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Octahedral Metal Carbonyls. 66.¹ Rates and Mechanism of Chelate Ring Displacement from Tetracarbonylmetal Complexes of Dithiaalkanes Forming Seven- and Eight-Membered Chelating Rings

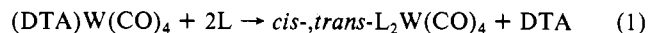
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The kinetics and mechanism of the stepwise displacement from (DTA)W(CO)₄ complexes (DTA = dithiaalkane) of DTD (2,2,9,9-tetramethyl-3,8-dithiadecane) and DTU (2,2,10,10-tetramethyl-3,9-dithiaundecane) have been investigated. DTD and DTU, which form seven- and eight-membered chelate rings, respectively, are displaced by Lewis bases (L = trialkyl, triaryl phosphite) in chlorobenzene solvent to afford L₂W(CO)₄ and DTA. The reactions are "biphasic", proceeding through the non-steady-state intermediates *cis*-(η¹-DTA)(L)W(CO)₄ after initial reversible ring opening. Complementary pulsed laser flash photolysis studies of chelate ring closure in [(η¹-DTA)W(CO)₄] in the absence of L have also been carried out. The results, together with those previously reported for the complexes containing the analogous four-, five-, and six-membered rings, DTHp, DTO, and DTN (2,2,6,6-tetramethyl-3,5-dithiaheptane, 2,2,7,7-tetramethyl-3,6-dithiaoctane, and 2,2,8,8-tetramethyl-3,7-dithianonane, respectively), permit a detailed comparison of reactivity in a series of five complexes differing only in chelate ring size. The dominant influences on reactivity are the rates of chelate ring opening, which increase with increasing ring size for the five- to eight-membered rings, and the steric nature of coordinated L in the *cis*-(η¹-DTA)(L)W(CO)₄ intermediates.

Introduction

Reaction of (DTA)W(CO)₄ complexes (DTA (dithiaalkane) = (CH₃)₂CS(CH₂)_xSC(CH₃)₂; x = 1-3), which contain 4-, 5- and 6-membered chelating rings, with phosphines and phosphites (=L), all exhibit the stoichiometry shown in eq 1. However, kinetics



studies have shown the rate laws for these reactions to be extremely sensitive to chelate ring size.²⁻⁴ Thus, for x = 1 (DTA = 2,2,6,6-tetramethyl-3,5-dithiaheptane (DTHp)), rate law 2 is

$$-d[(DTA)W(CO)_4]/dt = k[(DTA)W(CO)_4][L] \quad (2)$$

obeyed, and evidence supports an initial concerted ring opening and reclosure (path a, Scheme I).⁴ For x = 2, (DTA = 2,2,7,7-tetramethyl-3,6-dithiaoctane (DTO)), rate law 3 was

$$-d[(DTA)W(CO)_4]/dt = k'[(DTA)W(CO)_4]/(1 + k''[L]) \quad (3)$$

observed, which was interpreted in terms of initial reaction pathway b in Scheme I, where k' = k₁k₂/k₋₁ and k'' = k₂/k₋₁ and the ring-opening and ligand-attack steps governed by k₋₁ and k₂ were competitive. Other rapid steps then afforded the observed reaction products.² For x = 3 (DTA = 2,2,8,8-tetramethyl-3,7-dithianonane (DTN)) and for L = 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, P(OCH₂)₃CCH₃ (CP), at least (vide infra), "biphasic" behavior was observed, which thus indicated that the initial reversible ring-opening steps leading to formation of the *cis*-(η¹-DTN)(L)W(CO)₄ intermediate and the subsequent rate-determining loss of DTN from this species also were competitive.³ For other L, the observed rate behavior was interpreted in terms of competitive interchange and dissociative pathways (paths a and b in Scheme I). Parallel pulsed laser flash photolysis studies for these (DTA)W(CO)₄ complexes demonstrated that, upon flash photolysis, chelate ring-opening is induced; studies of the rates of reaction of the *cis*-(η¹-DTA)(solvent)W(CO)₄ species produced upon flash photolysis by chelate ring closure and by solvent displacement by L (Scheme I) also were important in the elucidation of mechanistic details.⁴⁻⁶ In view of the richness of

the mechanistic information that has been developed through studies of these systems and in view of the interest in further aspects of the influence of chelate ring size on the rates, energetics, and mechanism of chelate ring displacement in this series of complexes, we have extended the investigation to the seven- and eight-membered ring-containing species (x = 4, 5) (DTD)W(CO)₄ (DTD = 2,2,9,9-tetramethyl-3,8-dithiadecane) and (DTU)W(CO)₄ (DTU = 2,2,10,10-tetramethyl-3,9-dithiaundecane). The results of that investigation are the subject of this report.

Experimental Section

General Information. Infrared spectra were obtained by employing a Nicolet 20 XSB FTIR spectrometer. Proton NMR spectral measurements utilized a JEOL FX90Q spectrometer. Elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, IN.

Materials. Chlorobenzene (CB, Fisher) was stirred and refluxed over P₄O₁₀ under nitrogen for 24 h and was then fractionally distilled. The ligands P(OMe)₃ and P(O-*i*-Pr)₃ (Aldrich) were purified as described previously.^{2b,3a} P(OCH₂)₃CCH₃ (CP) was synthesized and purified through use of literature methods.^{7,8}

DTD and DTU were synthesized through use of method first employed by Federov and Savel'eva.⁹ The details of the syntheses of the crude ligands were identical with those described by Dobson and Cortés for preparation of DTHp.⁴ DTD was purified by vacuum distillation (bp 119-20 °C (1 Torr)), while DTU was fractionally distilled under nitrogen (bp 134-5 °C (0.1 Torr)). Purified yields were 42% and 38%, respectively. ¹H NMR (CDCl₃): DTD, δ 1.24 (18 H, s), 1.67 (4 H, m), 2.53 (4 H, t, J = 9 Hz); DTU, δ 1.25 (18 H, s), 1.50 (6 H, m), 2.45 (4 H, t, J = 9 Hz). ¹³C NMR (CDCl₃): DTD, δ 27.54 (t), 28.97 (t), 30.76 (q), 41.43 (s); DTU, δ 27.78 (t), 28.43 (t), 29.21 (t), 30.70 (q), 41.25 (s).

