Journal of Organometallic Chemistry, 131 (1977) 285—296
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

OCTAHEDRAL METAL CARBONYLS

XL *. A REINVESTIGATION OF THE KINETICS AND MECHANISM OF LIGAND EXCHANGE IN (2,2,8,8-TETRAMETHYL-3,7-DITHIANONANE)-TETRACARBONYLTUNGSTEN(0)

GERARD R. DOBSON * and LINDA D. SCHULTZ **
Department of Chemistry, North Texas State University, Denton, Texas 76203 (U.S.A.)

(Received August 27th, 1976)

Summary

A reinvestigation of the kinetics and mechanism of ligand-exchange reactions of (2,2,8,8-tetramethyl-3,7-dithianonane)tetracarbonyltungsten(0) ((DTN)W$(CO)_4$) with alkyl and aryl phosphites (L) to afford *trans*- and *cis*-$L_2W(CO)_4$ products supports a mechanism involving initial ring-opening, and subsequent competition between ring-reclosure and attack at the "ring-opened" five-coordinate, probably fluxional, intermediate, by L. A competing path, involving ring-reclosure in *cis*-(η^1-DTN)W$(CO)_4$(L) species with expulsion of L to afford the substrate is also to be inferred from the rate data. For L = $P(OCH_2)_3CCH_3$, an intermediate of this type, *cis*-(η^1-DTN)W$(CO)_4$(L) was isolated and characterized, and the kinetics of its formation and decomposition were studied. The data provide conclusive evidence for the operation of the ring-opening mechanism in these systems.

Introduction

Studies of the kinetics and mechanism of ligand-exchange reactions of (2,2,7,7-tetramethyl-3,6-dithiaoctane)W$(CO)_4$, (DTO)W$(CO)_4$, [1] and (2,2,8,8-tetramethyl-3,7-dithianonane)W$(CO)_4$, (DTN)W$(CO)_4$, [2] with phosphites (L), eq. 1,

$$(S_2)W(CO)_4 + 2\,L \rightarrow L_2W(CO)_4 + S_2 \qquad (1)$$

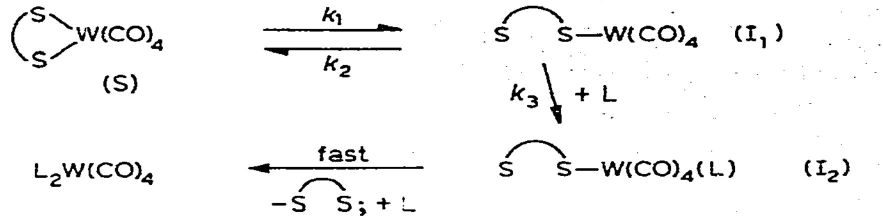
$$(S_2 = \text{DTO, DTN})$$

were interpreted in terms of a ring-opening mechanism (eq. 2). Assuming a

---

* Part XXXIX: see ref. 3.

** Robert A. Welch Predoctoral Fellow, 1973, 1975. Present address: Department of Chemistry, Texas Christian University, Ft. Worth, Texas 76129 (U.S.A.).



(2)

steady-state concentration of 2-I$_1$, eq. 2 affords the rate law, eq. 3. Under the

$$-d[S]/dt = k_1k_3[S][L]/(k_2 + k_3[L]) \tag{3}$$

pseudo first-order conditions (large excess of L) employed, eq. 3 may be arranged in terms of the pseudo first-order rate constants, k_{obs}, to afford:

$$1/k_{obs} = 1/k_1 + k_2/k_1k_3[L] \tag{4}$$

Thus eq. 4 predicts that the "reciprocal plots" will be linear, with plots for various L affording common intercepts, since k_1 should be independent of the identity of L. A recent detailed reinvestigation of the reaction of (DTO)W(CO)$_4$ with phosphines and phosphites has shown the rate data to be consistent with these expectations in every detail [3]. However, rate data for reaction of (DTN)-W(CO)$_4$ with L according to eq. 1 are inconsistent with eq. 4 in that noncommon intercepts of the "reciprocal plots" were observed [2]. No satisfying explanation for the qualitative differences observed for rate data for the corresponding (DTO)W(CO)$_4$ and (DTN)W(CO)$_4$ systems has been advanced [2], and thus a careful and detailed reinvestigation of the (DTN)W(CO)$_4$ system was also dictated. The results are the subject of this report.

Experimental

General. Except as noted, preparation and purification of reagents, the determination of reaction rates, and the analysis of rate data were as described previously [2,3]. Limits of error (in parentheses) for data are one standard deviation. Error limits for activation parameters are based on the uncertainties of the slopes and intercepts of the reciprocal plots (vide infra). Triethyl phosphite (Aldrich) was distilled over sodium under nitrogen, and was identified and found to be pure by GC/MS (Finnigan Model 3200 GC/MS).

