

## Articles

# Reactions of the Transient Species $W(CO)_5(\text{Cyclohexane})$ with Thiophene and Tetrahydrothiophene Studied by Time-Resolved Infrared Absorption Spectroscopy

Richard H. Schultz<sup>†</sup>

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel

Received June 7, 2004

The transient species  $W(CO)_5(\text{CyH})$  (CyH = cyclohexane) is prepared by laser photolysis of a CyH solution of  $W(CO)_6$ . Time-resolved infrared spectroscopy is used to probe the ligand substitution reactions of  $W(CO)_5(\text{CyH})$  with thiophene and tetrahydrothiophene (THT). From the temperature dependence of the second-order rate constants derived from the kinetic study, we obtain for reaction with thiophene  $\Delta H^\ddagger = 5.7 \pm 0.1 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -11.2 \pm 1.1 \text{ eu}$ , while for reaction with THT,  $\Delta H^\ddagger = 2.6 \pm 0.1 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -15.5 \pm 0.8 \text{ eu}$ . As expected, THT, the stronger electron donor, is the more reactive ligand of the two. THT is much more reactive than would be expected based on its strength as an electron donor, however. We show that the relative reactivities of O-, N-, and S-containing five-membered heterocycles toward ligand substitution at  $W(CO)_5(\text{CyH})$  can be accounted for by a model that takes into account the attacking ligand's polarizability in addition to its electron-donating ability.

## Introduction

Concerns about negative environmental effects arising from emissions of sulfur-containing species during combustion of fossil fuels have led to a significant effort toward development of efficient hydrodesulfurization (HDS) catalysts to reduce and remove sulfur from the fuel prior to combustion. The systems being developed as commercial HDS catalysts tend to be based on transition metals.<sup>1</sup> The development of practical HDS catalysts has thus seen a parallel research effort aimed at understanding at a more fundamental level the principles that guide the reactivity of transition-metal complexes with sulfur-containing organic species. In particular, many research groups have been working toward the goal of finding transition-metal systems that can perform homogeneous HDS under mild conditions in solution. Most of the systems thus far studied have used thiophene and its derivatives as models for the more complicated (and chemically heterogeneous) environment found in actual fossil fuel processing. In the course of the development of this chemistry, numerous

modes of reactivity have been found. Complexes have been developed in which a metal atom can insert into a  $C-S^{2-6}$  or  $C-H^{5a,7}$  bond of thiophene or one of its derivatives. In addition, numerous complexes are now known that can, under the proper conditions, reduce or desulfurize thiophenes in solution.<sup>6b,8–11</sup>

In addition to these studies of the reactivity of transition-metal complexes toward thiophene and related compounds, considerable research effort has gone into the more basic problem of the behavior of thiophene

(2) (a) Chen, J.; Angelici, R. A. *Organometallics* **1990**, *9*, 894. (b) Chen, J.; Daniels, L. M.; Angelici, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 2544. (c) Reynolds, M. A.; Guzei, I. A.; Angelici, R. A. *Chem. Commun.* **2000**, 513.

(3) (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Moneti, S.; Herrera, V.; Sánchez-Delgado, R. A. *J. Am. Chem. Soc.* **1994**, *116*, 4370. (b) Bianchini, C.; Jiménez, M. V.; Meli, A.; Vizza, F. *Organometallics* **1995**, *14*, 3196. (c) Bianchini, C.; Herrera, V.; Jiménez, M. V.; Laschi, F.; Meli, A.; Sánchez-Delgado, R.; Vizza, F.; Zanello, P. *Organometallics* **1995**, *14*, 4390. (d) Bianchini, C.; Jiménez, M. V.; Meli, A.; Moneti, S.; Vizza, F. *Inorg. Chim. Acta* **1998**, *272*, 55.

(4) Smith, V. C. M.; Aplin, R. T.; Brown, J. M.; Hursthouse, M. B.; Karalulov, A. I.; Abdul Malik, K. M.; Cooley, N. A. *J. Am. Chem. Soc.* **1994**, *116*, 5180.

(5) (a) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, *113*, 559. (b) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151. (c) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9851. (d) Jones, W. D.; Chin, R. M. *Organometallics* **1992**, *11*, 2698. (e) Jones, W. D.; Chin, R. M. *J. Organomet. Chem.* **1994**, *472*, 311. (f) Myers, A. W.; Jones, W. D. *Organometallics* **1996**, *15*, 2905. (g) Jones, W. D.; Chin, R. M.; Hoaglin, C. L. *Organometallics* **1999**, *18*, 1786. (h) Vico, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 7606. (i) Chantson, J.; Gorls, H.; Lots, S. *J. Organomet. Chem.* **2003**, *687*, 39.

(6) (a) Yu, K.; Li, H.; Watson, E. J.; Virkaitis, K. L.; Carpenter, G. B.; Sweigart, D. A. *Organometallics* **2001**, *20*, 3550. (b) Yu, K.; Li, H.; Watson, E. J.; Virkaitis, K. L.; D'Acchioli, J. S.; Carpenter, G. B.; Sweigart, D. A.; Czech, P. T.; Overly, K. R.; Coughlin, F. *Organometallics* **2002**, *21*, 1262.

<sup>†</sup> E-mail: schultr@mail.biu.ac.il. Fax: +972-3-535-1250.