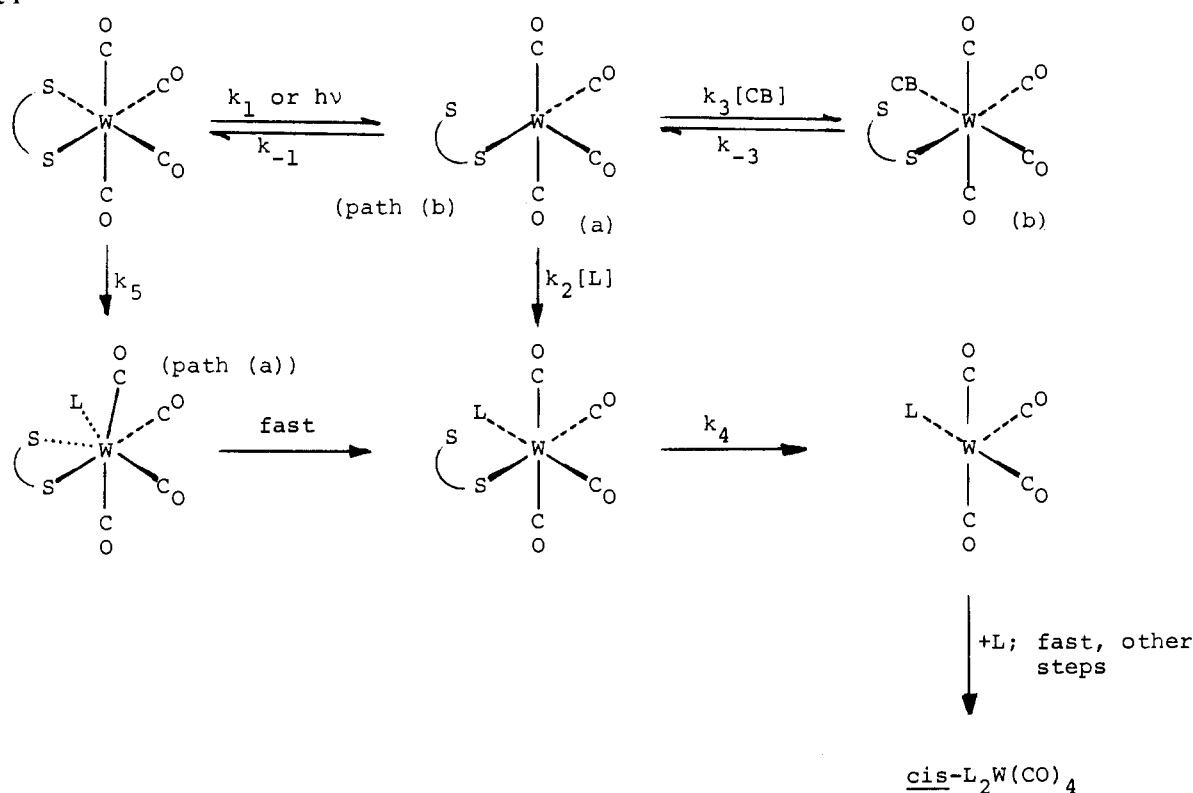
Synthesis of Complexes. (DTD)W(CO)₄. W(CO)₆ (Pressure Chemical Co.; 3.0 g, 8.5 mmol) and 3.12 g of DTD (13.3 mmol) were dissolved in 350 mL of hexanes (Fisher) and were placed in a photochemical reactor through which N₂ was continually bubbled through a sintered glass frit at the bottom. The solution was irradiated for 4 h by employing a 450-W Hanovia medium-pressure Hg lamp. Crystals of the yellow product precipitated from solution during irradiation. After the irradiation was complete, the crystals were recovered via suction filtration and were recrystallized from toluene/hexanes. Yield: 1.14 g (25.2%). Anal. Calcd for C₁₆H₂₆O₄S₂W: C, 36.23; H, 4.94. Found: C, 36.01; H, 4.99. ν(CO) (CB solution) = 2012.5 (m), 1894.5 (s), 1883.4 (s), 1852.0 (ms) cm⁻¹.

(DTU)W(CO)₄. The bright yellow complex was obtained from 3.0 g (8.5 mmol) of W(CO)₆ and 2.0 g (8.1 mmol) of DTU in 350 mL of

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Scheme I



hexanes from a procedure analogous to that employed in the synthesis of $(\text{DTD})\text{W}(\text{CO})_6$. The yield was 0.97 g (22%). Anal. Calcd for $\text{C}_{17}\text{H}_{28}\text{O}_4\text{S}_2\text{W}$: C, 37.51; H, 5.18. Found: C, 37.52; H, 5.13. $\nu(\text{CO})$ (CB solution) = 2012.3 (m), 1893.7 (s), 1882.7 (s), 1851.7 (ms) cm^{-1} .

***cis*- $(\eta^1\text{-DTD})(\text{CP})\text{W}(\text{CO})_4$.** This complex was characterized to confirm the presence of *cis*- $(\eta^1\text{-DTA})(\text{L})\text{W}(\text{CO})_4$ (DTA = DTD, DTU) complexes as intermediates in the overall DTA displacement reactions; it has been found for other DTA ligands (= DTHp,⁴ DTN³) that the *cis*- $(\eta^1\text{-DTA})(\text{CP})\text{W}(\text{CO})_4$ complexes are the most stable of those containing any L investigated. It was synthesized and purified (0.17 g, 43% yield) as described for its *cis*- $(\eta^1\text{-DTHp})(\text{CP})\text{W}(\text{CO})_4$ analogue⁴ from 0.30 g (0.57 mmol) of $(\text{DTD})\text{W}(\text{CO})_4$ and 0.15 g (0.64 mmol) of CP. Anal. Calcd for $\text{C}_{21}\text{H}_{36}\text{O}_7\text{PS}_2\text{W}$: C, 37.18; H, 5.20. Found: C, 37.06; H, 5.20. $\nu(\text{CO})$ (CB solution) = 2028.3 (m), 1921.6 (s), 1906.6 (vs), 1884.2 (s) cm^{-1} . The analogous complex, *cis*- $(\eta^1\text{-DTU})(\text{CP})\text{W}(\text{CO})_4$, was prepared similarly in CB solution but was not isolated; its carbonyl stretching spectrum, obtained in situ, exhibited bands at 2028.1 (m), 1922.7 (s), 1906.5 (vs), and 1883.2 (s) cm^{-1} .

