

**SYNTHESIS AND CHARACTERIZATION OF MOLYBDENUM AND
TUNGSTEN COMPLEXES CONTAINING *tert*-BUTYLCYCLOPENTADIENYL
LIGAND**

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Received 15-02-2001

Abstract

New molybdenum and tungsten complexes containing *tert*-butylcyclopentadienyl ligand ($\text{Cp}^+ = \text{}^t\text{Bu-C}_5\text{H}_4$) have been prepared and characterized. The reaction of $\text{M}(\text{CO})_3(\text{CH}_3\text{CN})_3$ with *tert*-butylcyclopentadiene provide improved route to the metal-metal bond compounds $[\text{Cp}^+\text{M}(\text{CO})_3]_2$ ($\text{M} = \text{Mo}$ (**Ia**), W (**Ib**)) in good isolated yields. New examples of mononuclear complexes have also been prepared. The yellow complexes $\text{Cp}^+\text{M}(\text{CO})_3\text{R}$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5$) (**IV**) and $[\text{Cp}^+\text{Mo}(\text{CO})_3\text{SO}_2(\text{p-C}_6\text{H}_4\text{X})]$ (**V**) ($\text{X} = \text{CH}_3, \text{Cl}$) have been prepared from the reaction of the anions, $[\text{Cp}^+\text{M}(\text{CO})_3]^-$, with alkyl halides or arylsulfonyl chlorides in THF solvent, respectively. Protonation of the anion $[\text{Cp}^+\text{M}(\text{CO})_3]^-$ with glacial acetic acid, which gave the hydride complexes, followed by stirring in CCl_4/THF or refluxing with CH_3I in benzene produce the corresponding halides $\text{Cp}^+\text{M}(\text{CO})_3\text{Cl}$ (**II**) or $\text{Cp}^+\text{M}(\text{CO})_3\text{I}$ (**III**), respectively.

Introduction

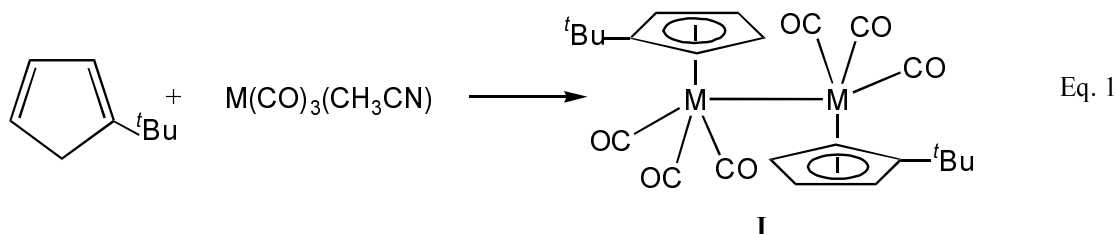
The synthesis of substituted cyclopentadienyl ligands and their complexes remains an active area of research.¹⁻²⁰ Although cyclopentadienyl metal carbonyl complexes of group VIB have been intensively studied, several examples of the corresponding substituted cyclopentadienyl complexes have been reported [20-27]. For example, the dimers $[\text{Cp}^+\text{M}(\text{CO})_3]_2$ ($\text{Cp}^+ = \text{C}_5\text{H}_4\text{COOH}, \text{C}_5\text{Me}_4(\text{CH}(\text{Et})(\text{Ph})), \text{}^t\text{BuC}_5\text{H}_4, \text{}^t\text{Bu}_2\text{C}_5\text{H}_3$) have been prepared and some are structurally characterized [20-23]. The mono-nuclear complexes $\text{Cp}^+\text{M}(\text{CO})_3\text{X}$ ($\text{Cp}^+ = \text{}^t\text{Bu}_2\text{C}_5\text{H}_3, \text{C}_5^i\text{Pr}_4\text{H}$; $\text{X} = \text{Cl}, \text{Br}$; $\text{M} = \text{Mo}$ and $\text{Cp}^+ = \text{C}_5\text{H}_4\text{COR}, \text{C}_5\text{H}_4\text{CH}(\text{OH})\text{Me}$; $\text{X} = \text{Me}$; $\text{M} = \text{Mo}, \text{W}$) were also prepared.^{20, 24-27}