(1) Recent reviews include, inter alia: (a) Breyse, M.; Djega-Mariadassou, G.; Pessayre, S.; Geantet, C.; Vrinat, M.; Perot, G.; Lemaire, M. *Catal. Today* **2003**, *84*, 129. (b) Oyama, S. T. *J. Catal.* **2003**, *216*, 343. (c) Song, C.; Ma, X. *Appl. Catal. B* **2003**, *41*, 207. (d) Furimsky, E. *Appl. Catal. A* **2003**, *240*, 1. (e) Chianelli, R. R.; Berhault, G.; Raybaud, P.; Kasztelan, S.; Hafner, J.; Toulhoat, H. *Appl. Catal. A* **2002**, *227*, 83. (f) Brorson, M.; King, J. D.; Kiriakidou, K.; Prestopino, F.; Nordlander, E. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH: Weinheim, Germany, 1999; Vol. 2, p 741. (g) Rodriguez, J. A.; Hrbek, J. *Acc. Chem. Res.* **1999**, *32*, 719. (h) Whitehurst, D. D.; Isoda, T.; Mochida, I. *Adv. Catal.* **1998**, *42*, 345.

and its derivatives as ligands independent of any subsequent reactions they may undergo at transition-metal centers. These ligands have been found to exhibit a rich and varied chemistry.<sup>12,13</sup> For example,  $\eta^1$ ,  $\eta^2$ ,  $\eta^4$ , and  $\eta^5$  binding modes have all been observed for thiophene,<sup>12</sup> and ligands such as benzothiophene (BT) or dibenzothiophene (DBT) can bind  $\eta^1$  through the S atom,  $\eta^6$  through a benzene ring, or  $\eta^2$  through two adjacent C atoms in a benzene or thiophene ring.<sup>14</sup> In fact, in room-temperature solution, the complexes CpRe(CO)<sub>2</sub>(BT) and Cp\*Re(CO)<sub>2</sub>(BT) are actually equilibrium mixtures of the  $\eta^1$ (S)-BT and 2,3- $\eta^2$ -BT linkage isomers.<sup>15</sup>

In our laboratory, we have been concerned primarily with the *kinetics* of the interaction between a coordinatively unsaturated transition-metal intermediate and an incoming ligand L to form a more stable complex and how the properties of the ligand and of the intermediate affect the reactivity. We have performed, inter alia, a series of studies of the reactions of the cyclohexane-solvated intermediate W(CO)<sub>5</sub>(CyH) (CyH = a molecule of the cyclohexane solvent) with five-membered heterocyclic molecules containing oxygen<sup>16–18</sup> or nitrogen.<sup>19</sup> We observed that in these systems, as the incoming ligand becomes more electron-donating,  $\Delta H^\ddagger$  (and  $\Delta G^\ddagger$  at temperatures around room temperature) for the sub-

stitution decreases, unless specific steric factors intervene.<sup>18</sup> In this report, we extend these studies to include reactions of two S-containing ligands, thiophene and tetrahydrothiophene (THT). Our goal was to see if the trends we observed for reaction partners containing first-row heterocyclic atoms would still occur with ligands containing a second-row heteroatom, and whether the model we developed in our previous studies can be extended to include the second-row analogues of furan and THF.

## Experimental Section

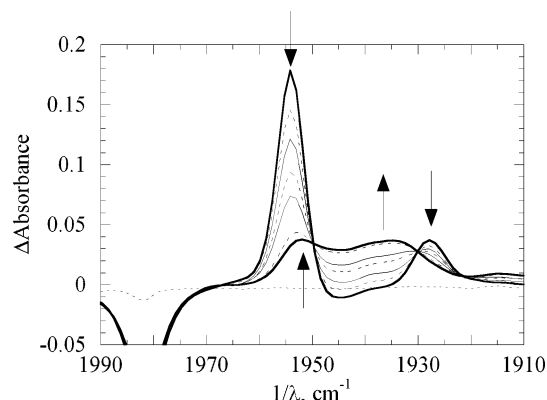
The spectrometer on which these experiments were performed has been described in detail previously,<sup>16</sup> so only a brief description will be given here. A CyH solution containing  $(0.5-1) \times 10^{-3}$  mol L<sup>-1</sup> W(CO)<sub>6</sub> and an at least 10-fold excess of the reaction partner L is prepared. The solution flows through a CaF<sub>2</sub> IR cell (0.5 mm path length, held to within  $\pm 0.3$  °C of the nominal reaction temperature), where reaction is initiated by the output of a pulsed XeCl excimer laser (308 nm,  $\sim 20$  ns/pulse, typically 2–5 Hz and 60–80 mJ/pulse). To ensure that each photolysis pulse irradiates fresh solution, the solution flows continuously through the cell. The UV flash leads to loss of a CO ligand and formation, within the photolysis pulse,<sup>20</sup> of the solvated W(CO)<sub>5</sub>(CyH) intermediate. The subsequent reaction of this intermediate is then monitored by following the time evolution of the solution's IR absorption.