Identification of the Final Reaction Products. Complete displacement of DTD and DTU from their $(\text{DTA})\text{W}(\text{CO})_4$ complexes by L affords, initially, *cis*- $(\text{L})_2\text{W}(\text{CO})_4$. These species were identified through their carbonyl stretching spectra observed in situ after completion of the reactions. The spectra are in agreement with those previously reported.^{8,10,11} The subsequent isomerization of these complexes to their trans analogues has been studied in detail^{4,10,12,13} and was not further considered here.

Thermal Kinetics Runs. Reactions of $(\text{DTD})\text{W}(\text{CO})_4$ and $(\text{DTU})\text{W}(\text{CO})_4$ in CB with L (=P(OMe)₃, P(O-*i*-Pr)₃) were observed to be biphasic (plots of $\ln(A_t - A_{bl})$ vs time consisted of two linear segments, corresponding to a fast rate and a slow rate) and therefore were carried out through the use of two methods. For the faster reactions, a "high-performance" kinetic photometry system, which allowed data acquisition to be within 5 s after mixing of the reaction solutions, was employed.

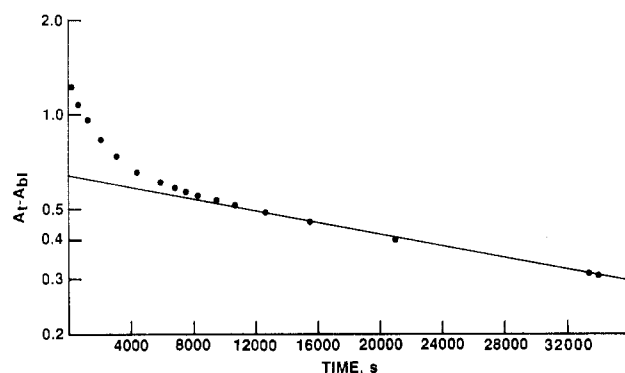


Figure 1. Plot of $\ln(A_t - A_{bl})$ vs time for the reaction of $(\text{DTD})\text{W}(\text{CO})_4$ with 0.6001 M P(O-*i*-Pr)₃ in chlorobenzene at 21.1 °C.

The slower of the two biphasic segments (involving reaction of $(\eta^1\text{-DTA})(\text{L})\text{W}(\text{CO})_4$ complexes with L) was studied kinetically by employing a Beckman DU-2 direct-reading spectrophotometer. The equipment and all procedures that were employed have been described in detail for studies of the analogous $(\text{DTHp})\text{W}(\text{CO})_4$ system.⁴ The analyzing wavelength monitored was 415 nm; 30 mg of complex in 50 mL of reaction solution was employed for the kinetics runs.

Flash Photolysis Studies. Pulsed laser flash photolysis investigations of $(\text{DTD})\text{W}(\text{CO})_4$ in CB solution were carried out as described previously;¹⁴ the cell temperature was held to within ± 0.1 °C. Absorbance due to the $(\eta^1\text{-DTA})(\text{CB})\text{W}(\text{CO})_4$ intermediate produced upon photolysis was monitored at 430 nm.

Data Analysis. Data for the thermal processes were analyzed by employing linear least-squares computer programs developed for our microcomputer. Limits of error, given in parentheses as the uncertainties of the last digit(s) of the cited value, are 1 standard deviation.

Results and Discussion

Stoichiometry. Reaction of $(\text{DTA})\text{W}(\text{CO})_4$ (DTA = DTD, DTU) with various L in CB monitored at 415 nm afforded segmented plots of $\ln(A_t - A_{bl})$ vs time (A_t and A_{bl} are the absorbance of the reaction solution at time t and of a solvent-ligand blank,

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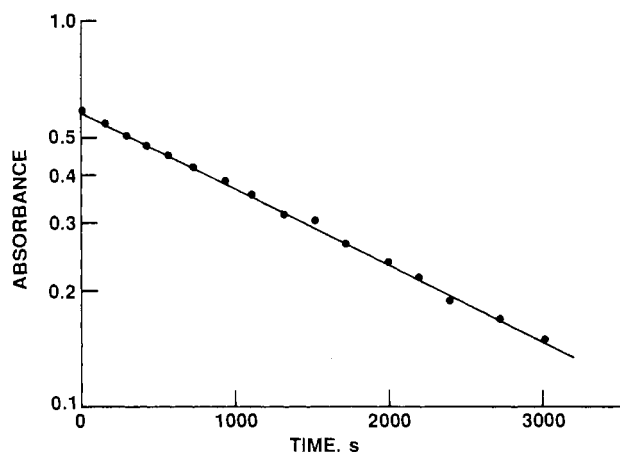
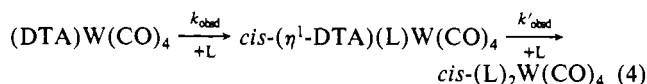


Figure 2. Plot of $\ln(A_t - A'_t)$ vs time for the reaction of $(\text{DTD})\text{W}(\text{CO})_4$ with 0.6001 M $\text{P}(\text{O}-i\text{-Pr})$ in chlorobenzene at 21.1 °C. A' is the absorbance obtained by extrapolation of the second (linear) segment of the plot illustrated in Figure 1 to time t .

respectively) corresponding to a very rapid first process and a much slower second one (Figure 1); parallel infrared studies indicated that the reactions rapidly afforded six-coordinate *cis*-(η^1 -DTA)(L) $\text{W}(\text{CO})_4$ intermediates, previously characterized for $\text{DTA} = \text{DTN}^3$ and DTHp and $\text{L} = \text{CP}^4$. The intermediate produced through reaction of $(\text{DTD})\text{W}(\text{CO})_4$ with CP was also characterized, while its DTU analogue was identified in solution from its carbonyl stretching spectrum. The slower second segment of the plot of $\ln(A_t - A_{bl})$ vs time is attributable to conversion of *cis*-(η^1 -DTA)(L) $\text{W}(\text{CO})_4$ intermediates into *cis*-(L) $_2\text{W}(\text{CO})_4$ products, identified in situ. The stoichiometry for these steps thus is