We are interested in preparing and characterizing organometallic complexes containing *tert*-butyl-substituted cyclopentadienyl ligands. To that end, we prepared the

iron dimers $[\text{Cp}^+\text{Fe}(\text{CO})_2]_2$ and the thiocarboxylate derivatives $\text{Cp}^+\text{Fe}(\text{CO})(\text{L})\text{SCOR}$ ($\text{Cp}^+ = {}^t\text{BuC}_5\text{H}_4$, ${}^t\text{Bu}_2\text{C}_5\text{H}_3$, $\text{L} = \text{CO}$, PPh_3 , AsPh_3 , SbPh_3).^{23, 28} The goal of the work reported here is to prepare and characterize the tungsten and molybdenum dimers $[\text{Cp}'\text{M}(\text{CO})_3]_2$ and some mono-nuclear carbonyl complexes of these metals that contain a *tert*-butylcyclopentadienyl ligand.

Results and discussion

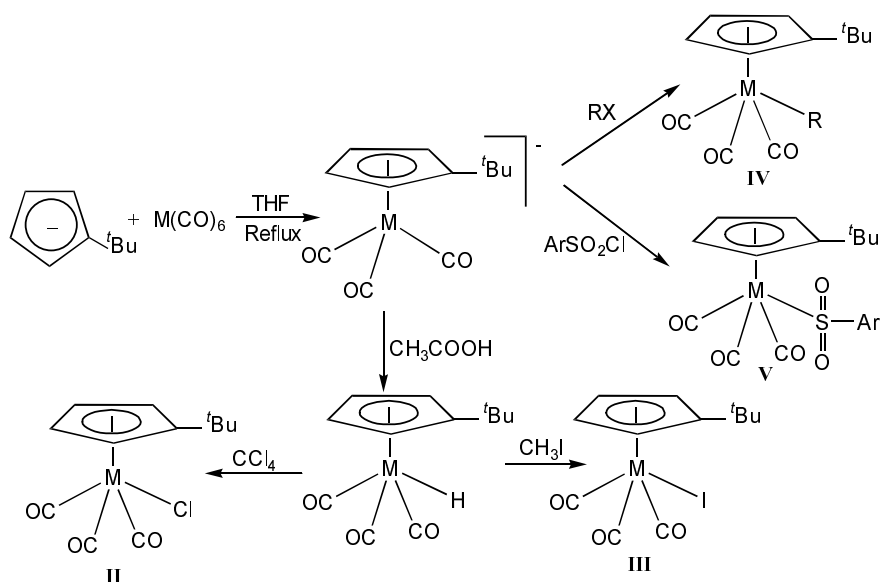
The dimers, $[({}^t\text{Bu-C}_5\text{H}_4)\text{M}(\text{CO})_3]_2$ ($\text{M} = \text{Mo}$ (**Ia**), W (**Ib**)), were synthesized in good yields by reacting of $\text{M}(\text{CO})_3(\text{CH}_3\text{CN})_3$ with *tert*-butylcyclopentadiene ligand (Equation 1).



These reactions were followed by IR spectroscopy. Progressive disappearance of the CO stretching bands of $\text{M}(\text{CO})_3(\text{CH}_3\text{CN})_3$ is a direct indication for the progress of the reaction. Compounds **I** are purple crystals, soluble in common organic solvent, and are stable in the solid state and in solution. These complexes were characterized by IR, ${}^1\text{H}$ -NMR spectroscopy as well as elemental analysis. The IR spectra of these compounds have three bands corresponding to the stretching frequencies of the terminal CO ligands. These were observed in the ranges 1950-1947, 1913-1905 and 1893-1887 cm^{-1} . These bands are indicative of the presence of $\text{M}(\text{CO})_3$ moieties which is consistent with the structure shown in Equation 1.²⁹ Comparison of the IR spectra of **I** and the unsubstituted analogs $[\text{CpM}(\text{CO})_3]_2$ ($\text{M} = \text{Mo}$, W) shows clearly the electronic effects of the *tert*-butyl group which results in a shift of ν_{CO} to lower values. The ${}^1\text{H}$ -NMR spectra of compounds **I** show a singlet in the range 1.25-1.26 ppm for the *tert*-butyl group, and two multiplets in the ranges 5.11-5.25 and 5.26-5.34 ppm for the (C_5H_4) ring protons.

