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Octahedral Metal Carbonyls.
XLV. *Kinetics and Mechanism of Ligand Exchange in Tungsten Carbonyl Complexes Containing Chelating Ligands Bonding Through Nitrogen

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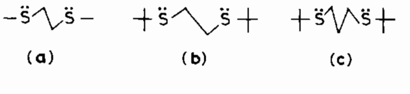
The kinetics and mechanism of the reaction of (tmen)W(CO)$_4$ (tmen = N,N,N',N'-tetramethylethylenediamine) and (tmpa)W(CO)$_4$ (tmpa = N,N,N',N'-tetramethyl-1,3-diaminopropane) with phosphines and phosphites (L) to afford L$_2$W(CO)$_4$ products have been investigated in detail. For both substrates, rate data support a mechanism involving two competing paths, one involving unimolecular, reversible ring-opening, the other a concerted process involving an interchange of L and one end of the bidentate chelating ligand; the former path predominates. The results are compared to studies of analogous systems containing chelating sulfur ligands. Intermediates of the type cis-*(η^1-tmpa)(L)W(CO)$_4$ (L = bicyclic phosphite) were identified. The nature of five-coordinate intermediates formed* via *ring-opening in (tmpa)-W(CO)$_4$ was also studied. (Tmpa)W(CO)$_4$ is a useful intermediate for the synthesis of (diolefin)W(CO)$_4$ complexes; thus (norbornadiene)W(CO)$_4$ was prepared in reasonable yield through reaction of (tmpa)W(CO)$_4$ with norbornadiene in hydrocarbon solvent under mild conditions.*

Introduction

Detailed investigations of the kinetics and mechanism of chelate ring-opening according to the overall reaction,

$$(L_2)W(CO)_4 + 2\ L' \rightarrow L'_2W(CO)_4 + (L_2), \qquad (1)$$

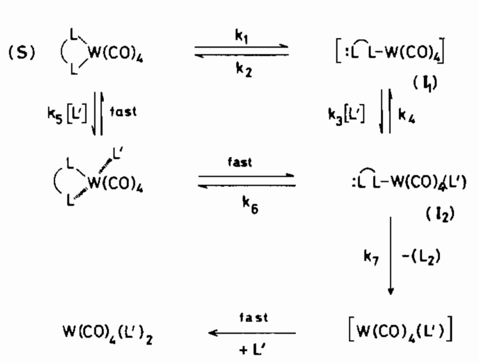
where (L$_2$) are bidentate chelating ligands (2-a–2-c)



(2)

(2-a = 2,5-dithiahexane (DTH); 2-b = 2,2,7,7-tetramethyl-3,6-dithiaoctane (DTO); and 2-c = 2,2,8,8-tetramethyl-3,7-dithianonane (DTN))

and L' = a variety of phosphines and phosphites, have been completed [1–5]. The rate data may be encompassed within an overall mechanism (3):



(3)

This mechanism, which envisions competing dissociative (governed by k$_1$) and interchange (governed by k$_5$) processes is particularly plausible in that it closely parallels the overall mechanism of substitution in "simple" ligand-exchange reactions of the octahedral metal carbonyls and derivatives [6], *e.g.*,

$$\begin{tikzcd}
L_xM(CO)_{6-x} \arrow[r, "k_a", "-CO"'] \arrow[d, "k_b{[L']}"'] & {[L_xM(CO)_{5-x}]} \arrow[d, "+L'"', "fast"] \\
{[L_xL'M(CO)_{6-x}]} \arrow[r, "-CO", "fast"'] & L_xL'M(CO)_{5-x}
\end{tikzcd} \qquad (4)$$

Interesting differences were observed with respect to the reactivity of the (L$_2$)W(CO)$_4$ complexes ((L$_2$) = 2-a–2-c with various L':

(a) The systems containing the chelating ligands 2-a and 2-b (five-membered chelate rings) do not undergo ring reclosure followed by expulsion of L' (the path governed by (3-k$_6$)), while the (DTN)W-(CO)$_4$ complex (six-membered chelate ring) does exhibit such a reaction path;

(b) The (DTN)W(CO)$_4$ complex reacted with the "constrained" phosphite (5), but not with other phosphines and phosphites, to afford an intermediate

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*Part LXIV: J.-C. Rousche and G. R. Dobson, *Inorg. Chim. Acta, 28,* L139 (1978).