The further isomerization of *cis*-(L) $_2\text{W}(\text{CO})_4$ to an equilibrium mixture also containing *trans*-(L) $_2\text{W}(\text{CO})_4$ was not further investigated since it has been studied in detail elsewhere; it has been found to take place via a nondissociative process probably involving formation of a trigonal-prismatic transition state.^{4,10,12,13}

Chelate Ring Opening in $(\text{DTA})\text{W}(\text{CO})_4$ in the Presence of L. The rapid reaction of $(\text{DTA})\text{W}(\text{CO})_4$ complexes ($\text{DTA} = \text{DTD}$, DTU) with L in CB to afford *cis*-(η^1 -DTA)(L) $\text{W}(\text{CO})_4$ intermediates was investigated as a function of the concentration of L ($\text{L} = \text{P}(\text{OMe})_3$, $\text{P}(\text{O}-i\text{-Pr})_3$) and of temperature under pseudo-first-order conditions ($[\text{L}] \gg [(\text{DTA})\text{W}(\text{CO})_4]$). The plots of $\ln(A_t - A_{bl})$ vs time, such as are illustrated in Figure 1 for a kinetics run for reaction of $(\text{DTD})\text{W}(\text{CO})_4$ with $\text{P}(\text{O}-i\text{-Pr})_3$, are typical of a "biphasic" reaction, and consist of two linear segments.¹⁵ The values of k'_{obsd} (eq 4) can be determined from the slopes of the second (slower) segment; a discussion of them will be deferred until the next section. The overall rate constants, k_{obsd} (eq 4), for the first reaction step may be evaluated by extrapolation of $\ln(A_t - A_{bl})$ for the second linear segment to zero time and subtraction of its value at any time from the corresponding value of $\ln(A_t - A_{bl})$ for the initial segment. Such a plot, derived from that in Figure 1, is illustrated in Figure 2. Plots of values of k_{obsd} vs $[\text{L}]$ obtained for the initial rapid decay for reaction of $(\text{DTD})\text{W}(\text{CO})_4$ with $\text{P}(\text{O}-i\text{-Pr})_3$ in CB at three temperatures are shown in Figure 3; these plots and those for rate data at other temperatures and for the analogous reactions of $(\text{DTU})\text{W}(\text{CO})_4$ obey the rate law

$$-d[\text{cis}-(\text{DTA})\text{W}(\text{CO})_4]/dt = k_{\text{obsd}}[\text{cis}-(\text{DTA})\text{W}(\text{CO})_4] \quad (5)$$

$$k_{\text{obsd}} = k'[\text{L}]/(1 + k''[\text{L}])$$

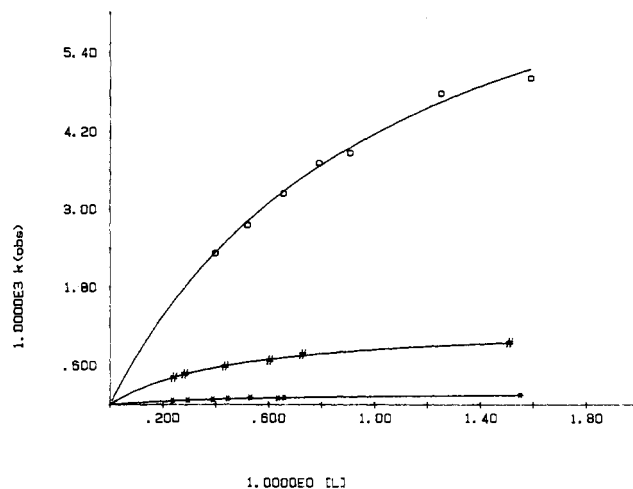


Figure 3. Plots of k_{obsd} vs $[\text{P}(\text{O}-i\text{-Pr})_3]$ for the reaction of $(\text{DTD})\text{W}(\text{CO})_4$ with $\text{P}(\text{O}-i\text{-Pr})_2$ in chlorobenzene at three temperatures: \times at 11.1 °C; $\#$ at 21.1 °C; \circ at 35.2 °C.

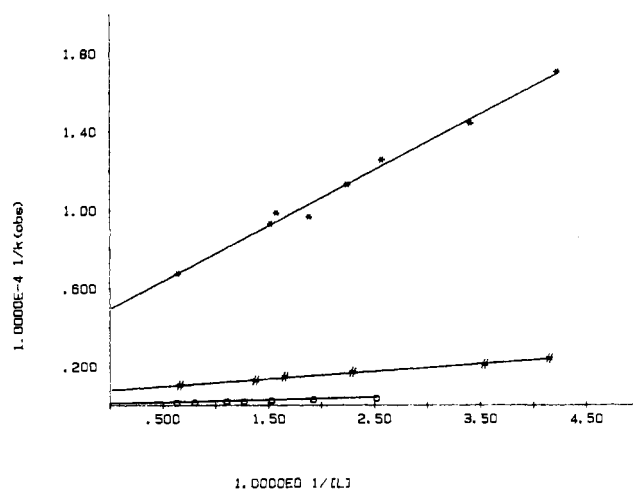


Figure 4. Plots of $1/k_{\text{obsd}}$ vs $1/[\text{P}(\text{O}-i\text{-Pr})_3]$ for the reaction of $(\text{DTD})\text{W}(\text{CO})_4$ with $\text{P}(\text{O}-i\text{-Pr})_3$ in chlorobenzene at three temperatures: \times at 11.1 °C; $\#$ at 21.1 °C; \circ at 35.2 °C.

Table I. Rate Constants and Activation Parameters for Chelate Ring Opening in $(\text{DTA})\text{W}(\text{CO})_4$ Complexes ($\text{DTA} = \text{DTD}$, DTU)

DTA	T , °C	L	$10^3 k_1$, s^{-1}	$10^3 k_1 k_2 / k_{-1}$, $\text{M}^{-1} \text{s}^{-1}$
DTD ^a	11.1	$\text{P}(\text{O}-i\text{-Pr})_3$	0.203 (11)	0.351 (13)
	21.1	$\text{P}(\text{O}-i\text{-Pr})_3$	1.13 (4)	1.36 (4)
		$\text{P}(\text{OMe})_3$	1.26 (4)	2.59 (7)
DTU ^b	35.2	$\text{P}(\text{O}-i\text{-Pr})_3$	8.1 (3)	8.4 (3)
	14.2	$\text{P}(\text{O}-i\text{-Pr})_3$	0.57 (3)	1.06 (4)
		$\text{P}(\text{OMe})_3$	0.53 (3)	1.46 (9)
	21.0	$\text{P}(\text{O}-i\text{-Pr})_3$	1.78 (6)	3.14 (6)
	35.2	$\text{P}(\text{O}-i\text{-Pr})_3$	12.1 (5)	17.4 (9)