To determine the C–O stretching frequencies of the species present during the course of the reaction, we use a step-scan FTIR (S<sup>2</sup>FTIR) spectrometer, which enables collection of the time-resolved IR spectrum with sub-microsecond time resolution. In the particular case of the experiments discussed here, the S<sup>2</sup>FTIR was run at 4 cm<sup>-1</sup> spectral resolution and with time steps of 200 ns. The temperature-dependent reaction kinetics of W(CO)<sub>5</sub>(CyH) are monitored by using a continuously tunable CW Pb-salt diode laser as the IR source. This source is tuned to a specific frequency corresponding to a C–O stretching absorption of W(CO)<sub>5</sub>(CyH) or of W(CO)<sub>5</sub>L, and the time dependence of the IR signal impinging upon an InSb detector (ca. 50 ns rise time) following the UV pulse is recorded. The raw IR signal is then converted to the change in absorbance  $\Delta A$ , and pseudo-first-order rate constants  $k_{\text{obs}}$  are determined by a linear fit to  $\ln|\Delta A_\infty - \Delta A_0|$ . The values of  $k_{\text{obs}}$  reported here were determined from the exponential decay of the 1954 cm<sup>-1</sup> W(CO)<sub>5</sub>(CyH) absorbance. In the case of reaction with thiophene, because of overlap of the peak of the W(CO)<sub>5</sub>(CyH) absorbance with a product C–O stretch, the best results were obtained when the laser was tuned  $\sim 2$  cm<sup>-1</sup> to the blue of the W(CO)<sub>5</sub>(CyH) absorbance peak. In some cases, the time dependence of the rise of the absorbance corresponding to W(CO)<sub>5</sub>L was measured as well. The value of  $k_{\text{obs}}$  for growth of the product was found to be identical to that for the decay of the W(CO)<sub>5</sub>(CyH) absorbance to within experimental error. The values of  $k_{\text{obs}}$  reported in Tables S-1 and S-2 represent averages of at least two independent measurements made at each temperature and concentration.

CyH was obtained in HPLC grade and distilled from Na/benzophenone. The concentration of benzophenone in the distilled solvent was confirmed by UV–vis spectroscopy to be  $< 10^{-6}$  mol L<sup>-1</sup>. Thiophene was obtained from Aldrich in  $\sim 98\%$  purity. The as-received thiophene was further purified by

- (7) (a) Bianchini, C.; Jiménez, M. V.; Meli, A.; Moneti, S.; Vizza, F. *J. Organomet. Chem.* **1995**, *504*, 27. (b) Stafford, P. R.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1995**, *34*, 5220. (c) Bianchini, C.; Casares, J. A.; Osman, R.; Pattison, D. I.; Peruzzini, M.; Perutz, R. N.; Zanobini, F. *Organometallics* **1997**, *16*, 4611. (d) Paneque, M.; Poveda, M. L.; Salazar, V.; Taboada, S.; Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Ruiz, C. *Organometallics* **1999**, *18*, 139.
- (8) (a) Eisch, J. J.; Im, K. R. *J. Organomet. Chem.* **1977**, *139*, C51. (b) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387.
- (9) (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sánchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 2731. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Herrera, V.; Sánchez-Delgado, R. A. *Organometallics* **1994**, *13*, 721. (c) Bianchini, C.; Frediani, P.; Herrera, V.; Jiménez, M. V.; Meli, A.; Rincón, L.; Sánchez-Delgado, R.; Vizza, F. *J. Am. Chem. Soc.* **1995**, *117*, 4333. (d) Bianchini, C.; Jiménez, M. V.; Meli, A.; Moneti, S.; Vizza, F.; Herrera, V.; Sánchez-Delgado, R. A. *Organometallics* **1995**, *14*, 2342. (e) Bianchini, C.; Fabbri, D.; Gladiali, S.; Meli, A.; Pohl, W.; Vizza, F. *Organometallics* **1996**, *15*, 4604. (f) Herrera, V.; Fuentes, A.; Rosales, M.; Sánchez-Delgado, R.; Bianchini, C.; Meli, A.; Vizza, F. *Organometallics* **1997**, *16*, 2465. (g) Bianchini, C.; Meli, A.; Moneti, S.; Oberhauser, W.; Vizza, F.; Herrera, V.; Fuentes, A.; Sánchez-Delgado, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 7071.
- (10) (a) Rosini, G. P.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 10767. (b) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1994**, *116*, 198. (c) Vicić, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 10855. (d) Vicić, D. A.; Jones, W. D. *Organometallics* **1998**, *17*, 3411.
- (11) (a) Frediani, P.; Salvini, A.; Finocchiaro, S. *J. Organomet. Chem.* **1999**, *584*, 265. (b) Janak, K. E.; Tanski, J. M.; Churchill, D. G.; Parkin, G. J. *Am. Chem. Soc.* **2002**, *124*, 4182. (c) Borowski, A. F.; Sabo-Étienne, S.; Donnadieu, B.; Chaudret, B. *Organometallics* **2003**, *22*, 4803. (d) Chérioux, F.; Therrien, B.; Süß-Fink, G. *Chem. Commun.* **2004**, 204.
- (12) (a) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259. (b) Harris, S. *Organometallics* **1994**, *13*, 2628. (c) Harris, S. *Polyhedron* **1997**, *16*, 3219. (d) Angelici, R. J. *Organometallics* **2001**, *20*, 1259.
- (13) (a) Sanger, M. J.; Angelici, R. J. *Organometallics* **1994**, *13*, 1821. (b) Mills, P.; Korlann, S.; Bussell, M. E.; Reynolds, M. A.; Ovichinnikov, M. V.; Angelici, R. J.; Stinner, C.; Weber, T.; Prins, R. *J. Phys. Chem. A* **2001**, *105*, 4418.
- (14) (a) Choi, M.-G.; Robertson, M. J.; Angelici, R. J. *Inorg. Chem.* **1991**, *113*, 4005. (b) Rao, K. M.; Day, C. L.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 5046.
- (15) Choi, M.-G.; Angelici, R. J. *Organometallics* **1992**, *11*, 3328–3334.
- (16) Paur-Afshari, R.; Lin, J.; Schultz, R. H. *Organometallics* **2000**, *19*, 1682.
- (17) Lugovskoy, A.; Paur-Afshari, R.; Schultz, R. H. *J. Phys. Chem. A* **2000**, *104*, 10587.
- (18) Krishnan, R.; Schultz, R. H. *Organometallics* **2001**, *20*, 3314.
- (19) Lugovskoy, A.; Shagal, A.; Lugovskoy, S.; Huppert, I.; Schultz, R. H. *Organometallics* **2003**, *22*, 2273.