Determination of reaction rates. For reaction of (DTN)W(CO)$_4$ with P(OCH$_2$)$_3$-CCH$_3$ in xylene, plots of ln(A_t — A_{bl}) vs. time (A_t and A_{bl} are the absorbances at time t, and of a solvent—ligand blank, respectively) at 425 nm [3] exhibited initial curvature, before becoming linear, suggestive of the formation of a reaction intermediate. Periodic scans of the carbonyl stretching region of the reaction solution (Perkin—Elmer Model 621 grating spectrophotometer) over the course of the reaction revealed the formation of an intermediate. Figure 1 exhibits changes in the carbonyl stretching spectrum (>2000 cm^{-1}) observed during the course of the reaction. The intermediate, (η^1-DTN)W(CO)$_4$[P(OCH$_2$)$_3$-CCH$_3$] was isolated and characterized as discussed below. A comparison of the visible spectra of the substrate, intermediate, and product showed the substrate to absorb much more strongly than the intermediate at 445 nm, and thus it was

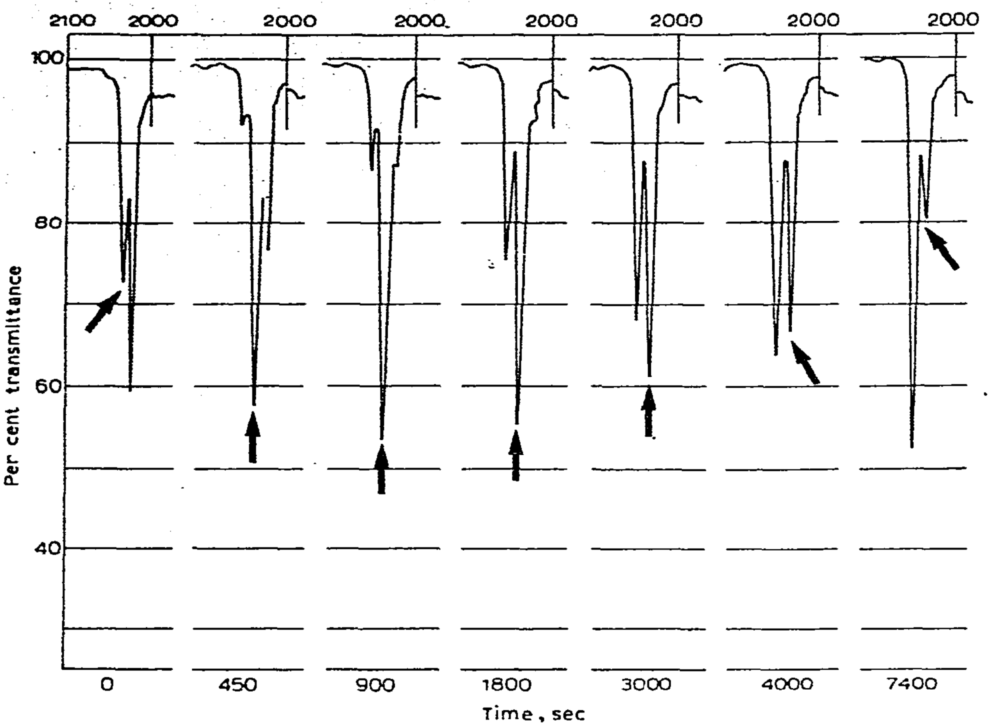


Fig. 1. Carbonyl stretching spectra (>2000 cm^{-1}) as a function of time for the reaction of (DTN)W$(CO)_4$ with $P(OCH_2)_3CCH_3$ in xylene at 66.5°C. The arrows indicate a band attributable to the intermediate B.

possible to obtain linear plots of $\ln(A_t - A_{bl})$ vs. time for the initial stages of the reaction at this wavelength (over about 1.5 half-lives). Figure 2 exhibits such plots at both 425 and 445 nm. For all other reactions, scans of the carbonyl stretching spectra over their course revealed the formation of only a negligible amount of (η^1-DTN)W$(CO)_4$(L) intermediates. Thus for L = $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(OCH(CH_3)_2)_3$ and $P(C_6H_5)_3$ the steady-state assumption for the change in concentration of the intermediate as a function of time was applicable, and rate data were obtained by methods wholly analogous to those described for the corresponding (DTO)W$(CO)_4$ systems [3].

Identification of reaction intermediate and products. Reaction products were found to be those observed for reaction of (DTO)W$(CO)_4$ with various L [3], *cis*- and *trans*-$L_2W(CO)_4$, and were identified by comparison of the carbonyl stretching spectra of reaction solutions to spectra reported for those complexes [1,4–8]. The intermediate (η^1-DTN)W$(CO)_4[P(OCH_2)_3CCH_3]$ was obtained in low yield as follows: (DTN)W$(CO)_4$ (0.5 g, 10^{-3} mol) and 3.0 g of $P(OCH_2)_3CCH_3$ (2×10^{-2} mol) were dissolved in 150 ml of xylene and placed in a 250 ml round-bottomed flask, which was flushed with nitrogen, sealed with a rubber septum, and placed in a constant temperature bath at 66.5° C. Samples of the reaction solution were withdrawn periodically and monitored in the carbonyl stretching region until the concentration of the intermediate had reached its maximum (ca. 1500 sec). The reaction was then quenched by cooling, and the solvent was removed under vacuum. Approximately 50 ml of hexane was added