^aDTD: $\Delta H_1^\ddagger = 26.0$ (7) kcal/mol; $\Delta S_1^\ddagger = 18.0$ (23) cal/(deg mol); $\Delta H_1^\ddagger + \Delta H_2^\ddagger - \Delta H_{-1}^\ddagger = 22.4$ (1) kcal/mol; $\Delta S_1^\ddagger + \Delta S_2^\ddagger - \Delta S_{-1}^\ddagger = 5.9$ (5) cal/(deg mol). ^bDTU: $\Delta H_1^\ddagger = 24.9$ (7) kcal/mol; $\Delta S_1^\ddagger = 14.7$ (23) cal/(deg mol); $\Delta H_1^\ddagger + \Delta H_2^\ddagger - \Delta H_{-1}^\ddagger = 22.6$ (9) kcal/mol; $\Delta S_1^\ddagger + \Delta S_2^\ddagger - \Delta S_{-1}^\ddagger = 8$ (3) cal/(deg mol).

On the basis of eq 5, plots of k_{obsd} vs $[\text{L}]$ are expected to be curved, with slopes decreasing with greater concentrations of L. Rearrangement of (5) affords eq 6.

$$1/k_{\text{obsd}} = k''/k' + 1/k'[\text{L}] \quad (6)$$

Plots of $1/k_{\text{obsd}}$ vs $1/[\text{L}]$ for the data plotted in Figure 3 are shown in Figure 4. This kinetics behavior is suggestive of successive reaction steps, one or more of which is reversible, and has been interpreted in several related studies, e.g., for reaction of $(\text{DTU})\text{W}(\text{CO})_4$ with L,^{2,5} in terms of path b in Scheme 1. For

(15) See: Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill Book Co.: New York, 1981; pp 65-71.

this mechanism, assuming steady-state concentrations of intermediates a and b in Scheme I, the rate law analogous to (6) is

$$1/k_{\text{obsd}} = 1/k_1 + k_{-1}/k_1k_2[L] \quad (7)$$

Values of k_{obsd} for this reaction step are given in Appendix I; values of the rate constants k_1 and k_1k_2/k_{-1} derived from eq 7, together with the corresponding activation parameters, are given in Table I.

Comparisons of (6) and (7) show that $k' = k_1k_2/k_{-1}$ and $k'' = k_2/k_{-1}$. Since for this mechanistic interpretation k_1 is the rate of unimolecular chelate ring opening, which is independent of the properties of the incoming nucleophile, L, the intercepts of plots of $1/k_{\text{obsd}}$ vs $1/[L]$ should be the same for all L. The values of k_1 obtained for L = P(OMe)₃ and P(O-*i*-Pr)₃ for reactions of (DTD)W(CO)₄ at 21.1 °C, $1.26(4) \times 10^{-3}$ and $1.13(4) \times 10^{-3}$ s⁻¹, and reactions of these ligands with (DTU)W(CO)₄ at 14.2 °C, $0.53(3) \times 10^{-3}$ and $0.57(3) \times 10^{-3}$ s⁻¹, respectively (Table I), are in agreement with this expectation.

The activation parameters obtained from this fast decay also are consistent with this mechanistic interpretation. ΔS_1^\ddagger for reactions of (DTD)W(CO)₄ and (DTU)W(CO)₄ with P(O-*i*-Pr)₃ are 18.0 (23) and 14.7 (23) cal/(deg mol), respectively, consistent with dissociative processes for chelate ring-opening. Values of $\Delta H_2^\ddagger - \Delta H_{-1}^\ddagger$ derived from the intercept/slope of the plots of $1/k_{\text{obsd}}$ vs $1/[L]$ are slightly negative (-3.6 (8) and -2.3 (16) kcal/mol, respectively). Such a trend also has been observed for chelate ring opening in (DTO)W(CO)₄² and (DTN)W(CO)₄,³ and has been interpreted in terms of an enthalpic barrier to chelate ring closure resulting from molecular distortions engendered upon ring closure as a consequence of the conformational preferences in the chelate rings.¹⁶ The corresponding entropies of activation, -12 (3) and -7 (5) cal/(deg mol), are consistent with the more negative values expected for bimolecular interaction of L with the five-coordinate *cis*-[(η¹-DTA)W(CO)₄] intermediates than for unimolecular chelate ring closure in these species.

Pulsed laser flash photolysis studies of other (DTA)W(CO)₄ complexes (DTA = DTHp,⁴ DTO⁵, and DTN⁶) have demonstrated that upon photolysis at 355 nm, chelate ring opening takes place and ring closure in the *cis*-[(DTA)(solvent)W(CO)₄] intermediates (path b in Scheme I) thus produced can be monitored. Unfortunately, the thermal reactions of (DTD)W(CO)₄ and (DTU)W(CO)₄ with L are so rapid under ambient conditions that these studies could be carried out in CB only in the absence of L. The studies that were performed, however, did permit the evaluation of the rates of ring closure in *cis*-[(η¹-DTD)(CB)W(CO)₄] and *cis*-[(η¹-DTU)(CB)W(CO)₄] intermediates over a temperature range of 9–35 °C. Values for the rate constants observed for these studies are given in Appendix II. According to the desolvation mechanism shown in Scheme I, the first-order rate constants observed for decay of the photogenerated transients should approximate $k_{-1}k_3/k_3[\text{CB}]$, i.e., $k_1K_{\text{eq}}/[\text{CB}]$.

