

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF SOUTH DAKOTA, VERMILION, SOUTH DAKOTA 57069**Octahedral Metal Carbonyls. XI.<sup>1</sup> Reactions of Group VIb Metal Carbonyl Derivatives of 2,2,7,7-Tetramethyl-3,6-dithiaoctane**

BY GERARD R. DOBSON

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Cr(CO)<sub>6</sub>, Mo(CO)<sub>6</sub>, and W(CO)<sub>6</sub> react with 2,2,7,7-tetramethyl-3,6-dithiaoctane (DTO) to give (DTO)M(CO)<sub>4</sub> complexes. The bidentate ligand is readily replaced in these complexes by phosphites (L) to give L<sub>2</sub>M(CO)<sub>4</sub> products. Kinetic data for all three metals indicate that the replacement occurs through a mechanism involving initial reversible dissociation of one end of the DTO ligand. DTO is also replaced by norbornadiene to give (C<sub>7</sub>H<sub>8</sub>)W(CO)<sub>4</sub>, thus suggesting the potential usefulness of (DTO)M(CO)<sub>4</sub> complexes as synthetic intermediates in the preparation of organometallic complexes of the group VIb metals.

**Introduction**

A recent kinetic investigation of the reactions of (DTH)M(CO)<sub>4</sub> complexes (DTH = 2,5-dithiahexane; M = Cr, Mo) with phosphites (L)<sup>2</sup>



showed the reactions for both metals to obey the second-order rate law

$$\text{rate} = k[(\text{DTH})\text{M}(\text{CO})_4][\text{L}] \quad (2)$$

The markedly different entropies of activation observed for the Cr and Mo systems led to the conclusion that for Cr the reaction proceeded through initial reversible dissociation of one end of the DTH ligand (reaction 5, below), while for Mo the reaction involved nucleophilic attack of L on (DTH)Mo(CO)<sub>4</sub> in the rate-determining step to give a seven-coordinate activated complex or intermediate (reaction 4, below).

The ease of replacement of the DTH ligand has also suggested the potential usefulness of (DTH)M(CO)<sub>4</sub> complexes as intermediates in the preparation of group VIb organometallic complexes. It has been shown<sup>3</sup> that DTH is replaced from (DTH)Cr(CO)<sub>4</sub> at 110° by norbornadiene, and the possible use of (bidentate)W(CO)<sub>4</sub> complexes as reaction intermediates in the synthesis of organometallic derivatives of tungsten which cannot be directly prepared from W(CO)<sub>6</sub> has been proposed, although the system investigated in this context, (tmen)W(CO)<sub>4</sub> (tmen = N,N,N',N'-tetramethylethylenediamine), failed in this regard.<sup>4</sup>

It appeared necessary both to further understanding of the mechanism of (bidentate)M(CO)<sub>4</sub> reactions and to the preparative use of such derivatives to investigate other (bidentate)M(CO)<sub>4</sub> systems in which dissociation of a bidentate ligand would be facilitated. This paper reports a kinetic and preparative investigation of group VIb metal carbonyl complexes of such a ligand, 2,2,7,7-tetramethyl-3,6-dithiaoctane [DTO, (CH<sub>3</sub>)<sub>8</sub>CS-C<sub>2</sub>H<sub>4</sub>SC(CH<sub>3</sub>)<sub>8</sub>].

**Experimental Section**

**General.**—Infrared spectra were recorded on high-resolution instruments (either a Perkin-Elmer Model 621 or a Beckman

Model IR-12 infrared spectrophotometer). Proton nmr spectra were obtained on a Varian Associates Model A-60A spectrometer. Chemical analyses and the molecular weight determination were performed by Midwest Microlab, Inc., Indianapolis, Ind. DTO was obtained from Phillips Petroleum Co., Special Products Division, Bartlesville, Okla., and was found to be suitable for use without further purification [proton nmr spectrum, CHCl<sub>3</sub> solution, internal TMS standard:  $\tau$  8.68 (singlet, *t*-butyl) and  $\tau$  7.30 (singlet, ethylene) in correct intensity ratio].

**Preparations.** (DTO)Cr(CO)<sub>4</sub>.—Cr(CO)<sub>6</sub> (4.4 g) and 30 ml of DTO in 75 ml of xylene were heated at reflux under nitrogen for 4 hr. The reaction solution was then filtered, and the volume was reduced to one-third under reduced pressure. Upon adding 150 ml of petroleum ether (bp 40–70°) to this solution and cooling overnight in a freezer, 3.8 g (51%) of moderately air-stable orange-yellow needles was obtained. The product was washed with small quantities of *n*-hexane and dried *in vacuo*. *Anal.* Calcd for C<sub>14</sub>H<sub>22</sub>O<sub>4</sub>S<sub>2</sub>Cr: C, 45.39; H, 5.89. Found: C, 45.30; H, 5.84. Carbonyl stretching spectra: cyclohexane solution on analytically pure sample: 2018 (m),<sup>5</sup> 1925 (m), 1917 (ms), 1908 (vs), 1902 (ms), 1885 (s) cm<sup>-1</sup>; CHCl<sub>3</sub> solution: 2016 (m), 1909 (vs), 1893 (s), 1859 (ms) cm<sup>-1</sup>. Proton nmr spectrum (CHCl<sub>3</sub> solution, internal TMS standard):  $\tau$  8.56 (singlet, *t*-butyl) and  $\tau$  7.30 (singlet, ethylene) in correct intensity ratio.

(DTO)Mo(CO)<sub>4</sub>.—Mo(CO)<sub>6</sub> (5.3 g) and 30 ml of DTO in 100 ml of *n*-heptane were heated at reflux under nitrogen for 5 hr. After the solution had cooled, the residue was separated by suction filtration and was twice recrystallized from toluene–hexane to give a high yield of lemon yellow, air-stable (DTO)Mo(CO)<sub>4</sub>, which was washed with *n*-hexane and dried *in vacuo*. *Anal.* Calcd for C<sub>14</sub>H<sub>22</sub>O<sub>4</sub>S<sub>2</sub>Mo: C, 40.57; H, 5.35; mol wt, 414.4. Found: C, 40.77; H, 5.41; mol wt, 438. Carbonyl stretching spectrum (CHCl<sub>3</sub> solution): 2023 (m), 1916 (vs), 1898 (s), 1861 (s) cm<sup>-1</sup>. Proton nmr spectrum (CHCl<sub>3</sub> solution, internal TMS standard):  $\tau$  8.56 (singlet, *t*-butyl) and  $\tau$  7.23 (singlet, ethylene) in correct intensity ratio.