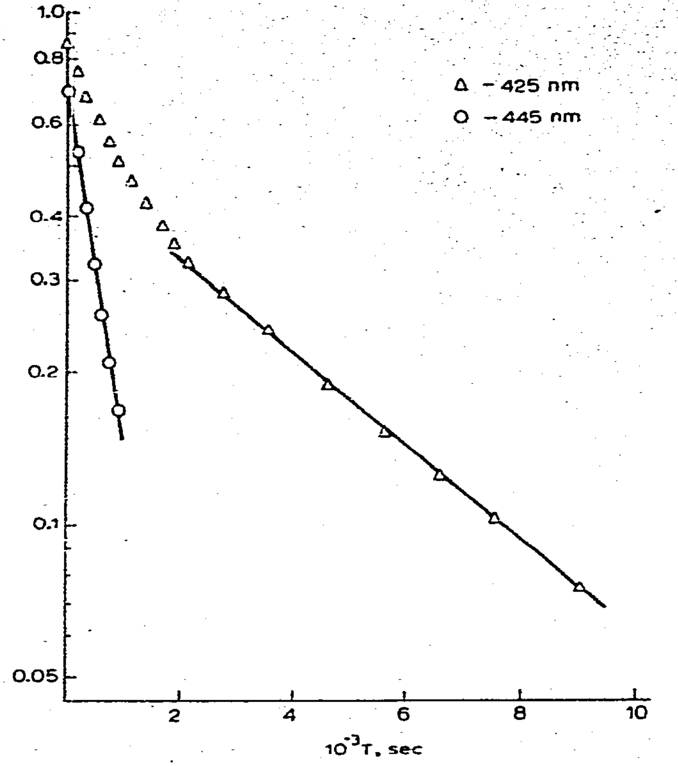


Fig. 2. Plots of $\ln(A_t - A_\infty)$ vs. time at 425 and 445 nm for reaction of $(DTN)W(CO)_4$ with $P(OCH_2)_3CCH_3$ in xylene at 66.5°C.

to the flask, which was then shaken and placed in a freezer for several hours. The mixture was then filtered to remove precipitated $W(CO)_4[P(OCH_2)_3CCH_3]_2$, substrate and ligand, and the filtrate was taken to dryness under vacuum. The pale yellow residue was then recrystallized four times from hexane to remove remaining ligand. Analysis: Found: C, 35.81; H, 5.11. $C_{20}H_{33}O_7PS_2W$ calcd.: C, 36.15; H, 5.01% (Galbraith Laboratories, Inc., Knoxville, Tennessee).

Results

Values of the pseudo first-order rate constants, k_{obs} as determined from plots of $\ln(A_t - A_{bl})$ or $\ln(A_t - A_\infty)$ vs. time for reactions of $(DTN)W(CO)_4$ with triphenylphosphine, triphenyl phosphite and alkyl phosphites in xylene at various temperatures are presented in Table 1. Plots of k_{obs} vs. [L] for reactions at 66.5°C for these substrates, and for $(\eta^1\text{-DTN})W(CO)_4[P(OCH_2)_3CCH_3]$ are exhibited in Fig. 3, while corresponding plots of $1/k_{obs}$ vs. $1/[L]$ (except for reaction of the intermediate) are shown in Fig. 4. Values of the intercepts and (intercept/slope) of the reciprocal plots (vide infra), together with the corresponding activation parameters for reaction of $(DTN)W(CO)_4$ with tri(isopropyl) phosphite in xylene are presented in Table 2.

(continued on p. 291)

TABLE 1

RATES OF REACTION OF (DTN)W(CO)$_4$ WITH PHOSPHINES AND PHOSPHITES IN XYLENE

Ligand (T, °C)	Conc'n (M)	$10^4\ k_{obs}$ (sec^{-1})	Ligand (T, °C)	Conc'n (M)	$10^4\ k_{obs}$ (sec^{-1})
P(OCH$_3$)$_3$					
(66.5)	0.134	6.12(7)	(76.5)	0.098	13.6(1)
	0.169	6.62(5)		0.126	16.4(1)
	0.248	7.52(8)		0.150	19.44(7)
	0.322	7.93(3)		0.206	25.4(2)
	0.502	8.40(4)		0.276	31.2(3)
	1.348	8.97(7)		0.338	36.5(3)
	1.643	9.5(1)		0.435	43.5(2)
P(OC$_2$H$_5$)$_3$			P(C$_6$H$_5$)$_3$		
(66.5)	0.114	6.9(1)	(66.5)	0.122	7.79(9)
	0.129	7.17(8)		0.156	8.9(3)
	0.173	8.62(7)		0.208	10.8(2)
	0.185	9.1(1)		0.245	12.9(7)
	0.277	10.8(2)		0.317	14.9(1)
	0.459	13.8(2)		0.470	17.3(1)
	0.682	14.8(3)	P(OCH$_2$)$_3$CCH$_3$		
	0.959	15.5(1)	(66.5)		
	1.098	16.15(8)	fast rxn	0.100	10.62(9)
	1.592	16.89(6)		0.127	11.9(1)
P[OCH(CH$_3$)$_2$]$_3$				0.153	13.5(1)
(56.5)	0.140	1.94(2)		0.241	17.2(4)
	0.183	2.42(3)		0.456	20.8(4)
	0.211	2.72(2)	slow rxn	0.101	2.14(1)
(56.5)	0.255	3.11(4)		0.107	1.99(5)
	0.341	3.70(3)		0.123	1.90(5)
	0.425	4.26(6)		0.160	1.96(2)
	0.663	5.73(5)		0.202	2.05(1)
	1.017	6.81(9)		0.227	2.06(1)
	1.196	7.96(3)		0.279	2.11(2)
(66.5)	0.101	4.68(1)		0.466	2.20(3)
	0.153	6.75(4)			
	0.207	8.25(4)			
	0.228	9.24(9)			
	0.302	11.4(3)			
	0.343	12.59(7)			
	0.493	15.8(2)			
	0.559	17.0(3)			

TABLE 2

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR REACTIONS OF (DTN)W(CO)$_4$ WITH PHOSPHITES AND PHOSPHINES IN XYLENE

