

## FUNCTIONALLY SUBSTITUTED CYCLOPENTADIENYLTRICARBONYLMETHYL DERIVATIVES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

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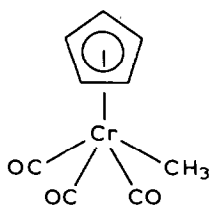
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### Summary

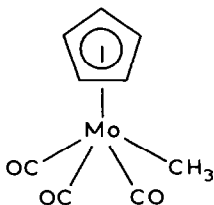
Functionally substituted cyclopentadienyltricarbonylmethyl derivatives of chromium, molybdenum, and tungsten have been prepared and their chemistry studied. The functional groups include carbomethoxy, acetyl, and formyl. The acetyl and formyl derivatives for molybdenum and tungsten were converted into their respective vinyl analogs with methylenetriphenylphosphorane. ( $\eta^5$ -Carboxycyclopentadienyl)tricarbonylmethyltungsten was prepared from ( $\eta^5$ -carbomethoxycyclopentadienyl)tricarbonylmethyltungsten using potassium hydroxide in methanol. The  $pK_a$  of this carboxylic acid was determined to be 4.5.

### Introduction

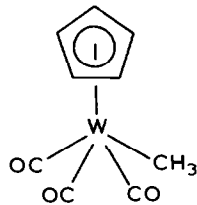
( $\eta^5$ -Cyclopentadienyl)tricarbonylalkyl derivatives of chromium (I), molybdenum (II), and tungsten (III) were first described by Fischer in 1955 [1], and by Wilkinson in 1956 [2]. Recently, considerable research has focused on the photochemistry of I–III [3–16]. ( $\eta^5$ -Cyclopentadienyl)tricarbonylalkyl derivatives of tungsten have also been incorporated into polymers [11,17–19]. Chemistry associated with the cyclo-



(I)



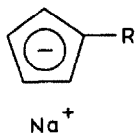
(II)



(III)

pentadienyl ring of I–III has been hampered because of the inability of these complexes to undergo electrophilic aromatic substitution.

We have recently reported the preparation of functionally substituted derivatives of I-III using reagents IV-VI as starting materials [20,21]. This report describes experimental details as well as the chemistry and physical properties of these complexes.



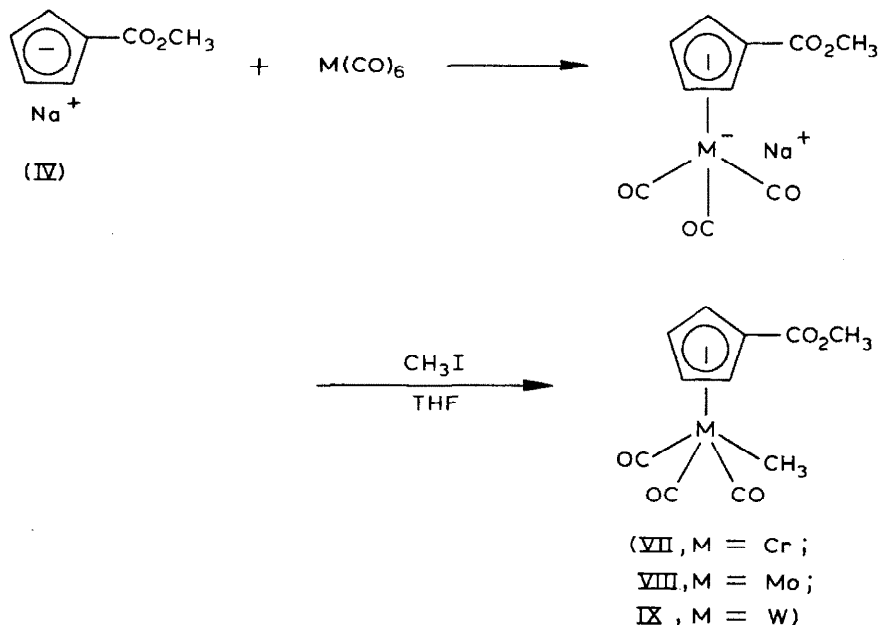
(IV, R = CO<sub>2</sub>CH<sub>3</sub>;

V, R = COCH<sub>3</sub>;

VI, R = CHO)

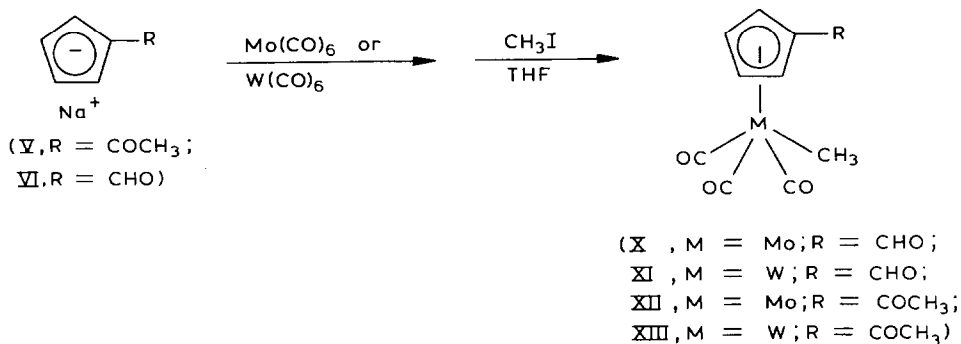
### Results and discussion

Reaction between organosodium reagent IV and the Group VIb metal hexacarbonyls produced intermediate cyclopentadienyltricarbonyl anions. Treatment of these anions with methyl iodide in THF gave complexes VII-IX in yields between 26 and 72%. The relative thermal stabilities of the chromium (VII) (dec.pt. > 40°C), molybdenum (VIII) (m.p. 61-62°C), and tungsten (IX) (m.p. 76-78°C) derivatives parallel the stabilities found earlier for the parent members ( $\eta^5\text{-C}_5\text{H}_5$ )M(CO)<sub>3</sub>CH<sub>3</sub> (M = Cr, Mo, W) [2].