(DTO)W(CO)<sub>4</sub>.—W(CO)<sub>6</sub> (7.25 g) and 30 ml of DTO were heated at reflux in xylene under nitrogen for 4 hr. The solution was then cooled and filtered, and the volume was reduced to one-third under reduced pressure. An excess of petroleum ether was then added to the remaining solution, whereupon the yellow crystalline product precipitated. The mixture was cooled in a freezer for 2 days, and the crystals were collected by suction filtration, washed with *n*-hexane, and dried *in vacuo*. The yield was 8.0 g (77% of theory) of air-stable product. *Anal.* Calcd for C<sub>14</sub>H<sub>22</sub>O<sub>4</sub>S<sub>2</sub>W: C, 33.48; H, 4.42. Found: C, 33.57; H, 4.34. Carbonyl stretching spectrum (CHCl<sub>3</sub> solution): 2019 (m), 1906 (vs), 1889 (vs), 1868 (s) cm<sup>-1</sup>. Proton nmr spectrum (CHCl<sub>3</sub> solution, internal TMS standard):  $\tau$  8.56 (singlet, *t*-butyl) and  $\tau$  7.22 (singlet, ethylene) in correct intensity ratio.

(5) Relative band intensities: s = strong; m = medium; w = weak; v = very; sh = shoulder.

(1) Part X: G. C. Faber and G. R. Dobson, *Inorg. Chim. Acta*, in press.  
(2) G. C. Faber and G. R. Dobson, *Inorg. Chem.*, **7**, 584 (1968).  
(3) H. C. E. Mannerskantz and G. Wilkinson, *J. Chem. Soc.*, 4454 (1962).  
(4) A. Fronzaglia and R. B. King, *Inorg. Chem.*, **5**, 1837 (1966).

**Reaction of (DTO)W(CO)<sub>4</sub> with Diolefins.**—(DTO)W(CO)<sub>4</sub> (3.06 g) and 4 ml of norbornadiene were refluxed under nitrogen in 100 ml of *n*-hexane for 19 hr. The mixture was cooled and filtered, and the residue was taken up in a minimal amount of toluene. Suction filtration of this solution and addition of an excess of petroleum ether followed by cooling in a freezer for 1 day resulted in the recovery of 2.14 g of (DTO)W(CO)<sub>4</sub>. The original filtrate was evaporated to dryness at reduced pressure and the residue was three times vacuum-sublimed to give 0.16 g (23% based upon unrecovered (DTO)W(CO)<sub>4</sub>) of (C<sub>7</sub>H<sub>8</sub>)W(CO)<sub>4</sub> as shown by infrared spectrum<sup>4</sup> and melting point (mp 90–91.5°; lit.<sup>4</sup> 90–92°). The same reaction run under nitrogen in refluxing benzene resulted in polymerization of the norbornadiene after 1 hr. Polymerization of norbornadiene by W(CO)<sub>6</sub> occurs under much more drastic conditions.<sup>6</sup> 1,5-Hexadiene and (DTO)W(CO)<sub>4</sub> were heated at reflux for several hours, but no evidence for formation of the (diene)W(CO)<sub>4</sub> complex was obtained.

[(C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>P]<sub>2</sub>W(CO)<sub>4</sub>.—(DTO)W(CO)<sub>4</sub> (0.6 g) and 3 ml of triethyl phosphite were heated to 98° in 25 ml of toluene in a vessel sealed with a rubber septum (under conditions approximating those employed for the kinetic runs). When the solution had become nearly colorless, an infrared spectrum showed the solution to contain only *trans*- and *cis*-[(C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>P]<sub>2</sub>W(CO)<sub>4</sub> ( $\nu_{CO}$ , toluene: 2035 (w), 1960 (w, sh), 1936 (s, sh), 1920 (vs) cm<sup>-1</sup>). The toluene was removed at reduced pressure, and the remaining oil was taken up in a few milliliters of *n*-hexane. The resulting solution was cooled over Dry Ice for 2 days, after which the white crystalline product, which melted to an oil at room temperature, was collected by suction filtration and dried *in vacuo*. *Anal.* Calcd for C<sub>18</sub>H<sub>30</sub>O<sub>10</sub>P<sub>2</sub>W: C, 30.59; H, 4.82. Found: C, 30.43; H, 4.71.

**Kinetic Runs.**—Spectrograde 1,2-dichloroethane (Matheson Coleman and Bell) and reagent grade xylene (Fisher) were used as obtained. Purification of the phosphites used has previously been described.<sup>1</sup> With exceptions to be discussed, kinetic runs for (DTO)Cr(CO)<sub>4</sub> and (DTO)Mo(CO)<sub>4</sub> were carried out under pseudo-first-order conditions as described for the analogous (DTH)M(CO)<sub>4</sub> complexes.<sup>2</sup> For the reaction of (DTO)Cr(CO)<sub>4</sub> with triethyl phosphite in 1,2-dichloroethane, a standard  $A_\infty$  value, which differed from the absorption observed for the solvent–ligand blank ( $A_{bl}$ ) by ca. 1% of the  $A_0 - A_{bl}$  value, was employed. Kinetic runs were monitored to at least 80% of completion, and plots of  $\ln(A_t - A_\infty)$  vs.  $t$  were linear over this time interval. The absorption at infinite time for reaction of (DTO)Mo(CO)<sub>4</sub> with phosphites was found to be appreciably greater than the  $A_{bl}$  values, despite the fact that the observed reaction products do not absorb at the wavelength monitored (4000 Å; see Discussion).<sup>2</sup> The rate law for the reaction of (DTO)Mo(CO)<sub>4</sub> with trimethyl phosphite was therefore determined from the initial slopes of the  $\ln(A_t - A_{bl})$  vs.  $t$  plots. For kinetic runs of (DTO)W(CO)<sub>4</sub> with phosphites under pseudo-first-order reaction conditions, approximately 80 mg of substrate in 50 ml of xylene and at least a 20-fold excess of phosphite were employed in each run. A standard  $A_\infty$  value which differed from  $A_{bl}$  by ~1% of the  $A_0 - A_{bl}$  value was employed. Reactions were monitored at 4300 Å on a Beckman DU spectrophotometer to at least 80% of completion, and plots of  $\ln(A_t - A_\infty)$  vs.  $t$  were linear over this time interval. Other procedures were the same as employed for the (DTO)Cr(CO)<sub>4</sub> system.