The synthesis of $\text{Cp}'\text{M}(\text{CO})_3\text{X}$ ($\text{X} = \text{Cl}$, **I**; $\text{M} = \text{Mo}$, W) (**II**, **III**) started by deprotonation of ${}^t\text{Bu-C}_5\text{H}_5$ ligand using sodium metal to give sodium *tert*-butyl

cyclopentadienide that reacted with $M(\text{CO})_6$ ($M = \text{Mo}, \text{W}$) to yield $\text{Cp}'\text{M}(\text{CO})_3\text{Na}$. This salt was protonated with glacial acetic acid in THF to give the hydride complex, which was utilized *insitu* as outlined in Scheme 1.



The progress of these reactions was also followed by withdrawing samples of the solution, and monitoring the disappearance of the bands of $\text{Cp}'\text{M}(\text{CO})_3\text{Na}$. The newly prepared compounds **II** and **III** are orange-red crystals, air stable as solids and in solutions. They are soluble in organic solvents such as hexane, CH_2Cl_2 and diethyl ether. The IR spectra (ν_{CO} region) of **II** in CCl_4 solution exhibited three absorbances in the ranges 2051–2045, 1980–1962 cm^{-1} and 1952–1946 cm^{-1} while two bands (2038–2034, 1968–1956 cm^{-1}) are observed for compounds **III**.^{30, 31} $^1\text{H-NMR}$ spectra of compounds **II** and **III** exhibit signals which are in good agreement with the proposed structures. All chemical shift values of the protons appear in the expected region. However, they shift to high field compared to those of the unsubstituted cyclopentadienyl carbonyl analogs.²⁹ For example: the Cp-ring protons of $\text{CpMo}(\text{CO})_3\text{I}$ appear as singlet at 5.57 ppm, in CDCl_3 solution²⁹ while those of **IIIa** appear as two multiplet at 5.45 and 5.52 ppm.

The reaction of $\text{Cp}'\text{M}(\text{CO})_3\text{Na}$ ($\text{M} = \text{Mo}, \text{W}$) with CH_3I or $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ in THF afforded the mononuclear complexes $(t\text{-Bu-C}_5\text{H}_4)\text{M}(\text{CO})_3\text{R}$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5$; $\text{M} = \text{Mo}$ (**IVa**, **IVc**), $\text{M} = \text{W}$ (**IVb**)) in moderate yields as shown in Scheme 1. Complexes **IV** are yellow powders and stable under N_2 for several days. Their solutions in organic solvents are slowly decomposed even under N_2 atmosphere and increased upon exposure to air (require several minutes for complete decomposition). This instability, which is a general feature of transition metal alkyl complexes³² alters the elemental analysis results of complexes **IV**. Complexes **IV** are soluble in common organic solvents and insoluble in hexane. Infrared and $^1\text{H-NMR}$ spectroscopic data have confirmed the structures of these compounds.³⁴ The IR spectra for **IVa** and **IVb** have two bands and in the case of **IVc** three bands are found in the C-O stretching region. The assignment of these bands was made on the basis of reported results of similar compounds.^{30, 33} For the unsubstituted analogs, where $\text{R} = \text{Et}, i\text{Pr}$, two strong bands in the C-O stretching region have also been reported.²⁴⁻²⁷ The $^1\text{H-NMR}$ spectra of compounds **IV** show a singlet in the range 1.15-1.18 ppm for the *tert*-butyl group, a singlet in the range 5.38-5.58 ppm for the (C_5H_4) ring protons and the protons of the alkyl group with the appropriate multiplicity and integration. The chemical shift values of the protons for the methyl and methylene groups are smaller than those found for methyl and methylene groups attached to carbon atoms.

