

## PENTAMETHYLCYCLOPENTADIENYL DERIVATIVES OF TRANSITION METALS

### VI\*. CARBONYLATION OF METAL–METAL TRIPLE BONDS: A HIGH PRESSURE INFRARED SPECTROSCOPIC STUDY

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(Received October 20th, 1978)

#### Summary

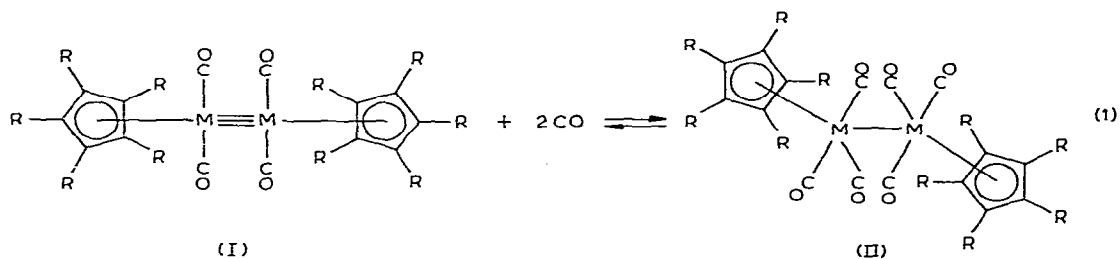
Reactions of appropriate metal carbonyl derivatives with pentamethylcyclopentadiene in boiling n-decane provide improved routes to the metal–metal triple bond compounds  $[(\text{CH}_3)_5\text{C}_5\text{M}(\text{CO})_2]_2$  (M = Cr, Mo, and W) as well as  $(\text{CH}_3)_5\text{C}_5\text{M}(\text{CO})_3$  (M = Mn and Re) and  $[(\text{CH}_3)_5\text{C}_5\text{Ru}(\text{CO})_2]_2$ . Infrared spectroscopic studies at elevated pressures indicate that the ease of CO addition in n-tetradecane solution to the metal–metal triple bond in the analogous compounds  $[(\text{CH}_3)_5\text{C}_5\text{M}(\text{CO})_2]_2$  (M = Cr, Mo, and W) to form the corresponding  $[(\text{CH}_3)_5\text{C}_5\text{M}(\text{CO})_3]_2$  derivatives increases in the sequence Cr < W < Mo. These carbonylations have also been carried out on the preparative scale leading to the isolation of the three metal–metal single bonded  $[(\text{CH}_3)_5\text{C}_5\text{M}(\text{CO})_3]_2$  derivatives (M = Cr, Mo, and W) in the solid state. The chromium derivative  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_3]_2$ , reported here for the first time, is the least stable of these compounds and is red-purple in contrast to the green  $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$ .

One of the most interesting developments in transition metal organometallic chemistry during the past decade has been the discovery of stable metal carbonyl derivatives containing metal–metal multiple bonds [2]. Among the more important such compounds are the cyclopentadienylmetal dicarbonyl dimers of chromium and molybdenum of the type  $[\text{R}_5\text{C}_5\text{M}(\text{CO})_2]_2$  (I: R = CH<sub>3</sub>, M = Cr [3,4,5] and Mo [3,4,6]; R = H, M = Cr [7], Mo [8] and W [9]). In 1975 two research groups [8,10] first reported the reversible addition of CO to the molybdenum–molybdenum triple bond in  $[\text{R}_5\text{C}_5\text{Mo}(\text{CO})_2]_2$  derivatives (I: R = H and CH<sub>3</sub>,

\* For part V of this series see ref. 1. Portions of this paper were presented at the 176th National Meeting of the American Chemical Society, Miami Beach, Florida, September, 1978, paper INOR50 in abstracts.

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M = Mo) to give the corresponding molybdenum—molybdenum single bond  $[\text{R}_5\text{C}_5\text{Mo}(\text{CO})_3]_2$  derivatives II as in eq. 1. A subsequent paper [9] reports a



study of the equilibria represented by eq. 1 for all five known cases  $[\text{R}_5\text{C}_5\text{M}(\text{CO})_2]_2$  ( $\text{R} = \text{CH}_3$ ,  $\text{M} = \text{Cr}$  and  $\text{Mo}$ ;  $\text{R} = \text{H}$ ,  $\text{M} = \text{Cr}$ ,  $\text{Mo}$ , and  $\text{W}$ ) using photochemical conditions to effect the decarbonylation of the  $[\text{R}_5\text{C}_5\text{M}(\text{CO})_3]_2$  derivatives II. We have now obtained for the first time the sixth and final system of this type  $[(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_2]_2$  (I:  $\text{R} = \text{CH}_3$ ,  $\text{M} = \text{W}$ ) and have isolated  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_3]_2$  (II:  $\text{R} = \text{CH}_3$ ,  $\text{M} = \text{Cr}$ ) for the first time in a reasonably pure state. The availability of the complete series of pentamethylcyclopentadienyl derivatives I ( $\text{M} = \text{Cr}$ ,  $\text{Mo}$ , and  $\text{W}$ ) and of high pressure infrared spectroscopic equipment [11] has allowed us to make a comparative study of the relative reactivities of the analogous metal—metal triple bonded derivatives  $[(\text{CH}_3)_5\text{C}_5\text{M}(\text{CO})_2]_2$  (I:  $\text{R} = \text{CH}_3$ ,  $\text{M} = \text{Cr}$ ,  $\text{Mo}$ , and  $\text{W}$ ) towards CO addition. This work is described in detail in this paper.