Ligand	T (°C)	$\frac{10^4 k_3(k_6+k_7)}{k_7(k_1k_3+k_2k_5}$ (sec^{-1})	$\frac{k_3(k_6+k_7)}{k_2(k_4+k_6+k_7)}$ (M^{-1})
P(OCH$_3$)$_3$	66.5	9.8(1)	12.7(7)
P(OC$_2$H$_5$)$_3$	66.5	19.3(4)	4.71(9)
P[OCH(CH$_3$)$_2$]$_3$ [a]	56.5	11.8(5)	1.40(9)
	66.5	40.9(4)	1.28(2)
	76.5	125.(8)	1.23(9)
P(OCH$_2$)$_3$CCH$_3$	66.5	29.3(14)	5.6(5)
P(C$_6$H$_5$)$_3$	66.5	32.5(38)	2.5(4)

[a] Activation parameters. Intercepts: ΔH^* 26.3(14) kcal mol^{-1}, ΔS^* 8(4) cal deg^{-1} mol^{-1}; intercepts/slopes: $\Delta H^* = 2.1(18)$ kcal mol^{-1}, $\Delta S^* = -6(5)$ cal deg^{-1} mol^{-1}.

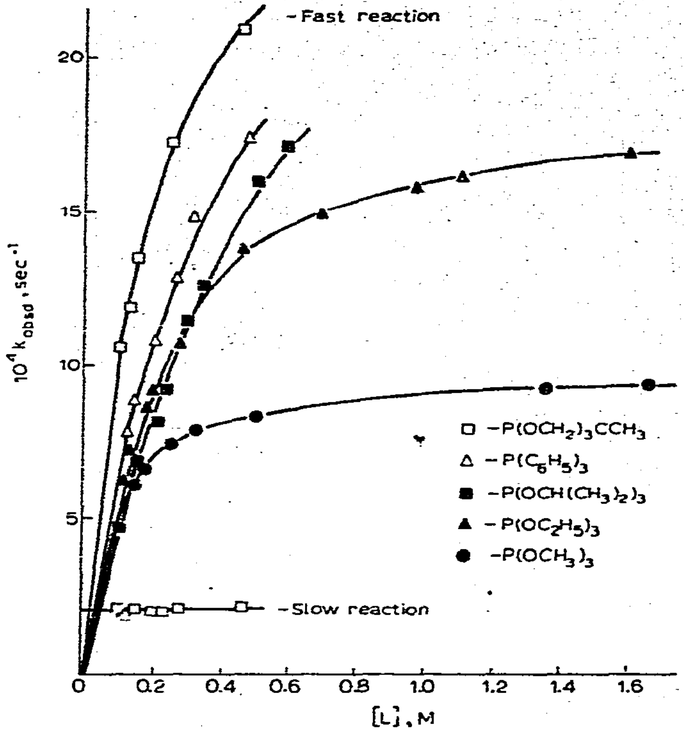


Fig. 3. Plots of k_{obs} vs. [L] for reaction of (DTN)W(CO)$_4$ with phosphines and phosphites (L) in xylene at 66.5°C.

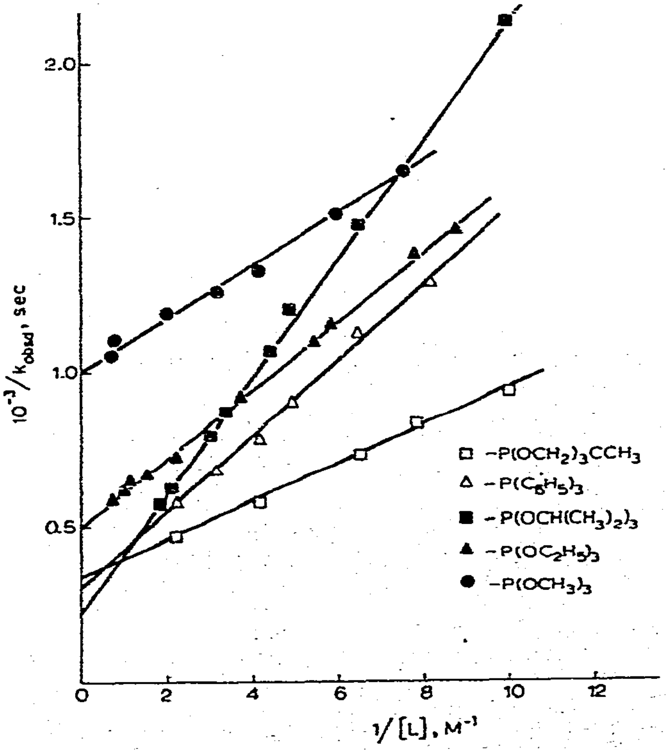
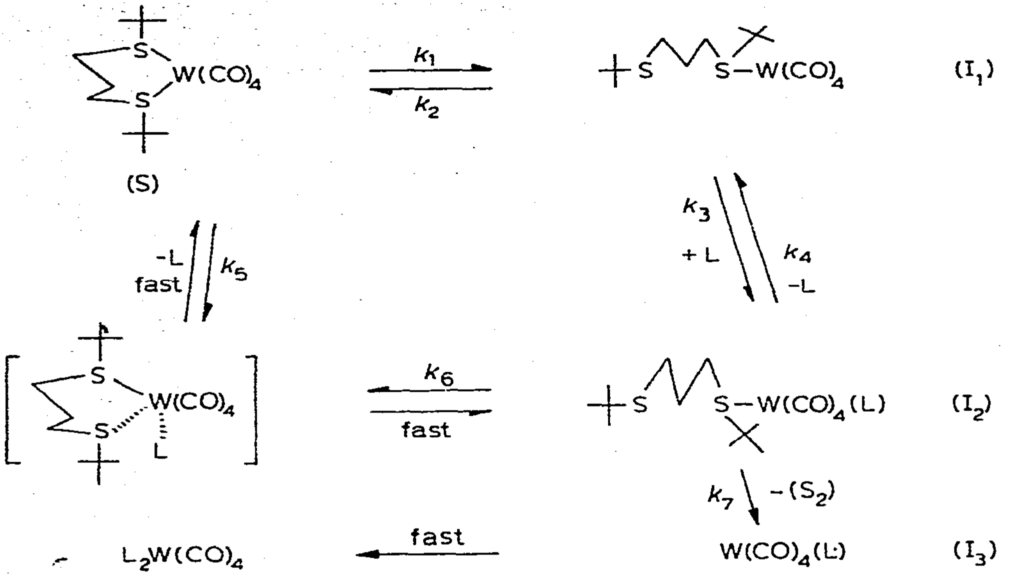