The products for reactions of (DTO)Cr(CO)<sub>4</sub> and (DTO)Mo(CO)<sub>4</sub> with phosphites were the same as those obtained for the analogous DTH systems as shown by a comparison of carbonyl stretching spectra. The characterization of [P(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>W(CO)<sub>4</sub>, a reaction product of the (DTO)W(CO)<sub>4</sub> system, has been described in an earlier section. The analogous isopropyl phosphite derivative was identified through comparison of its carbonyl stretching spectrum with that of the ethyl product.

## Results and Discussion

**Kinetics and Mechanism.** (a) (DTO)Cr(CO)<sub>4</sub>.—Rate data for the reaction of (DTO)Cr(CO)<sub>4</sub> with

triethyl phosphite are given in Table I. At ligand concentrations  $\geq 0.5$  M, plots of  $k_{obsd}$  vs. [L] are linear (Figure 1), and a mixed-order rate law

$$\text{rate} = k_a[(\text{DTO})\text{Cr}(\text{CO})_4] + k_b[(\text{DTO})\text{Cr}(\text{CO})_4][\text{L}] \quad (3)$$

is obeyed. At higher ligand concentrations there is significant deviation of the  $k_{obsd}$  vs. [L] plots from linearity. Rate constants (Table II) and activation parameters (Table III) have been calculated from the

TABLE I  
PSEUDO-FIRST-ORDER RATE CONSTANTS FOR REACTION OF (DTO)M(CO)<sub>4</sub> WITH PHOSPHITES

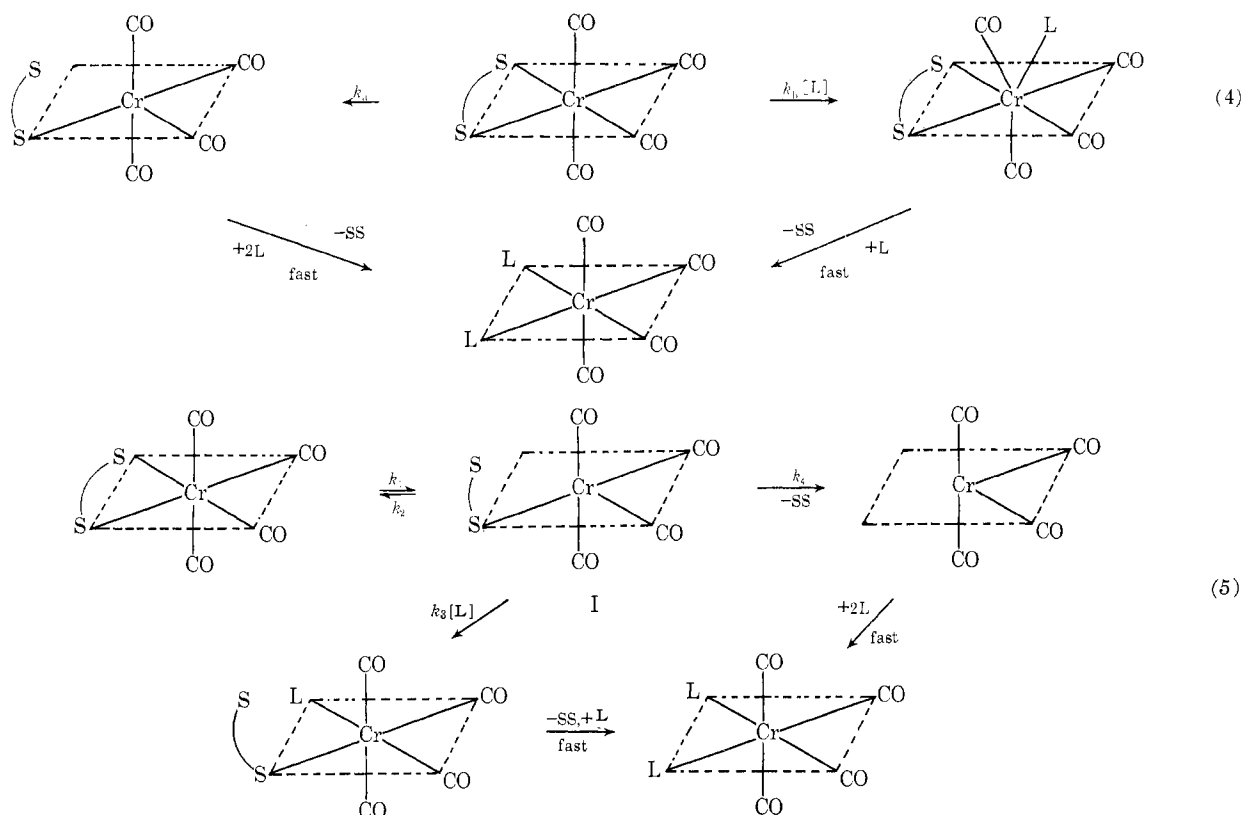
Temp, °C	[L], M	10 <sup>4</sup> k <sub>obsd</sub> , sec <sup>-1</sup>	Temp, °C	[L], M	10 <sup>4</sup> k <sub>obsd</sub> , sec <sup>-1</sup>			
31.9	(DTO)Cr(CO) <sub>4</sub> + P(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (in 1,2-dichloroethane)	0.1294	0.387	55.35	(DTO)Mo(CO) <sub>4</sub> + P(OCH <sub>3</sub> ) <sub>3</sub> (in 1,2-dichloroethane)			
		0.3275	0.712			0.2628	3.64	
		0.4879	0.930			0.6019	6.08	
		0.4881	0.929			1.0073	9.08	
		0.6682	1.12			1.4236	12.0	
	0.8872	1.40	(DTO)W(CO) <sub>4</sub> + P(OCH <sub>3</sub> ) <sub>3</sub> (in xylene)		79.8	0.2205	0.410	
	1.0326	1.52				0.3183	0.545	
	1.3867	1.88				0.4096	0.707	
	42.1	0.0629				1.31	0.7341	1.04
	0.1212	1.56				1.524	1.71	
50.7	(DTO)Cr(CO) <sub>4</sub> + P(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (in 1,2-dichloroethane)	0.2080	2.31	89.2	(DTO)W(CO) <sub>4</sub> + P(OCH <sub>3</sub> ) <sub>3</sub> (in xylene)			
		0.2750	2.48			0.2635	1.41	
		0.3860	3.21			0.4055	1.93	
		0.4881	3.82			0.7574	3.12	
		0.4889	3.75			0.9611	3.79	
	(DTO)Mo(CO) <sub>4</sub> + P(OCH <sub>3</sub> ) <sub>3</sub> (in 1,2-dichloroethane)	0.6966	4.81		99.9	(DTO)W(CO) <sub>4</sub> + P(OCH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>3</sub> (in xylene)		
		0.8254	5.62				0.1123	2.20
		0.9584	5.91				0.1321	2.61
		1.4560	7.65				0.2089	4.31
		50.7	0.0721				4.66	0.3982
(DTO)Cr(CO) <sub>4</sub> + P(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (in 1,2-dichloroethane)	0.1046	5.20	99.9	(DTO)W(CO) <sub>4</sub> + P(OCH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>3</sub> (in xylene)				
	0.2487	7.57			0.8117	8.22		
	0.3648	9.42			1.318	11.3		
	0.4850	11.7						