- (20) (a) Welch, J. A.; Peters, K. S.; Vaida, V. *J. Phys. Chem.* **1982**, *86*, 1941. (b) Wang, L.; Zhu, X.; Spears, K. G. *J. Am. Chem. Soc.* **1988**, *110*, 8695. (c) Lee, M.; Harris, C. B. *J. Am. Chem. Soc.* **1989**, *111*, 8963. (d) Xie, X.; Simon, J. D. *J. Phys. Chem.* **1989**, *93*, 4401. (e) Joly, A. G.; Nelson, K. A. *Chem. Phys.* **1991**, *152*, 69. (f) Dougherty, T. P.; Heilweil, E. J. *J. Chem. Phys.* **1994**, *100*, 4006. (g) Dougherty, T. P.; Grubbs, W. T.; Heilweil, E. J. *J. Phys. Chem.* **1994**, *98*, 9396. (h) Perutz, R. N. *Pure Appl. Chem.* **1993**, *70*, 2211. (i) Wang, C.; Mohney, B. K.; Akremitchev, B. B.; Walker, G. C. *J. Phys. Chem. A* **2000**, *104*, 4314.

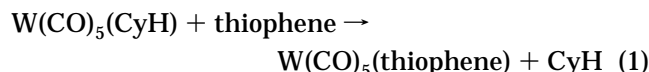


**Figure 1.** Time-resolved step-scan FTIR spectra for the reaction of  $W(CO)_5(\text{CyH})$  with thiophene. Shown are IR spectra  $-1, 0, 2, 5, 10, 15, 30,$  and  $40 \mu\text{s}$  after photolysis of a room-temperature CyH solution containing  $7 \times 10^{-4} \text{ mol L}^{-1} W(CO)_6$  and  $0.160 \text{ mol L}^{-1}$  thiophene.

storage for 10 days over  $AgNO_3$ , followed by filtration, reflux for 24 h over a mixture of  $CaH_2$  and activated charcoal, and distillation.<sup>21</sup> The purified thiophene was then stored in a clean, dry bottle over molecular sieves. THF was obtained from Aldrich in  $>99\%$  purity (confirmed by NMR spectroscopy) and used without further purification except for storage over molecular sieves to remove any residual  $H_2O$ .

## Results

**$W(CO)_5(\text{CyH}) + \text{Thiophene}$ .**  $S^2$ FTIR results for the reaction of  $W(CO)_5(\text{CyH})$  are shown in Figure 1. The intermediate decays cleanly to a single product with two strong C–O stretches at  $1950$  and  $1933 \text{ cm}^{-1}$  and a much weaker one at  $2080 \text{ cm}^{-1}$ . We identify this product as  $W(CO)_5(\text{thiophene})$ , produced in reaction 1:



To our knowledge, the sole report of this species that has so far appeared in the literature is an IR study from 1965,<sup>22</sup> in which the C–O stretching frequencies for  $W(CO)_5(\text{thiophene})$  at  $20^\circ\text{C}$  in *n*-hexane were reported to be  $2085, 1953,$  and  $1937 \text{ cm}^{-1}$ , quite similar to the frequencies reported in the present work (Table 1). The authors of the 1965 study also reported that at  $-180^\circ\text{C}$  in a 1:4 isopentane/methylcyclohexane mixture the C–O stretches of  $W(CO)_5(\text{thiophene})$  appear at  $2092, 1952,$  and  $1921 \text{ cm}^{-1}$ , but that upon warming to about  $-110^\circ\text{C}$ , the peaks shift to those of the room-temperature species. They proposed that the two spectra reflected different structures and hypothesized that at low temperature they had trapped  $W(CO)_5(\eta^5\text{-thiophene})$ , which converted to the  $\eta^1$  structure as the temperature was raised.

In our experiment, we found no evidence for the existence at room temperature of more than one product appearing on a microsecond time scale. Efforts to synthesize a sufficiently large quantity of  $W(CO)_5$ -

(21) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897. This procedure demonstrates that while the label of the commercially supplied sample indicates that thiophene has a "stench", the observed foul odor actually arises from the alkanethiols present as  $<1\%$  impurities rather than from the thiophene itself.