Fig. 4. Plots of $1/k_{obs}$ vs. 1/[L] for reaction of (DTN)W(CO)$_4$ with phosphines and phosphites (L) in xylene at 66.5°C.

Discussion

For reactions of (DTN)W(CO)$_4$ with phosphines and phosphites in xylene, plots of k_{obs} vs. [L] exhibit marked curvature (Fig. 3), as was observed for the analogous reactions of (DTO)W(CO)$_4$ [1,3]. However, the linear reciprocal plots of $1/k_{obs}$ vs. $1/[L]$ do not exhibit common intercepts (Fig. 4, Table 2) [2], as was observed for reactions of (DTO)W(CO)$_4$ [3] and are expected on the basis of mechanism 2. In the absence of any evidence for a ligand—substrate interaction which would facilitate ring-opening [2], and on the basis of recent results which have noted ring-reclosure in six-coordinate metal carbonyls containing *monohapto* bidentate ligands coordinating through nitrogen [9], sulfur [10], or phosphorus [11], mechanism 5 is proposed to explain these observations.



(5)

Employing the assumption of steady-state concentrations of 5-I$_1$ and 5-I$_2$, the rate law (eq. 6) is obtained. Assuming $k_1 >> k_5$, this rate law is of the same

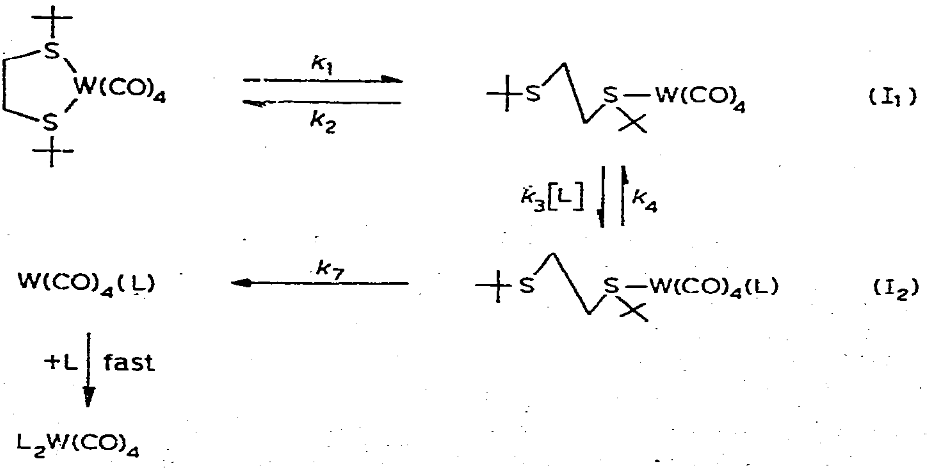
$$-d[S]/dt = \frac{k_7(k_1k_3 + k_2k_5)[S][L] + k_3k_5[S][L]^2}{k_2(k_4 + k_6 + k_7) + k_3(k_6 + k_7)[L]} \qquad (6)$$

form as that obtained from mechanism 2 through assumption of a steady-state concentration of 2-I$_1$, and thus the "curved" plots of k_{obs} vs. [L], are expected, and observed, for ligand-exchange reactions of both substrates, as are linear "reciprocal plots" of $1/k_{obs}$ vs. $1/[L]$ (eq. 4). However, in contrast to the expected and observed independence of the intercepts of the reciprocal plots for 2 ($1/k_1$), [3], the intercepts for the reciprocal plots for 5 are $k_3(k_6 + k_7)/k_7(k_1k_3 + k_2k_5)$, which should vary with the identity of L, since the rate constants k_3, k_6 and k_7 involve either attack by L or transformation of intermediate 5-I$_2$, which contains coordinated L. Thus, mechanism 5 predicts non-common intercepts of the reciprocal plots, as is observed.