Although the four protons of $(t\text{-Bu-C}_5\text{H}_4)$ constitute an AA'BB' system. Their splitting pattern is markedly affected by the structural and electronic environment around the metal center. It has been found that the ring protons of this system appear as symmetrical multiplet in $\text{Cp}'_2\text{TiCl}_2$,³⁴ as an unsymmetrical multiplet in $\text{Cp}'_2\text{Ti}(\text{Cl})(\text{NCS})$,³⁴ as a singlet in $\text{Cp}'_2\text{Ti}(\text{NCS})_2$, as two multiplets in $\text{Cp}'\text{Fe}(\text{CO})_2\text{SCOR}$ [23] and as four multiplets in $\text{Cp}'\text{Fe}(\text{CO})(\text{PPh}_3)\text{SCOR}$.²⁸ Accordingly, the $^1\text{H-NMR}$ spectra of **IV**, in which the C_5H_4 -ring protons appear as singlet, could be possible.

The reaction of $\text{Cp}'\text{Mo}(\text{CO})_3\text{Na}$ with sulfonyl chlorides afforded the S-bonded sulfinato (SO_2Ar) compounds of molybdenum $\text{Cp}'\text{Mo}(\text{CO})_3\text{SO}_2\text{Ar}$ ($\text{Ar} = p\text{-C}_6\text{H}_4\text{CH}_3$ (**Va**), $p\text{-C}_6\text{H}_4\text{Cl}$ (**Vb**)) as shown in Scheme 1. These reactions were monitored by IR spectroscopy, the production of the sulfinato compounds was evidenced by the shift (to higher values) in the carbonyl stretching frequencies and a change in the color of the

solution from yellow brown to red. The complexes are yellow powders and stable under N₂; however, their solutions in organic solvents slowly decomposed when exposed to air. They are soluble in CH₂Cl₂, CHCl₃ and insoluble in hexane. On the basis of the observed positions of the CO and SO₂ stretching frequencies and the ¹H-NMR signals and their similarity to the corresponding absorption in the spectrum of CpMo(CO)₃SO₂Ph,³⁵ these complexes are assigned the S-sulfinato structures. A satisfactory elemental analysis has confirmed the structures of these compounds.

The IR spectra of complexes **V** have three bands in the ranges 2046-2024, 1986-1967 and 1927 cm⁻¹, which are indicative of the presence of the M(CO)₃ moieties. The presence of an S-sulfinato ligand (SO₂Ar) is confirmed by the observation of strong infrared bands in the ranges 1322-1199 and 1146-1035 cm⁻¹ (KBr).³⁵⁻³⁷ The ¹H-NMR spectra of compounds **V** show that all chemical shift values of the protons appear in the expected region. Comparison of the ¹H-NMR data of **Va** and **Vb** shows clearly the electronic effects of the para substituent group (-SO₂-p-C₆H₄X, X= Cl, CH₃). The ¹H-NMR spectrum of **Va** show two multiplets at 5.52 and 5.82 ppm for the (C₅H₄) ring protons, while those of **Vb** appear at 5.80 and 6.23 ppm. The method used to prepare complexes **V** are novel and simple one. The use of this method to prepare the unsubstituted analogs, CpM(CO)₃SO₂Ar, which have been prepared by more difficult methods, may be tested in the future.

Experimental

All reactions were carried out under a dinitrogen atmosphere using standard Schlenk or vacuum line techniques.³⁸ Diethyl ether, tetrahydrofuran (THF) and hexane were dried by refluxing over sodium/benzophenone. Dichloromethane and acetonitrile were dried over P₂O₅. All solvents were distilled just prior to use. The following chemicals were used as received: M(CO)₆ (M= Mo, W; Aldrich), *tert*-butyl chloride and glacial acetic acid (Fluka), methyl iodide, carbon tetrachloride (BDH), 4-chlorobenzenesulfonyl chloride and *p*-toluenesulfonyl chloride (Acros). The complex M(CO)₃(CH₃CN)₃³⁹ and the *tert*-butyl cyclopentadiene ligand⁴⁰ were prepared as reported in the literature.

IR spectra: Nicolet-Impact 410 FT-IR spectrometer; in cm^{-1} . $^1\text{H-NMR}$ spectra: Bruker WP80SY spectrometer with TMS as an internal standard; in ppm. Elemental analysis: Laboratoire D'Analyse Élémentaire Université de Montréal, Montréal, Canada. M.p.: Thomas Hoover Capillary melting point apparatus and are uncorrected.

