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OCTAHEDRAL METAL CARBONYLS

XXXIX [*] A REINVESTIGATION OF THE KINETICS AND MECHANISM OF LIGAND-EXCHANGE IN (2,2,7,7-TETRAMETHYL-3,6-DITHIAOCTANE)-TETRACARBONYLTUNGSTEN(0)

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Summary

A reinvestigation of the kinetics and mechanism of ligand-exchange reactions of (2,2,7,7-tetramethyl-3,6-dithiaoctane)tetracarbonyltungsten(0), (DTO)W(CO)$_4$, with alkyl and aryl phosphites and phosphines (L) to afford *trans*- and *cis*-L$_2$W(CO)$_4$ products has been completed Data support a "simple" ring-opening mechanism involving reversible dissociation of one end of the bidentate DTO ligand, and competition for the resulting five coordinate intermediate between ring-reclosure and attack by L. Comparison of "competition ratios" between attack by L and ring reclosure in this intermediate, probably fluxional, with abilities of other metal carbonyls and intermediates to discriminate among the same nucleophiles provides evidence that reactions of octahedral metal carbonyls with Lewis bases via the associative path are best described as a "dissociative interchange" (I_d) process. Activation parameters indicate, however, that the intermediate exhibits significant ability to discriminate between ring-reclosure and reaction with L

Introduction

Studies of the kinetics and mechanism of reactions of tetracarbonyltungsten complexes containing the bidentate sulfur-containing ligands (S$_2$), 2,2,7,7-tetra-

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methyl-3,6-dithiaoctane (DTO) [1] and 2,2,8,8-tetramethyl-3,7-dithianonane (DTN) [2] (I and II), respectively, with phosphorus-containing Lewis bases (L) have been reported These reactions involve exclusive replacement of S_2 (eq 1)


(I)


(II)

and the kinetic results obtained have been interpreted in terms of a ring-opening mechanism (eq 2) [1,2]

$$(S_2)W(CO)_4 + 2\,L \rightarrow \textit{cis-}\text{ and }\textit{trans-}L_2W(CO)_4 + S_2 \tag{1}$$

$$\begin{tikzcd} I + (S_2)W(CO)_4 \arrow[r, shift left, "k_1"] & \underset{(III)}{[\,S{-}S{-}W(CO)_4\,]} \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_2 + L"] & (2a) \\ S_2 + L_2W(CO)_4 & \underset{(IV)}{[\,S{-}S{-}W(CO)_4(L)\,]} \arrow[l, "fast", "other\ steps"'] & (2b) \end{tikzcd}$$

Through the assumption of a steady-state concentration of the intermediate (III the rate law 3 was proposed to explain the rate data Plots of k_{obsd}, the pseudo-

$$-d[(S_2)W(CO)_4]/dt = k_1k_2[(S_2)W(CO)_4][L]/(k_{-1} + k_2[L]) \tag{3}$$

first-order rate constants (excess of L) vs. [L] were observed to exhibit marked curvature, as expected from eq 3, for $k_{-1} \sim k_2[L]$ Rearrangement of eq. 3 in terms of k_{obsd} afforded eq 4, which predicted linear "reciprocal plots" of $1/k_{obsd}$

$$1/k_{obsd} = 1/k_1 + k_{-1}/k_1k_2\,[L], \tag{4}$$

vs 1/[L] Such linear plots were obtained for reactions of both (DTO)W(CO)$_4$ and (DTN)W(CO)$_4$ [2] For the latter, however, the reciprocal plots had non-common intercepts as a function of L, inconsistent with a term ($1/k_1$, eq 4) whose magnitude would be expected to be invariant to the identity of L The anomaly was attributed to a ligand-substrate interaction which facilated ring-opening, but no spectroscopic evidence for such an interaction was observed [2] For ligand-exchange reactions of (DTO)W(CO)$_4$, data were obtained for only tw ligands, $P(OC_2H_5)_3$ and $P[OCH(CH_3)_2]_3$, and while the values of k_1 agreed closel the data were insufficient to permit a definite conclusion as to whether or not the b havior of the two substrates differed Thus, to obtain a more detailed mechanist picture it was necessary to investigate the rate behavior for (DTO)W(CO)$_4$ in greater depth, over a wider range of nucleophiles The results of that investigation are the subject of this report.