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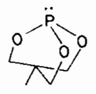


(5)

(4-methyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]-octane)

($3\text{-}I_2$) of sufficient stability to be isolated and characterized.

Moreover, the bidentate ligands in the substrates are readily displaced under mild reaction conditions, and thus such systems afford useful entrees to the synthesis of substitution products of tungsten hexacarbonyl which are difficult or impossible to synthesize directly.

Given that all of the systems studied in detail contain chelating ligands bonding through sulfur, possible influences on mechanism or reactivity of the identity of the coordinating atom have not been investigated. Thus it was of interest to study related systems in which the donor atom differs significantly in its coordinating properties. It is generally accepted that sulfur functions both as a σ-donating and π-accepting ligand ligand in its coordination in organometallic complexes. Nitrogen, on the other hand, possesses no energetically-accessible orbitals of correct symmetry to enter into π-bonding; thus complexes containing chelating ligands coordinating through nitrogen were of special interest for study.

In this report are detailed studies of the kinetics and mechanism of reactions analogous to (1), where (L_2) are 6-a and 6-b which form five- and six-membered chelate rings, respectively.

(6)

(6-a = N,N,N′,N′-tetramethylethylenediamine (tmen); 6-b = N,N,N′,N′-tetramethyl-1,3-diaminopropane (tmpa)).

Preliminary data had been reported for the reaction of $(tmpa)W(CO)_4$ with tri(isopropyl) phosphite and triethyl phosphite [2], and an examination of those data in light of the studies on $(DTN)W(CO)_4$ [4] suggests that the two systems react *via* mechanistically-similar paths; no result for reaction of $(tmen)W(CO)_4$ have been reported.

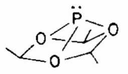
Experimental

General

Infrared spectra were recorded employing a Perkin Elmer Model 621 grating spectrophotometer, and were calibrated against a bond of water vapor at 1869.4 cm^{-1} [7]. Kinetics data were obtained employing that instrument or a Beckman DU-2 direct reading ultraviolet–visible spectrophotometer. Melting points were obtained in open capillaries (Hoover melting point apparatus) and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preparation and Purification of Reaction Materials

The substrates, $(tmen)W(CO)_4$ and $(tmpa)W(CO)_4$ were prepared from $W(CO)_6$ (Pressure Chemical) and tmen or tmpa (Aldrich) according to the procedures of Poilblanc [8] and of Dobson and Faber [1]. The ligands trimethyl phosphite, tri(isopropyl phosphite, triphenyl phosphite, triphenylphosphine and $P(OCH_2)_3CCH_3$ (5), were obtained or synthesized, purified, and checked for purity as described by Schultz and Dobson [3]. 1-Phospha-2,8,9-trioxa-ademantane, $P(O_3C_6H_9)$, (7) was some of that



(7)

employed in a study by Memering and Dobson [9], and had been stored under nitrogen in a freezer.

Kinetics Runs

Kinetics runs were carried out employing the Beckman uv–visible spectrophotometer for triphenylphosphine; for other ligands, runs were carried out both in the visible (425 nm) and infrared regions. For the latter, the disappearance of substrate carbonyl stretching bands at 1834 cm^{-1} ($(tmen)W(CO)_4$) and 1840 cm^{-1} ($(tmpa)W(CO)_4$) was monitored; the infrared method was employed for the majority of runs. Results employing the two methods were in excellent agreement. Runs were carried out under pseudo first-order reaction conditions (at least a tenfold excess of L), and plots of $\ln(A_t - A_\infty)$ *vs.* time (triphenylphosphine) or of $\ln(A_t - A_{bl})$ *vs.* time (other ligands) were linear to at least 80 per cent of reaction completion (A_t, A_∞, A_{bl} are the absorbances of reaction solutions at time t, at infinite time, and of a solvent-ligand blank, respectively). Values of the pseudo first order rate constants obtained from the slopes of these plots are given in Tables I ($(tmen)W(CO)_4$) and II ($(tmpa)W(CO)_4$). Other experimental details, including procedures employed in determination of rates of reaction of $(tmpa)W(CO)_4$ with $P(OCH_2)_3CCH_3$ (analogous to methods employed for reaction of $(DTN)W(CO)_4$ with this L) [4] and sampling techniques, have been described elsewhere [3, 10].