[Cp'M(CO)₃]₂: A solution of 7.00 mmol of $\text{M}(\text{CO})_6$ in 60 mL acetonitrile was refluxed for 4 hours when $\text{M} = \text{Mo}$ and for 6 days when $\text{M} = \text{W}$. The resulting bright yellow solution of $\text{M}(\text{CO})_3(\text{CH}_3\text{CN})_3$ was evaporated under reduced pressure to give yellow solid residue. To this solid a freshly distilled (5.0 mL, 32.1 mmol) *tert*-butyl cyclopentadiene was added directly. The mixture was refluxed for 3 hours and the color of the solution turned to dark red. The volatiles were removed under vacuum at room temperature to give a dark red solid. The solid was washed with hexane and collected by filtration as purple crystals of $[\text{Cp}'\text{M}(\text{CO})_3]_2$ and air-dried.

[Cp'Mo(CO)₃]₂ (Ia): Yield = 90 %. M.p. = 164–165 °. IR (CH_2Cl_2): ν_{CO} : 1950 (vs), 1913 (s, br), 1893 (sh). $^1\text{H-NMR}$ (CDCl_3): 1.25 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 5.11 (m, 2 H, C_5H_4), 5.26 (m, 2 H, C_5H_4). Anal. calc. for $\text{C}_{24}\text{H}_{26}\text{Mo}_2\text{O}_6$: C 47.85, H, 4.35; found: C 47.45, H 4.33.

[Cp'W(CO)₃]₂ (Ib): Yield = 70 %. M.p. = 210–212 °. IR (CH_2Cl_2): ν_{CO} : 1947 (vs), 1905 (s), 1887 (sh). $^1\text{H-NMR}$ (CDCl_3): 1.26 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 5.25 (s, 2 H, C_5H_4), 5.34 (s, 2 H, C_5H_4). Anal. calc. For $\text{C}_{24}\text{H}_{26}\text{O}_6\text{W}_2$: C 37.04, H 3.36; found: C 37.04; H 3.36

Cp'M(CO)₃Na: In a 100 mL schlenk flask fitted with a reflux condenser and a magnetic stirrer, sodium (0.200 g, 8.70 mmol) was finely dispersed by rapid stirring in refluxing toluene (40 mL). Toluene was replaced by THF (40 mL) and freshly distilled *tert*-butyl cyclopentadiene (3.0 mL, 19.3 mmol) was added dropwise to the stirred suspension at room temperature. When all sodium was dissolved, a pale pink solution of sodium *tert*-butyl cyclopentadienide was formed. To the resulting solution, $\text{M}(\text{CO})_6$ (8.70 mmol) was added. The solution was refluxed until no unreacted $\text{M}(\text{CO})_6$ found in the solution, producing yellow to yellow-brown solution of the salt $\text{Cp}'\text{M}(\text{CO})_3\text{Na}$. The progress of the reaction was followed by withdrawing samples of the solution at various time

intervals; and monitoring the appearance of the bands of $\text{Cp}'\text{M}(\text{CO})_3\text{Na}$ (1897 (s), 1793 (s), 1744 cm^{-1} (s) where $\text{M} = \text{Mo}$ and 1891 (s), 1790 (s), 1739 cm^{-1} (s) where $\text{M} = \text{W}$). No attempt has been made to isolate the pure sodium salts, and the products were utilized *insitu* for further reactions.

$\text{Cp}'\text{M}(\text{CO})_3\text{Cl}$: To the tetrahydrofuran solution of $\text{Cp}'\text{M}(\text{CO})_3\text{Na}$ prepared as described above; glacial acetic acid (1.0 mL, 17.5 mmol) was added. The mixture was stirred for one hour and the solvent was removed under reduced pressure. The resulting hydride was dissolved in 2.0 mL (20.8 mmol) of CCl_4 and stirred for 25 minutes. The volatiles were evaporated under reduced pressure and the remaining residue was recrystallized from CH_2Cl_2 /hexane mixture. The solid was collected as orange-red crystals and air-dried.

$\text{Cp}'\text{Mo}(\text{CO})_3\text{Cl}$ (IIa): Yield= 50 %. M.p.= 48-50°. IR (CCl_4): ν_{CO} : 2051 (s), 1980 (vs), 1952 (s). ^1H NMR (CDCl_3): 1.25 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 5.11(m, 2 H, C_5H_4), 5.25 (m, 2 H, C_5H_4). Anal. calc. for $\text{C}_{12}\text{H}_{13}\text{ClMoO}_3$: C 42.81, H, 3.89; found: C 43.41, H 4.34.