TABLE II  
RATE CONSTANTS FOR REACTION OF (DTO)M(CO)<sub>4</sub> WITH PHOSPHITES

Temp, °C	10 <sup>4</sup> k <sub>1</sub> k <sub>4</sub> /k <sub>2</sub> , sec <sup>-1</sup>	10 <sup>4</sup> k <sub>1</sub> k <sub>3</sub> /k <sub>2</sub> , l. mol <sup>-1</sup> sec <sup>-1</sup>	Temp, °C	10 <sup>4</sup> k <sub>1</sub> , sec <sup>-1</sup>	k <sub>2</sub> /k <sub>3</sub> , mol l. <sup>-1</sup>								
31.9	0.198	1.48	79.8	0.358	1.71								
						42.1	0.925	5.93	89.2	0.986	1.60		
												50.7	3.50
(DTO)Mo(CO) <sub>4</sub> + P(OCH <sub>3</sub> ) <sub>3</sub> (in 1,2-dichloroethane)	(DTO)W(CO) <sub>4</sub> + P(OCH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>3</sub>	55.35	1.51	7.55	99.9								

linear portion of the data. The two-term rate expression might be interpreted in terms of two competing mechanisms, dissociation of DTO ( $k_a$ ) and nucleophilic attack of triethyl phosphite on (DTO)-Cr(CO)<sub>4</sub>, followed by loss of DTO ( $k_b$ ) (see eq 4).

(6) J. R. Leto and L. M. Olsen, U. S. Patent 3,192,191 (1965).



Comparison of the calculated activation parameters for the second-order term with those reported for the reaction of  $\text{Cr}(\text{CO})_6$  with tri-*n*-butylphosphine in decalin<sup>7</sup> would indicate, however, that this mechanism is not the correct one, the possible influence of the difference in solvents notwithstanding. The second-order enthalpies of activation are quite similar ( $24.1 \pm 0.9$  kcal/mol for the reaction of  $(\text{DTO})\text{Cr}(\text{CO})_4$  with triethyl phosphite *vs.*  $25.5 \pm 2.9$  kcal/mol for the reaction of  $\text{Cr}(\text{CO})_6$  with tri-*n*-butylphosphine) although consideration of steric effects, the relative basicities of the attacking ligands, and the bonding properties of CO and DTO would all support a higher second-order enthalpy of activation for  $(\text{DTO})\text{Cr}(\text{CO})_4$ .<sup>8</sup> A more negative entropy of activation than the observed  $2.9 \pm 2.3$  eu might also be expected for an associative process.

For most observed cases of rate dependence upon ligand concentration which have been reported for octahedral metal carbonyl complexes of the first transition series a chelating group is present<sup>9</sup> and a mechanism involving initial reversible dissociation of one end of the chelating group followed by attack of the ligand on the resulting five-coordinate activated complex or intermediate will also explain the kinetic data. In at least one reported instance unequivocal preference for such an alternate mechanism has been expressed.<sup>9</sup> The experimental data to be presented for both  $(\text{DTO})\text{Cr}(\text{CO})_4$  and  $(\text{DTO})\text{W}(\text{CO})_4$  also support this mechanism (eq 5).

(7) J. R. Graham and R. J. Angelici, *Inorg. Chem.*, **6**, 2082 (1967).

(8) For a recent review on kinetics and mechanism of substitution reactions of metal carbonyls, see R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

(9) G. C. Faber, T. D. Walsh, and G. R. Dobson, *J. Am. Chem. Soc.*, **90**, 4178 (1968).

TABLE III  
ACTIVATION PARAMETERS FOR REACTIONS OF  $(\text{DTO})\text{Cr}(\text{CO})_4$   
AND  $(\text{DTO})\text{W}(\text{CO})_4$  WITH TRIETHYL PHOSPHITE

Complex	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu
$(\text{DTO})\text{Cr}(\text{CO})_4$	$\sim 24^a$	$\sim +2$
(1,2-dichloroethane soln)	$29.6 \pm 1.1^b$	$+16.9 \pm 3.0$
	$24.1 \pm 0.9^c$	$+2.9 \pm 2.4$
$(\text{DTO})\text{W}(\text{CO})_4$	$25.7 \pm 0.7^a$	$+1.6 \pm 2.0$
(xylene soln)	$-4.7 \pm 1.7^d$	$-23.9 \pm 4.6$

<sup>a</sup>  $\Delta H^\ddagger = \Delta H_1^\ddagger$ . <sup>b</sup>  $\Delta H^\ddagger = \Delta H_1^\ddagger + \Delta H_4^\ddagger - \Delta H_2^\ddagger$ .  
<sup>c</sup>  $\Delta H^\ddagger = \Delta H_1^\ddagger + \Delta H_3^\ddagger - \Delta H_2^\ddagger$ . <sup>d</sup>  $\Delta H^\ddagger = \Delta H_2^\ddagger - \Delta H_3^\ddagger$ .