## Experimental

Microanalyses were performed by Atlantic Microanalytical Laboratory, Atlanta, Georgia, and by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Melting and decomposition points were taken on samples in capillaries and are uncorrected. A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions with metal carbonyl derivatives; (b) handling filtered solutions of organometallic compounds; (c) filling evacuated vessels containing organometallic compounds.

### *Preparation of the pentamethylcyclopentadienylmetal carbonyl derivatives*

Recent developments [12], have made pentamethylcyclopentadiene readily accessible from 2-bromo-2-butene (purchased from Columbia Organic Chemicals, Columbia, South Carolina) in 75% yield. Accordingly the pentamethylcyclopentadienylmetal carbonyls used in this work were obtained by reactions of pentamethylcyclopentadiene rather than the previously used [5,6] acetylpentamethylcyclopentadiene with appropriate metal carbonyls. Use of boiling n-decane (b.p.  $174^\circ\text{C}$ ) as a solvent appeared to offer some significant improvements over some of the reaction conditions used in the original study [6] of reactions of metal carbonyls with pentamethylcyclopentadiene. Details of some of the reactions of pentamethylcyclopentadiene in boiling n-decane with some of the metal carbonyls relevant to this project are given below.

A.  $\text{Cr}(\text{CO})_6$ . A mixture of 3.0 g (13.7 mmol) of  $\text{Cr}(\text{CO})_6$ , 2.0 g (14.7 mmol) of pentamethylcyclopentadiene, and 50 ml of n-decane was boiled under reflux for

22 h. The color of the solution initially turned purple-red but ultimately became the characteristic green color of  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$  (I: R = CH<sub>3</sub>, M = Cr). After completion of the reaction, the mixture was cooled to room temperature and then kept at 0°C for several hours. The resulting deep green crystals were filtered, washed with hexane, and dried at 50–60°C/35 mmHg for 3 h. Recrystallization from hexane gave 1.75 g (53% yield) of deep green  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$  identified by its melting point and infrared spectrum (Table 1).

A similar reaction of Cr(CO)<sub>6</sub> with pentamethylcyclopentadiene in the lower boiling 2,2,4-trimethylpentane (b.p. 99°C) also formed  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$  but only very slowly reaching a 5% yield after boiling under reflux for 6 days.

**B. Mo(CO)<sub>6</sub>.** A mixture of 1.0 g (4.0 mmol) of Mo(CO)<sub>6</sub>, 0.54 g (4.0 mmol) of pentamethylcyclopentadiene, and 25 ml of n-decane was boiled under reflux for 6 h. The mixture was then cooled to 0°C for 3 h. The resulting red crystals were filtered, washed with small amounts of hexane, and dried at 60°C/35 mmHg for 16 h. The infrared  $\nu(\text{CO})$  spectrum of this red solid indicated it to be a mixture of  $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]_2$  (I) and  $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_3]_2$  (II: R = CH<sub>3</sub>, M = Mo).

In order to separate these pure components, a concentrated dichloromethane solution of this red solid was chromatographed on a 2 × 60 cm Florisil column. The first orange-red band was eluted with 1/1 diethyl ether/hexane. Removal of solvent from the eluate followed by crystallization from a mixture of diethyl ether and hexane gave 0.64 g (56% yield) of deep red crystalline  $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]_2$  identified by its  $\nu(\text{CO})$  infrared spectrum and decomposition point. The second orange-red band was eluted with diethyl ether. Evaporation of the eluate followed by low temperature crystallization from diethyl ether gave 0.10 g (9% yield) of red crystalline  $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_3]_2$ , m.p. 175°C, anal.: Found: C, 49.7; H, 4.8. C<sub>26</sub>H<sub>30</sub>Mo<sub>2</sub>O<sub>6</sub> calcd.: C, 49.5; H, 4.8%.

Use of lower boiling saturated hydrocarbon solvents for the reaction of Mo(CO)<sub>6</sub> with pentamethylcyclopentadiene gave lower yields of  $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]_2$ : e.g. 40% in 2,2,5-trimethylhexane (b.p. 124°C) after 20 h boiling under reflux and only 10% in boiling 2,2,4-trimethylpentane.

**C. W(CO)<sub>6</sub>.** A mixture of 3.52 g (10 mmol) of W(CO)<sub>6</sub>, 1.5 g (11 mmol) of pentamethylcyclopentadiene, and 50 ml of n-decane was boiled under reflux for 22 h. The purple-red solution was kept at 0°C for 3 h. The resulting deep red crystals were filtered, washed with small amounts of hexane, and dried at 50–60°C/35 mmHg for 12 h. A concentrated solution of this red solid in dichloro-

TABLE 1

THE PENTAMETHYLCYCLOPENTADIENYLMETAL CARBONYLS OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

Compound	Color	M.p. (°C)	Infrared $\nu(\text{CO})^a$ (cm <sup>-1</sup> )
$[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$	deep green	dec. >200	1871, 1852
$[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]_2$	red	dec. 219	1867, 1842
$[(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_2]_2$	red	dec. 237	1874, 1828
$[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_3]_2$	dark purple	dec. 137–138	1915, 1886
$[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_3]_2$	orange-red	175	1933, 1898
$[(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_3]_2$	orange-red	207	1920, 1893