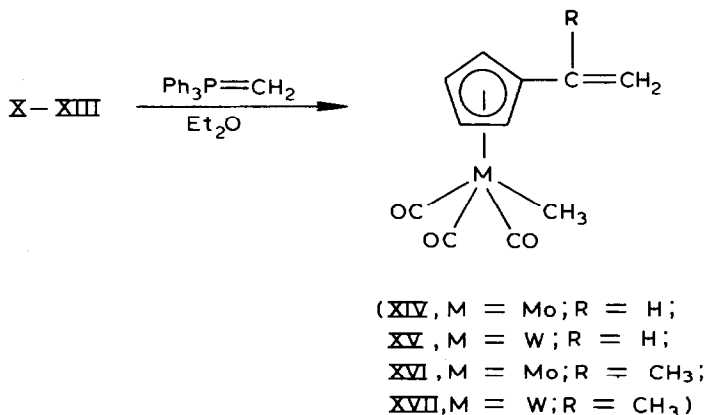


Organosodium reagents V and VI reacted in a manner similar to IV with Mo(CO)<sub>6</sub> (THF, reflux) and W(CO)<sub>6</sub> (DMF, reflux). Following methylation of the intermediate tricarbonyl anions with methyl iodide, the derivatives X-XIII were obtained in good yields. Aldehyde XI has been previously reported by us in the

preparation of organotungsten monomers and polymers [18]. These molybdenum and tungsten derivatives (VIII–XIII) are all air-stable yellow crystalline solids.



We next turned our attention to the chemistry of these derivatives. For example, treatment of X–XIII with methylenetriphenylphosphorane, which was generated from methyltriphenylphosphonium iodide and *n*-butyllithium in ether, produced the vinyl derivatives XIV–XVII in 11–26% yields. A better route to vinyl derivative XV



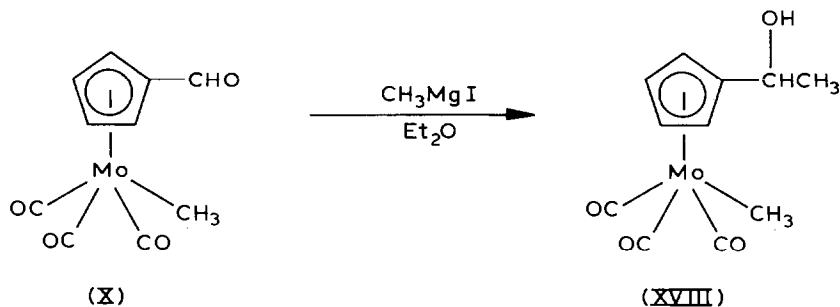
has recently been reported by us, using a Wittig reaction under phase-transfer conditions, and the polymerization of this monomer has been studied [18,19].

The low yields in these reactions are believed to be due to the base-sensitivity of compounds X–XIII. Upon treatment of these compounds with Wittig reagents extensive decomposition was observed.

Owing to the low yields of these reactions using methylenetriphenylphosphorane, alternative methods of preparation were investigated. For example, treatment of XIII with methylmagnesium iodide followed by aqueous hydrochloric acid produced the isopropenyl derivative (XVII) in 38% overall yield.

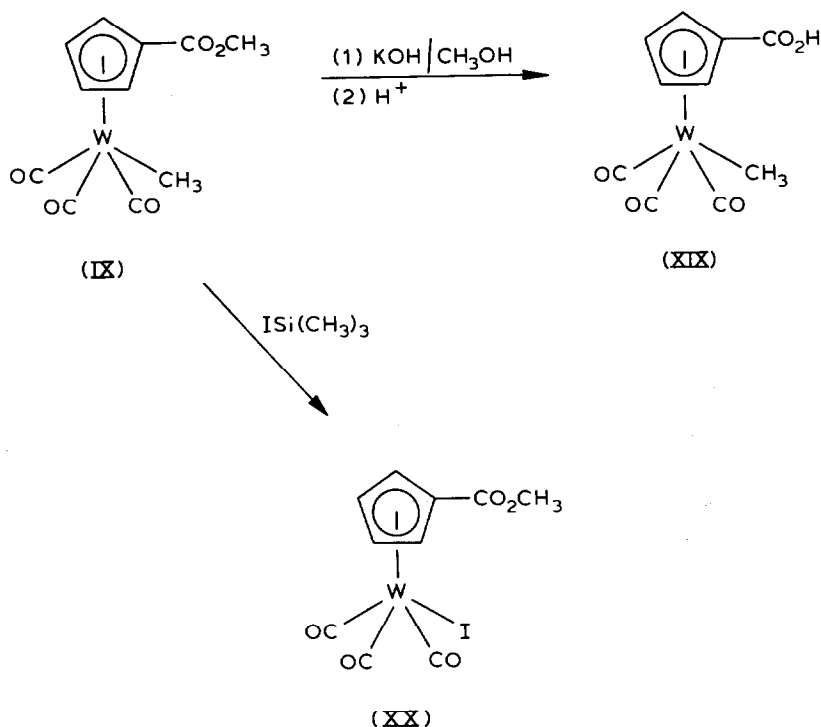
A similar reaction between X and methylmagnesium iodide gave the secondary alcohol XVIII in 32% yield. During the course of this reaction considerable decomposition of the organometallic compounds occurred, requiring tedious purification to obtain pure XVIII. Dehydration of XVIII with *p*-toluenesulfonic acid in refluxing benzene produced the vinyl derivative XIV in 2% yield; 39% of the starting alcohol was recovered. Considerable decomposition also occurred during this reaction.