Employing the steady-state approximation for the rate of formation of I the rate expression

$$\text{rate} = \frac{k_1 k_4 [(\text{DTO})\text{Cr}(\text{CO})_4] + k_1 k_3 [(\text{DTO})\text{Cr}(\text{CO})_4][\text{L}]}{k_2 + k_3[\text{L}] + k_4} \quad (6)$$

is obtained. For the reasonable conditions  $k_3[\text{L}] \sim k_4 \ll k_2$ , this expression becomes

$$\text{rate} = k_a [(\text{DTO})\text{Cr}(\text{CO})_4] + k_b [(\text{DTO})\text{Cr}(\text{CO})_4][\text{L}] \quad (7)$$

$(k_a = k_1 k_4 / k_2; k_b = k_1 k_3 / k_2)$

and thus a two-term rate law, as observed for  $[\text{L}] \geq 0.5 M$ , should be expected. Moreover, the negative deviation from linearity of the  $k_{\text{obsd}}$  *vs.*  $[\text{L}]$  plots for  $[\text{L}] > 0.5 M$  (Figure 1) would be expected as the contribution of  $k_3[\text{L}]$  to the denominator of (6) becomes significant. It can be shown for  $k_2 \gg k_4$  that

$$1/(k_{\text{obsd}} - k_a) = (k_2/k_1 k_3[\text{L}]) + (1/k_1) \quad (8)$$

and thus that plots of  $1/(k_{\text{obsd}} - k_a)$  *vs.*  $1/[\text{L}]$  should be linear, with intercept  $1/k_1$ . Such plots for  $[\text{L}] > 0.2 M$  are shown in Figure 2; mechanism 5 is seen to be entirely consistent with the kinetic data.

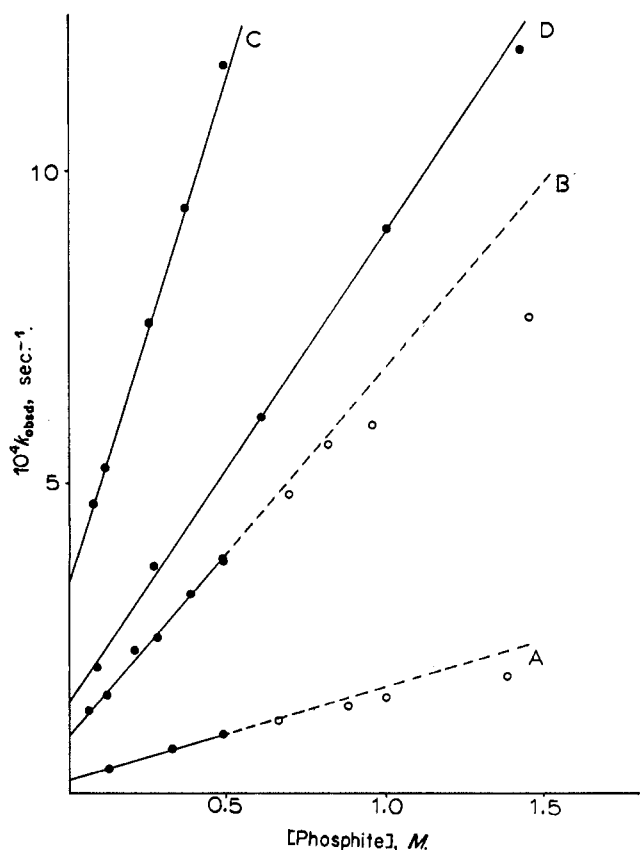


Figure 1.—Plots of  $k_{\text{obsd}}$  vs. phosphite concentration for reactions of  $(\text{DTO})\text{Cr}(\text{CO})_4$  and  $(\text{DTO})\text{Mo}(\text{CO})_4$  in 1,2-dichloroethane: (A)  $(\text{DTO})\text{Cr}(\text{CO})_4$  with triethyl phosphite,  $31.9^\circ$ ; (B)  $(\text{DTO})\text{Cr}(\text{CO})_4$  with triethyl phosphite,  $42.1^\circ$ ; (C)  $(\text{DTO})\text{Cr}(\text{CO})_4$  with triethyl phosphite,  $50.7^\circ$ ; (D)  $(\text{DTO})\text{Mo}(\text{CO})_4$  with trimethyl phosphite,  $55.35^\circ$ .

The calculated second-order activation parameters may be directly compared to those reported for the reaction of  $(\text{DTH})\text{Cr}(\text{CO})_4$  with triethyl phosphite in 1,2-dichloroethane (Table III). It is seen that the enthalpy of activation for  $(\text{DTO})\text{Cr}(\text{CO})_4$  is somewhat smaller than that for  $(\text{DTH})\text{Cr}(\text{CO})_4$ . If it is assumed that steric factors predominate and that their effects on  $k_2$  and  $k_3[\text{L}]$  will be about equal, the observed difference may be attributed to a greater ease of breaking a Cr-S bond in the DTO complex.