<sup>a</sup> In n-tetradecane solution.

methane was chromatographed on a  $2 \times 60$  cm Florisil column packed in hexane. The first orange-red band was eluted with 1/10 diethyl ether/hexane. Removal of solvent from the red-orange eluate followed by low temperature crystallization from diethyl ether gave 1.14 g (31% yield) of deep red crystalline  $[(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_2]_2$ , dec.  $237^\circ\text{C}$ ; proton NMR in  $\text{CDCl}_3$   $\delta$  2.02 ppm; anal. Found: C, 38.6; H, 4.0.  $\text{C}_{24}\text{H}_{30}\text{O}_4\text{W}_2$  calcd.: C, 38.4; H, 4.0%. A second orange band was eluted with diethyl ether. Removal of solvent from the eluate followed by low temperature crystallization from diethyl ether gave 1.0 g (25% yield) of red-orange  $[(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_3]_2$ , m.p.  $207^\circ\text{C}$ ; anal. Found: C, 38.2; H, 4.3.  $\text{C}_{26}\text{H}_{30}\text{O}_6\text{W}_2$  calcd.: C, 38.7; H, 3.7%.

*D. Ru<sub>3</sub>(CO)<sub>12</sub>.* A mixture of 1.28 g (2 mmol) of  $\text{Ru}_3(\text{CO})_{12}$  [13], 0.82 g (6 mmol) of pentamethylcyclopentadiene, and 40 ml of n-decane was boiled under reflux for 4 h to give a deep red solution. After standing at room temperature for 12 h the resulting red crystals were filtered. A concentrated dichloromethane solution of this red solid was chromatographed on a  $2 \times 60$  cm Florisil column packed in hexane. A yellow band was first eluted with hexane. Evaporation of the eluate gave 0.215 g (17% recovery) of orange crystals of unreacted  $\text{Ru}_3(\text{CO})_{12}$ . The next band (orange-yellow) was eluted with dichloromethane. Removal of solvent followed by crystallization from a mixture of dichloromethane and hexane gave 0.56 g (70% yield) of  $[(\text{CH}_3)_5\text{Ru}(\text{CO})_2\text{C}_5\text{Ru}(\text{CO})_2]_2$ , m.p.  $297^\circ\text{C}$  (dec.), infrared  $\nu(\text{CO})$  in  $\text{CH}_2\text{Cl}_2$ : 1925 s and 1744 s  $\text{cm}^{-1}$ , proton NMR in  $\text{CDCl}_3$   $\delta$  1.84 ppm; anal. Found: C, 49.3; H, 5.1; Ru, 34.8.  $\text{C}_{24}\text{H}_{30}\text{O}_4\text{Ru}_2$  calcd.: C, 49.3; H, 5.1; Ru, 34.8%.

Ultraviolet irradiation of a solution of 0.075 g of  $[(\text{CH}_3)_5\text{C}_5\text{Ru}(\text{CO})_2]_2$  in 200 ml of benzene for 20 h led only to the production of poorly defined carbonyl-free products with no evidence for the formation of  $[(\text{CH}_3)_5\text{C}_5\text{RuCO}]_2$  containing a ruthenium-ruthenium triple bond or the tetrahedral cluster  $[(\text{CH}_3)_5\text{C}_5\text{RuCO}]_4$  analogous to the reported compounds  $[\text{C}_5\text{H}_5\text{MCO}]_4$  (M = Fe [14] and Ru [15]).

*E. CH<sub>3</sub>Mn(CO)<sub>5</sub>.* Reaction of 0.52 g (2.5 mmol) of  $\text{CH}_3\text{Mn}(\text{CO})_5$  [16,17] with 0.34 g (2.5 mmol) of pentamethylcyclopentadiene in 25 ml of boiling n-decane for 1.5 h gave a 36% yield of pale yellow crystalline  $(\text{CH}_3)_5\text{C}_5\text{Mn}(\text{CO})_3$ , m.p.  $77^\circ\text{C}$  (lit. [4] m.p.  $77.5^\circ\text{C}$ ) after low temperature crystallization from hexane.

*F. Mn<sub>2</sub>(CO)<sub>10</sub>.* Reaction of 1.6 g (4.1 mmol) of  $\text{Mn}_2(\text{CO})_{10}$  [18] with 0.75 g (5.6 mmol) of pentamethylcyclopentadiene in 25 ml of boiling n-decane for 12 h gave 0.16 g (10% recovery) of unchanged  $\text{Mn}_2(\text{CO})_{10}$  and 0.46 g (30% yield) of  $(\text{CH}_3)_5\text{C}_5\text{Mn}(\text{CO})_3$ , separated by chromatography on Florisil in hexane solution.

*G. CH<sub>3</sub>Re(CO)<sub>5</sub>.* Reaction of 0.40 g (1.2 mmol) of  $\text{CH}_3\text{Re}(\text{CO})_5$  [19] with 0.175 g (1.3 mmol) of pentamethylcyclopentadiene in 25 ml of boiling n-decane for 3 h gave 0.12 g (26% yield) of white crystalline  $(\text{CH}_3)_5\text{C}_5\text{Re}(\text{CO})_3$ , m.p.  $151^\circ\text{C}$  (lit. [6] m.p.  $151-153^\circ\text{C}$ ), after crystallization from hexane.