Identification of Reaction Products

For each system, preliminary kinetics runs were carried out by scanning the carbonyl stretching region of the infrared (2200–1700 cm^{-1}) as a function of time. The infrared spectra (carbonyl stretching region) of the $L_2W(CO)_4$ reaction products for L = $P(OCH_3)_3$ (*cis*), $P(OCH_2)_3CCH_3$ (*cis*), $P(OC_6H_5)_3$

TABLE I. Rate Data for the Reaction of (Tmen)W(CO)$_4$ with Phosphines and Phosphites in Xylene at Various Temperatures.

[L], M	10^4 k_{obsd} (sec^{-1})
L = $P(OCH_2)_3CCH_3$; T = 120.0 °C	
0.0752	4.62(8)
0.1024	5.70(2)
0.1425	7.14(2)
0.2282	9.95(4)
0.2733	11.76(6)
0.3031	12.20(4)
0.3387	13.5(1)
0.3448	13.22(4)
0.4364	15.8(1)
0.4398	15.22(7)
0.4698	15.84(5)
0.5096	16.46(6)
......	
L = $P(OC_6H_5)_3$; T = 120.0 °C	
0.0763	0.43(1)
0.3880	1.91(4)
0.4561	2.24(4)
0.5230	2.48(4)
0.7349	3.19(4)
0.8737	4.34(13)
0.9748	3.79(6)
1.170	4.78(6)
1.344	5.11(4)
1.435	5.79(5)
1.521	5.59(9)
1.669	5.78(27)
1.784	6.14(7)
1.865	6.34(12)
......	
L = $P(C_6H_5)_3$; T = 120.0 °C	
0.0312	0.58(2)
0.0623	1.22(1)
0.0858	1.58(3)
0.1532	2.97(3)
0.2023	4.03(5)
0.2389	4.61(3)
0.2689	5.15(4)
0.3183	5.65(4)
0.3526	5.61(6)
0.4183	6.45(4)
0.6116	7.07(5)
0.7241	8.16(8)
0.8286	8.38(15)
......	
L = $P[OCH(CH_3)_2]_3$; T = 110.0 °C	
0.1311	0.90(2)
0.1650	1.10(1)
0.1880	1.21(1)
0.2074	1.31(2)
0.2754	1.80(1)
0.3982	2.37(2)
0.5698	2.99(1)
0.6602	3.36(2)
0.7733	3.80(2)
0.9691	4.84(2)
......	
L = $P[OCH(CH_3)_2]_3$, T = 120.0 °C	
0.1018	1.95(5)
0.1068	2.16(5)
0.1146	2.28(3)
0.1410	2.90(3)
0.1418	2.94(5)
0.1721	3.30(2)
0.1877	3.30(10)
0.1877	3.58(5)
0.3027	5.23(2)
0.4729	7.08(3)
0.5113	7.86(3)
0.6183	9.07(3)
0.8121	11.44(5)
......	
L = $P[OCH(CH_3)_2]_3$, T = 130.0 °C	
0.1164	7.34(11)
0.1362	8.36(7)
0.1617	9.29(9)
0.1788	10.41(6)
0.2153	12.06(14)
0.2606	13.30(8)
0.3008	15.08(9)
0.3847	18.43(6)
0.4578	19.85(10)
0.5243	22.26(5)
0.6565	25.7(2)
0.8283	32.0(2)

TABLE II. Rate Data for the Reaction of (Tmpa)W(CO)$_4$ with Phosphines and Phosphites in Xylene at 43.0 °C.