(22) Stolz, I. W.; Haas, H.; Sheline, R. K. *J. Am. Chem. Soc.* **1965**, *87*, 716.

**Table 1.** C–O Stretch IR Absorption Frequencies and Force Constants for  $M(CO)_5L$  in CyH Solution<sup>a</sup>

L	$\nu_{CO}, \text{cm}^{-1}$			$k_{CO}, \text{mdyn C}^{-1}$		
	$A_1(1)$	$A_1(2)$	E	$k_{cis}$	$k_{trans}$	$k_i$
CyH	2087	1928	1954	16.075	15.233	0.326
thiophene	2080	1933	1950	15.995	15.305	0.317
THF	2073	1926	1939	15.839	15.202	0.326
furan <sup>b</sup>	2078	1936	1949	15.974	15.35	0.315
THF <sup>c</sup>	2074	1911	1933	15.778	14.98	0.342
pyrrole <sup>d</sup>	2074	1918	1939	15.844	15.079	0.328
pyrrolidine <sup>d</sup>	2067	1910	1923	15.634	14.969	0.348

<sup>a</sup>  $k_{cis}$ , C–O *cis* to L;  $k_{trans}$ , C–O *trans* to L;  $k_i$ , interaction force constant for mutually *cis* carbonyls. Force constants were calculated using the Cotton–Kraihanzel method (ref 34). <sup>b</sup> Ref 17. <sup>c</sup> Ref 16. <sup>d</sup> Ref 19.

(thiophene) to enable structural elucidation by  $^1\text{H}$  NMR have thus far been unsuccessful, and the  $W(CO)_5$ -(thiophene) product seems to be particularly unstable compared to other  $W(CO)_5L$  complexes we have observed.  $W(CO)_5(\text{thiophene})$  produced by exposure of a CyH solution containing  $W(CO)_6$  and an excess of thiophene to several laser shots decomposes within several minutes at room temperature to as yet unidentified products. Similarly, Ruetter et al.<sup>23</sup> reported that they were unable to isolate any  $Mo(CO)_n(\text{thiophene})$  complexes, and other reports in the literature have indicated that S-bound thiophene complexes are particularly reactive toward replacement of the thiophene ligand.<sup>24</sup> To try to obtain some additional insight into the structure of  $W(CO)_5(\text{thiophene})$ , we performed a DFT calculation on the complex using the Gaussian 03 program<sup>25</sup> (B3LYP level, using the Stuttgart 1997 ECP and basis sets for W,<sup>26</sup> 6-31++G(2d,2p) basis set for C, H, and O, and 6-31++G(3df) basis set for S). This calculation predicts that the  $\eta^1$  structure is an energy minimum, with the plane of the thiophene ring at an angle of  $\sim 140^\circ$  to the plane of the *cis* carbonyls. This calculated structure is quite similar to the X-ray structure reported for  $W(CO)_5(\eta^1\text{-DBT})$ ,<sup>27</sup> and such bent

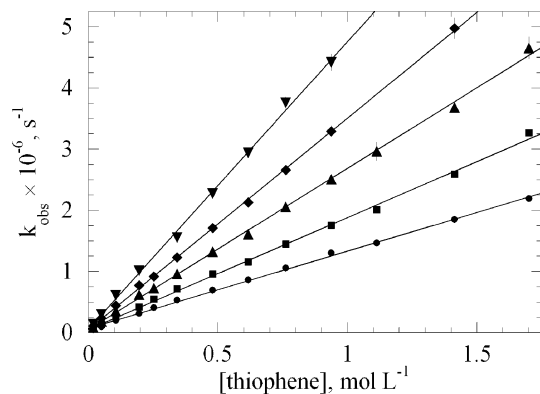
(23) Ruetter, F.; Valencia, N.; Sánchez-Delgado, R. *J. Am. Chem. Soc.* **1989**, *111*, 40.

(24) (a) Draganjac, M.; Ruffing, D. G.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 1909. (b) Constable, E. C.; Henney, R. P. G.; Tocher, D. A. *J. Chem. Soc., Chem. Commun.* **1989**, 913. (c) Liu, C.; Lucas, C. R.; Newlands, M. J.; Charland, J. P. *Inorg. Chem.* **1990**, *29*, 4380.

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. W.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03* (Revision B.04); Gaussian, Inc.: Pittsburgh, PA, 2003.

(26) Dolg, M.; Stoll, H.; Preuss, H.; Pitzer, R. M. *J. Phys. Chem.* **1993**, *97*, 5852. Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/25/04, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, funded by the U.S. Department of Energy, and available for free download at <http://www.emsl.pnl.gov/forms/basisform.html>.

(27) Reynolds, M. A.; Guzei, I. A.; Logsdon, B. C.; Thomas, L. M.; Jacobson, R. A.; Angelici, R. A. *Organometallics* **1999**, *18*, 4075.

