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Note

# Metal carbonyls of telluroether formed by the oxygen atom transfer reaction to $M(CO)_6$ (M = Mo, W) in the presence of $(p-CH_3OC_6H_4)_2$ TeO and relative kinetic investigation $\stackrel{\text{}_{\sim}}{\rightarrow}$

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#### Abstract

A new synthetic process is reported for the preparation of two substituted metal carbonyls,  $(p-CH_3OC_6H_4)_2TeM(CO)_5$  (M = Mo, W). In the presence of  $(p-CH_3OC_6H_4)_2TeO$  as O atom transfer reagent in tetrahydrofuran solvent, a CO ligand is replaced by telluroether when  $M(CO)_6$  (M = Mo, W) is reacted with  $(p-CH_3OC_6H_4)_2TeO$  under very mild experimental conditions (r.t.). The products were characterized by elemental analysis, mass, IR and <sup>1</sup>H NMR spectroscopies. The spectra suggest that the coordination geometry is distorted from a regular octahedral structure due to an asymmetrical bulky telluroether ligand on the metal atom. Kinetics of these reactions of  $M(CO)_6$  with  $(p-CH_3OC_6H_4)_2TeO$  show the reactions are first order in the concentration of  $M(CO)_6$  and of Te oxide. The rates of reaction decrease in the order  $W(CO)_6 > Mo(CO)_6 > Cr(CO)_6$ , and the results obtained are discussed in term of a presumed mechanism.

Keywords: Transition metal complexes; Carbonyl complexes; Telluroether complexes; Oxygen atom transfer reaction; Kinetics and mechanism

## 1. Introduction

We have studied in detail the kinetics and mechanisms of oxygen atom transfer reactions occurring in carbonyl complexes [1-5]. One of the important applications of these reactions is its use in the synthesis of organometallic compounds [6-10]. The reactions involve an O atom transfer from the O atom reagent to a carbonyl carbon to form  $CO_2$  and an active intermediate 'M solvent' which is a key step in the synthesis (Eq. (1)).

$$M-CO + E-O \longrightarrow M \cdot \text{solvent} + E + CO_2 \uparrow$$
(1)

The active intermediate then readily reacts with E or an added entering ligand (amine, phosphine, arsine or stibine) to afford the expected substituted product. The conditions for O atom transfer reactions are very mild, usually proceeding at room temperature or below.

We were successful in the synthesis of two metal carbonyl complexes of telluroether using  $M(CO)_6$  as metal substrate and telluroxide as O atom transfer reagent in the absence of entering ligand. The preparation and characterization of the

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title complexes by elemental analysis, IR, <sup>1</sup>H NMR and MS are discussed in this article. Kinetic data obtained provide a comparison of the relative reactivities of  $M(CO)_6$  towards  $(p-CH_3OC_6H_4)_2$ TeO decreasing in the order  $W > M_0 > Cr$ . The same reactivity order was obtained for reactions of the Cr triad of carbonyls with Me<sub>3</sub>NO [11].

#### 2. Experimental

#### 2.1. Reagents

 $Mo(CO)_6$  and  $W(CO)_6$  were purchased from Aldrich, (*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>TeO was prepared by reacting tellurium(IV) chloride and anisole and by refining in C<sub>2</sub>H<sub>5</sub>OH according to standard literature procedures [12]. Manipulations involving metal carbonyl and telluroxide were routinely carried out under an N<sub>2</sub> atmosphere by using standard Schlenk techniques. All solvents were dried and distilled under nitrogen before use.

#### 2.2. Preparation of $(p-CH_3OC_6H_4)_2TeMo(CO)_5$

This new substituted carbonyl was prepared by adding stoichiometric amounts of  $Mo(CO)_6$  (132 mg, 0.50 mmol)

<sup>\*</sup> This paper is dedicated to Professor F. Basolo.