[L], M	10^4 k_{obsd} (sec^{-1})
L = $P[OCH(CH_3)_2]_3$	
0.0742	0.96(1)
0.1636	2.12(1)
0.3676	4.59(3)
0.4905	6.32(3)
0.5763	7.08(5)
0.6504	8.23(7)
0.8196	9.81(3)
0.8624	10.29(8)
1.405	17.00(9)
1.460	17.6(2)
1.717	20.5(2)
......	
L = $P(C_6H_5)_3$	
0.2198	1.56(1)
0.3200	2.38(2)
0.4003	2.62(3)
0.5058	3.41(2)
0.6482	4.46(2)
0.8005	4.60(2)
0.8006	4.61(4)
0.9371	5.23(4)
0.9963	4.87(3)
1.066	5.40(3)
......	
L = $P(OC_6H_5)_3$	
0.1273	0.532(2)
0.1798	0.73(1)
0.2425	0.92(1)
0.3512	1.31(1)
0.3955	1.47(2)
0.7767	2.24(3)
1.232	2.90(2)
1.268	3.16(3)
1.793	3.64(1)
......	
L = $P(OCH_2)_3CCH_3$ (first step)	
0.0808	2.18(1)
0.1012	2.68(1)
0.1122	3.01(1)
0.1394	3.56(2)
0.2756	5.58(6)
0.3268	6.35(3)
0.4379	8.26(4)
0.4411	7.05(4)
0.5038	9.16(3)
0.5042	9.43(4)
0.6732	10.02(3)
0.7400	10.86(9)
......	
L = $P(OCH_2)_3CCH_3$ (second step)	
0.0884	1.08(1)
0.3291	0.95(2)
0.4308	0.87(4)
0.5120	0.81(4)
0.5668	0.75(2)
0.6417	0.81(1)
0.7270	0.87(1)

(*cis*), and $P(C_6H_5)_3$ (*trans* and *cis*) have been reported elsewhere [11–14]; the product for L = $P[OCH(CH_3)_2]_3$ had not been synthesized previously and was prepared as follows:

Cis-$\{P[OCH(CH_3)_2]_3\}_2W(CO)_4$

2.0 grams of (tmpa)W(CO)$_4$ and 10 ml (*ca.* 9.7 g) of tri(isopropyl) phosphite were dissolved in 100 ml of xylene in a three-necked flask equipped with a gas-seal (bubbler), condenser and rubber septum. The solution was stirred magnetically at 90 °C for 20 minutes. The solution was then cooled, its volume reduced to about 5 ml under vacuum, and 50 ml of *n*-heptane was added. The solution was then cooled to 0 °C for 24 hr; the pale yellow crystals which preci-

TABLE III. Rate Constants for Reaction of (Tmen)W(CO)$_4$ and (Tmpa)W(CO)$_4$ with Phosphines and Phosphites at Various Temperatures, from Reciprocal Plots of $1/k_{obsd}$ *vs.* $1/[L']$.

L′	T, °C	10^2 slope $\frac{k_2(k_4+k_6+k_7)}{k_7(k_1k_3+k_3k_5)}$ (M^{-1})	10^2 intercept $\frac{k_3(k_6+k_7)}{k_7(k_1k_3+k_2k_5)}$ (sec^{-1})
(tmen) W(CO)$_4$			
$P(OCH_2)_3CCH_3$	120.0°	1.51(3)	3.14(9)
$P(OC_6H_5)_3$	120.0	17.9(6)	5.8(5)
$P(C_6H_5)_3$	120.0	4.2(3)	5.9(8)
$P[OCH(CH_3)_2]_3$	110.0	14.1(6)	7.1(10)
	120.0	4.6(1)	3.6(4)
	130.0	1.50(5)	1.6(1)
(tmpa) W(CO)$_4$			
$P(OCH_3)_3CCH_3$	43.0°	7.8(1)	0.50(15)
$P(OC_6H_5)_3$	43.0	11.3(9)	7.7(12)
$P(C_6H_5)_3$	43.0	21.9(3)	15.5(4)
$P[OCH(CH_3)_2]_3$	43.0	3.2(1)	4.8(4)

TABLE IV. Carbonyl Stretching Spectra for (Tmpa)W(CO)$_4$, its Reaction Intermediates, and Products.

