactions, also that CO insertion leads to termination, with alcohol and aldehyde formation but not to carbon chain growth.

Compounds 7 and 9 were found to be less reactive towards synthesis gas.

(c) With  $SO_2$ 

Since some mononuclear aryl complexes are known to react with SO<sub>2</sub> to form the corresponding S-sulphinates,<sup>18,19</sup> we were interested to investigate similar reactions with  $\mu$ -phenylene complexes. Thus, we find that compounds **7–9** react with liquid SO<sub>2</sub> according to the following equation

$$1,4-C_{6}H_{4}M_{2}+2SO_{2} \longrightarrow 1,4-C_{6}H_{4}(SO_{2}M)_{2} \qquad (3)$$

$$10 \ M = Mn(CO)_{5}$$

$$11 \ M = Re(CO)_{5}$$

$$12 \ M = CpFe(CO)_{2}.$$

Data for compounds 1–12 are given in Table 1. In general, the reactions of the binuclear  $\mu$ -phenylene complexes with SO<sub>2</sub> are significantly slower than analogous reactions with mononuclear phenyl compounds.

# (d) With halogens

Compared to the corresponding  $\mu$ -phthaloyl compounds, the  $\mu$ -phenylene compounds 7–9 react more readily with the halogens Br<sub>2</sub> or I<sub>2</sub> in THF to yield the corresponding metal carbonyl halides and 1,4-dihalobenzenes [eq. (4)]:

1,4-C<sub>6</sub>H<sub>4</sub>M<sub>2</sub>+2X<sub>2</sub>
$$\longrightarrow$$
 1,4-C<sub>6</sub>H<sub>4</sub>X<sub>2</sub>+2MX (4)  
[M = Mn(CO)<sub>5</sub>, Re(CO)<sub>5</sub> or CpFe(CO)<sub>2</sub>;  
X = Br or I].

Similar results have been found for the reactions of the manganese and iron compounds.<sup>9</sup> We find the rate of metal-carbon cleavage by halogen in  $1,4-C_6H_4M_2$  to be CpFe(CO)<sub>2</sub> > Re(CO)<sub>5</sub> > Mn(CO)<sub>5</sub>; exactly the same order as we found for the  $\mu$ -phthaloyl compounds.

#### (e) With tertiary phosphines

The reactions of **8** and **9** with PPh<sub>3</sub> or PMePh<sub>2</sub> were carried out under various conditions and gave substitution products according to eq. (5):

$$1,4-C_{6}H_{4}[M(CO)]_{2}+2PR_{3} \longrightarrow$$

$$1,4-C_{6}H_{4}[M(PR_{3})]_{2}+2CO \quad (5)$$

$$13 \ M = Mn(CO)_{4}, PR_{3} = PMePh_{2}$$

$$14 M = Mn(CO)_4, PR_3 = PPh_3$$

15  $M = CpFe(CO), PR_3 = PPh_3$ .

This CO substitution reaction is analogous to that reported for  $Mn(CO)_5Ph$  with PPh<sub>3</sub>, although the rate of reaction of the  $\mu$ -phenylene complex **8** with PPh<sub>3</sub> is slower than that for  $Mn(CO)_5Ph$ .<sup>20</sup> Products resulting from aryl migration were not observed. Our results agree well with those reported by others for the reaction of **8** with PPh<sub>3</sub>.<sup>9</sup> In the presence of Me<sub>3</sub>NO, the reactions to give **13** and **14** in eq. (5) proceded much faster. Similar rate enhancement has been found for the substitution of CO by PPh<sub>3</sub> in Mn(CO)<sub>5</sub>Ph.<sup>21</sup> On the basis of IR spectra in the v(CO) region, compounds **13** and **14** adopt a *cis*-configuration at manganese.

#### CONCLUSIONS

The reactivity of the  $\mu$ -phthaloyl and  $\mu$ -phenylene complexes of several metals give similar products to analogous reactions of mononuclear compounds, although the rates of some of the reactions are different. We are at present obtaining quantitative data on these rate differences. These findings may have significance in catalytic reactions that yield difunctional aryl products.

Acknowledgements—We thank the University of Cape Town and FRD for support, Johnson Matthey for a generous loan of rhodium trichloride and Nazir Ahmed for help with the manuscript.

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