and  $(p-CH_3OC_6H_4)_2$ TeO (180 mg, 0.50 mmol) to 20 ml THF at room temperature. A yellow suspension formed, and the reaction was allowed to stir for 6 h under N<sub>2</sub>. The solvent was evaporated under vacuum and toluene (10 ml) was added to the residue. The yellow toluene solution was filtered and concentrated under vacuum until yellow crystals formed. Recrystallization under refrigeration was effected from toluene-pentane (3:1 vol./vol.). Yield 120 mg (41.5%). Anal. Calc. for C<sub>19</sub>H<sub>14</sub>O<sub>7</sub>MoTe: C, 39.49; H, 2.44. Found: C, 39.67; H 2.32%. IR (KBr;  $\nu$ (CO), cm<sup>-1</sup>): 2071.7 (m), 2000.6 (s, sh), 1956.6 (vs), 1922.8 (s, sh). <sup>1</sup>H NMR (CDCl<sub>3</sub>;  $\delta$ ): 3.84 (s, 6H), 6.87 (d, 4H), 7.55 (d, 4H). MS (*m/e*; relative intensity): 580 (21.0), 552 (25.5), 524 (100), 496 (37.0), 468 (18.0), 440 (86.5), 379 (62.0).

This same general procedure was followed for the next complex.

#### 2.3. Preparation of $(p-CH_3OC_6H_4)_2TeW(CO)_5$

To a THF (30 ml) solvent, W(CO)<sub>6</sub> (120 mg, 0.57 mmol) and (*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>TeO (200 mg, 0.56 mmol) were added and the mixture was stirred for 4 h under nitrogen at 20 °C. A yellow solid was obtained. Yield 95 mg (29%). Anal. Calc. for C<sub>19</sub>H<sub>14</sub>O<sub>7</sub>TeW: C, 34.28; H, 2.10. Found: C, 34.45; H, 2.16%. IR (KBr:  $\nu$ (CO), cm<sup>-1</sup>): 2070.6 (m), 1994.2 (s, sh), 1924.1 (vs), 1906.5 (s, sh). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 3.85 (s, 6H), 6.80 (d, 4H), 7.52 (d, 4H).

#### 2.4. Kinetic measurements

Kinetic data were obtained by monitoring IR absorbance changes  $(A_{\infty} - A_t)$  in the  $\nu$ (CO) region (Fig. 1) with time, and IR spectra were recorded on a Nicolet-5DX FT-IR spectrophotometer using a special variable temperature IR cell with 0.5 mm CaF<sub>2</sub> windows. The reactions were carried out under pseudo-first-order conditions where concentrations of telluroxide were more than 10 times greater than those of



Fig. 1. Time-dependent IR spectra recorded in the  $\nu$ (CO) region for reaction (2).

 $M(CO)_6$ . The thermostatic systems maintained the temperature in a range  $\pm 0.2$  °C. For comparison with  $Cr(CO)_6$  [9], the reactions were investigated in CHCl<sub>3</sub> solvent. Plots of  $\ln(A_{\infty}-A_i)$  versus time monitoring the disappearance of  $M(CO)_6$  were linear over two half-lives (linear correlation coefficients > 0.995). The slopes of these lines gave values of  $k_{obs}$ .

#### 3. Results and discussion

The new substituted carbonyl complexes were formed directly from the reductive reactions involving O atom transfer to  $M(CO)_6$  with telluroxide (Eq. (2)).

$$M(CO)_{6} + R_{2}TeO \xrightarrow{r.t. N_{2}}{THF} R_{2}TeM(CO)_{5} + CO_{2} \uparrow$$
$$M = Mo, W; R = p-CH_{3}OC_{6}H_{4}$$
(2)

The reaction shown in Eq. (2) is driven by the formation of a good leaving group  $CO_2$  and an active intermediate 'M(CO)<sub>5</sub> solvent' which readily reacts with telluroether. The products are stable at room temperature, even in the air for 2–3 months.

A molecular ion peak observed by mass spectroscopy (FABH) with middle intensity is consistent with the molecular weight expected. Other fairly strong peaks are also observed in the spectra. The relative abundance of metalcontaining fragments and their probable assignment for the Mo complex are given in Table 1. The mass spectral data in Table 1 provide possible fragmentation processes of eliminating CO.

The four bands and their relative intensity patterns (m; s, sh; vs; s, sh) of the IR spectra for the new complexes of the type  $LM(CO)_5$  (M=Mo, W; L = (p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Te) suggest that telluroether as an asymmetrical ligand coordinates with the metal after oxygen atom transfer, according to the structural information about the substituted metal carbonyl complexes provided from the numbers of  $\nu$ (CO) stretching bands and relative intensity [13]. These IR spectra are similar to those of the corresponding compounds (p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>TeCr(CO)<sub>5</sub> [9] and (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>TeW(CO)<sub>5</sub> [14] with crystal structures showing the coordination geometry at M is distorted from a regular octahedral structure.