$\text{Cp}'\text{W}(\text{CO})_3\text{Cl}$ (IIb): Yield= 70 %. M.p.= 64-65°. IR (CCl_4): ν_{CO} : 2045 (s), 1962 (vs), 1946 (w). ^1H NMR (CDCl_3): 1.31 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 5.41 (m, 2 H, C_5H_4), 5.72 (m, 2 H, C_5H_4). Anal. calc. for $\text{C}_{12}\text{H}_{13}\text{ClO}_3\text{W}$: C 33.95, H 3.08; found: C 34.35, H 3.30.

$\text{Cp}'\text{M}(\text{CO})_3\text{I}$: A similar procedure to that described for $\text{Cp}'\text{Mo}(\text{CO})_3\text{Cl}$ was followed. Except that the resulting hydride was refluxed with (1.0 mL, 16.1 mmol) of methyl iodide in 30 mL of benzene for 24 hours.

$\text{Cp}'\text{Mo}(\text{CO})_3\text{I}$ (IIIa): Yield = 45 %. M.p.= 51-53°. IR (CCl_4): ν_{CO} : 2038 (vs), 1968 (vs). ^1H -NMR (CDCl_3): 1.25 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 5.45 (m, 2 H, C_5H_4), 5.52 (m, 2 H, C_5H_4). Anal. calc. for $\text{C}_{12}\text{H}_{13}\text{IMoO}_3$: C 33.67, H 3.06; found: C 33.19, H 2.91.

$\text{Cp}'\text{W}(\text{CO})_3\text{I}$ (IIIb): Yield= 52 %. M.p.= 71-73°. IR (CCl_4): ν_{CO} : 2034 (vs), 1956 (vs). ^1H NMR (CDCl_3): 1.28 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 5.48 (m, 2 H, C_5H_4), 5.64 (m, 2 H, C_5H_4). Anal. calc. for $\text{C}_{12}\text{H}_{13}\text{IO}_3\text{W}$: C 27.93, H 2.53; found: C 27.86, H 2.36.

$\text{Cp}'\text{M}(\text{CO})_3\text{R}$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5$): To the tetrahydrofuran solution of $\text{Cp}'\text{M}(\text{CO})_3\text{Na}$ prepared as above; the alkyl halide (16.0 mmol) was added. A rapid reaction occurred

with methyl iodide and the mixture was stirred for 2 hours at 40 °C to ensure complete reaction. However, the reaction with benzyl chloride was stirred for 16 hours at room temperature. After the removal of tetrahydrofuran under reduced pressure, the residue was extracted with 25 mL of CH₂Cl₂. The solution was filtered, the solvent was removed, and the resultant yellow solid was recrystallized from CH₂Cl₂/hexane mixture.

Cp'Mo(CO)₃CH₃ (IVa): Yield= 60 %. M.p. = 143° (dec.). IR (CCl₄): ν_{CO}: 2017 (vs), 1931 (vs, br). ¹H-NMR (DMSO-*d*₆): 0.32 (s, 3 H, CH₃), 1.16 (s, 9 H, C(CH₃)₃), 5.45 (s, 4 H, C₅H₄). Anal. calc. for C₁₃H₁₆MoO₃: C 49.37, H 5.10; found: C 46.47, H 3.48.

Cp'W(CO)₃CH₃ (IVb): Yield= 55 %. M.p. = 160°. IR (CCl₄): ν_{CO}: 2015 (vs), 1923 (vs, br). ¹H-NMR (DMSO-*d*₆): 0.38 (s, 3 H, CH₃), 1.18 (s, 9 H, C(CH₃)₃), 5.58 (m, 4 H, C₅H₄). Anal. calc. for C₁₃H₁₆O₃W: C 38.63, H 3.99; found: C 36.13, H 2.21

Cp'Mo(CO)₃CH₂C₆H₅ (IVc): Yield= 65 %. M.p.= 123° (dec.). IR (CCl₄): ν_{CO}: 2013 (vs), 1953 (s), 1925 (vs). ¹H NMR (DMSO-*d*₆): 1.15 (s, 9 H, C(CH₃)₃), 2.89 (s, 2 H, CH₂) 5.38 (m, 2 H, C₅H₄), 5.56 (m, 2 H, C₅H₄), 7.15 (m, 5 H, C₆H₅). Anal. calc. for C₁₉H₂₀MoO₃: C 58.17, H 5.13; found: C 56.67, H 3.58.