Complex	$^a\nu$(CO), cm^{-1}	Solvent
(tmpa)W(CO)$_4$ [2]	2011w, 1883vs, 1864s, 1816s	$CHCl_3$
cis-(η^1-tmpa)[P(OCH$_2$)$_3$CCH$_3$]W(CO)$_4$	2030m, 1913s, 1900vs, 1880	xylene
cis-(η^1-tmpa)[P(O$_3$C$_6$H$_9$)]W(CO)$_4$	2029m, 1915s, 1902vs, 1874m	xylene
cis-[P(OCH$_2$)$_3$CCH$_3$]W(CO)$_4$ [11]	2045m, 1950sh, 1924vs	CH_2Cl_2
cis-[P(O$_3$C$_6$H$_9$)]$_2$W(CO)$_4$ [11]	2053m, 1950sh, 1927vs	CH_2Cl_2

^{a}Relative band intensitesi: s-strong, m-medium, w-weak, v-very, sh-shoulder.

pitated were filtered (cold), were washed with cold *n*-heptane, and were dried under vacuum. *Anal.*. Calc'd for $C_{22}H_{42}O_{10}WP_2$: C, 37.09; H, 5.94. Found: C, 37.24; H, 6.02. Carbonyl stretching spectrum ($CHCl_3$ solution): 2037(w), 1953(m), 1900(vs) cm^{-1}. The complex melted at 92–4 °C.

Reaction intermediates of the type, *cis*-(η^1-tmpa)-(L)W(CO)$_4$ were also identified for L = P(OCH$_2$)$_3$-CCH$_3$ and P(O$_3$C$_6$H$_9$).

Cis-(η^1-tmpa)[P(OCH$_2$)$_3$CCH$_3$] W(CO)$_4$

(Tmpa)W(CO)$_4$ (4.0 g) and 14 g of P(OCH$_2$)$_3$-CCH$_3$ in 60 ml of xylene were placed in the apparatus described above in a constant temperature bath at 43 °C. After one hr the solution was cooled and the solvent removed under vacuum. The residue was sublimed at 50 °C/0.1 torr for three days, during which time 9.7 g of unreacted P(OCH$_2$)$_3$CCH$_3$ was recovered. The residue was then dissolved in 30 ml of xylene, cooled in a dry ice–acetone bath, and filtered, to separate [P(OCH$_2$)$_3$CCH$_3$]$_2$W(CO)$_4$. The filtrate was evaporated to dryness to afford the product (1.5 g). *Anal.* Calc'd for $C_{16}H_{27}O_7WN_2P$: C, 33.47; H, 4.74. Found: C, 33.29; H, 4.75. The carbonyl stretching spectrum (xylene solution) is given in Table IV.

The complex *cis*-(η^1-tmpa)[P(O$_3$C$_6$H$_9$)] W(CO)$_4$ was identified *in situ* through a similar procedure employing 0.63 g (tmpa)W(CO)$_4$ and 0.65 g P(O$_3$C$_6$-H$_9$) in xylene at 43 °C (3200 sec reaction time). The carbonyl stretching spectrum (xylene solution) is given in Table IV.