Table 1

The relative abundances of metal-containing fragments in the mass spectra of  $(p-CH_3OC_6H_4)_2TeMo(CO)_5$ 

Fragment ion	Relative abundances	Tentative assignment	
580	21.0	$[(p-CH_3OC_6H_4)_2TeM_0(CO)_5]^+$	
552	25.5	$[(p-CH_3OC_6H_4)_2TeMo(CO)_4]^+$	
524	100	$[(p-CH_3OC_6H_4)_2TeM_0(CO)_3]^+$	
496	37.0	$[(p-CH_3OC_6H_4)_2TeM_0(CO)_2]^+$	
468	18.0	$[(p-CH_3OC_6H_4)_3TeM_0(CO)]^+$	
440	86.5	$[(p-CH_3OC_4H_4)_3TeM_0]^+$	
399	62.0	$[(C_6H_5)_2$ TeMo] <sup>+</sup>	



Fig. 2. <sup>1</sup>H NMR spectrum for the (*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>TeW(CO)<sub>5</sub> complex.



Fig. 3. Plots of  $k_{obs}$  vs.  $(p-CH_3OC_6H_4)_2$ TeO concentration. <sup>a</sup> Ref. [9]. <sup>b</sup> This work.





Table 2 The second-order rate constants for reaction (2) (solvent: CHCl<sub>3</sub>)

M(CO) <sub>6</sub>	<i>T</i> (°C)	$k_2 (M^{-1} s^{-1})$	Relative ratio
$Cr(CO)_6^a$	30.0	1.17×10 <sup>-2</sup>	1
Mo(CO) <sub>6</sub> <sup>b</sup>	30.0	$5.24 \times 10^{-2}$	4.4
W(CO) <sub>6</sub> <sup>b</sup>	30.0	$11.2 \times 10^{-2}$	9.5

<sup>a</sup> Ref. [9].

<sup>b</sup> This work.

Signals were detected in the <sup>1</sup>H NMR spectrum of  $(p-CH_3OC_6H_4)_2TeW(CO)_5$  in CDCl<sub>3</sub> (Fig. 2), which indicate the coordination of telluroether to metal. There are three resonances for the compound: one single and sharp peak ( $\delta$  3.85 ppm) for six protons of methoxy groups on two benzene rings; the first doublet resonance at higher field ( $\delta$ 6.80 ppm) is ascribed to four of the phenyl protons adjacent to the Te

atom; the second one at lower field ( $\delta$  7.52 ppm) belongs to another four phenyl protons far away from the Te atom.

Spectral changes for all the reaction mixtures show good isosbestic points (Fig. 1), suggesting stoichiometric reactions affording monosubstituted products. The new bands appear at  $\nu(CO) = 2071.7$  and 1950.1 cm<sup>-1</sup> (M=Mo) in agreement with the fundamental bands in the IR spectrum of the monosubstituted solid compound synthesized in this work. Plots of  $k_{obs}$  versus (*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>TeO concentration (Fig. 3) ( show first-order dependence in substrate and telluroxide concentrations. Thus, CO substitution obeys a second-order rate law (Eq. (3)).

$$r = k_2[M(CO)_6][(p-CH_3OC_6H_4)_2TeO]$$
 (3)

This rate law and kinetic behavior are the same as those reported earlier [1-5]. A four-centered mechanism (Scheme 1) is postulated as the reaction pathway, consistent with an earlier [15] suggestion. Any electronic or steric factors that benefit such an increase in the coordination number would reduce the energy of this intermediate and of the transition state species as well.

The second-order rate constants for the chromium triad are given in Table 2. The reaction rates of  $M(CO)_6$  with  $R_2$ TeO for changes in M decrease in the order W>Mo>Cr(W:Mo:Cr=9.5:4.4:1) and are consistent with what was observed for the  $M(CO)_6/Me_3NO$  system [11]. These results are attributed to steric effects on the stabilities of the transition state of the reaction, destabilizing for the smaller Cr atom relative to the larger W atom of the triad.

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