It also has been shown that the enthalpies of activation for solvent displacement reactions of photogenerated intermediates such as *cis*-[(P(O-*i*-Pr)₃)(CB)W(CO)₄], closely related to those studied here, are dominated largely by the strength of the solvent-W interaction since they involve initial W-solvent bond breaking followed by interaction of L at the resulting five-coordinate *cis*-[(L)W(CO)₄] intermediate.⁸ Intermediates such as these have been found to be highly reactive, with rates approaching the diffusion-controlled limit.¹⁷ Consequently, values of ΔH_{-1}^\ddagger and ΔH_3^\ddagger should approach zero. That this situation applies here, also, is supported by the similarity in the enthalpy of activation observed for displacement of CB from *cis*-[(P(O-*i*-Pr)₃)(CB)W(CO)₄], 12.8 (9) kcal/mol, and those observed here for CB-displacement upon chelate ring closure in *cis*-[(η¹-DTD)(CB)W-

Table II. Rate Constants and Activation Parameters for W-S Bond Fission in *cis*-(η¹-DTA)(L)W(CO)₄ Complexes (DTA = DTD, DTU)

DTA	T, °C	L	10 ³ k ₄ , s ⁻¹	
DTD ^a	11.1	P(O- <i>i</i> -Pr) ₃	0.0044 (3)	
			0.0239 (18)	
	21.1	P(OMe) ₃	0.0038 (3)	
			0.100 (5)	
		P(O- <i>i</i> -Pr) ₃	0.160 (4)	
			0.65 (3)	
DTU	14.2	P(OMe) ₃	1.77 (4)	
			0.00758 (16)	
	21.0	P(O- <i>i</i> -Pr) ₃	0.00159 (7)	
			0.0235 (4)	
		33.9	P(O- <i>i</i> -Pr) ₃	0.157 (4)
				0.180 (3)
44.4	P(O- <i>i</i> -Pr) ₃	0.6255 (5)		
		1.77 (3)		

^aDTD: $\Delta H_4^\ddagger = 26.0(3)$ kcal/mol; $\Delta S_4^\ddagger = 11.1(11)$ cal/(deg mol).

^bDTU: $\Delta H_4^\ddagger = 25.8(2)$ kcal/mol; $\Delta S_4^\ddagger = 10.4(5)$ cal/(deg mol).

Table III. Comparisons of Rate Constants for Reactions of (DTA)W(CO)₄ Complexes (DTA = DTHp, DTO, DTN, DTD, DTU) with P(O-*i*-Pr)₃ at 35.2 °C in CB

rate const ^f	DTHp ^a	DTO ^b	DTN ^c	DTD	DTU
10 ⁵ k ₁ , s ⁻¹	<i>d</i>	0.16 (3)	6.5 (5)	81 (3)	1210 (50)
10 ⁻⁵ k ₋₁ K _{eq} /[CB]	<i>d</i>	5.67 (2)	2.04 (3)	0.94 (12)	0.62 (2)
10 ⁻⁵ k ₂ K _{eq} /[CB]	<i>d</i>	1.2 (2)	1.78 (5)	0.97 (22)	0.89 (9)
10 ⁵ k ₄ , s ⁻¹	32.7 (1)			16.0 (14)	18.0 (3)
k ₂ /k ₋₁	<i>d</i>	0.21 (5)	0.87 (4)	1.03 (9)	1.44 (9)
		0.28 (7) ^e	0.97 (9) ^e		

^aReference 4. ^bReferences 2 and 5. ^cReferences 3 and 6. ^dInterchange mechanism observed. ^eComplementary data from thermal ligand-exchange studies, rather than via flash photolysis studies.^{5,6} ^fRelative rates as a function of coordinated L for k₄, DTA = DTHp, at 44.5 °C in CB: CP (1); P(OMe)₃ (3.6); P(OPh)₃ (27); P(O-*i*-Pr)₃ (35); P(*n*-Bu)₃ (67).⁴

(CO)₄] and *cis*-[(η¹-DTU)(CB)W(CO)₄], 11.11 (6) and 10.5 (5) kcal/mol, respectively. By way of further comparison, these values are 8.8 (5) kcal/mol for chelate ring closure in *cis*-[(η¹-DTO)(CB)W(CO)₄]⁵ and 11.5 (3) kcal/mol in *cis*-[(η¹-DTN)(CB)W(CO)₄]⁶ respectively. The somewhat lower value observed in the DTO complex may indicate that desolvation upon chelate ring closure is an interchange process, as is the case in *cis*-[(η¹-DTHp)(DCE)W(CO)₄], (DCE = 1,2-dichloroethane), for which the enthalpy of activation is 5.6 (5) kcal/mol.⁴ Entropies of activation for chelate ring closure along the series *cis*-[(η¹-DTA)(CB)W(CO)₄], DTA = DTN, DTD, DTU, are 2.6 (15), 0.2 (18), and -2.3 (16) cal/(deg mol). This decrease may be related to that expected for the freezing of internal rotation about an increasing number of -CH₂- bonds upon ring closure.¹⁸

Reaction of *cis*-(η¹-DTA)(L)W(CO)₄ with L To Afford *cis*-(L)₂W(CO)₄. The slow subsequent conversion of the thermally produced *cis*-(η¹-DTA)(L)W(CO)₄ complexes to *cis*-(L)₂W(CO)₄ afforded the pseudo-first-order rate constants k'_{obsd} (eq 4) given in Appendix III, which were found to obey the pseudo-first-order rate law

$$k'_{\text{obsd}} = k_4 \quad (8)$$

This reaction step is best attributed to a mechanism involving rate-determining dissociation of the coordinated end of the bidentate ligand, governed by k₄ in Scheme I, followed by other rapid steps (*vide infra*). The step has been observed and has been discussed in detail for the very similar reaction of *cis*-(η¹-DTHp)(L)W(CO)₄ with various L.⁴ Values of k₄ are given in Table II. Enthalpies of activation for loss of DTD and DTU from their *cis*-(η¹-DTA)(P(O-*i*-Pr)₃)W(CO)₄ complexes are very similar, 26.0 (3) and 25.8 (2) kcal/mol, respectively, as might be anticipated for such similar complexes and are also similar to those observed for W-S bond breaking upon chelate ring opening in

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these complexes, 26.0 (7) and 24.9 (7) kcal/mol. The observed entropies of activation, 11.1 (11) and 10.4 (5) cal/(deg mol), respectively, for the DTD and DTU complexes are consistent with a dissociative process.