The complex nature of the values of the slopes ($k_2(k_4 + k_6 + k_7)/k_7(k_1k_3 + k_2k_5)$) and intercepts of the "reciprocal plots" of $1/k_{obs}$ vs. $1/[L]$ precludes a detailed interpretation of the manner in which they vary as a function of the identity of L. Several qualitative conclusions can, however, be drawn. Since it is observed experimentally that $k_1 >> k_5$, the principle of microscopic reversibility dictates that $k_4 >> k_6$. It can also be shown that $k_6 \sim k_7$ where non-common intercepts of the reciprocal plots are observed (vide infra). It follows that the values for (intercept/slope) of the reciprocal plots (Table 2) are $1.23 < k_3(k_6 + k_7)/k_2(k_4 + k_6 + k_7) < 12.7$ at 66.5°C. Thus, since $k_4 >> k_6 \sim k_7$, $k_3(k_6 + k_7)/k_2(k_4 + k_6 + k_7) \sim k_3(k_6 + k_7)/k_2k_4$, and $k_3 >> k_2$. This observation is to be contrasted to results which show that five-coordinate intermediates derived from octahedral metal carbonyls possess very limited abilities to discriminate among monodentate nucleophiles [12—14]. Thus ring-reclosure is inhibited relative to the ability of free nucleophiles to interact with 5-I_1, an observation which may be a consequence of the constraint placed upon the potentially-coordinating sulfur atom by the trimethylene bridge in the bidentate ligand.

Based upon the relative magnitudes of the rate constants as adduced above, the intercepts of the reciprocal plots, $k_3(k_3 + k_7)/k_7(k_1k_3 + k_2k_5) \sim k_6/k_1k_7 + 1/k_1$. Thus higher values for the intercepts support greater ratios k_6/k_7, which vary $P[OCH(CH_3)_2]_3 < P(C_6H_5)_3 \sim P(OCH_2)_3CCH_3 < P(OC_2H_5)_3 < P(OCH_3)_3$. While these values depend both upon the ease of ring-reclosure to afford the substrate and the ease of W—S bond-breaking, they can be seen to be related to some degree to the steric demands imposed by L in 5-I_2.

The mechanistic results have implications to the mechanism of ligand-exchange for $(DTO)W(CO)_4$ with L [1,3], which proceeds at temperatures some 30—35°C higher for comparable rates than does ligand-exchange in $(DTN)W(CO)_4$. In view of the great similarity of intermediates 2-I_2 and 5-I_2 and the fact that k_4 and k_7 both govern dissociative processes which should exhibit similar entropies of activation, it is highly probable that k_4 also is important in the mechanism of ligand-exchange for $(DTO)W(CO)_4$, and that there also, $k_4 >> k_7$. Thus the preferred mechanism is not 2, but rather, 7.



(7)

The steady-state rate law for 7 is;

$$-d[S]/dt = k_1k_3k_7[S][L]/(k_2(k_4 + k_7) + k_3k_7[L]) \qquad (8)$$

This rate law affords the "reciprocal relationship", eq. 9, which encompasses all

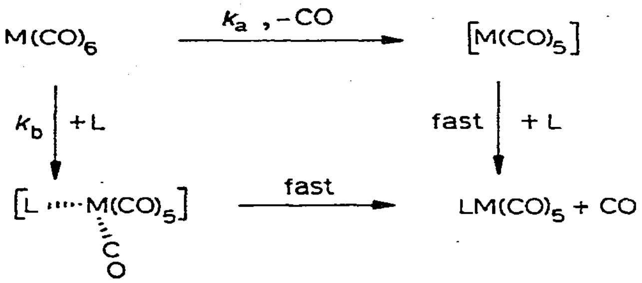
$$1/k_{obs} = 1/k_1 + k_2(k_4 + k_7)/k_1k_3k_7[L], \qquad (9)$$

of the qualitative features of the observed rate behavior, e.g., linear reciprocal plots with common intercepts as a function of the identity of L.

However, values of (intercept/slope) now become $k_3k_7/k_2(k_4 + k_7)$ rather than k_3/k_2 (eq. 4), and, since k_3, k_4 and k_7 all should vary with the identity of L, the values of (intercept/slope) do not reflect the "competition ratios" of attack at 2-I_1 by L vs. ring-reclosure, as claimed [3].

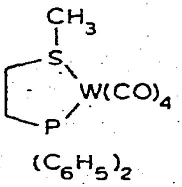
It thus is evident that discussions of observations which were based upon the assumed * mechanistic simplicity of 2 are most probably without basis.

It is also worth mentioning that mechanism 5, which envisions two competing reaction paths, one involving dissociation, the other a concerted process, is consistent with other proposed mechanisms of ligand-exchange in ochabedral metal carbonyls, in which analogous competitive pathways (e.g. 10) are often invoked [15].

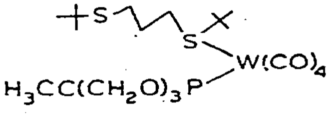


(10)

The operation of a ring-opening mechanism as shown in 5 is also strongly supported by the isolation of an intermediate of the type 5-I_2, *cis*-(η^1-DTN)W(CO)$_4$-[P(OCH$_2$)$_3$CCH$_3$]. The carbonyl stretching spectrum of this species (Table 3) exhibits absorptions characteristic of C_{2v} local symmetry of the four carbonyls (*cis*-orientation of the two substituents) [16]. Additionally, band positions, when compared to those exhibited by the substrate, product and a "model" complex containing both coordinating P(III) and S(II), *cis*-(SPE)W(CO)$_4$ (SPE = 1-(methylthio)-2-(diphenylphosphino)ethane (A) [17], provide strong evidence that the intermediate is (B) (Table 3).