Experimental

General Infrared spectra were obtained employing a Perkin—Elmer Model 62 infrared spectrophotometer, and were calibrated against a band of water vapor at 1869.4 cm^{-1} [3] NMR spectra were obtained using a Jeolco Model PS-100 NMR spectrometer

Preparation and purification of materials 2,2,7,7-Tetramethyl-3,6-dithiaoctane was obtained from Phillips Petroleum Co , Special Products Division, Bartlesville, Okla , and was found to be suitable for use without further purification (NMR spectrum) The substrate, (DTO)W(CO)$_4$, was prepared and purified as described in the literature [1] Technical grade xylenes were obtained from Scientific Products, Inc , were purified by fractional distillation over sodium (138—140°C) and were stored in a brown bottle under nitrogen prior to use. Decalin was shaken with concentrated sulfuric acid, washed with water until neutral, allowed to stand overnight over anhydrous CaCl$_2$, and vacuum distilled over sodium (nitrogen bleed) at 78°C, 19 torr

While trialkyl and triaryl phosphites have often been used 'as obtained" or with minimal precautions as to purity, it was found necessary to purify rigorously such nucleophiles to insure reproducibility of results Trimethyl phosphite (Aldrich) was fractionally-distilled over sodium under nitrogen Triisopropyl phosphite (Aldrich) was fractionally-distilled over sodium under reduced pressure (60—62°C/10 torr, nitrogen bleed) The "constrained phosphite", 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2 2 2]octane, P(OCH$_2$)$_3$CCH$_3$ was prepared by the method of Verkade et al [4], and was purified by vacuum-sublimation (five times, 50°C/0 2 torr) Triphenyl phosphite (Aldrich and Eastman) was fractionally distilled (160°C/0 1 torr) over a small quantity of sodium, and was then again fractionally distilled (no sodium, four times) until the odor of phenol could no longer be detected in the distillate The purity of each liquid ligand was then assayed employing a Finnigan Corporation Model 3200 gas chromatograph/mass spectrometer, no evidence for any impurity in any ligand was observed The liquids were stored in foil-wrapped flasks under nitrogen, and were used within one week of the final distillation Triphenylphosphine (Cincinnati Milachron, Reading, Ohio) was recrystallized from absolute ethanol (four times), was dried under high vacuum, stored under nitrogen in a foil-wrapped flask and was then redried under vacuum immediately prior to use Kinetic runs were found to be reproducible among different batches of a given ligand

Determination of reaction rates Reaction rates were monitored employing a Beckman DU-2 direct-reading, or Beckman DB spectrophotometer through observation of a substrate band at 425 nm in the visible region The substrate was found to obey the Lambert—Beer Law over the concentration range monitored The absorbance at infinite time (t_∞) differed from that of a solvent-ligand blank by less than one per cent of the initial absorbance (A_0) for all ligands except triphenylphosphine, for those ligands the solvent-ligand blank was thus employed in lieu of a value of A_∞ Plots of ln ($A_t - A_{bl}$) vs. time were linear to at least two half-lives For triphenylphosphine, appreciable absorption at t_∞ was noted as a consequence of the formation of substantial quantities of yellow *trans*-[(C$_6$H$_5$)$_5$P]$_2$W(CO)$_4$ as a reaction product Therefore, a value for A_∞ was obtained for each run for this ligand after at least seven half-lives Plots of ln ($A_t - A_\infty$) vs. t employing these A_∞ values were linear to at least two half-lives At least a forty-fold excess of ligand was employed to insure pseudo first-order reaction conditions. Sampling techniques, and other details of the experimental procedures, have been given [1,2].

Data were treated employing a linear least-squares computer program utilizing an IBM 360 Model 50 computer. Limits of error (uncertainty of last digit(s) for reported value) are one standard deviation for values of k_{obsd}. Cited deviations of k_1, k_2/k_{-1} and activation parameters are based upon the standard deviations of the slopes and intercepts of the "reciprocal plots" (eq. 4).