Cp'Mo(CO)₃SO₂Ar: To the tetrahydrofuran solution of Cp'Mo(CO)₃Na prepared as described above; ArSO₂Cl (Ar= C₆H₄CH₃ and C₆H₄Cl) (8.00 mmol) was added. The color of the solution changed from yellow brown into red. The mixture was stirred for 4 hours at ~ 50 °C to ensure complete reaction. The solvent was removed under vacuum. The resultant solid material was extracted with 25 mL of CH₂Cl₂. Removal of the solvent from the filtered dichloromethane extracts left yellow solid of crude Cp'Mo(CO)₃SO₂Ar. This solid was recrystallized from CH₂Cl₂/hexane mixture.

Cp'Mo(CO)₃SO₂C₆H₄CH₃ (Va): Yield= 75 %. M.p. = 120° (dec.). IR (CH₂Cl₂, cm⁻¹): ν_{CO}: 2048 (vs), 1965 (vs, br). IR (KBr): ν_{CO}: 2041 (vs), 1986 (s), 1927 (vs). ν_{SO₂}: 1199 (vs), 1035 (vs). ¹H-NMR (CDCl₃): 1.22 (s, 9 H, C(CH₃)₃), 2.41 (s, 3H, CH₃), 5.52 (m, 2 H, C₅H₄), 5.82 (m, 2 H, C₅H₄), 7.48 (m, 4 H, C₆H₄). Anal. calc. for C₁₉H₂₀MoO₅S: C 50.0, H 4.41, S 7.02; found: C 49.6, H 4.11, S 6.52.

Cp'Mo(CO)₃SO₂C₆H₄Cl (Vb): Yield= 72 %. M.p.= 122° (dec.). IR (CH₂Cl₂): ν_{CO}: 2051 (s), 2029 (m) 1970 (vs). IR (KBr): ν_{CO}: 2046 (s), 2024 (w), 1967 (vs). ν_{SO₂}: 1322 (vs), 1146 (vs). ¹H-NMR (CDCl₃): 1.53 (s, 9 H, C(CH₃)₃), 5.80 (m, 2 H, C₅H₄), 6.23

(m, 2 H, C₅H₄), 7.41 (m, 4 H, C₆H₄). Anal. calc. for C₁₈H₁₇MoO₅S: C 45.34, H 3.59, S 6.72; found: C 44.89, H 3.34, S 6.27.

Acknowledgements

The authors thank the Deanship of Research, Jordan University of Science & Technology for financial support, Grant No. 57/98.