(A)



(B)

The observation that both *trans* and *cis*-[P(C$_6$H$_5$)$_3$]$_2$W(CO)$_4$ are formed through reaction of triphenylphosphine with (DTN)W(CO)$_4$ and that plots of ln. ($A_t - A_\infty$) vs. t for reaction of (DTN)W(CO)$_4$ with P(C$_6$H$_5$)$_3$ are linear over

---

* "Essentia non sunt multiplicanda praeter necessitatem" — Venerabilis Inceptor.

TABLE 3

CARBONYL STRETCHING SPECTRA FOR cis-$(\eta^1$-DTN)W(CO)$_4$[P(OCH$_2$)$_3$CCH$_3$] AND RELATED COMPLEXES

Complex	ν(CO) (cm^{-1}) [a]
cis-W(CO)$_4$[P(OCH$_2$)$_3$CCH$_3$]$_2$ [b]	2045m, 1950(sh), 1924vs
cis-$(\eta^1$-DTN)W(CO)$_4$[P(OCH$_2$)$_3$CCH$_3$] [c]	2031m, 1921s, 1905vs, 1882vs
cis-CH$_3$SC$_2$H$_4$P(C$_6$H$_5$)$_2$W(CO)$_4$ [d]	2023m, 1914s, 1897s, 1871ms
cis-(DTN)W(CO)$_4$ [e]	2019m, 1902vs, 1883s, 1848ms

[a] Relative band intensities: s = strong; m = medium; v = very; sh = shoulder. [b] Ref. 4, CH$_2$Cl$_2$ solution. [c] This work, CHCl$_3$ solvent. [d] Ref. 17, CHCl$_3$ solution. [e] Ref. 2, CHCl$_3$ solution.

two or more half lives support fluxionality of intermediates such as 5-I$_1$ on the time-scale of the ligand-substitution process. The results parallel those observed for reaction of (DTO)W(CO)$_4$ with this nucleophile [3], for which they were discussed in detail. Similar results have been noted for reaction of (tmpa)W(CO)$_4$ (tmpa = N,N,N',N'-tetramethyl-1,3-diaminopropane) with triphenylphosphine [18]. If intermediate 5-I$_1$, which is probably square-pyramidal *, is indeed fluxional (eq. 11) the observation that the isolated intermediate B exhibits exclusively cis geometry suggests the more stable five-coordinate species to be that in which the substituent is in the equatorial plane of the square pyramid, D. Unless this is the case, 5-I$_2$ would be expected to exhibit $trans$-stereochemistry, since on steric grounds interaction of P(OCH$_2$)$_3$CCH$_3$ should be more probable with the axially-substituted species, C. Thus, the equatorially-substituted species D must be thermodynamically more stable, in agreement with the "site preference" model of reactivity via carbonyl dissociation in substituted octahedral metal carbonyls advanced by Atwood and Brown [19].

(C) (D) (11)

Rate data for the formation and disappearance of cis-$(\eta^1$-DTN)W(CO)$_4$[P(OCH$_2$)$_3$CCH$_3$] offer additional support for the operation of mechanism 5. The plot of k_{obs} vs. [P(OCH$_2$)$_3$CCH$_3$] (Fig. 3) exhibits curvature, and the corresponding reciprocal plot (Fig. 4) is linear, as expected if the isolated intermediate is formed via the ring-opening mechanism.

It is, however, evident that the presence of significant concentrations of this intermediate during the course of the reaction invalidates the usual steady-state assumption, that $-d[5\text{-}I_2]/dt = 0$. Through the assumption that $-d[5\text{-}I_2]/dt$ may be significant, the more general rate law, eq. 12, is applicable.

---

* Evidence which indicates that sixteen valence electron, pentacoordinate species such as 5-I$_1$ exhibit square-pyramidal geometry has been cited: see ref. 18.

$$-\mathrm{d}[\mathrm{S}]/\mathrm{d}t = \frac{k_7\{(k_1k_3 + k_2k_5)[\mathrm{S}][\mathrm{L}] + k_3k_5[\mathrm{S}][\mathrm{L}]^2\} + (k_2k_4 + k_2k_6 + k_3k_6)[\mathrm{L}]\mathrm{d}[\mathrm{I}_2]/\mathrm{d}t}{k_2(k_4 + k_6 + k_7) + k_3(k_6 + k_7)[\mathrm{L}]} \tag{12}$$

This rate law imposes the less stringent requirement, (eq. 13) as the steady-state

$$k_1k_3[\mathrm{S}][\mathrm{L}] >> (k_2k_4 + k_3k_6)[\mathrm{L}]\ \mathrm{d}[\mathrm{I}_2]/\mathrm{d}t \tag{13}$$

criterion. The observation (Fig. 4) that the plot of $1/k_{\mathrm{obs}}$ vs. $1/[\mathrm{L}]$ is linear under the conditions employed indicates that the requirement 13 is met in this system.

Data for the decomposition of 5-I_2 to afford the observed reaction product were also obtained, and the plot of k_{obs} vs. $[\mathrm{P(OCH_2)_3CCH_3}]$ indicates that this process obeys the rate law, eq. 14, confirming, as is a requirement of the overall

$$-\mathrm{d}[(\eta^1\text{-DTN})\mathrm{W(CO)_4(P(OCH_2)_3CCH_3)}]/\mathrm{d}t = k[(\eta^1\text{-DTN})\mathrm{W(CO)_4(P(OCH_2)_3CCH_3)}] \tag{14}$$

mechanism 5, that conversion of the intermediate to product proceeds via a unimolecular process.