Identification of reaction products. Infrared spectra of solutions at t_∞ were compared to those for the authentic *trans*- and *cis*-$L_2W(CO)_4$ complexes [6–11]. In each case the spectrum revealed reaction products to be those disubstituted species; in no instance was there evidence for the formation of a trisubstituted reaction product.

Results

Values of k_{obsd} as determined from plots of ln $(A_t - A_{bl})$ or ln $(A_t - A_\infty)$ vs. time for reactions of (DTO)W(CO)$_4$ with the five ligands in xylene and with $P[OCH(CH_3)_2]_3$ in decalin at 89.9–109.9°C are presented in Table 1. Plots of

TABLE 1

RATES OF REACTION OF (DTO)W(CO)$_4$ WITH PHOSPHORUS-CONTAINING LIGANDS

Ligand	Temperature (°C)	[L] (*M*)	$10^4 k_{obsd}$ (sec^{-1})
$P(OCH_3)_3$ [a]	99.9	0.155	3.42(1)
		0.183	3.62(1)
		0.208	4.35(1)
		0.270	5.20(1)
		0.347	6.49(5)
		0.541	8.67(4)
		1.041	13.28(4)
$P[OCH(CH_3)_2]_3$ [a]	89.9	0.491	1.65(1)
		0.566	1.87(1)
		0.663	2.10(1)
		0.729	2.22(1)
		0.849	2.51(1)
		1.199	3.35(2)
		1.296	3.48(2)
		1.472	3.61(2)
	99.9	0.173	2.04(1)
		0.266	2.97(1)
		0.340	3.70(2)
		0.428	4.39(2)
		0.512	5.20(1)
		0.590	6.60(2)
		0.823	7.31(3)
		1.215	9.7(1)
	109.9	0.179	6.06(4)
		0.197	6.71(3)
		0.246	7.84(7)
		0.269	8.40(1)
		0.312	9.74(2)
		0.386	11.1(1)
		0.468	13.09(6)
		0.590	16.55(8)
		0.808	19.01(1)

TABLE 1 (continued)

Ligand	Temperature (°C)	[L] (M)	$10^4 k_{obsd}$ sec^{-1}
		1 280	24 7(1)
		1 702	30 3(2)
$P(C_6H_5)_3$ [a]	99 9	0 182	2 75(5)
		0 243	3 32(4)
		0 278	4 09(2)
		0 326	4 33(4)
		0 392	5 16(9)
		0 967	9 25(8)
$P(OCH_2)_3CCH_3$ [a]	99 9	0 138	4 89(2)
		0 190	6 07(7)
		0 227	6 91(4)
		0 323	8 43(8)
		0 406	9 86(7)
		0 527	12 7(2)
		0 710	12 97(5)
$P(OC_6H_5)_3$ [a]	99 9	0 125	1 15(2)
		0 167	1 54(1)
		0 245	2 21(2)
		0 303	2 61(1)
		0 383	3 40(6)
		0 399	3 53(2)
		0 432	3 56(6)
		0 752	6 1(1)
		1 100	6 8(2)
		1 798	8 5(2)
$P[OCH(CH_3)_2]_3$ [b]	89 9	0 170	1 410(3)
		0 263	1 966(6)
		0 439	2 99(1)
		0 629	3 71(1)
		0 864	4 25(2)
		1 203	5 30(6)
		1 369	5 54(1)
	99 9	0 109	2 71(1)
		0 144	3 43(2)
		0 181	4 02(2)
		0 227	4 8(1)
		0 399	7.16(3)
		0 560	8 8(1)
		0 884	11 5(1)
		1 365	14 3(2)
	109 9	0 088	5 65(8)
		0 149	8 0(1)
		0 227	12 3(1)
		0 353	16 5(1)
		0 574	22 1(3)
		0 643	22 9(3)

[a] Xylene solvent. [b] Decalin solvent.

k_{obsd} vs. [L] for reactions at 99.9°C in xylene are illustrated in Fig. 1, while the corresponding plots of $1/k_{obsd}$ vs. $1/[L]$ are shown in Fig. 2. Values of the rate constants k_1 and k_2/k_{-1} (eq. 3), together with activation parameters for reaction of $(DTO)W(CO)_4$ with triisopropyl phosphite in xylene and decalin are presented in Table 2.