( $\eta^5$ -Carbomethoxycyclopentadienyl)tricarbonylmethyltungsten (IX) was saponi-



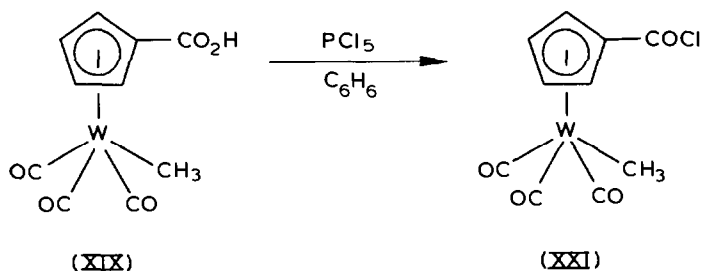
fied under mild conditions with potassium hydroxide in aqueous methanol at 25°C to give, after acidification, the corresponding carboxylic acid (XIX) in 82% yield. When ester VIII was treated under identical conditions a dark solution resulted. The anticipated carboxylic acid corresponding to VIII was not obtained upon acidification with dilute hydrochloric acid. Presumably VIII was unstable to the basic conditions of saponification.

Olah and co-workers have developed a method of converting esters into carboxylic acids, under neutral conditions, using iodotrimethylsilane [22]. A reaction between IX and iodotrimethylsilane, which was generated from sodium iodide and chlorotrimethylsilane, did not produce the expected acid XIX. The only compound isolated from this reaction was ( $\eta^5$ -carbomethoxycyclopentadienyl)tricarbonyliodotungsten (XX), which resulted from cleavage of the tungsten–methyl bond.



Compound XX was identified by its  $^1\text{H}$  NMR, IR, and mass spectra. The  $^1\text{H}$  NMR spectrum of XX exhibited a pair of triplets ( $A_2B_2$  pattern) at  $\delta$  5.84 and 6.11 ppm for protons H(3,4) and H(2,5), respectively. The  $^1\text{H}$  NMR spectrum of  $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{I}$  showed a single resonance at  $\delta$  5.68 ppm. [23]. Cleavage of the tungsten–methyl bond was indicated by the absence of resonances in the range of  $\delta$  0.30–0.50 ppm. Compound XX also exhibited a sharp singlet at  $\delta$  3.86 ppm for the carbomethoxy protons. The IR spectrum of XX showed two metal carbonyl bands and an organic carbonyl absorption at 2035, 1940, and 1710  $\text{cm}^{-1}$ , respectively. The mass spectrum of XX showed parent peaks at  $m/e$  516 ( $^{182}\text{W}$ ),  $m/e$  517 ( $^{183}\text{W}$ ),  $m/e$  518 ( $^{184}\text{W}$ ), and  $m/e$  520 ( $^{186}\text{W}$ ).

Carboxylic acid XIX was converted into  $(\eta^5\text{-chloroformylcyclopentadienyl})\text{tricarboxylmethyltungsten}$  (XXI) in 38% yield by means of  $\text{PCl}_5$  in benzene. Acid chloride XXI was identified on the basis of its  $^1\text{H}$  NMR, IR, and mass spectra. The  $^1\text{H}$  NMR spectrum of XXI exhibited a pair of apparent triplets ( $A_2B_2$  pattern) at  $\delta$  5.57 and 5.81 ppm for cyclopentadienyl protons H(3,4) and H(2,5), respectively. The IR spectrum of XXI in ether showed an organic carbonyl band at 1770  $\text{cm}^{-1}$ ; the organic carbonyl band of the starting acid XIX in ether occurred at 1730  $\text{cm}^{-1}$ . The



mass spectrum of XXI showed parent peaks at  $m/e$  408 ( $^{182}\text{W}$ ,  $^{35}\text{Cl}$ ),  $m/e$  409 ( $^{183}\text{W}$ ,  $^{35}\text{Cl}$ ),  $m/e$  410 ( $^{184}\text{W}$ ,  $^{35}\text{Cl}$  and  $^{182}\text{W}$ ,  $^{37}\text{Cl}$ ), and 412 ( $^{184}\text{W}$ ,  $^{37}\text{Cl}$ ).

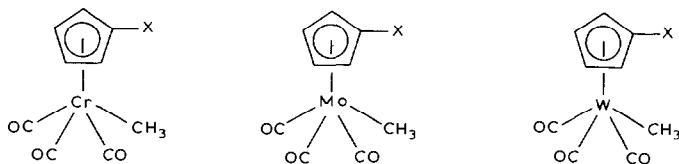
The  $^1\text{H}$  NMR spectra of monosubstituted cyclopentadienylmetal compounds vary greatly in complexity, depending upon the transition metal and the nature of the substituent. In general, compounds with substituents other than simple alkyl groups exhibit an  $A_2B_2$  pattern for the cyclopentadienyl protons [24]. The spectrum consists of a pair of apparent triplets, in which the downfield triplet has been assigned to the H(2,5) protons.