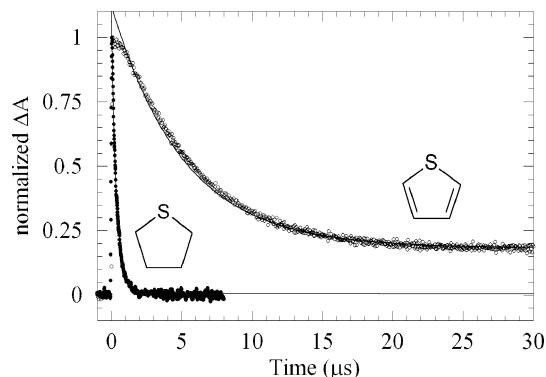
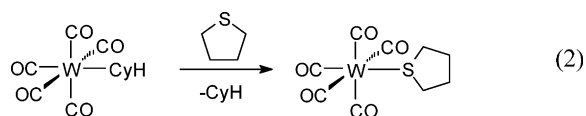


**Figure 2.** Experimentally determined pseudo-first-order reaction rate constant  $k_{\text{obs}}$  for reaction 1 as a function of thiophene concentration at 20 °C (●), 30 °C (■), 40 °C (▲), 50 °C (◆), and 60 °C (▼). The solid lines represent least-squares linear fits to  $k_{\text{obs}}$  as a function of [thiophene].

structures are typical of  $\eta^1$ -thiophene complexes in general. A second DFT calculation performed at the same level of theory predicts that the  $\eta^2$  (side-bound) structure of  $\text{W}(\text{CO})_5(\text{thiophene})$  is  $\sim 4$  kcal/mol higher in energy than the  $\eta^1$  structure. While assignment of the hapticity of the thiophene ligand in the  $\text{W}(\text{CO})_5(\text{thiophene})$  product that appears within microseconds of the photolysis does not affect any of the conclusions of the present study, the results of the theoretical calculations, the similarity of its IR spectrum to other  $\text{W}(\text{CO})_5(\eta^1\text{-L})$  complexes, and our experimental observation that the kinetic product of the reaction of  $\text{W}(\text{CO})_5(\text{CyH})$  with an ambidentate heterocyclic ligand adopts the  $\eta^1$  structure even if the  $\eta^2$  structure is thermodynamically more stable<sup>28</sup> lead us to the conclusion that the immediate product of reaction 1 is S-bound  $\text{W}(\text{CO})_5(\eta^1\text{-thiophene})$ .

For our temperature-dependent kinetic studies, we measured the pseudo-first-order rate constants  $k_{\text{obs}}$  for reaction 1 over the concentration range  $0.0184 \text{ mol L}^{-1} \leq [\text{thiophene}] \leq 1.702 \text{ mol L}^{-1}$  at 20, 30, and 40 °C. Above 40 °C,  $k_{\text{obs}}$  was too large for accurate measurement in our apparatus at the highest thiophene concentrations used at lower temperatures. Thus, at 50 °C,  $k_{\text{obs}}$  was measured to a maximum thiophene concentration of  $1.414 \text{ mol L}^{-1}$ , while at 60 °C,  $[\text{thiophene}]_{\text{max}}$  was  $0.938 \text{ mol L}^{-1}$ . The results of the measurements of  $k_{\text{obs}}$  as a function of [thiophene] are plotted in Figure 2, and the experimental values of  $k_{\text{obs}}$  as a function of temperature and [thiophene] are given in the Supporting Information in Table S-1. As can be seen in the figure, and as is typical for ligand substitution reactions of solvated transition-metal intermediates,  $k_{\text{obs}}$  is a linear function of [thiophene] over the entire concentration range at which the experiments were performed.

**$\text{W}(\text{CO})_5(\text{CyH}) + \text{THT}$ .** Qualitatively, the reaction of  $\text{W}(\text{CO})_5(\text{CyH})$  with THT is similar to its reaction with thiophene. The IR absorptions of the intermediate decay with the simultaneous appearance of a new set of absorptions, Table 1. We attribute these new absorptions to  $\text{W}(\text{CO})_5(\eta^1\text{-THT})$ , formed in reaction 2. We see



**Figure 3.** IR absorption traces for reaction of  $\text{W}(\text{CO})_5(\text{CyH})$  with thiophene (●) and THT (○). The graph shows the normalized change in absorbance in the band corresponding to the E symmetry C–O stretch of  $\text{W}(\text{CO})_5(\text{CyH})$  following the photolysis of a CyH solution of  $\text{W}(\text{CO})_6$  in the presence of  $0.11 \text{ mol L}^{-1}$  ligand at 20 °C. The solid lines represent exponential fits to the decay of the absorbance with  $k_{\text{obs}} = 1.98 \times 10^5 \text{ s}^{-1}$  for reaction with thiophene and  $k_{\text{obs}} = 2.94 \times 10^6 \text{ s}^{-1}$  for reaction with THT.

no evidence for formation of any other product on any time scale from microseconds to minutes. C–O stretching frequencies for  $\text{W}(\text{CO})_5(\eta^1\text{-THT})$  have been previously reported as  $2073 \text{ cm}^{-1}$  in  $\text{CS}_2$ ,<sup>29</sup>  $1930.5$ ,  $1941.5$ , and  $2075 \text{ cm}^{-1}$  in 2,2,4-trimethylpentane,<sup>30</sup> and  $1919$ ,  $1939$ , and  $2078 \text{ cm}^{-1}$  in pentane.<sup>31</sup>