(b)  $(\text{DTO})\text{Mo}(\text{CO})_4$ .—For the reactions in 1,2-dichloroethane of  $(\text{DTO})\text{Mo}(\text{CO})_4$  with phosphites, it was found that  $k_{\text{obsd}}$  plots deviated from linearity at longer reaction times as the result of  $A_\infty$  values significantly greater than those of the ligand-solvent blanks. The reaction products have been shown,<sup>2</sup> however, not to absorb at the wavelength monitored ( $4000 \text{ \AA}$ ). The high  $A_\infty$  values evidently arise from decomposition since infrared spectra of the reaction solutions failed to demonstrate the presence of other possible products, e.g.,  $(\text{DTO})(\text{L})\text{Mo}(\text{CO})_3$ , from which the absorbance might result. Accordingly, the rate law was determined for the reaction of  $(\text{DTO})\text{Mo}(\text{CO})_4$  with trimethyl phosphite from the initial slopes of the plots of  $\ln(A_t - A_{\text{bl}})$  vs.  $t$  at various ligand concentrations (Table I). It is seen (Figure 1) that the rate law for Mo is similar to that for Cr. It may be es-

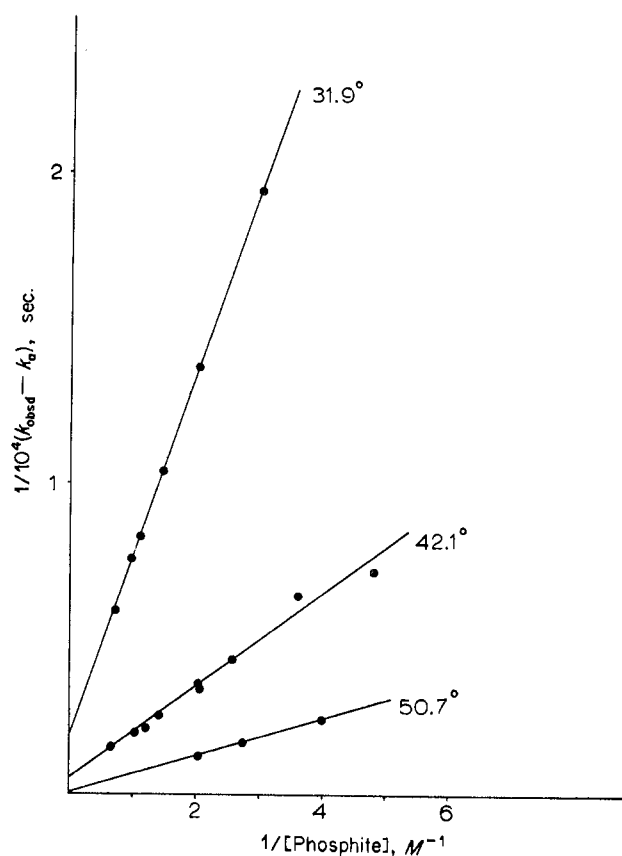


Figure 2.—Plots of  $1/(k_{\text{obsd}} - k_a)$  vs.  $1/[\text{phosphite}]$  for the reaction of  $(\text{DTO})\text{Cr}(\text{CO})_4$  with triethyl phosphite in 1,2-dichloroethane.

timated that second-order reaction rates with triethyl phosphite in 1,2-dichloroethane vary as:  $(\text{DTH})\text{Mo}(\text{CO})_4^2 > (\text{DTO})\text{Cr}(\text{CO})_4 > (\text{DTH})\text{Cr}(\text{CO})_4^2 > (\text{DTO})\text{Mo}(\text{CO})_4$ . This order may be rationalized through the assumption that reactions of  $(\text{DTO})\text{Cr}(\text{CO})_4$  and  $(\text{DTO})\text{Mo}(\text{CO})_4$  proceed through similar mechanisms, while those of  $(\text{DTH})\text{Cr}(\text{CO})_4$  and  $(\text{DTH})\text{Mo}(\text{CO})_4$  proceed through different ones, as has been proposed. The slower rate for  $(\text{DTO})\text{Mo}(\text{CO})_4$  than for  $(\text{DTH})\text{Mo}(\text{CO})_4$  might thus be attributed to inhibition of nucleophilic attack on Mo by the bulky DTO ligand. It thus would appear probable that the reaction of  $(\text{DTO})\text{Mo}(\text{CO})_4$  proceeds through mechanism 5; no reasonable explanation for the observed order of reaction rates can be offered if it is assumed that the reaction of  $(\text{DTO})\text{Mo}(\text{CO})_4$  proceeds through (4) and that the preferred mechanisms for  $(\text{DTH})\text{M}(\text{CO})_4$  complexes are, in fact, the correct ones.

In an attempt to obtain information about the mechanism of decomposition in this system, the initial rates for the reactions of  $(\text{DTO})\text{Mo}(\text{CO})_4$  with 0.5 M solutions of various phosphites and the extents of decomposition as indicated by  $A_\infty$  values were compared. The rates of reaction varied as:  $\text{P}(\text{OCH}_3)_3 > \text{P}(\text{OC}_2\text{H}_5)_3 > \text{P}(\text{OCH}(\text{CH}_3)_2)_3 > \text{P}(\text{OC}_6\text{H}_5)_3$ , the same order as was observed for reactions of  $(\text{DTH})\text{Mo}(\text{CO})_4$  with these ligands.<sup>2</sup> It was further found that the  $A_\infty$  values increased in the reverse order, and with decreasing  $[\text{L}]$ . Thus it would appear that the extent of

decomposition is inversely related to the relative sizes of the  $k_3[L]$  terms, and it would thus seem reasonable to attribute decomposition to the presence of  $\text{Mo}(\text{CO})_4$ , the formation of which is more favored for lower values of  $k_3[L]$ .

(c)  $(\text{DTO})\text{W}(\text{CO})_4$ .—Plots of  $k_{\text{obsd}}$  vs.  $[\text{L}]$  (Figure 3) for the reaction of  $(\text{DTO})\text{W}(\text{CO})_4$  with triethyl phosphite in xylene are not linear but show decreased dependence of rate on  $[\text{L}]$  as  $[\text{L}]$  increases and may be extrapolated to the origin. Thus mechanism 5, with  $k_3[L] \sim k_2$  and  $k_4 = 0$ , is consistent with the data. The appropriate rate expression is

$$\text{rate} = k_1 k_3 [(\text{DTO})\text{W}(\text{CO})_4] [\text{L}] / (k_2 + k_3 [\text{L}]) \quad (9)$$

which may be rearranged to

$$1/k_{\text{obsd}} = (1/k_1) + (k_2/k_1 k_3 [\text{L}]) \quad (10)$$

Thus plots of  $1/k_{\text{obsd}}$  vs.  $1/[\text{L}]$  should be linear with slope  $k_2/k_1 k_3$  and intercept  $1/k_1$ , as is found (Figure 4).