*H. CH<sub>3</sub>Mo(CO)<sub>3</sub>C<sub>5</sub>H<sub>5</sub>.* Reaction of 0.32 g (1.25 mmol) of  $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$  [20] with 0.23 g (1.7 mmol) of pentamethylcyclopentadiene in 25 ml of boiling n-decane for 2 h resulted in a red solution from which  $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$  (0.056 g, 18% yield), identified by its melting point and infrared  $\nu(\text{CO})$  spectrum, was the only identifiable organometallic compound that could be isolated. No evidence for any pentamethylcyclopentadienylmolybdenum derivatives was obtained from this reaction.

### Preparative carbonylation studies

The following reactions of  $[(CH_3)_5C_5M(CO)_2]_2$  derivatives with CO were carried out under the indicated conditions using a 300 ml stainless steel rocking autoclave.

A.  $[(CH_3)_5C_5Cr(CO)_2]_2$ . A solution of 0.39 g (0.61 mmol) of  $[(CH_3)_5C_5Cr(CO)_2]_2$  in 80 ml of toluene was heated under 200 atm. CO for 30 min at 175°C. Removal of solvent from the resulting filtered purple-red solution followed by crystallization of the residue from benzene with the rigorous exclusion of air gave 0.24 g (44% yield) of deep purple-red (almost black) crystalline air sensitive  $[(CH_3)_5C_5Cr(CO)_3]_2$ ; proton NMR in  $C_6D_6$   $\delta$  1.56 ppm; anal.: Found: C, 56.2; H, 6.3; Cr, 18.0  $C_{26}H_{30}Cr_2O_6$  calcd.: C, 57.5; H, 5.5; Cr, 19.2%.

B.  $[(CH_3)_5C_5Mo(CO)_2]_2$ . A solution of 0.12 g (0.22 mmol) of  $[(CH_3)_5C_5Mo(CO)_2]_2$  in 80 ml of toluene was heated to 75°C under 50 atm CO. Removal of solvent from the resulting filtered orange-red solution gave 0.055 g (40% yield)

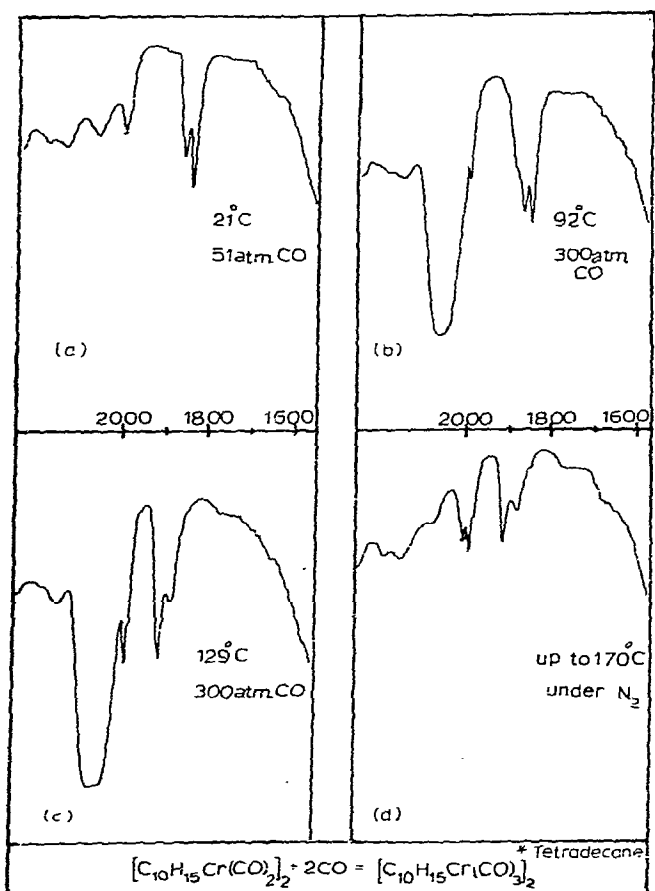


Fig. 1. Infrared spectra obtained upon heating  $[(CH_3)_5C_5Cr(CO)_2]_2$  in *n*-tetradecane solution under CO pressure: (a) initial solution; (b) solution obtained after heating under 300 atm CO up to 92°C over a 5 h period; (c) solution obtained after further heating of the solution in b up to 129°C over an additional half hour; (d) solution obtained by further heating under 300 atm CO up to 170°C followed by cooling to room temperature and releasing the CO pressure.

of red-orange crystalline  $[(CH_3)_5C_5Mo(CO)_3]_2$ , identified by its melting point and infrared  $\nu(CO)$  frequencies (Table 1).

C.  $[(CH_3)_5C_5W(CO)_2]_2$ . A solution of 0.10 g (0.13 mmol) of  $[(CH_3)_5C_5W(CO)_2]_2$  in 80 ml of toluene was heated to  $120^\circ C$  under 200 atm CO. Removal of solvent from the resulting filtered orange-red solution followed by crystallization from a mixture of benzene and hexane gave 0.065 g (64% yield) of orange-red crystalline  $[(CH_3)_5C_5W(CO)_3]_2$ , identified by its melting point and infrared  $\nu(CO)$  frequencies (Table 1).