Table 1 summarizes the  $^1\text{H}$  NMR spectra for various  $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Cr}(\text{CO})_3\text{CH}_3$ ,  $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mo}(\text{CO})_3\text{CH}_3$ , and  $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{W}(\text{CO})_3\text{CH}_3$  compounds. It can be seen from Table 1 that the cyclopentadienyl protons occur at lowest field for tungsten, intermediate field for molybdenum, and highest field for chromium. There is a larger difference in chemical shift between the proton resonances of the chromium compounds and the molybdenum compounds than between the latter and the tungsten compounds. The acyl metallocenes of iron, ruthenium, and osmium show a similar trend [24]. It also can be seen from Table 1 that the ring substituent has a slight effect on the chemical shift of the methyl group attached to the metal. Electron-withdrawing substituents (e.g. formyl, acetyl, etc.) deshield the methyl groups for the chromium, molybdenum, and tungsten compounds.

The  $\text{p}K_a$  values of  $(\eta^5\text{-carboxycyclopentadienyl})\text{tricarboxylmethyltungsten}$  (XIX) and benzoic acid were determined to be 4.5 and 4.3, respectively. As can be seen

TABLE 1

$^1\text{H}$  NMR COMPARISONS OF VARIOUS CHROMIUM, MOLYBDENUM, AND TUNGSTEN COMPOUNDS <sup>a</sup>



X	$\delta(\text{H-}(3,4))$	$\delta(\text{H-}(2,5))$	$\delta(\text{M-CH}_3)$	$\delta(\text{H-}(3,4))$	$\delta(\text{H-}(2,5))$	$\delta(\text{M-CH}_3)$	$\delta(\text{H-}(3,4))$	$\delta(\text{H-}(2,5))$	$\delta(\text{M-CH}_3)$
H	4.76 <sup>b</sup>	4.76 <sup>b</sup>	0.68 <sup>b</sup>	5.27 <sup>b</sup>	5.27 <sup>b</sup>	0.34 <sup>b</sup>	5.38 <sup>b</sup>	5.38 <sup>b</sup>	0.40 <sup>b</sup>
$\text{CO}_2\text{CH}_3$	4.90	5.28	0.82	5.32	5.32	0.38	5.48	5.83	0.48
CHO				5.39	5.78	0.45	5.71 <sup>c</sup>	5.82 <sup>c</sup>	0.48 <sup>c</sup>
$\text{C}(\text{O})\text{CH}_3$				5.52	5.72	0.45	5.52	5.72	0.45
$\text{C}(\text{CH}_3)=\text{CH}_2$				5.47	5.73	0.44	5.34	5.44	0.39
$\text{CH}=\text{CH}_2$				5.28	5.38	0.33	5.36 <sup>c</sup>	5.48 <sup>c</sup>	0.40 <sup>c</sup>
$\text{CH}(\text{OH})\text{CH}_3$				5.22	5.31	0.32	5.39 <sup>c</sup>	5.39 <sup>c</sup>	0.46 <sup>c</sup>

<sup>a</sup> Recorded in  $\text{CDCl}_3$ ; estimated accuracy  $\pm 0.02$  ppm; this work. <sup>b</sup> Recorded in  $\text{CCl}_4$ ; ref. 25. <sup>c</sup> Ref. 18.

TABLE 2.  $\text{p}K_a$  VALUES OF VARIOUS ACIDS IN AQUEOUS SOLUTION AT 25°C

Acid	$\text{p}K_a$	Reference
Benzoic	4.2	26
Benzoic	4.3	this work
Ferrocenoic	4.4	27
Anisic	4.5	26
XIX	4.5	this work

from Table 2, acid (XIX) is a slightly weaker acid than ferrocenoic acid, and approximately as strong as anisic acid.

### Experimental

All operations were carried out under a nitrogen atmosphere using standard Schlenk or vacuum line techniques. Pentane, hexane, and dimethylformamide (DMF) were dried over calcium hydride and distilled under argon. Diethyl ether was predried over sodium wire and distilled from sodium-benzophenone under argon. Tetrahydrofuran and dimethoxyethane (DME) were predried over KOH, then sodium wire, and distilled under argon from sodium-benzophenone.

Column chromatography was carried out using Fischer brand Florisil or Alfa-Ventron neutral CAMAG alumina. The Florisil and alumina were heated under vacuum (0.01 mmHg) on a rotary evaporator to remove water and oxygen. The alumina was then deactivated with 5% (by weight) argon-saturated water.

Chromium, molybdenum, and tungsten hexacarbonyls were obtained from Pressure Chemical Co. Sodium carbomethoxycyclopentadienide (IV), sodium acetylcyclopentadienide (V), and sodium formylcyclopentadienide (VI) were prepared according to literature procedures [20,28,29].