The primary difference between the kinetics of reactions 1 and 2 is that THT reacts considerably more rapidly at any given temperature and concentration than does thiophene. This difference is illustrated by the experimental traces shown in Figure 3. Because of the rapidity of the reaction, the maximum concentration at which we could accurately measure  $k_{\text{obs}}$  in our apparatus was considerably lower for reaction with THT than it was for thiophene. At 20 and 30 °C,  $k_{\text{obs}}$  was measured over the concentration range  $6.07 \times 10^{-3} \text{ mol L}^{-1} \leq [\text{THT}] \leq 0.218 \text{ mol L}^{-1}$ ; at 40 °C,  $[\text{THT}]_{\text{max}}$  was  $0.130 \text{ mol L}^{-1}$ ; and at 50 and 60 °C,  $[\text{THT}]_{\text{max}}$  was  $0.113 \text{ mol L}^{-1}$ . The experimental results ( $k_{\text{obs}}$  as a function of [THT]) are shown graphically in Figure 4, and the values of  $k_{\text{obs}}$  are given in Table S-2 of the Supporting Information. As with reaction 1,  $k_{\text{obs}}$  for reaction 2 is a linear function of [THT] over the concentration range measured.

## Discussion

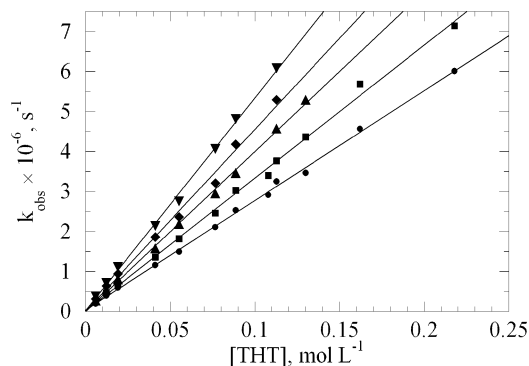
**Activation Parameters and Reaction Mechanism.** For each temperature at which kinetic measurements were made, we derive second-order rate constants  $k_a$  as the slopes of linear fits to  $k_{\text{obs}}$ ; the values of  $k_a$  are summarized in Table 2. An Eyring analysis of the temperature dependence of  $k_a$  for reactions 1 and 2 is shown in Figure 5. From these analyses, we derive  $\Delta H^\ddagger = 5.7 \pm 0.1 \text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger = -11.2 \pm 1.1 \text{ eu}$  for reaction with thiophene and  $\Delta H^\ddagger = 2.6 \pm 0.1 \text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger = -15.5 \pm 0.8 \text{ eu}$  for reaction with THT.

(28) Shagal, A.; Schultz, R. H. *Organometallics* **2003**, *21*, 5657.

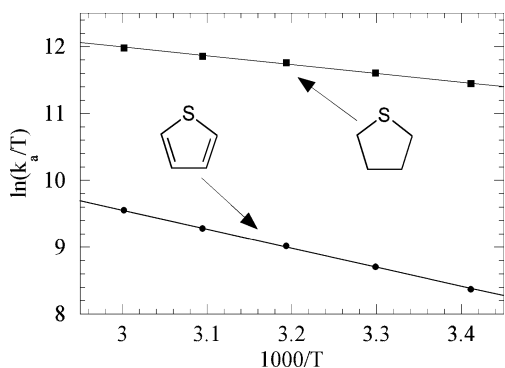
(29) Strohmeier, W.; Guttenberger, J. F.; Popp, G. *Chem. Ber.* **1965**, *98*, 2248.

(30) Brown, R. A.; Dobson, G. R. *Inorg. Chim. Acta* **1972**, *6*, 65.

(31) Sauer, N. N.; Angelici, R. J. *Inorg. Chem.* **1987**, *26*, 2160.



**Figure 4.** Experimentally determined pseudo-first-order reaction rate constant  $k_{\text{obs}}$  for reaction 2 as a function of THT concentration at 20 °C (●), 30 °C (■), 40 °C (▲), 50 °C (◆), and 60 °C (▼). The solid lines represent least-squares linear fits to  $k_{\text{obs}}$  as a function of [THT].



**Figure 5.** Eyring analyses of reactions 1 (●) and 2 (■). The solid lines are weighted least-squares linear fits to the experimental data points.

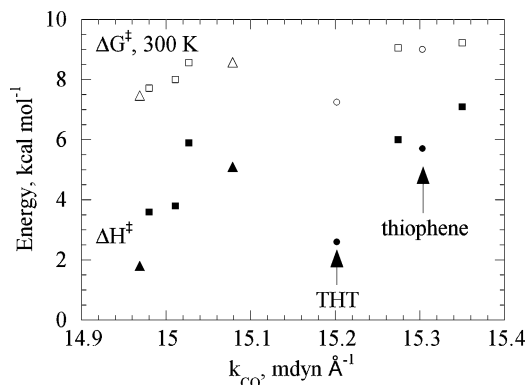
**Table 2. Second-Order Rate Constants for Reactions 1 and 2 (1 $\sigma$  uncertainties in parentheses)**

$T, ^\circ\text{C}$	$k_a, 10^6 \text{ mol L}^{-1} \text{ s}^{-1}$	
	thiophene	THT
20	1.25 (0.01)	27.45 (0.35)
30	1.86 (0.02)	33.25 (0.58)
40	2.57 (0.02)	40.00 (0.61)
50	3.45 (0.02)	45.52 (1.59)
60	4.69 (0.07)	53.19 (1.03)