#### Decarbonylation studies

A.  $[(CH_3)_5C_5Cr(CO)_3]_2$ . Boiling a purple-red solution of  $[(CH_3)_5C_5Cr(CO)_3]_2$  in *p*-xylene (b.p.  $138^\circ C$ ) under reflux for 1 h caused its color to change to deep green. From this solution deep green crystalline  $[(CH_3)_5C_5Cr(CO)_2]_2$ , identified by its melting point and  $\nu(CO)$  infrared spectrum, could be isolated. A similar

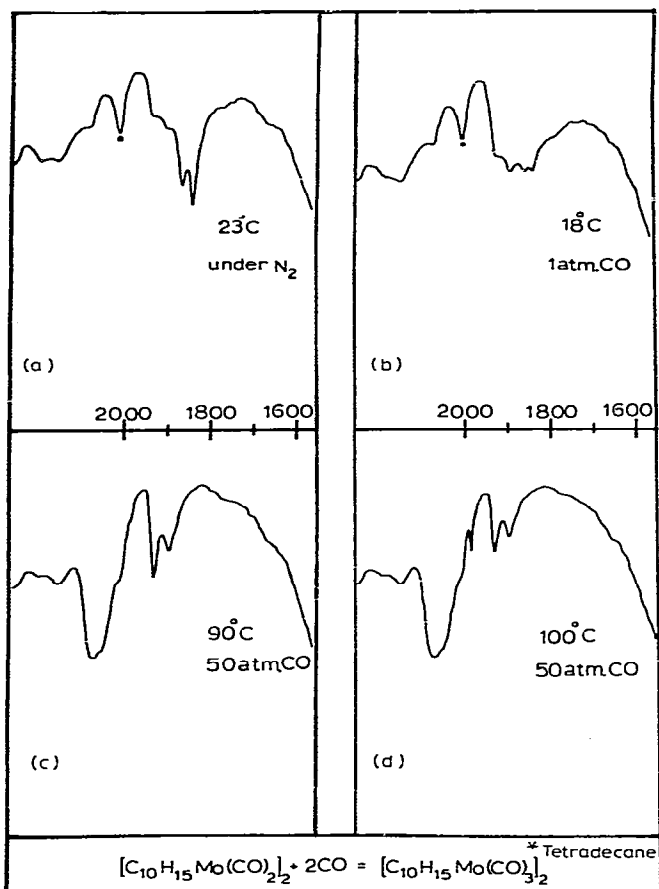


Fig. 2. Infrared spectra obtained upon heating  $[(CH_3)_5C_5Mo(CO)_2]_2$  in *n*-tetradecane solution under CO pressure: (a) initial solution (under 30 atm nitrogen); (b) solution obtained immediately after flushing with 1 atm CO at  $18^\circ C$ ; (c) solution obtained after heating under 50 atmospheres CO to  $90^\circ C$ ; (d) solution obtained after further heating of the solution in c to  $100^\circ C$  over a period of 8 minutes (note appearance of  $Mo(CO)_6$  peak at  $1885\text{ cm}^{-1}$  during this additional heating).

conversion of  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_3]_2$  to  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$  was not observed in boiling benzene ( $80^\circ\text{C}$ ). However, keeping a solid sample of  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_3]_2$  for several days in vacuum ( $25^\circ\text{C}/0.01\text{ mmHg.}$ ) resulted in conversion to  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$ .

B.  $[(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_3]_2$ . Boiling a solution of  $[(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_3]_2$  in *p*-xylene under reflux for 48 h resulted in conversion to  $[(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_2]_2$  as indicated by the  $\nu(\text{CO})$  infrared spectrum.

#### High pressure infrared spectroscopic studies

The infrared spectra at elevated pressures (Fig. 1, 2 and 3) were run in the previously described [11] stainless steel high pressure infrared cell with Irtran I windows and recorded on Perkin-Elmer Model 281 spectrometer with grating optics. Eastman highest purity n-tetradecane was used as the solvent for all of the spectra reported here.