$^1\text{H}$  NMR spectra were recorded on a Varian A-60 spectrometer, IR spectra were recorded on either a Perkin-Elmer 237B or a Beckman IR-10 spectrometer. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

*( $\eta^5$ -Carbomethoxycyclopentadienyl)tricarbonylmethylchromium (VII)*

A mixture of sodium carbomethoxycyclopentadienide (0.75 g, 5.1 mmol) and chromium hexacarbonyl (1.10 g, 5.0 mmol), in 50 ml of DMF, was refluxed for 7 h. The DMF was removed under vacuum (0.01 mmHg) and the resulting black oil taken up in 50 ml of THF. The solution was cooled in an ice-salt bath and iodomethane (0.63 ml, 10.0 mmol) added. The mixture was stirred at this temperature for 2 h and then evaporated on Florisil under reduced pressure. The resulting residue was added to a column of Florisil ( $5 \times 1.5$  cm) and the column eluted with hexane/ether to give a yellow-brown band. This band was collected under nitrogen at  $-78^\circ\text{C}$  and the solvent reduced to a quarter of its original volume under vacuum. The Schlenk tube was cooled to  $-78^\circ\text{C}$  and allowed to stand overnight to give 0.36 g (26%) of VII. An analytical sample was obtained by several recrystallizations from pentane at  $-78^\circ\text{C}$  as yellow crystals m.p.  $40^\circ\text{C}$  dec. (Found: 47.91; H, 3.69.  $\text{C}_{11}\text{H}_{10}\text{CrO}_5$  calcd.: C, 48.18; H, 3.68%). IR (Pentane):  $\nu(\text{CO})$  2030(s), 1950(s), 1740(m)  $\text{cm}^{-1}$ .

*( $\eta^5$ -Carbomethoxycyclopentadienyl)tricarbonylmethylmolybdenum (VIII)*

Sodium cyclopentadienide was prepared from sodium sand (0.80 g, 34.3 mmol) and cyclopentadiene (4.00 ml, 48.5 mmol) in 100 ml of THF. To this was added dimethyl carbonate (5.80 ml, 69.0 mmol) and the mixture refluxed for 3 h. The solution was cooled to  $25^\circ\text{C}$ , molybdenum hexacarbonyl (7.26 g, 27.5 mmol) was added, and the mixture refluxed for 6 h. Iodomethane (2.10 ml, 33.0 mmol) was added with continued stirring for 5 h. The THF was removed under vacuum on alumina and the resulting residue added to a column of alumina ( $15 \times 1.5$  cm). Elution of the column with hexane produced a small yellow band which was not collected. The column was eluted further with hexane/ether to give another yellow band which was collected under nitrogen. Removal of the solvent under vacuum gave 3.12 g (36%) of VIII. An analytical sample was obtained by sublimation at  $45^\circ\text{C}/0.01$  mmHg as lemon-yellow crystals, m.p.  $61$ – $62.5^\circ\text{C}$ . (Found: C, 41.49; H, 3.18.  $\text{C}_{11}\text{H}_{10}\text{MoO}_5$  calcd.: C, 41.53; H, 3.17%). IR (KBr):  $\nu(\text{CO})$  2010(s), 1915(s), 1710(m)  $\text{cm}^{-1}$ .

*( $\eta^5$ -Carbomethoxycyclopentadienyl)tricarbonylmethyltungsten (IX)*

Sodium cyclopentadienide was prepared from sodium sand (0.80 g, 34.3 mmol) and cyclopentadiene (4.00 ml, 48.5 mmol) in 100 ml of DME. To this was added dimethyl carbonate (5.80 ml, 69.0 mmol) and the mixture refluxed for 2.5 h. The solution was cooled to  $25^\circ\text{C}$ , tungsten hexacarbonyl (11.00 g, 27.5 mmol) was added, and the mixture refluxed for 20 h. Iodomethane (2.10 ml, 33.0 mmol) was added with continued stirring for 4.5 h at  $25^\circ\text{C}$ . The DME was then removed under vacuum, resulting in a brown oil. The oil was extracted with a total of 400 ml of hexane and filtered to give a yellow solution. The solvent was removed under vacuum to produce 8.00 g (72%) of IX. An analytical sample was obtained by sublimation at  $60^\circ\text{C}/0.01$  mmHg as yellow crystals, m.p.  $76$ – $78^\circ\text{C}$ . (Found: C, 32.84; H, 2.43.  $\text{C}_{11}\text{H}_{10}\text{O}_5\text{W}$  calcd.: C, 32.54; H, 2.48%). IR (KBr):  $\nu(\text{CO})$  2005(s), 1910(s), 1715(m)  $\text{cm}^{-1}$ .

*( $\eta^5$ -Formylcyclopentadienyl)tricarbonylmethylmolybdenum (X)*

Sodium formylcyclopentadienide (2.40 g, 20.7 mmol) and molybdenum hexacarbonyl (5.28 g, 20.0 mmol) were added to a 250 ml three-neck round-bottom flask equipped with a condenser and gas inlet and outlet valves. To this was added 150 ml of THF and the mixture refluxed for 48 h. The solution was cooled to 25°C, excess iodomethane was added, and the mixture stirred for 20 h. The THF was removed under vacuum on alumina. The resulting residue was added to a column of alumina (15 × 1.5 cm) and the column eluted with pentane. The column was then eluted with pentane/ether to produce a yellow band which was collected under nitrogen. The solvent was removed under vacuum to give 3.65 g (63%) of X. An analytical sample was obtained by sublimation at 50°C/0.01 mmHg as yellow crystals, m.p. 75°C dec. (Found: C, 41.85; H, 2.94.  $C_{10}H_8MoO_4$  calcd.: C, 41.69; H, 2.80%). IR (KBr):  $\nu(CO)$  2020(s), 1920(s), 1680(m)  $cm^{-1}$ .