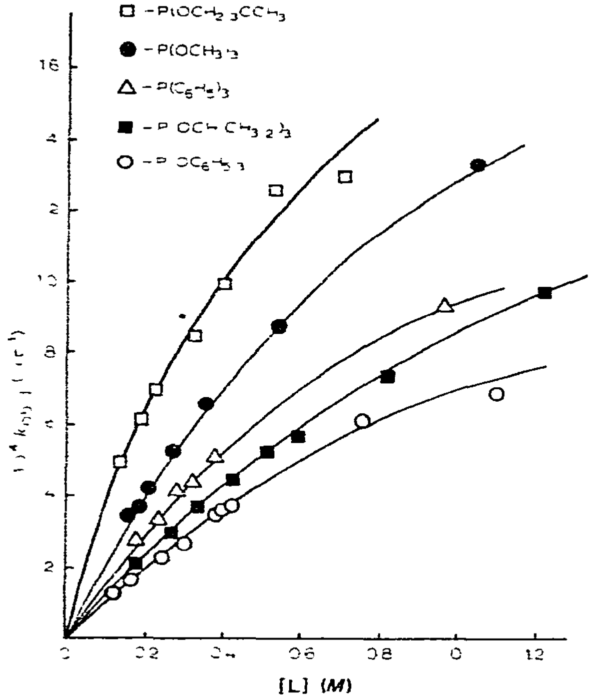

Fig 1 Plot of k_{obsd} vs [L] for reactions of various phosphorus ligands (L) with (DTO)W(CO)$_4$ in xylene at 99 9°C

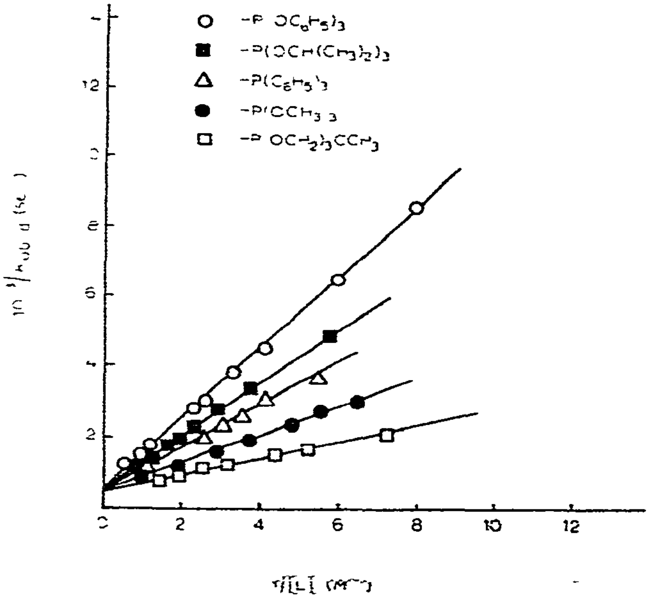

Fig. 2 Plot of $1/k_{obsd}$ vs. 1/[L] for reactions of (DTO)W(CO)$_4$ with various phosphorus ligands (L) in xylene at 99.9°C.

TABLE 2

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR REACTIONS OF (DTO)W(CO)$_4$ WITH PHOSPHORUS-CONTAINING LIGANDS

Ligand	Temperature (°C)	$10^4 k_1$ [a] (sec^{-1})	k_2/k_{-1} [a] (M)
$P(OCH_3)_3$	99.9	26.2(48)	0.93(20)
$P(OC_2H_5)_3$	99.9	27.5 [b]	0.79 [b]
$P[OCH(CH_3)_2]_3$ [c]	89.9	9.8(7)	0.41(4)
		9.3(4) [d]	1.04(6) [d]
	99.9	23.2(11)	0.56(3)
		20.2(11) [d]	1.41(9) [d]
	109.9	51.0(36)	0.75(7)
		45.6(10) [d]	1.60(5) [d]
$P(OC_6H_5)_3$	99.9	23.8(40)	0.41(7)
$P(C_6H_5)_3$	99.9	20.4(46)	0.85(25)
$P(OCH_2)_3CCH_3$	99.9	22.6(19)	1.97(25)