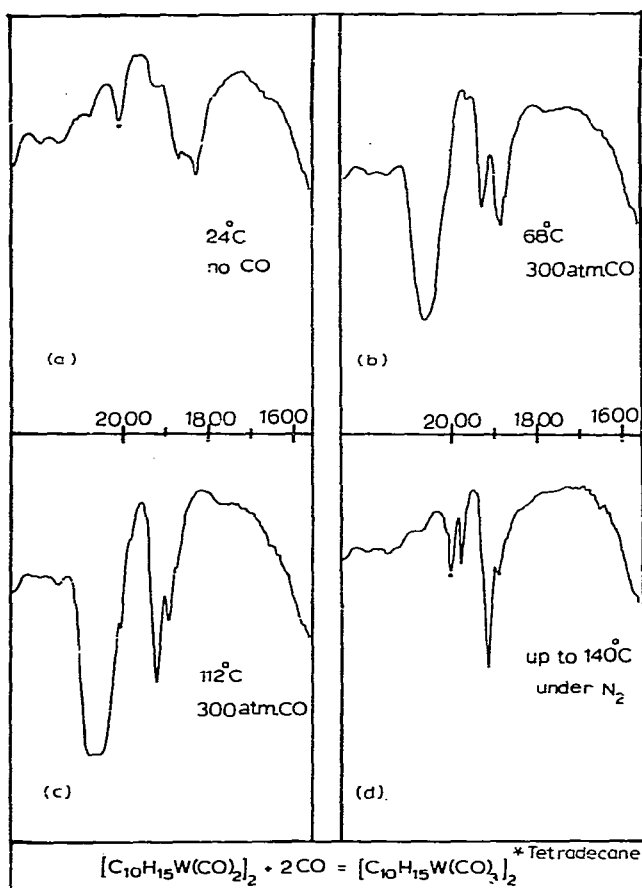


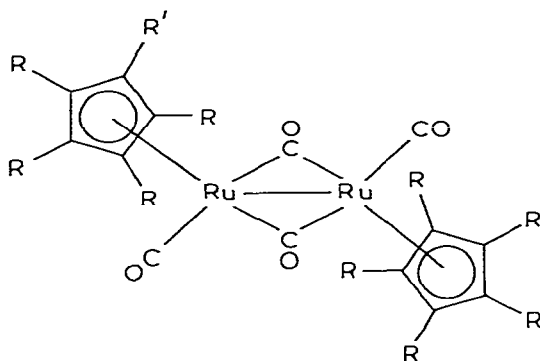
Fig. 3. Infrared spectra obtained upon heating  $[(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_2]_2$  in n-tetradecane solution under CO pressure: (a) initial solution; (b) solution obtained after heating under 300 atmospheres CO up to  $68^\circ\text{C}$  over a 3 h period; (c) solution obtained after further heating of the solution in b up to  $112^\circ\text{C}$  over an additional hour; (d) solution obtained by further heating under 300 atmospheres CO up to  $140^\circ\text{C}$  followed by cooling to room temperature and releasing the CO pressure.

## Results and discussion

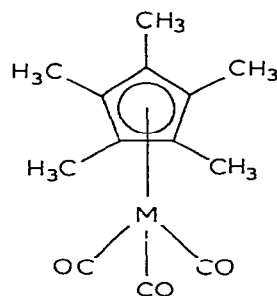
### Preparative studies

The easy availability of pentamethylcyclopentadiene from 2-bromo-2-butene [12] makes the reactions of the metal hexacarbonyls  $M(CO)_6$  ( $M = Cr, Mo,$  and  $W$ ) with pentamethylcyclopentadiene in boiling *n*-decane an attractive method for the preparation of the metal-metal triple bonded derivatives  $[(CH_3)_5C_5M(CO)_2]_2$  (I:  $M = Cr, Mo,$  and  $W$ ). The chromium and molybdenum derivatives are well-known [3-6] but the tungsten derivative is reported here for the first time. The molybdenum and tungsten triple-bonded derivatives  $[(CH_3)_5C_5M(CO)_2]_2$  (I:  $M = Mo$  and  $W$ ) are obtained as mixtures with smaller quantities of the corresponding metal-metal single bonded derivatives  $[(CH_3)_5C_5M(CO)_3]_2$  (II:  $M = Mo$  and  $W$ ) but these mixtures can readily be separated by column chromatography.

Several reactions of pentamethylcyclopentadiene with other relatively stable metal carbonyl derivatives in boiling *n*-decane were also investigated. Such a reaction of  $Ru_3(CO)_{12}$  with pentamethylcyclopentadiene was found to give a relatively good yield of  $[(CH_3)_5C_5Ru(CO)_2]_2$  (III:  $R = R' = CH_3$ ) completely analogous to the recently reported [21] ethyltetramethylcyclopentadienyl derivative  $[C_2H_5(CH_3)_4C_5Ru(CO)_2]_2$  (III:  $R = CH_3, R' = C_2H_5$ ) of which the structure was determined by X-ray diffraction. Similar reactions of  $CH_3M(CO)_5$  ( $M = Mn$  and  $Re$ ) or  $Mn_3(CO)_{10}$  with pentamethylcyclopentadiene were found to give ~30% yields of the corresponding  $(CH_3)_5C_5M(CO)_3$  derivatives (IV:  $M = Mn$  and  $Re$ ), which represent appreciable improvements over the ~10% yields reported in the literature [4,6] for the preparation of these substances.



(III)



(IV)

### Carbonylation and decarbonylation studies

The reactions of the three  $[(CH_3)_5C_5M(CO)_2]_2$  derivatives (I:  $M = Cr, Mo,$  and  $W$ ) in *n*-tetradecane solution with CO under pressure were followed by infrared spectroscopy in the  $\nu(CO)$  region using our previously developed [11] stainless steel high pressure infrared cell with Irtran I windows (Fig. 1, 2, and 3). The  $\nu(CO)$  frequencies used to identify the relevant pentamethylcyclopentadienyl metal derivatives are listed in Table 1.