*( $\eta^5$ -Acetylcyclopentadienyl)tricarbonylmethylmolybdenum (XII)*

Sodium acetylcyclopentadienide (1.30 g, 10.0 mmol) and molybdenum hexacarbonyl (2.64 g, 10.0 mmol) were added to a 250 ml three-neck round-bottom flask equipped with a condenser and gas inlet and outlet valves. THF (150 ml) was added, the mixture was refluxed for 12 h and cooled to 25°C. To this was added iodomethane (0.75 ml, 12.0 mmol) and the mixture stirred for 5 h. The THF was then evaporated on alumina under reduced pressure and the resulting residue added to a column of alumina (15 × 1.5 cm). Elution of the column with hexane followed by hexane/ether gave a yellow band which was collected under nitrogen. The solvent was removed under vacuum to give 2.75 g (91%) of XII. An analytical sample was obtained by sublimation at 50°C/0.01 mmHg, m.p. 61.5–63°C. (Found: C, 43.86; H, 3.44.  $C_{11}H_{10}MoO_4$  calcd.: C, 43.73; H, 3.34%). IR(Melt):  $\nu(CO)$  2020(s), 1920(s), 1665(s)  $cm^{-1}$ .

*( $\eta^5$ -Acetylcyclopentadienyl)tricarbonylmethyltungsten (XIII)*

Sodium acetylcyclopentadienide (5.00 g, 38.4 mmol) and tungsten hexacarbonyl (12.30 g, 35.0 mmol) were added to a 250 ml three-neck round-bottom flask equipped with a condenser and gas inlet and outlet valves. To this was added 150 ml of DMF and the mixture refluxed for 2 h. The DMF was removed under vacuum (0.01 mmHg) to give a black oil. The oil was taken up in 150 ml of THF, and iodomethane (2.90 ml, 45.0 mmol) added. The mixture was stirred for 2.5 h at 25°C and the THF removed under vacuum. The resulting residue was extracted with pentane/ether and the extracts filtered through a plug of Florisil. The solvent was removed under vacuum to give 7.83 g (57%) of XIII. An analytical sample was obtained by sublimation at 55°C/0.01 mmHg as yellow crystals, m.p. 73.5–75°C. (Found: C, 34.00; H, 2.64.  $C_{11}H_{10}O_4W$  calcd.: C, 33.87; H, 2.58%). IR (KBr):  $\nu(CO)$  2010(s), 1920(s), 1670(m)  $cm^{-1}$ .

*( $\eta^5$ -Vinylcyclopentadienyl)tricarbonylmethylmolybdenum (XIV)*

In a 100 ml single-neck round-bottom flask with a side arm were placed methyltriphenylphosphonium iodide (2.02 g, 5.5 mmol) and 60 ml ether. To this was added 1.8 M methylolithium (3.0 ml, 5.5 mmol) and the mixture stirred at 25°C for 4 h. This Wittig reagent was then added dropwise to a solution of X (1.44 g, 5.5 mmol) in 50 ml of ether. The mixture was stirred at 25°C for 24 h. The solvent was



evaporated on Florisil under reduced pressure and the resulting residue added to a column of Florisil ( $15 \times 1.5$  cm). Elution of the column with hexane brought down a yellow band which was collected under nitrogen. The solvent was removed under vacuum to give 0.15 g (11%) of XIV as a yellow liquid. An analytical sample was obtained by molecular distillation. (Found: C, 46.14; H, 3.67.  $C_{11}H_{10}MoO_3$  calcd.: C, 46.17; H, 3.52%). IR (Neat):  $\nu(CO)$  2005(s), 1920(s)  $cm^{-1}$ .

*( $\eta^5$ -Isopropenylcyclopentadienyl)tricarbonylmethylmolybdenum (XVI)*

In a 100 ml single-neck round-bottom flask with a side arm were placed methyltriphenylphosphonium iodide (1.21 g, 3.0 mmol) and 50 ml of ether. To this was added 1.8 M methyllithium (1.70 ml, 3.0 mmol) and the mixture stirred for 4 h at 25°C. This Wittig reagent was then added dropwise to a solution of XII (0.91 g, 3.0 mmol) in 50 ml of ether. The mixture was stirred at 25°C for 18 h. The solvent was evaporated on Florisil under reduced pressure and the resulting residue added to a column of Florisil ( $15 \times 1.5$  cm). Elution of the column with hexane gave a yellow band which was collected under nitrogen. The solvent was removed under vacuum to give 0.23 g (26%) of XVI as a yellow solid. An analytical sample was obtained by sublimation at 40°C/0.01 mmHg, m.p. 54.5–56°C. (Found: C, 48.12; H, 4.19.  $C_{12}H_{12}MoO_3$  calcd.: C, 48.01; H, 4.03%). IR (KBr):  $\nu(CO)$  2005(s), 1915(s)  $cm^{-1}$ .

*( $\eta^5$ -Isopropenylcyclopentadienyl)tricarbonylmethyltungsten (XVII)*

*Method A:* In a 100 ml single-neck round-bottom flask with a side arm were placed methyltriphenylphosphonium iodide (2.02 g, 5.0 mmol) and 75 ml of ether. To this was added 1.9 M n-butyllithium (2.60 ml, 5.0 mmol) and the solution stirred for 5 h at 25°C. This Wittig reagent was then added dropwise to a solution of XIII (1.95 g, 5.0 mmol) in 100 ml of ether. The mixture was stirred at 25°C for 12 h. The solution was filtered and the solvent removed under vacuum on alumina. The resulting residue was added to a column of alumina ( $15 \times 1.5$  cm) and the column eluted with hexane. A small yellow band came down the column and was collected under nitrogen. The solvent was removed under vacuum to give 0.21 g (11%) of XVII as a yellow solid. An analytical sample was obtained by sublimation at 40°C/0.01 mmHg, m.p. 73–75°C. (Found: C, 37.23; H, 3.30.  $C_{12}H_{12}O_3W$  calcd.: C, 37.14; H, 3.12%). IR (KBr):  $\nu(CO)$  2000(s), 1910(s)  $cm^{-1}$ .