The observation that an intermediate, $(\eta^1\text{-DTN})\mathrm{W(CO)_4[P(OCH_2)_3CCH_3]}$, was isolated, but that no other intermediate of the reaction of either $\mathrm{(DTO)W(CO)_4}$ [3] or $\mathrm{(DTN)W(CO)_4}$ with any other L exhibited stability sufficient for observation, requires comment. If it is assumed that the intermediates of DTO 7-I_2 and DTN 5-I_2 exhibit about the same stabilities [2], the failure to observe a DTO intermediate may be attributed to the (35° C) higher reaction temperature required for the ligand-substitution process. At the higher temperature a DTO-containing intermediate might not persist long enough to be observed.

In view of early reports of the relative instability of simple substitution products containing monodentate sulfur(II) ligands [20,21], the isolation of the intermediate might also seem surprising. Recently, however, it has been found that substituted metal carbonyls containing *monohapto* bidentate sulfur ligands exhibit significantly greater stabilities [10,22]. The enhanced stability has been attributed in part to steric protection afforded the M—S linkage by the bulky bidentate ligands [22].

It is not surprising that the "constrained phosphite" should form a complex of unusual stability. In a number of instances, phosphites exhibiting the "caged" structure have been found to form coordination compounds not formed with similar but non-"caged" phosphites [23]. Moreover, the anomalously high dipole moment exhibited by the "constrained phosphite" [24], and chemical shift and coupling constant data [23], indicate that a change in hybridization occurs at phosphorus upon constraint which increases the "s" character of the lone pair of phosphorus, resulting in a more stable P—W bond. It is also possible that the steric properties and rigidity of $\mathrm{P(OCH_2)_3CCH_3}$ contribute to the stability of its complexes. The unusual ability of caged phosphites to stabilize species such as $(\eta^1\text{-DTN})\mathrm{W(CO)_4[P(OCH_2)_3CCH_3]}$ is further indicated by the preparation of the stable intermediates, $(\eta^1\text{-tmpa})\mathrm{W(CO)_4(L)}$ (L = $\mathrm{P(OCH_2)_3CCH_3}$ and 1-phospha-2,8,9-trioxaademantane), both of which contain a "caged" phosphite ligand; in no instance was an intermediate containing a non-"caged" phosphite observed [7].

Other questions concerning the contrasting behavior of the (DTO)W(CO)$_4$ and (DTN)W(CO)$_4$ complexes, which contain five- and six-membered chelate rings, e.g., differences in mechanism, are of interest, but a discussion of such questions is best deferred until the results of structural studies for both substrates, being conducted in collaboration with Prof. Ivan Bernal, have been completed.

Acknowledgements

The support of this research by the Robert A. Welch Foundation, under Grant #B-434, and the North Texas State University Faculty Research Fund is gratefully acknowledged. We thank Prof. Martin Schwartz for fruitful discussions and a referee for a key comment.

References

1 G.R. Dobson, Inorg. Chem., 8 (1969) 90.
2 G.R. Dobson and G.C. Faber, Inorg. Chim. Acta, 4 (1970) 87.
3 L.D. Schultz and G.R. Dobson, J. Organometal. Chem., 124 (1977) 19.
4 A. Vanderbroucke, Jr., D.G. Hendricker, R.E. McCarley and J.G. Verkade, Inorg. Chem., 7 (1968) 825.
5 R. Mathieu and R. Poilblanc, C.R. Acad. Sci. Paris, Sér. C, 264 (1967) 1053.
6 G.C. Mather and A. Pidcock, J. Chem. Soc., A (1970) 1226.
7 G.R. Dobson and A. Moradi-Araghi, manuscript in preparation.
8 D.J. Darensbourg, personal communication, 1976.
9 B.J. McKerley, G.C. Faber and G.R. Dobson, Inorg. Chem., 14 (1975) 2275.
10 J.A. Connor and G.A. Hudson, J. Chem. Soc. Dalton, (1975) 1025.
11 J.A. Connor, J.P. Day, E.M. Jones and G.K. McEwen, J. Chem. Soc. Dalton, (1973) 347.
12 C.L. Hyde and D.J. Darensbourg, Inorg. Chem., 12 (1973) 1286.
13 W.D. Covey and T.L. Brown, Inorg. Chem., 12 (1973) 2820.
14 J.M. Kelly, D.V. Bent, H. Hermann, D. Schulte-Frohlinde and E. Koerner von Gustorf, J. Organometal. Chem., 69 (1974) 259.
15 G.R. Dobson, Acc. Chem. Res., 8 (1976) 300.
16 L.E. Orgel, Inorg. Chem., 1 (1962) 25.
17 E.P. Ross and G.R. Dobson, J. Inorg. Nucl. Chem., 30 (1968) 2363.
18 D.J. Darensbourg, G.R. Dobson and A. Moradi-Araghi, J. Organometal. Chem., 116 (1976) C17.
19 J.D. Atwood and T.L. Brown, J. Amer. Chem. Soc., 98 (1976) 3160.
20 F.A. Cotton and F. Zingales, Inorg. Chem., 1 (1962) 145.
21 G. Bouquet and M. Bigorgne, Bull. Soc. Chim. Fr. (1962) 433.
22 E.W. Ainscough, E.J. Birch and A.M. Brodie, Inorg. Chim. Acta, 20 (1976) 187; E.W. Ainscough, personal communication, 1976.
23 J.G. Verkade and T.S. Piper, Inorg. Chem., 1 (1962) 453.
24 T.L. Brown, J.G. Verkade and T.S. Piper, J. Phys. Chem., 65 (1961) 2051.