The chromium-chromium triple bond in  $[(CH_3)_5C_5Cr(CO)_2]_2$  (I:  $R = CH_3,$



M = Cr) was found to be relatively resistant towards CO addition in accord with previous work [9]. Thus heating a tetradecane solution of  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$  with 300 atm CO results in no significant attack of the chromium—chromium triple bond even at 92°C (Fig. 1b). Further heating to 129°C (Fig. 1c) results in complete loss of  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$  (I) to give  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_3]_2$  (II) as indicated by the disappearance of the 1871, 1852  $\text{cm}^{-1}$  pair of  $\nu(\text{CO})$  frequencies and the formation of a 1915, 1886  $\text{cm}^{-1}$  pair of  $\nu(\text{CO})$  frequencies (Table 1). A small amount of  $\text{Cr}(\text{CO})_6$  also forms in a side reaction as recognized by an additional sharp band at 1995  $\text{cm}^{-1}$  (spike on the strong 2140  $\text{cm}^{-1}$  free CO band in Fig. 1b and 1c). Further heating to 170°C in a closed system results in no further alteration of the  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_3]_2$  spectrum, even if the CO pressure is replaced by nitrogen at atmospheric pressure (Fig. 1d).

The corresponding reactions of the molybdenum—molybdenum triple bond in  $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]_2$  (I: R = CH<sub>3</sub>, M = Mo) with CO proceed under considerably milder conditions again in accord with previous work [8]. Carbonylation to form  $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_3]_2$  (II: R = CH<sub>3</sub>, M = Mo) already begins at room temperature and atmospheric pressure (Fig. 2b) and is complete at 90°C and 50 atm CO (Fig. 2c). Further heating to 100°C under 50 atmospheres CO results in the formation of some  $\text{Mo}(\text{CO})_6$  as indicated by the appearance of a new  $\nu(\text{CO})$  frequency at 1985  $\text{cm}^{-1}$  (Fig. 2d).

The reaction of the tungsten—tungsten triple bond in  $[(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_2]_2$  (I: R = CH<sub>3</sub>, M = W) with CO is of greater interest than the corresponding reactions of the chromium and molybdenum derivatives since this tungsten system has not been previously available. The results illustrated in Fig. 3 indicate that the reactivity of the tungsten—tungsten triple bond in  $[(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_2]_2$  is intermediate between that of the relatively unreactive chromium—chromium triple bond in  $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]_2$ . Thus in a typical experiment an n-tetradecane solution of  $[(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_2]_2$  (I: R = CH<sub>3</sub>, M = W) was heated under 300 atm CO while recording the infrared spectra in the  $\nu(\text{CO})$  region at approximately 20°C intervals. At 68°C the formation of  $[(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_3]_2$  (II: R = CH<sub>3</sub>, M = W) was first detected by appearance of a new  $\nu(\text{CO})$  band at 1920  $\text{cm}^{-1}$  (Fig. 3b). Further heating to 112°C results in incipient formation of  $\text{W}(\text{CO})_6$  ( $\nu(\text{CO})$  1980  $\text{cm}^{-1}$ ) as well as complete disappearance of  $[(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_2]_2$  (Fig. 3c). The bands due to  $[(\text{CH}_3)_5\text{C}_5\text{W}(\text{CO})_3]_2$  (as well as, of course, that due to  $\text{W}(\text{CO})_6$ ) were stable in a closed system (e.g. Fig. 3d).

The results from these high pressure infrared spectroscopic experiments summarized in Table 2 indicate that there is a large difference in the reactivity of metal—metal triple bonds in completely analogous compounds towards addition reactions. Furthermore, the ease of addition reactions to the metal—metal triple bond increases in the sequence Cr < W < Mo. The relatively high reactivity of molybdenum—molybdenum triple bonds towards CO addition as compared with corresponding chromium—chromium and tungsten—tungsten triple bonds is reminiscent of the high chemical reactivity of molybdenum—carbon bonds as compared with corresponding chromium—carbon and tungsten—carbon bonds [22].

The reactions of  $[(\text{CH}_3)_5\text{C}_5\text{M}(\text{CO})_2]_2$  (I: R = CH<sub>3</sub>, M = Cr, Mo, and W) with CO to give  $[(\text{CH}_3)_5\text{C}_5\text{M}(\text{CO})_3]_2$  (II: R = CH<sub>3</sub>, M = Cr, Mo, and W) observed spectroscopically in the high pressure infrared cell have also been verified on a preparative

TABLE 2

SUMMARY OF REACTIONS OF  $[(\text{CH}_3)_5\text{C}_5\text{M}(\text{CO})_2]_2$  WITH CARBON MONOXIDE STUDIED BY INFRARED SPECTROSCOPY AT ELEVATED PRESSURES

$[(\text{CH}_3)_5\text{C}_5\text{M}(\text{CO})_2]_2$ derivative used	CO pressure (atm.)	Temperature of formation <sup>a</sup> of $[(\text{CH}_3)_5\text{C}_5\text{M}(\text{CO})_3]_2$ (°C)	Temperature of formation <sup>a</sup> of $\text{M}(\text{CO})_6$ (°C)
M = Cr	300	116	92
M = Mo <sup>b</sup>	50	18	106
M = W	50	82	>103
M = W	300	68	112

<sup>a</sup> These represent the first temperatures at which the infrared  $\nu(\text{CO})$  frequencies characteristic of the indicated products were observed at the indicated pressures. <sup>b</sup> Immediate conversion of  $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]_2$  to  $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_3]_2$  was also observed when an n-tetradecane solution of  $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]_2$  was flushed with CO at one atmosphere pressure in accord with reported observations of Ginley and Wrighton (ref. 9).