Reaction Rates of Chelate Ring Displacement as a Function of Chelate Ring Size. Table III presents rate constants associated with displacement of various DTA ligands from the five (DTA)W(CO)₄ complexes (DTA = DTHp, DTO, DTN, DTD, and DTU) by P(O-*i*-Pr)₃ in CB at 35.2 °C. It first should be recalled that the evidence suggests that the mechanism of ring opening in (DTHp)W(CO)₄ is a concerted process and thus obeys path a shown in Scheme I,⁴ while ring opening in (DTO)W(CO)₄, (DTN)W(CO)₄, (DTD)W(CO)₄, and (DTU)W(CO)₄ is dissociative in nature (path b of Scheme I). Thus, the rate of chelate ring opening in (DTHp)W(CO)₄ is anomalously fast and does not follow the trend of increasing rate as a function of chelate ring size observed for the other four complexes. For them, however, there is a regular increase in values of k_1 , the rate constants for chelate ring opening, as ring size increases from five to eight atoms. The increase over the series is some 7500-fold. On the other hand, while as might be expected rates of chelate ring closure decrease with increasing chelate ring-size, the decrease is only some 9-fold from DTU to DTO. Since the relative rates of attack by L at the *cis*-[(η^1 -DTA)W(CO)₄] intermediates, governed by $K_{eq}k_2$, are nearly invariant, changes in the rates of chelate ring opening to produce *cis*-(η^1 -DTA)(P(O-*i*-Pr)₃)W(CO)₄ complexes are largely attributable to a greatly enhanced value of k_1 with increasing ring size. Through the application of Hammond's postulate¹⁹ to this observation, it may be concluded that there is a great deal of W-S bond breaking in attaining the transition state leading to chelate ring opening; i.e., it is a "late" transition state that closely resembles the five-coordinate "ring-opened" intermediate. In this regard it should be recalled that there is much evidence which suggests that such intermediates are highly reactive and, consequently, that they should possess little discriminating ability among potential incoming nucleophiles.¹⁷ Entropies of activation accompanying chelate ring opening are observed, roughly, to increase along the series from the five-membered to the eight-membered ring system, consistent, as noted earlier, with an increase in the number of -CH₂- groups that can undergo internal rotation after chelate ring opening.¹⁸

Since changes in the rates of the step governed by k_{obsd} (eq 4) as a function of chelate ring size are dominated by k_1 , a comparison of the rate constants k_1 and k_4 (Table III) affords trends in the ratios k_{obsd}/k'_{obsd} (eq 4) for a given concentration of L, the ratios of rate constants for the two steps of the biphasic process observed here. This ratio determines which limiting form of the overall rate law for displacement of DTA by P(O-*i*-Pr)₃ for the series DTO, DTN, DTD, and DTU will be observed or if the two steps of the biphasic process are competitive. For (DTO)W(CO)₄ and (DTN)W(CO)₄ in their reactions with P(O-*i*-Pr)₃, for which biphasic behavior was not observed and thus for which it may be presumed that $k_{obsd} \ll k'_{obsd}$, values of k'_{obsd} could not be determined. However, the constancy of k'_{obsd} for the DTD and DTU complexes, $16.0 (14) \times 10^{-5} \text{ s}^{-1}$ and $18.0 (3) \times 10^{-5} \text{ s}^{-1}$, makes it reasonable to presume that this value is also similar for the DTO and DTN complexes, that is, that the length of the alkane chain in the chelate ring backbone does not significantly affect the value of k_4 . Assuming a value of 18×10^{-5} for k'_{obsd} , the ratios k_{obsd}/k'_{obsd} are as follows: DTO, 0.089; DTN, 0.36; DTD, 5.1; DTU, 67. These values indicate that the rate-limiting step changes from that governed by k_{obsd} for DTO to that governed by k'_{obsd} for DTU. The observed increase in rates of chelate ring opening along the series DTO, DTN, DTD, and DTU and the similar rates of dissociation of these ligands from their *cis*-(η^1 -DTA)(P(O-*i*-Pr)₃)W(CO)₄ complexes thus has as its consequences, as is observed, that, for reaction of (DTO)W(CO)₄ and (DTN)W(CO)₄ with P(O-*i*-Pr)₃, ring opening is rate determining while, for the analogous reactions of (DTD)W(CO)₄ and (DTU)W(CO)₄,

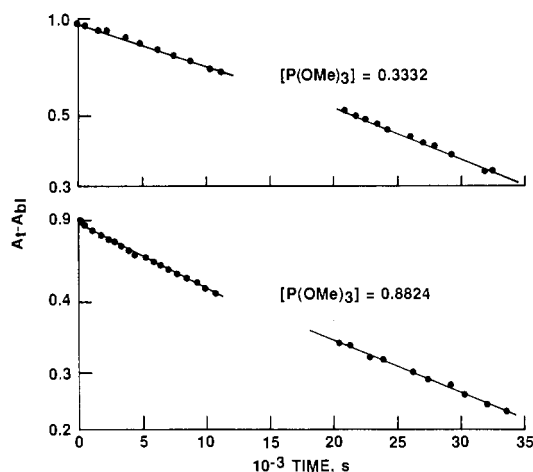


Figure 5. Plots of $\ln(A_t - A_{\infty})$ vs time for reactions of (DTN)W(CO)₄ with P(OMe)₃ in chlorobenzene at 43.3 °C at two concentrations of P(OMe)₃.

dissociation of DTA from *cis*-(η^1 -DTA)(L)W(CO)₄ is rate determining.

Another factor that may influence the rate law observed for reactions of a particular (DTA)W(CO)₄ is the effect of the steric nature of coordinated L on k_4 . For example, for (η^1 -DTHp)(L)W(CO)₄ at 44.5 °C (Table III), these rates vary some 67-fold from L = CP (Tolman cone angle²⁰ = 101°) to L = P(*n*-Bu)₃ (cone angle = 132°). This suggests, for reactions of (DTN)W(CO)₄, for which the k_{obsd}/k'_{obsd} ratio is closest to unity, that the rate law observed will depend critically on the steric nature of L. For bulky L, $k_{obsd} \gg k'_{obsd}$ and "monophasic" behavior consistent with the rate laws 5-7 is expected, while for nonbulky L, $k_{obsd} \ll k'_{obsd}$, for which biphasic behavior should be observed.