*Method B:* Methylmagnesium iodide was prepared in ether from magnesium (0.29 g, 12.0 mmol) and iodomethane (0.75 ml, 12.0 mmol). To this was added dropwise a solution of XIII (3.12 g, 8.0 mmol) in 20 ml of THF. After the addition was complete the mixture was refluxed for 3 h. The solution was cooled to 25°C, 30 ml of 30% hydrochloric acid added, and the mixture stirred for 17 h. The solution was then extracted with methylene chloride, the combined organic extracts washed with dilute sodium bicarbonate solution, and the extracts dried over anhydrous magnesium sulfate. The solution was filtered and the solvent evaporated on Florisil under reduced pressure. The resulting residue was added to a column of Florisil ( $15 \times 1.5$  cm) and the column eluted with hexane. A yellow band came down the column and was collected under nitrogen. The solvent was removed under vacuum to give 1.19 g (38%) of XVII.

*( $\eta^5$ -1-Hydroxyethylcyclopentadienyl)tricarbonylmethylmolybdenum (XVIII)*

Methylmagnesium iodide was prepared in ether from magnesium metal (0.13 g,

5.2 mmol) and excess iodomethane. This Grignard reagent was added dropwise to X (1.00 g, 3.5 mmol) in 30 ml of ether. After the addition was complete the reaction mixture was stirred for 2 h at 25°C, and then hydrolyzed with dilute ammonium chloride solution. The layers were separated and the ether layer was washed with water. The ether layer was dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated on alumina under reduced pressure and the resulting residue added to a column of alumina (15 × 1.5 cm). Elution of the column with pentane/ether gave a yellow band which was collected under nitrogen. Removal of the solvent under vacuum gave 0.34 g (32%) of XVIII as a yellow liquid. An analytical sample was obtained by molecular distillation. (Found: C, 43.57; H, 3.89. C<sub>11</sub>H<sub>12</sub>MoO<sub>4</sub> calcd.: C, 43.44; H, 3.98%). IR (Neat):  $\nu(\text{CO})$  2005(s), 1910(s) cm<sup>-1</sup>.

*( $\eta^5$ -Carboxycyclopentadienyl)tricarbonylmethyltungsten (XIX)*

Compound IX (406 mg, 1.0 mmol) and potassium hydroxide (130 mg, 2.3 mmol) were dissolved in a solution of 8 ml of methanol and 0.2 ml of water. The mixture was stirred at 25°C for 23 h, and then poured into 50 ml of water. The solution was acidified with concentrated hydrochloric acid and cooled in ice. The precipitate was collected and dried at 25°C/0.01 mmHg to give 310 mg (82%) of XIX as a yellow powder. An analytical sample was obtained by sublimation at 100°C/0.01 mmHg, m.p. 187°C dec. (Found: C, 30.80; H, 2.21. C<sub>10</sub>H<sub>8</sub>O<sub>5</sub>W calcd.: C, 30.64; H, 2.06%). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  (ppm) 0.48, s, W-CH<sub>3</sub>; 5.73, t, H(3,4); 5.94, t, H(2,5). IR (KBr):  $\nu(\text{CO})$  2020(s), 1915(s) cm<sup>-1</sup>.

*( $\eta^5$ -Carbomethoxycyclopentadienyl)tricarbonyliodotungsten (XX)*

Compound IX (406 mg, 1.0 mmol) was dissolved in 15 ml of acetonitrile and chlorotrimethylsilane (0.25 ml, 2.0 mmol) was added. To this was added sodium iodide (300 mg, 2.0 mmol) and the mixture refluxed for 24 h. The reaction mixture was poured into water, extracted with two portions of ether, and the combined extracts dried over anhydrous magnesium sulfate. The solution was filtered and the solvent removed under vacuum to give 410 mg (79%) of XX as red plates. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 3.86, s, OCH<sub>3</sub>; 5.84, t, H(3,4); 6.11, t, H(2,5). IR (KBr):  $\nu(\text{CO})$  2035(s), 1940(s), 1710(m) cm<sup>-1</sup>. Mass Spectrum: *M*<sup>+</sup> *m/e* 518 (<sup>184</sup>W).

*( $\eta^5$ -Chloroformylcyclopentadienyl)tricarbonylmethyltungsten (XXI)*

Compound XIX (1.00 g, 2.5 mmol) was dissolved in 50 ml of benzene and phosphorus pentachloride (0.59 g, 2.8 mmol) was added. The mixture was stirred at 25°C for 2 h and the solvent removed under vacuum. The resulting residue was extracted with pentane and filtered through Celite under nitrogen. The solvent was removed under vacuum to give 0.40 g (38%) of XXI as a yellow solid. An analytical sample was obtained by sublimation at 60°C/0.01 mmHg followed by several recrystallizations from pentane/ether, m.p. 70–72.5°C. (Found: C, 29.47; H, 1.91. C<sub>10</sub>H<sub>7</sub>ClO<sub>4</sub>W calcd.: C, 29.26; H, 1.72%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 0.51, s, W-CH<sub>3</sub>; 5.57, t, H(3,4); 5.81, t, H(2,5). IR (ether):  $\nu(\text{CO})$  2015(s), 1940(s), 1770(m) cm<sup>-1</sup>. Mass Spectrum: *M*<sup>+</sup> *m/e* 410 (<sup>184</sup>W).