(Norbornadiene) W(CO)$_4$

(Tmpa)W(CO)$_4$ (1.2 g) and norbornadiene (15 ml) were placed in the apparatus described above and heated at 50 °C for 4 hr. The solution was then cooled to room temperature, the excess norbornadiene was removed under vacuum, and the residue was then extracted with several portions of hexane (total volume, 120 ml). The volume of the extracts was then reduced to 20 ml, and the yellow precipitate which was formed was filtered, and dried under

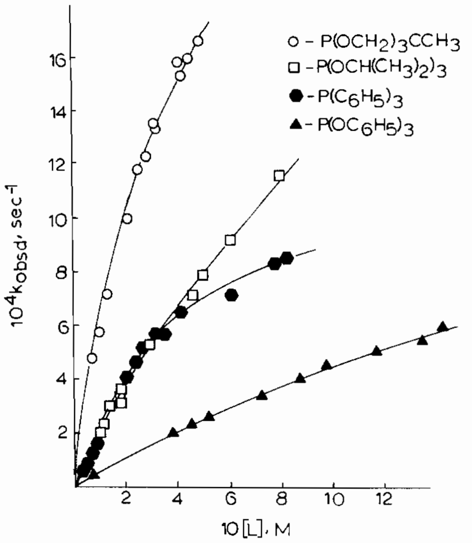


Figure 1. Plots of k_{obsd} *vs.* [L] for reactions of (tmen)W-$(CO)_4$ with phosphines and phosphites at 120.0 °C in xylene solvent.

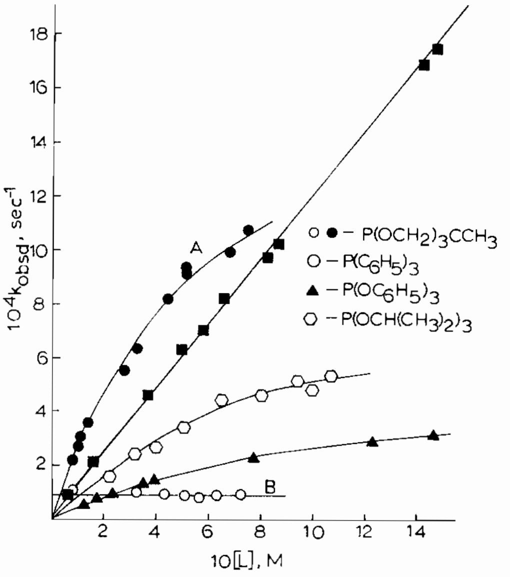


Figure 2. Plots of k_{obsd} *vs.* [L] for reactions of (tmpa)W-$(CO)_4$ with phosphines and phosphites at 43.0 °C in xylene solvent. For reaction with L = $P(OCH_2)_3CCH_3$, (A) represents the plot of k_{obsd} *vs.* $[P(OCH_2)_3CCH_3]$ for the disappearance of the substrate, and (B) for the disappearance of the *cis*-(η^1-tmpa)$[P(OCH_2)_3CCH_3]W(CO)_4$ intermediate; see text.

vacuum. The crude product was then vacuum-sublimed (80 °C/0.1 torr) to afford 0.56 g (51.3%) of product. The complex was identical (mp, carbonyl stretching spectrum), to that prepared by King and Fronzaglia [15] *via* $(CH_3CN)_3W(CO)_3$.

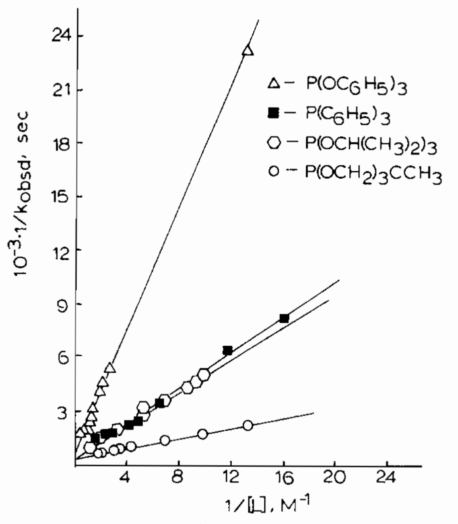


Figure 3. Plots of $1/k_{obsd}$ *vs.* 1/[L] for reaction of (tmen)-$W(CO)_4$ with phosphines and phosphites at 120.0 °C in xylene solvent.