The latter observation is in fact noted for reaction of (DTN)W(CO)₄ with CP.³ However, noncoincident intercepts were observed for the plots of $1/k_{obsd}$ vs $1/[L]$ (differing values of " k_1 ") for the somewhat larger ligands P(OMe)₃ (cone angle = 107°) and P(OEt)₃ (cone angle = 109°).²⁰ This behavior was attributed to competition between paths a and b in Scheme I.⁴ For still larger ligands, such as P(OPh)₃, P(O-*i*-Pr)₃, and PPh₃ (cone angles = 128, 130, and 145°, respectively), observed values for k_1 were roughly similar. For P(O-*i*-Pr)₃ in its reaction with (DTN)W(CO)₄, the coincidence of the "competition ratios", k_2/k_{-1} , obtained thermally³ and via pulsed laser flash photolysis,⁶ given in Table III, supports the accessibility only of pathway b in Scheme I.

These observations suggest that the differing values for " k_1 " with "intermediate" ligands such as P(OMe)₃ and P(OEt)₃, rather than being the result of a competitive interchange pathway, could in fact be due to unrecognized biphasic behavior, in which k_{obsd} and k'_{obsd} were sufficiently similar that plots of $\ln(A_t - A_{\infty})$ vs time were taken to be linear. It has been noted by Espenson that slight curvature of plots of $\ln(A_t - A_{\infty})$ vs time often is attributable to a small difference between the experimentally determined value of A_{∞} and the true value; it is much less common that such curvature should be attributable to biphasic behavior.¹⁵

To address this question, preliminary studies of the reaction of (DTN)W(CO)₄ with P(OMe)₃ in CB were undertaken in which many more data points were acquired than in the previous³ studies. Figure 5 illustrates two plots of $\ln(A_t - A_{\infty})$ vs time obtained from that study. The plots clearly indicate biphasic behavior; in particular, it is to be noted that the increase of the value of k_{obsd} with increased concentration of P(OMe)₃ produces a plot that is concave downward at low [P(OMe)₃], but concave upward at higher [P(OMe)₃]. Thus, tentatively, it may be concluded that no interchange pathway (path a in Scheme I) is operative in this system, which is under current further study.

Conclusions. The diverse kinetics behavior observed for reactions of (DTA)W(CO)₄ with various L is largely influenced by

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the rates of unimolecular chelate ring opening, which increase with increasing chelate ring size, and the rates of W-S bond breaking in the *cis*-(η^1 -DTA)(L)W(CO)₄ intermediates produced after chelate ring opening, which increase with increasing steric demands of L.

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ciated.

Registry No. (DTD)W(CO)₄, 118297-74-8; (DTU)W(CO)₄, 118297-75-9; P(O-*i*-Pr)₃, 513-02-0; P(OMe)₃, 121-45-9; *cis*-(η^1 -DTD)(P(O-*i*-Pr)₃)W(CO)₄, 118297-76-0; *cis*-(η^1 -DTU)(P(O-*i*-Pr)₃)W(CO)₄, 118297-79-3; *cis*-(η^1 -DTD)(P(OMe)₃)W(CO)₄, 118297-77-1; *cis*-(η^1 -DTU)(P(OMe)₃)W(CO)₄, 118297-78-2; (η^1 -DTD)W(CO)₄, 118297-80-6; (η^1 -DTU)W(CO)₄, 118297-81-7.

Supplementary Material Available: Listings of values of k_{obsd} for reactions of (DTA)W(CO)₄ with L to afford *cis*-(η^1 -DTA)(L)W(CO)₄ complexes in chlorobenzene at various temperatures (Appendix I), rate constants for chelate ring reclosure in *cis*-[(η^1 -DTA)(CB)W(CO)₄] intermediates produced via pulsed laser flash photolysis at various temperatures (Appendix II), and values of k_4 for dissociation of DTA from *cis*-(η^1 -DTA)(L)W(CO)₄ complexes in the presence of L in CB at various temperatures (Appendix III) (8 pages). Ordering information is given on any current masthead page.

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Natural Bond Orbital (NBO) Analysis of Substituent Effects in Borazine Derivatives

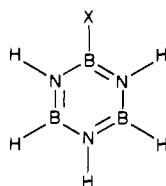
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The natural bond orbital (NBO) method of wave function analysis has been applied to characterize electronic substituent effects in B-monosubstituted borazine derivatives. The calculations indicate that the highly polar nature of the ipso B-N π^* antibonds and π bonds allows for enhanced interaction with π donors and limits the interaction with π acceptors relative to benzene. Calculated para π -electron density changes are smaller in magnitude than those in benzene derivatives, indicating decreased but still significant resonance delocalization. Calculated substituent/ring interaction energies and para π -electron density changes for B-monosubstituted borazines give improved Hammett correlations over those for analogous benzene systems.

Introduction

Borazine (Ia) has often been referred to as the "inorganic benzene" because its physical and structural properties are similar to those of benzene.¹



- Ia. X = H
 b. X = NH₂
 c. X = OH
 d. X = F
 e. X = Cl
 f. X = CN
 g. X = NO₂

Recent interest in borazine derivatives has intensified due to their utility as precursors to high molecular weight polymers and boron-nitrogen ceramics.² Electron diffraction studies have shown that the borazine molecule has a planar D_{3h} symmetry with all B-N bond lengths being equivalent ($r_{\text{B-N}} = 1.44 \text{ \AA}$).³ The B-N bond lengths are shorter than a representative B-N single bond (cf. H₃BNH₃, $r_{\text{B-N}} = 1.56 \text{ \AA}$) and suggest the B-N bond order in borazine is significantly greater than 1.

Chemically, however, borazine behaves very differently from benzene. Unlike benzene, borazine undergoes addition reactions quite readily. Also, electrophilic substitution is not found in borazine chemistry. Thus, it is generally agreed that the chemical properties of borazine are dictated to a greater extent by the polarity of the B-N σ bonds than by the aromaticity of the π system.¹

Intriguing, however, are the properties of substituted borazine derivatives. Relative ¹H NMR shifts of ortho and para N-H protons of B-monosubstituted borazines are strikingly similar to those of the analogous benzene derivatives.⁴⁻⁶ This suggests that indeed the borazine ring π system is capable of transmitting substituent effects transannularly. Although experimentally known for quite some time, a mechanistic discussion of substituent effects have been ignored in ab initio theoretical studies of borazine.⁷⁻¹² In this contribution, we theoretically characterize the magnitude and nature of the aromaticity in borazine and examine the mechanism of transmission of substituent effects through the borazine π system. Results are interpreted within the natural bond orbital (NBO) framework, which has been successfully applied to both localized and delocalized systems.¹³ This represents a

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