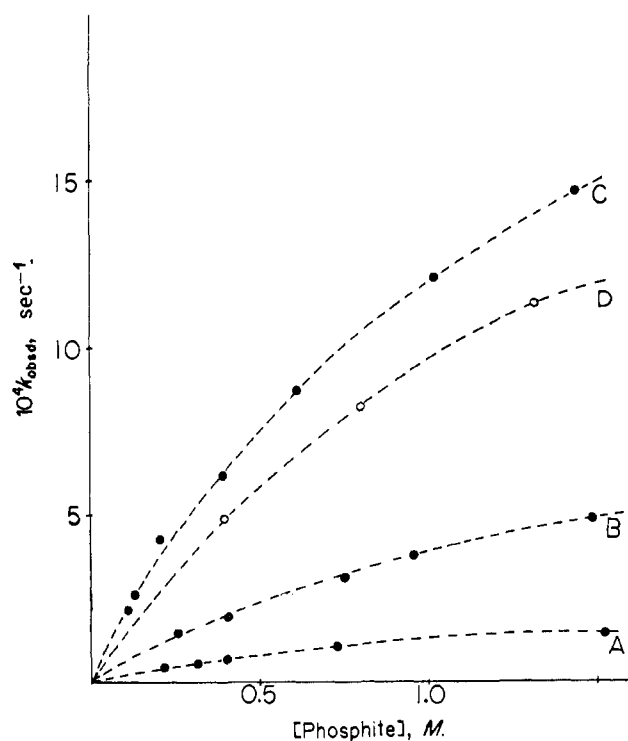


Figure 3.—Plots of  $k_{\text{obsd}}$  vs.  $[\text{phosphite}]$  for the reaction of  $(\text{DTO})\text{W}(\text{CO})_4$  with phosphites in xylene: (A) with triethyl phosphite, 79.8°; (B) with triethyl phosphite, 89.2°; (C) with triethyl phosphite, 99.9°; (D) with triisopropyl phosphite, 99.9°.

Since the observed value of  $k_1$  should be independent of the phosphite chosen, the reaction at 99.9° of triisopropyl phosphite with  $(\text{DTO})\text{W}(\text{CO})_4$  was also investigated. The  $k_1$ 's obtained for the two ligands (Table II) agree to within 6%. The larger value for  $k_2/k_3$  observed for triisopropyl phosphite (Table II) is also to be expected since data<sup>2</sup> indicate triisopropyl phosphite to be the poorer nucleophile. The failure to observe complete dissociation of DTO in the absence of ligand attack supports a greater difficulty in breaking W-S than Mo-S or Cr-S bonds as has been observed in many instances. No other plausible mechanism would appear to satisfy the experimental data.

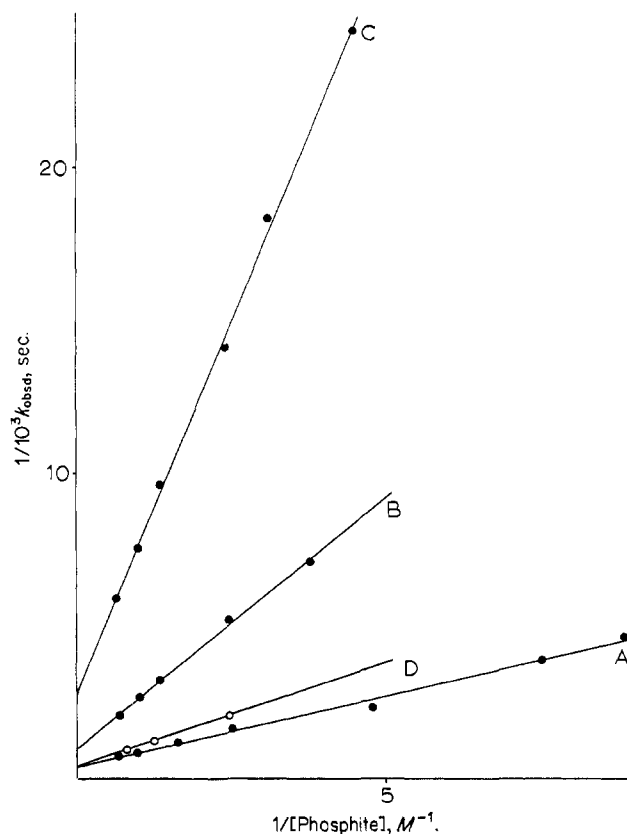


Figure 4.—Plots of  $1/k_{\text{obsd}}$  vs.  $1/[\text{phosphite}]$  for the reaction of  $(\text{DTO})\text{W}(\text{CO})_4$  with phosphites in xylene: (A) with triethyl phosphite, 99.9°; (B) with triethyl phosphite, 89.2°; (C) with triethyl phosphite, 79.8°; (D) with triisopropyl phosphite, 99.9°.

The evidence obtained for all three  $(\text{DTO})\text{M}(\text{CO})_4$  systems demonstrates that the ring-opening mechanism, alone of all mechanisms which have been considered for systems of this type, is consistent with the kinetic data. It further suggests that it is highly possible that other reactions of  $[(\text{bidentate})\text{M}(\text{CO})_4]_n$  ( $n = 1, 2$ ) with Lewis bases for which rate dependence on ligand concentration is noted, e.g.,  $(\text{DTH})\text{Mn}(\text{CO})_4$ <sup>10</sup> and  $[\text{M}(\text{CO})_4\text{X}]_2$  ( $\text{M} = \text{Mn}, \text{Re}; \text{X} = \text{Cl}, \text{Br}, \text{I}$ )<sup>11</sup> proceed by way of this mechanism. This would appear to be particularly true for metals of the first transition series (Cr, Mn) for which the small sizes of the metal atoms make an associative mechanism less plausible.

**Infrared and Proton Nmr Spectra.**—Carbonyl stretching and proton nmr spectra in chloroform (see Experimental Section) for  $(\text{DTO})\text{M}(\text{CO})_4$  species ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) may be interpreted in a straightforward manner. Four terminal carbonyl stretching bands are observed ( $2A_1 + B_1 + B_2$ ) as anticipated for a molecule in which the carbonyl groups possess  $C_{2v}$  local symmetry. The frequencies are 4–7  $\text{cm}^{-1}$  lower than are those reported for analogous  $(\text{DTH})\text{M}(\text{CO})_4$  complexes.<sup>3</sup> A number of possible interpretations based upon steric or upon  $\sigma$ - or  $\pi$ -bonding effects would be consistent with the data; thus there would appear to be little to be gained through extensive discussion of the observed differences. Proton nmr spec-

(10) G. C. Faber and G. R. Dobson, unpublished results.