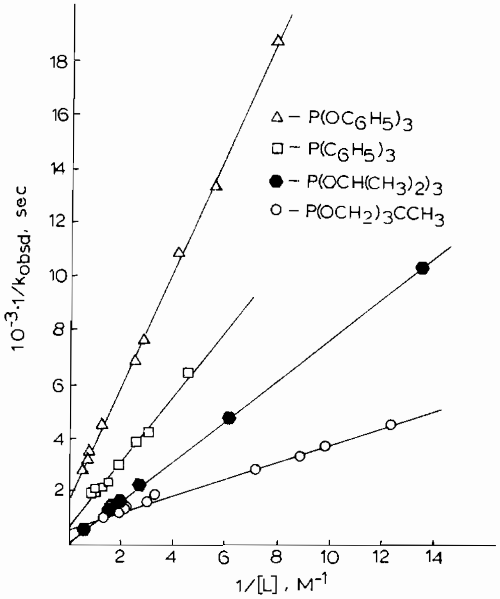


Figure 4. Plots of $1/k_{obsd}$ *vs.* 1/[L] for reaction of (tmpa)-$W(CO)_4$ with phosphines and phosphites at 43.0 °C in xylene solvent.

Statistical Analysis of Rate Data

Values of the pseudo first order rate constants, k_{obsd}, (Tables I, II) were determined employing a semi-logarithmic least-squares computer program on the North Texas State University IBM 360 Model 50 computer. Limits of error (one standard deviation, given in parentheses in Tables I–II) were then employed in the determination of the slopes and intercepts of plots of $1/k_{obsd}$ *vs.* 1/[L] (*vide infra*). A weighted least-squares program was employed in this analysis [16].

Results and Discussion

Figures 1 and 2 exhibit plots of k_{obsd} *vs.* [L] for reactions of (tmen)W(CO)$_4$ and (tmpa)W(CO)$_4$ with phosphines and phosphites, based upon data exhibited in Tables I and II. These plots are qualitatively consistent with those expected on the basis of mechanism (3). Based upon the assumption of steady-state concentrations of (3-I$_1$) and (3-I$_2$), the applicable rate law is,

$$-d[S]/dt = \frac{k_7\{(k_1k_3 + k_2k_5)[S][L]\} + k_3k_5[S][L]^2}{k_2(k_4 + k_6 + k_7) + k_3(k_6 + k_7)[L]} \quad (8)$$

Assuming that $k_1 >> k_5$, the "reciprocal relationship",

$$1/k_{obsd} = \frac{k_2(k_4 + k_6 + k_7)}{k_7(k_1k_3 + k_3k_5)[L]} + \frac{k_3(k_6 + k_7)}{k_7(k_1k_3 + k_2k_5)} \quad (9)$$

may be derived, which predicts linear plots of $1/k_{obsd}$ *vs.* 1/[L] which have non-common intercepts, in view of the complexity of the second term on the right-hand side of (9). Values of the slopes and intercepts of these plots are exhibited in Table III. The predicted behavior is observed for both reactions of (tmen)W(CO)$_4$ (Fig. 3) and (tmpa)W(CO)$_4$ (Fig. 4).

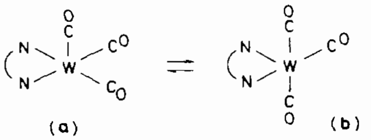
Data for the corresponding five-membered ring systems (DTO)W(CO)$_4$ and (tmen)W(CO)$_4$ differ qualitatively. For reaction of (DTO)W(CO)$_4$ with L [3], common intercepts for the "reciprocal plots" for various L indicate that the path governed by k_5 and k_6 is not operative. In contrast, the statistically-significant non-congruence of these intercepts for reaction of (tmen)W(CO)$_4$ with L indicates that this path is accessible. The reason for this difference in rate behavior is not evident, but it is clear that ring-size alone does not determine the mechanism of ring-opening in these systems.

The data for (tmpa)W(CO)$_4$ is qualitatively similar to that observed for the analogous sulfur-containing six-membered chelate ring substrate, (DTN)W(CO)$_4$ [4] in the following respects:

(a) "Reciprocal plots" of $1/k_{obsd}$ *vs.* 1/[L] are linear, with non-common intercepts, consistent with mechanism (3), in which the dissociative and interchange paths are both accessible.