[a] Xylene solvent unless otherwise noted. [b] Ref. 3; the values of k_1 given in that reference are one-tenth of the true values. [c] Activation parameters: xylene $\Delta H_1^{\ddagger} = 22.2(27)$ kcal mol^{-1}, $\Delta S_1^{\ddagger} = -14(8)$ cal deg^{-1} mol^{-1}, $\Delta H_2^{\ddagger} - \Delta H_{-1}^{\ddagger} = 8.2(34)$ kcal mol^{-1}, $\Delta S_2^{\ddagger} - \Delta S_{-1}^{\ddagger} = 22(9)$ cal deg^{-1} mol^{-1}; Decalin $\Delta H_1^{\ddagger} = 21.3(19)$ kcal mol^{-1}, $\Delta S_1^{\ddagger} = -14(5)$ cal deg^{-1} mol^{-1}, $\Delta H_2^{\ddagger} - \Delta H_{-1}^{\ddagger} = 5.1(24)$ kcal mol^{-1}, $\Delta S_2^{\ddagger} - \Delta S_{-1}^{\ddagger} = 20(9)$ cal deg^{-1} mol^{-1}. [d] Decalin solvent.

Discussion

Plots of k_{obsd} vs. [L] for reaction of (DTO)W(CO)$_4$ with all ligands studied exhibit curvature (Fig. 1), suggestive of a complex reaction mechanism. The linear reciprocal plots of $1/k_{obsd}$ vs. $1/[L]$, consistent with mechanism 2, have a common intercept within experimental error (Table 2). The coincidence of these intercepts is expected in that their values ($1/k_1$) should be independent of the identity of the nucleophile. The rate data thus are fully consistent with mechanism 2 *.

For reaction of triphenylphosphine with (DTO)W(CO)$_4$, the substrate and the *trans*-[$(C_6H_5)_3P]_2W(CO)_4$ product absorb at 425 nm, and a second reaction product, *cis*-[$(C_6H_5)_3P]_2W(CO)_4$, is also observed in the reaction solution at infinite time. Under such circumstances, plots of ln $(A_t - A_\infty)$ vs. time should not be linear unless the ratio of the concentrations of the products is constant over the course of the reaction. That such linear plots are in fact observed over two or more half-lives strongly suggests that the ratio of reaction products, [*cis*]/[*trans*] indeed remains constant over the reaction's course. Such a constant ratio is most likely to arise as a result of fluxionality (rapid on the time-scale of the overall ligand-substitution process of a five-coordinate intermediate III and/or [$(C_6H_5)_3PW(CO)_4$], formed through dissociation of DTO from IV. A similar explanation has been advanced to account for the product stereochemistry observed for reaction of triphenylphosphine with $(C_6H_5)_3E$—Mn(CO)$_5$ (E = Ge, Sn) [12]. Detailed supporting evidence for fluxionality of species such as [$(C_6H_5)_3PW(CO)_4$] under still milder reaction conditions has also been reported for a related system [13].

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[*] This behavior may be contrasted to that for reaction of (DTN)W(CO)$_4$ with phosphines and phosphites, for which it has been shown, and confirmed through a much more extensive study [31] that non-common intercepts of reciprocal plots, indicative of a more complex mechanism, are obtained.

The strong evidence presented for the very probable operation of the simple ring-opening mechanism 2 in these systems under the non-limiting conditions, $k_{-1} \sim k_2$ [L] permits the calculation of the "competition ratios", k_2/k_{-1}, between attack at III and ring-reclosure. These ratios can provide more detailed insight into the nature of the intermediate and of the reaction mechanism. Since it is reasonable to presume that the rate of ring-reclosure (governed by k_{-1}) should be independent of the identity of L, the ratios should reflect the ability of III to discriminate among the various L.