(11) F. Zingales and U. Sartorelli, *Inorg. Chem.*, **6**, 1243 (1967).

tra for (DTO)M(CO)<sub>4</sub> complexes all show singlet absorptions due to *t*-butyl protons and another singlet which may be ascribed to the ethylene protons; these occur in the expected 4.5:1 intensity ratios and are shifted somewhat downfield with respect to the absorptions for the free ligand. Deshielding of the protons is to be expected upon coordination of sulfur.

The solubility of (DTO)Cr(CO)<sub>4</sub> was sufficient to permit an infrared spectrum to be taken in cyclohexane. The spectrum was run on a sample the purity of which was verified by chemical analysis; it was also observed that no decomposition occurred over the time required to scan the carbonyl stretching region several times. Six bands in the carbonyl stretching region, suggesting the presence of more than one species, are observed (see Experimental Section). Rough estimates of the relative sizes of *k*<sub>1</sub> and *k*<sub>2</sub> for (DTO)Cr(CO)<sub>4</sub> do not rule out the possibility that the second species is (DTO)Cr(CO)<sub>4</sub> in which one end of the DTO molecule is dissociated. Unfortunately, it was not possible to obtain a proton nmr spectrum in a deuterated hydrocarbon solvent, and thus the origin of the two additional carbonyl stretching bands cannot be assigned with confidence.

**Reactions of (DTO)W(CO)<sub>4</sub>.**—The inertness of W(CO)<sub>6</sub> toward carbonyl replacement has prevented the direct preparation of some organometallic com-

plexes of tungsten. An indirect route to the preparation of such compounds, *e.g.*, (diolefin)W(CO)<sub>4</sub>, through use of (CH<sub>3</sub>CN)<sub>3</sub>W(CO)<sub>3</sub> has been reported.<sup>4</sup> The potential usefulness of (DTO)W(CO)<sub>4</sub> as such an intermediate has been briefly investigated; details are given in the Experimental Section. Reaction of (DTO)W(CO)<sub>4</sub> with norbornadiene in refluxing *n*-hexane gives a 23% yield of (C<sub>7</sub>H<sub>8</sub>)W(CO)<sub>4</sub> as shown by the infrared spectrum and melting point of the product. Although the yield of (C<sub>7</sub>H<sub>8</sub>)W(CO)<sub>4</sub> was lower than those reported by Fronzaglia and King,<sup>4</sup> who obtained a 56% yield based on moles of (CH<sub>3</sub>CN)<sub>3</sub>W(CO)<sub>3</sub> used, the ease of preparation and air stability of (DTO)W(CO)<sub>4</sub> would appear to offer advantages for the indirect synthesis of organometallic complexes of tungsten, particularly so for cases in which the use of large excesses of the substituent ligand is economically feasible.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, BRITISH COLUMBIA, CANADA

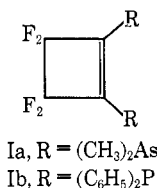
## The Characterization of $(\text{CH}_3)_2\text{AsC}=\overline{\text{CAs}(\text{CH}_3)_2\text{CF}_2\text{CF}_2\text{Fe}_2(\text{CO})_6}$ and Related Complexes

BY W. R. CULLEN, D. A. HARBOURNE, B. V. LIENGME, AND J. R. SAMS

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The complexes  $\text{RC}=\overline{\text{CR}(\text{CF}_2)_n\text{CF}_2\text{Fe}_2(\text{CO})_6}$  [ $\text{R} = (\text{CH}_3)_2\text{As}$  or  $(\text{C}_6\text{H}_5)_2\text{P}$ ,  $n = 1$ ;  $\text{R} = (\text{C}_6\text{H}_5)_2\text{P}$ ,  $n = 2$ ] have been isolated and evidence is presented that the phosphorus compounds have structures analogous to that of the known arsenic derivative (Figure 1). In particular, information about their structure and bonding has been obtained from their Mössbauer spectra.

The novel cyclobutene derivatives Ia, ffars, and Ib, ffos, have recently been found to form chelate complexes when treated with derivatives of the heavier



transition metals and with certain metal carbonyls.<sup>1</sup> It has also been reported<sup>2</sup> that ffars forms a complex (ffars)Fe<sub>2</sub>(CO)<sub>6</sub> whose structure is indicated in Figure

1. Here the ligand is not only acting as a chelating group to one iron atom in the usual way<sup>3</sup> but is also using the double bond of the cyclobutene bridging group to coordinate to the second iron atom. Olefins,<sup>4</sup> including perfluorocycloalkenes,<sup>5</sup> are known to react with iron carbonyls to give derivatives of the type (olefin)Fe(CO)<sub>4</sub>. Furthermore, iron pentacarbonyl and its derivatives, like some other metal car-

(2) (a) F. W. B. Einstein and J. Trotter, *J. Chem. Soc., A*, 824 (1967); (b) F. W. B. Einstein, W. R. Cullen, and J. Trotter, *J. Am. Chem. Soc.*, **88**, 5670 (1966).

(3) T. A. Manuel, *Advan. Organometal. Chem.*, **3**, 181 (1965).

(4) *E.g.*, P. Corradini, C. Pedone, and A. Sirigu, *Chem. Commun.*, 341 (1966); A. R. Luxmore and M. R. Truter, *Acta Cryst.*, **15**, 1117 (1962); E. K. Gustorf, M. C. Henry, and C. D. Pietro, *Z. Naturforsch.*, **19b**, 284 (1964).

(5) R. Fields, M. M. Germain, R. N. Haszeldine, and P. W. Wiggans, *Chem. Commun.*, 243 (1967).

(1) W. R. Cullen, P. S. Dhaliwal, and C. J. Stewart, *Inorg. Chem.*, **6**, 2256 (1967).