*Determination of the pKa values of benzoic acid and ( $\eta^5$ -carboxycyclopentadienyl)tricarbonylmethyltungsten (XIX)*

The titrations were made on a Radiometer Titrigraph-Type SBR2c, Copenhagen

(U.S. distributor, The London Co., West Lake, Ohio) coupled with the Radiometer Titrator II and pH meter 25 with a combination glass electrode. An analog data collection was performed using an X-Y recorder.

Twenty ml solutions of 0.02 M benzoic acid and 0.008 M ( $\eta^5$ -carboxycyclopentadienyl)tricarbonylmethyltungsten (XIX) were titrated with 0.5 ml of 0.8758 N sodium hydroxide at 23°C. The  $pK_a$  values were obtained experimentally from the titration curve by determining the pH at half-neutralization.

The  $pK_a$  for benzoic acid was determined to be  $4.3 \pm 0.1$ . The  $pK_a$  for XIX was determined to be  $4.5 \pm 0.1$ .

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### References

- 1 E.O. Fischer, W. Hafner, and H.O. Stahl, *Z. Anorg. Allgem. Chem.*, 282 (1955) 47.
- 2 T.S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3 (1956) 104.
- 3 R.J. Kazlauskas and M.S. Wrighton, *J. Am. Chem. Soc.*, 102 (1980) 1727.
- 4 H.G. Alt and M.E. Eichner, *Angew. Chem., Int. Ed. Engl.*, 21 (1982) 78.
- 5 R.G. Severson and A. Wojcicki, *J. Organomet. Chem.*, 157 (1978) 173.
- 6 H.G. Alt and M.E. Eichner, *J. Organomet. Chem.*, 212 (1981) 397.
- 7 K.A. Mahmoud, R. Narayanaswamy, and A.J. Rest, *J. Chem. Soc., Dalton Trans.*, (1981) 2199.
- 8 R.B. Hitam, R.H. Hooker, K.A. Mahmoud, R. Narayanaswamy, and A.J. Rest, *J. Organomet. Chem.*, 222 (1981) C9.
- 9 H.G. Alt, J.A. Schwärzle, and C.G. Kreiter, *J. Organomet. Chem.*, 153 (1978) C7.
- 10 C.G. Kreiter, K. Nist, and H.G. Alt, *Chem. Ber.*, 114 (1981) 1845.
- 11 B. Klein, R.J. Kazlauskas, and M.S. Wrighton, *Organometallics*, 1 (1982) 1338.
- 12 R.J. Kazlauskas and M.S. Wrighton, *J. Am. Chem. Soc.*, 104 (1982) 6005.
- 13 H.G. Alt, *J. Organomet. Chem.*, 124 (1977) 167.
- 14 D.R. Tyler, *Inorg. Chem.*, 20 (1981) 2257.
- 15 H.G. Alt, *J. Organomet. Chem.*, 127 (1977) 349.
- 16 M.D. Rausch, T.E. Gismondi, H.G. Alt, and J.A. Schwärzle, *Z. Naturforsch. B*, 32 (1977) 998.
- 17 C.U. Pittman, Jr., B.T. Kim, and W.M. Douglas, *J. Org. Chem.*, 40 (1975) 590.
- 18 D.W. Macomber, M.D. Rausch, T.V. Jayaraman, R.D. Priester, and C.U. Pittman, Jr., *J. Organomet. Chem.*, 205 (1981) 353.
- 19 C.U. Pittman, Jr., T.V. Jayaraman, R.D. Priester, Jr., S. Spencer, M.D. Rausch, and D.W. Macomber, *Macromolecules*, 14 (1981) 237.
- 20 W.P. Hart, D.W. Macomber, and M.D. Rausch, *J. Am. Chem. Soc.*, 102 (1980) 1196.
- 21 D.W. Macomber, W.P. Hart, M.D. Rausch, C.U. Pittman, Jr., and R.D. Priester, Jr., *J. Am. Chem. Soc.*, 104 (1982) 884.
- 22 T.L. Ho and G.A. Olah, *Synthesis*, (1977) 417.
- 23 D.G. Alway and K.W. Barnett, *Inorg. Chem.*, 19 (1980) 1533.
- 24 M.D. Rausch and V. Mark, *J. Org. Chem.*, 28 (1962) 3225.
- 25 A. Davison, J.A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, (1963) 1133.
- 26 R.C. Weast, *Handbook of Chemistry and Physics*, 47 ed., The Chemical Rubber Co., Cleveland, Ohio, 1966 p. D86.
- 27 K.L. Rinehart, Jr., K.L. Motz, and S. Moon, *J. Am. Chem. Soc.*, 79 (1957) 2749.
- 28 K. Hafner, G. Schultz, and K. Wagner, *Justus Liebigs Ann. Chem.*, 678 (1964) 39.
- 29 R.D. Rogers, J.L. Atwood, M.D. Rausch, D.W. Macomber, and W.P. Hart, *J. Organomet. Chem.*, 238 (1982) 79.