(b) For both systems, for bicyclic phosphites L′ but for no other ligands (in this study, L′ = ligands (5) and (7)) intermediates of the type *cis*-(η^1-L$_2$)(L′)W(CO)$_4$, of sufficient stability to allow isolation and kinetics studies of their rates of appearance and disappearance, have been observed. For L′ = P(OCH$_2$)$_3$CCH$_3$, rate data indicate the intermediate to be produced predominately *via* unimolecular ring-opening (linear plot of $1/k_{obsd}$ *vs.* 1/[P(OCH$_2$)$_3$CCH$_3$], Fig. 4), and to disappear *via* a unimolecular process (plot of k_{obsd} *vs.* [P(OCH$_2$)$_3$CCH$_3$] with zero slope, Fig. 2). These observations are fully consistent with mechanism (3). The stability of these intermediates thus must be attributed largely to the bicyclic phosphites themselves, and to the relative instability of the six-membered ring systems relative to the five, which permits intermediate formation under relatively mild conditions. The unusual bonding properties of the bicyclic phosphites have been well-documented [17]. It has been hypothesized that "constraint" about the O–P–O bond angles produced in these systems results in a change in hybridization at P, significantly altering the coordination properties of these ligands; it is to be noted that rates of reaction of (L$_2$)W(CO)$_4$ complexes with P(OCH$_2$)$_3$CCH$_3$ are significantly faster than with other nucleophiles.

The four carbonyl stretching bands observed in the infrared spectra of these intermediates support exclusively *cis*-orientation of (L$_2$) and L′, a fact which could be attributed either to the non-fluxionality of the five-coordinate, probably square-pyramidal



(10)

intermediate (10-a) or, in the event of fluxionality of this intermediate as shown in (10) to the greater thermodynamic stability of (10-a) relative to (10-b), or to the relative thermodynamic instability of *trans*-(η^1-L$_2$)L′W(CO)$_4$.

For L = PPh$_3$, as reported elsewhere, both *trans* and *cis* L$_2'$W(CO)$_4$ products are obtained. This observation, together with results from ^{13}CO labeling experiments involving species similar to the inferred (η^1-tmpa)(PPh$_3$)W(CO)$_4$ intermediate (3-I$_2$) suggest that the five-coordinate intermediates (10) are in fact fluxional, and that (10-a) is thermodynamically more stable than (10-b), in accord with the "site preference" model of reactivity in these systems put forth by Atwood and Brown [19, 20].

The correspondence of mechanistic details as outlined above for bidentate ligands containing nitrogen or sulfur donor atoms suggests that in six-membered ring systems, the bonding properties of the coordinating atoms in the chelating ring do not alter qualitatively the observed rate-behavior: ring size must therefore play an important role in the differences observed in reactivity of complexes of five- and six-membered chelate ring systems. A recent X-ray study of the structures of (DTN)W(CO)$_4$ and (DTN)W(CO)$_4$ is consistent with this view [21].

It is to be noted that replacement of tmpa from (tmpa)W(CO)$_4$ by various L proceeds under very mild conditions, proceeding at a reasonable rate even at 40 °C. Thus this air-stable substrate is a useful intermediate to the synthesis of (diolefin)W(CO)$_4$

species which are difficult or impossible to synthesize directly from the relatively inert $W(CO)_6$: King and Fronzaglia have prepared a variety of such species from $(CH_3CN)_3W(CO)_3$. The reaction of (tmpa)W-$(CO)_4$ with norbornadiene proceeds smoothly in hydrocarbon solvent at 50 °C to afford (NBD)W-$(CO)_4$ in yield comparable (*ca.* 50%) to that obtained employing the more difficult to prepare and air-sensitive $(CH_3CN)_3W(CO)_3$; thus (tmpa)$W(CO)_4$ promises to be of significant synthetic utility.

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