References and Notes

1. Ginely D. S., Wrighton M. S., *J. Am. Chem. Soc.* **1975**, *97*, 3533.
2. Jones S. S., Rausch M. D., Bitterwolf T. E., *J. Organomet. Chem.* **1993**, *450*, 27.
3. Krimmer H.Pstowasser B., Hafner K., *Tetrahedron Lett.* **1982**, *23*, 5135.
4. Hughes A. K., Meetsma A., Teuben J. H., *Organometallics*, **1993**, *12*, 1936.
5. Wang T. F., Lee T. Y., Wen, Y. S., Liu L. K., *J. Organomet. Chem.* **1991**, *403*, 353.
6. Rieger B., Steimannand M., Fawzi R., *Chem. Ber.* **1992**, *125*, 2373.
7. Donovan, T. B., Hughes R. P., Trujilo H. A., Rheingold A. L., *Organometallics*, **1992**, *11*, 64.
8. Hughes R. B., Kowalski A. S., Lompfrey J. R., Rheingold A. L., *Organometallics*, **1994**, *13*, 2691.
9. Venier C. F., Casserly E. W., *J. Am. Chem. Soc.* **1990**, *112*, 2808.
10. Stizmann H., *Z. Naturforsch.* **1989**, *44b*, 1293.
11. Hughes R. P., Lompfrey J. R., *Inorg. Chim. Acta.* **1995**, *240*, 653.
12. Hughes R. B., Kowalski A. S., Lompfrey J. R., Neithamer D. R., *J. Org. Chem.* **1996**, *61*, 401.
13. Heeg M. J., Janiak C., Zukerman J. J., *J. Am. Chem. Soc.* **1984**, *106*, 4259.
14. Dormand A., Elboudadili A., Moise C., *Tetrahedron Lett.* **1983**, *24*, 3087.
15. Oukda J., Herdtweck E., *Chem. Ber.* **1989**, *121*, 1899.
16. Okuda J., *Chem. Ber.* **1989**, *122*, 1075.
17. Weinmann D. J., Abrahamson H. B., *Inorg. Chem.* **1987**, *26*, 2133.
18. Petillon F. Y., Lequere J. L., Roue J., Guerschais J. E., Sharp D. W. A., *J. Organomet. Chem.* **1980**, *204*, 207.
19. Curtis M. D., *Polyhedron*, **1987**, *6*, 759.
20. Hughes R. P., Lompfrey J. R., Rheingold A., Yop J. P. A., *J. Organomet. Chem.* **1996**, *517*, 63.
21. Watikns W. C., Jaeger T., Kidd C. E., Fortier S., Baird M. C., Kiss G., Roper G. C., Hoff D. C., *J. Am. Chem. Soc.* **1992**, *114*, 907.
22. Avey A., TenHaeff S. C., Weakley T. G. R., Tyler D. R., *Organometallics*, **1991**, *10*, 3607, (1991).
23. El-Hinnawi M. A., El-khateeb M., Jibril I., Abu-Orabi S. T., *Synth. React. Inorg. Met.-Org. Chem.* **1989**, *19*, 809.
24. Stizmann H., *Chem. Ber.* **1990**, *123*, 2311.
25. Macomber D. W., Rausch M. D., Jayaraman T. V., Priester R. D., Pittman C. U., *J. Organomet. Chem.* **1981**, *205*, 353.
26. Hart W. P., Macomber D. W., Rausch M. D., *J. Am. Chem. Soc.* **1980**, *102*, 1196.
27. Macomber D. W., Rausch M. D., *J. Organomet. Chem.* **1983**, *258*, 331.
28. Jibril I., El-Hinnawi M. A., El-khateeb M., *Polyhedron*, **1991**, *10*, 2095.
29. Always D G., Barnett K. W., *Inorg. Chem.* **1980**, *19*, 1533.
30. Piper T. S., Wilkinson G., *Inorg. Nucl. Chem.* **1956**, *3*, 104.
31. Tyler D. R., *Inorg. Chem.* **1981**, *20*, 2257.
32. Haiduc H., Zuckerman J. J., in 'Basic Organometallic Chemistry' Walter de Gruyter, Berlin, New York, 1985.
33. King R. B., Fronzaglia A., *J. Am. Chem. Soc.* **1966**, *88*, 709.
34. Jibril I., Abu-Orabi S. T., Klaib S., Zsolani L., Huttner G., *J. Organomet. Chem.* **1994**, *467*, 189.
35. Pannell K. H., Kapoor R. N., *J. Organomet. Chem.* **1984**, *269*, 59.

36. Severson R. G., Wojcicki, A. *J. Am. Chem. Soc.* **1979**, *101*, 877.
37. Weinmannand, D. G., Abrahamson H. B., *Inorg. Chem.* **1987**, *26*, 3034.
38. Shriver D., Drezdson M., in 'The Manipulation of Air Sensitive Compounds', 2nd Ed., Wiley Interscience, Toronto, 1986.
39. Keppie S. A., Lappert M. F., *J. Chem. Soc. (A)*, **1971**, 3216.
40. Abu-Orabi S. T., Jutzi P., *J. Organomet. Chem.* **1987**, *329*, 169.

Povzetek

Opisana je priprava in karakterizacija novih kompleksov molibdena in volframa, ki vsebujejo *tert*-butilciklopentadienilni ligand ($t\text{-Bu-C}_5\text{H}_4$; Cp'), s sestavo $[\text{Cp}'\text{M}(\text{CO})_3]_2$ in $\text{Cp}'\text{M}(\text{CO})_3\text{X}$ (X= halogen, alkil, alkilsulfonil).