scale in a rocking autoclave. Solid samples of the three metal-metal single bonded derivatives  $[(\text{CH}_3)_5\text{C}_5\text{M}(\text{CO})_3]_2$  (II: R = CH<sub>3</sub>, M = Cr, Mo, and W) have now been isolated, the chromium and tungsten compounds for the first time. The chromium compound  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_3]_2$  is by far the least stable of these pentamethylcyclopentadienylmetal carbonyl derivatives towards air, particularly in solution. It therefore could not be obtained completely analytically pure. The instability of  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_3]_2$  suggests some steric hindrance when a bulky pentamethylcyclopentadienyl ring is bonded to a first row transition metal which concurrently is bonded to four other ligands (three CO groups and the other chromium atom). The dark red-purple color of  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_3]_2$  is also striking in view of the green color [23] of the unsubstituted cyclopentadienyl derivative  $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$  (II: R = H, M = Cr). This means, for example, that the decarbonylation of a boiling *p*-xylene solution of  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_3]_2$  (II: R = CH<sub>3</sub>, M = Cr) to  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$  can be observed visually by the originally red-violet solution becoming dark green. Also the purple intermediate colors observed in the reactions of  $\text{Cr}(\text{CO})_6$  with pentamethylcyclopentadiene to give ultimately green  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$  and in the sodium amalgam reduction of  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$  to give yellow-brown  $\text{Na}[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_3]$  may suggest the intermediacy of purple  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_3]_2$  in both of these reactions. This suggestion is reasonable in light of the chemistry involved. Also our observed  $\nu(\text{CO})$  frequencies of 1915 and 1886  $\text{cm}^{-1}$  for  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_3]_2$  in n-tetradecane solution differ considerably from the frequencies of 1985 and 1900  $\text{cm}^{-1}$  previously [9] assigned to  $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_3]_2$  in benzene solution. Since this difference is too great to be a solvent effect, we suspect that the previously observed 1985  $\text{cm}^{-1}$  frequency arises from a  $\text{Cr}(\text{CO})_6$  impurity ( $\nu(\text{CO})$  for  $\text{Cr}(\text{CO})_6$  is 1995  $\text{cm}^{-1}$  in n-tetradecane) and that the 1915 and 1886  $\text{cm}^{-1}$  bands are incompletely resolved in the relatively poor infrared spectroscopy solvent benzene leading to the observed 1900  $\text{cm}^{-1}$  frequency.

## Acknowledgement

We are indebted to the Division of Basic Energy Sciences of the U.S. Department of Energy for partial support of this work under Contract EY-76-S-09-0933.

## References

- 1 R.B. King, W.M. Douglas, and A. Efraty, *J. Organometal. Chem.*, 69 (1974) 131.
- 2 R.B. King, *Coord. Chem. Revs.*, 20 (1976) 155.
- 3 R.B. King and A. Efraty, *J. Amer. Chem. Soc.*, 93 (1971) 4950.
- 4 R.B. King and A. Efraty, *J. Amer. Chem. Soc.*, 94 (1972) 3773.
- 5 J. Potenza, P. Giordano, D. Mastropaolo, A. Efraty, and R.B. King, *Chem. Commun.*, (1972) 1333.
- 6 R.B. King and M.B. Bisnette, *J. Organometal. Chem.*, 8 (1967) 287.
- 7 P. Hackett, P.S. O'Neill, and A.R. Manning, *J. Chem. Soc. Dalton*, (1974) 1625.
- 8 R.J. Klingler, W. Butler, and M.D. Curtis, *J. Amer. Chem. Soc.*, 97 (1975) 3535.
- 9 D.S. Ginley, C.R. Bock, and M.S. Wrighton, *Inorg. Chim. Acta*, 23 (1977) 85.
- 10 D.S. Ginley and M.S. Wrighton, *J. Amer. Chem. Soc.*, 97 (1975) 3533.
- 11 R.B. King, A.D. King, Jr., M.Z. Iqbal, and C.C. Frazier, *J. Amer. Chem. Soc.*, 100 (1978) 1687.
- 12 R.S. Threlkel and J.E. Bercaw, *J. Organometal. Chem.*, 136 (1977) 1.
- 13 B.R. James, G.L. Rempel, and W.K. Teo, *Inorg. Syn.*, 16 (1976) 45.
- 14 R.B. King, *Inorg. Chem.*, 5 (1966) 2227.
- 15 T. Blackmore, J.D. Cotton, M.I. Bruce, and F.G.A. Stone, *J. Chem. Soc. A*, (1968) 2931.
- 16 W. Hieber and G. Wagner, *Liebigs Ann.*, 618 (1958) 24.
- 17 R.B. King, *Organometal. Syn.*, 1 (1965) 147.
- 18 R.B. King, J.C. Stokes, and T.F. Korenowski, *J. Organometal. Chem.*, 11 (1968) 641.
- 19 W. Beck, W. Hieber, and H. Tengler, *Ber.*, 94 (1961) 862.
- 20 T.S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3 (1956) 104.
- 21 N.A. Bailey, S.L. Radford, J.A. Sanderson, K. Tabatabaian, C. White, and J.M. Worthington, *J. Organometal. Chem.*, 154 (1978) 343.
- 22 R.B. King, *Inorg. Nucl. Chem. Letters*, 5 (1969) 905.
- 23 E.O. Fischer and W. Hafner, *Z. Naturforsch.*, B10 (1955) 140.