Table 3 presents data which bear on the abilities of III, other intermediates and coordinatively-saturated metal carbonyl substrates to "discriminate" among various nucleophiles. Based on Hammond's postulate [14], this ability should be related to the extent of bond-making in the transition state leading to product formation.* For metal carbonyls, substrates of lower coordination number generally exhibit the greater discriminating abilities [15] as is indicated by the data (Table 3) for four-coordinate $Co(CO)_3NO$ [16], and as might be expected, based upon steric considerations. It is of interest to note that the discriminating abilities of the intermediates, $[(C_6H_5)_3PMo(CO)_4]$ [17] and $[(h^1\text{-}DTO)W(CO)_4]$ do not differ too greatly from those of the hexacarbonyls themselves. Based upon limited data, $[Mo(CO)_5]$ [18] may be less discriminating, although flash photolysis studies have shown the rates of combination of a variety of basic solvents with $[Cr(CO)_5]$ to vary some twenty-fold [19]. These data may suggest that "nucleophilic attack" at the hexacarbonyls may not be too different from the bimolecular interaction of L with the five-coordinate intermediates themselves. Thus, as discussed by Covey and Brown for ligand-exchange reactions of $(amine)Mo(CO)_5$ complexes [18], "associative" reactions of the octahedral metal carbonyls may better be described as a "dissociative interchange" (I_d) [20] in which a properly-positioned L fills a coordination site vacated by a dissociating carbonyl. The general observation

TABLE 3

DISCRIMINATION ABILITIES $k_2[L]/k_2[P(C_6H_5)_3]$ FOR ASSOCIATIVE REACTIONS OF METAL CARBONYLS[a]

Metal carbonyl	$P(n\text{-}C_4H_9)_3$	$P(OR)_3$	$P(C_6H_5)_3$	$P(OCH_2)_3CR$	$P(OC_6H_5)_3$	$As(C_6H_5)_3$
$[Mo(CO)_5]$[b]	—	1.14	1.00	—	—	0.85
$[PPh_3Mo(CO)_4]$[c]	0.46	—	1.00	1.62	—	0.32
$[h^1\text{-}DTOW(CO)_4]$[d]	—	1.04	1.00	2.32	0.48	—
$Mo(CO)_6$[e]	11.6	3.78	1.00	2.01	0.84	0.58
$W(CO)_6$[e]	8.0	1.91	1.00	1.67	—	—
$Co(CO)_3NO$[f]	90	1.8	1.00	0.65	0.034	0.0023

[a] Error limits omitted. [b] Ref. 18. R = CH_3; data taken in n-hexane solvent at 35°C. [c] Ref. 17. R' = C_2H_5; data taken in n-hexane at 36.5°C. [d] This work, R = R = CH_3; data taken in xylene solvent at 99.9°C. [e] Ref. 30. R = R = C_2H_5; $Mo(CO)_6$, decalin solvent at 112.0°C. $W(CO)_6$, decalin solvent at 165.7°C. [f] Ref. 16; R = R' = CH_3; toluene solvent at 25°C.

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* However, in the absence of information about the relative ground-state energies of the reaction products, it is difficult to assess the extent of transition state bond-making on this basis.

** h^1 = *monohapto* [32]

that reactions of the hexacarbonyls of Cr, Mo and W (S) with L obey a rate law, (eq 5) supportive of parallel ligand-independent "dissociative" and ligand-dependent "associative" reaction paths over the observed wide range of substrate reactivity also indicates much the same factors to be important in determining reactivity by each path [21,22].

$$-d[S]/dt = k_1[S] + k_2[S][L] \qquad (5)$$

The "competition ratios", k_2/k_{-1} (Table 2) also reveal the relative strengths of the nucleophiles in their reactions with $[(h^1\text{-DTO})W(CO)_4]$, which, with the exception of triphenylphosphine, increase in the order of the decreasing steric requirement of L, as is reflected in their Tolman cone angles [23] The observed order is not that generally observed for S_N2 processes involving metal carbonyl substrates [15] and suggests that significant steric demands are imposed in the intermediates

For reaction of $(DTO)W(CO)_4$ with triisopropyl phosphite, activation parameters in xylene and decalin for competition between "attack" by L and ring-reclosure (Table 2) are of particular interest Significantly positive values for both $\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger}$ (5—8 kcal mol^{-1}) and $\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$ (20 cal deg^{-1} mol^{-1}) are observed, which indicate marked differences in the ligand-attack and ring-reclosure processes While comparison of the values of k_2/k_{-1} and the activation parameters in the two solvents indicate some solvation of the intermediate by xylene *, these data also support more bond-making (less bond-breaking) upon ring-reclosure than upon addition of L This effect is, perhaps, not unexpected, since enhanced nucleophilicity of the free end of a bidentate ligand, attributable to an increased "local concentration" of the Lewis base, has been previously noted, and in several instances, concerted ring-reclosure involving expulsion of a coordinated ligand has been proposed in reactions of octahedral substrates [25—28] These results indicate that the $[h^1\text{-(DTO)}W(CO)_4]$ intermediate exhibits significant ability to discriminate between ring-reclosure and uptake of L

Acknowledgements

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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 E K. Plyler, A Danti, R L Blaine and E D Tidwell, J Res. Nat. Bur Stand , A, 64 (1960) 29
4 J G Verkade, T.J. Huttemann, M.K. Fung and R.W King, Inorg. Chem., 4 (1965) 83
5 W. Hieber and J Peterhans, Z Naturforsch. B, 14 (1959) 462.

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* There is substantial evidence that coordinatively-unsaturated metal carbonyl intermediates may be strongly solvated by aromatic solvents [33] Changes in values for k_2/k_{-1} and activation parameters from xylene to decalin may be interpreted in terms of a "concerted" ring-reclosure involving displacement of solvent with a "dissociative interchange" type addition of L to the solvated intermediate.

6 A Vanderbroucke Jr D G Hendricker, R E McCarley and J G Verkade Inorg. Chem 7 (1968) 825
7 R Mathieu and R Poilblanc C R Acad Sci. Paris, Ser C 264 (1967) 1053
8 G C Mather and A Pidcock, J Chem. Soc A (1970) 1226
9 M Graziani, F. Zingales and U Belluco Inorg. Chem. 6 (1967) 1582.
10 G R Dobson and A Moradi-Araghi, in preparation.
11 D.J Darensbourg, personal communication.
12 G R Dobson and E.P Ross, Inorg. Chim Acta 5 (1971) 199
13 D J Darensbourg G R Dobson and A Moradi-Araghi J Organometal Chem 116 (1976) C17
14 G S Hammond, J Amer Chem Soc 77 (1955) 334
15 R J Angelici, Organometal. Chem Rev 3 (1968) 173
16 E.M Thorsteinson and F Basolo J Amer Chem Soc 88 (1966) 3929
17 C L Hyde and D J Darensbourg, Inorg. Chem , 12 (1973) 1286
18 W D Covey and T L Brown, Inorg. Chem 12 (1973) 2820
19 J M Kelley, D V Bent H Hermann D Schulte-Frohlinde and E Koerner von Gustorf, J Organometal Chem 69 (1974) 259
20 C H. Langford and H B Gray Ligand Substitution Processes 2nd ed Benjamin Menlo Park Calif 1974 Chapter 1
21 G R Dobson Accounts Chem Research 8 (1976) 300
22 J E Pardue and G R Dobson, Inorg. Chim Acta in press
23 C A Tolman J Amer Chem Soc 92 (1970) 2957
24 E.P Ross, R T Jernigan and G R Dobson J Inorg. Nucl Chem. 33 (1971) 3375
25 J A. Connor J P Day E M Jones and G K McEwen, J. Chem Soc (Dalton) (1973) 347
26 B J McKerley G C Faber and G R Dobson Inorg. Chem 14 (1975) 2275
27 J A Connor and G A Hudson, J Chem Soc , (Dalton), (1975) 1025
28 L D Schultz and G R Dobson J Coord Chem 5 (1976) 163
29 G R Dobson and H T Strunk J. Inorg. Nucl Chem in press.
30 J R Graham and R J Angelici, Inorg. Chem , 6 (1967) 2082
31 L D Schultz and G R Dobson J Organometal Chem submitted
32 F A Cotton, J Amer. Chem. Soc 90 (1968) 6230
33 R J Angelici and B E Leach J Organometal. Chem 11 (1968) 203 I W Stolz H. Haas and R K. Sheline J Amer Chem Soc 87 (1965) 716