While reactions of solvated intermediates can show mechanistically ambiguous kinetics,<sup>32</sup> we believe that the results for reactions 1 and 2 are best explained by an associative interchange ( $I_a$ ) mechanism. The low values of  $\Delta H^\ddagger$  relative to the  $(\text{CO})_5\text{W}-\text{CyH}$  bond dissociation energy (estimated<sup>33</sup> to be  $\sim 10\text{--}15 \text{ kcal mol}^{-1}$ ) and the negative values of  $\Delta S^\ddagger$  are typical of associative ligand exchange reactions. In addition, the strong dependence of the activation parameters on the identity of the incoming ligand and the greater reactivity of the stronger electron donor imply involvement of the incoming ligand in the transition state. We reached similar

(32) (a) Childs, G. I.; Colley, C. S.; Dyer, J.; Grills, D. C.; Sun, X.-Z.; Yang, J.; George, M. W. *J. Chem. Soc., Dalton Trans.* **2000**, 1901. (b) Schultz, R. H. *Int. J. Chem. Kinet.* **2004**, *36*, 427.

(33) (a) Yang, G. K.; Vaida, V.; Peters, K. S. *Polyhedron* **1988**, *7*, 1619. (b) Morse, J. M., Jr.; Parker, G. H.; Burkey, T. J. *Organometallics* **1989**, *8*, 2471. (c) Braslavsky, S. E.; Heibel, G. E. *Chem. Rev.* **1992**, *92*, 1381. (d) Hester, D. M.; Sun, J.; Harper, A. W.; Yang, G. K. *J. Am. Chem. Soc.* **1992**, *114*, 5234. (e) Leu, G.-L.; Burkey, T. J. *J. Coord. Chem.* **1995**, *34*, 87. (f) Zarić, S.; Hall, M. B. *J. Phys. Chem. A* **1997**, *101*, 4646. (g) Burkey, T. J. Personal communication.



**Figure 6.**  $\Delta H^\ddagger$  (solid symbols) and  $\Delta G^\ddagger$  at 300 K (open symbols) for ligand substitution at  $W(\text{CO})_5(\text{CyH})$  by L as a function of  $k_{\text{CO}}^{\text{trans}}$ , the stretching force constant of the carbonyl *trans* to L in the product  $W(\text{CO})_5\text{L}$ . Shown are results for five-membered heterocycles containing O (■, □), NH (▲, △), or S (●, ○).

mechanistic conclusions in our other studies of ligand substitution at  $W(\text{CO})_5(\text{CyH})$ .<sup>16–19</sup>

**Reactivity Trends.** In our previous studies of the reactions of  $W(\text{CO})_5(\text{CyH})$  with N- and O-containing analogues of thiophene and THT,<sup>16,17,19</sup> we found that  $\Delta H^\ddagger$  (and  $\Delta G^\ddagger$  at 300 K) for the exchange correlates with  $k_{\text{CO}}^{\text{trans}}$ , the Cotton–Kraihanzel stretching force constant<sup>34</sup> of the carbonyl *trans* to L in the product  $W(\text{CO})_5\text{L}$ . We explained this correlation in terms of a stronger electron donor being better able to stabilize the electron-poor transition state.<sup>35</sup> This correlation of the reaction barrier with a property of the product is further evidence for a late (i.e., associative) transition state. In contrast, no such effect is seen in the analogous reactions of  $\text{CpMn}(\text{CO})_2(\text{CyH})$ , which appears to react more dissociatively.<sup>36</sup>

Figure 6 shows a plot of  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  (300 K) for ligand exchange at  $W(\text{CO})_5(\text{CyH})$  as a function of  $k_{\text{CO}}^{\text{trans}}$ .<sup>37</sup> It is immediately clear that THT fails to fit in with the correlation that we previously noted for the first-row heterocycles.<sup>38</sup> Once thiophene and THT are included, one can also question whether pyrrolidine (the leftmost point on the graph) follows the trend in  $\Delta H^\ddagger$  either. We had previously argued<sup>19</sup> that the deviation of  $\Delta H^\ddagger$  for the reaction with pyrrolidine is consistent with an asymptotic rise in  $\Delta H^\ddagger$  with  $k_{\text{CO}}^{\text{trans}}$  to the  $(\text{CO})_5\text{W}-\text{CyH}$  bond dissociation energy, rather than with a purely linear relationship between  $\Delta H^\ddagger$  and  $k_{\text{CO}}^{\text{trans}}$ . The addition of thiophene and (in particular) THT to the collection of ligands studied may call this interpretation into question as well.

To develop a more accurate model for the relative reactivities of the various ligands studied thus far, we

(34) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

(35) Angelici has observed that more strongly electron-donating thiophenes bind more strongly to the metal in the Ru complexes  $(\eta^5\text{-thiophene})\text{Ru}(\eta^5\text{-Cp})^+$  (Hachgenei, J. W.; Angelici, R. J. *Organometallics* **1989**, *8*, 14) and  $(\eta^1(\text{S-thiophene})\text{Ru}(\eta^5\text{-Cp})(\text{CO})(\text{PPh}_3))^+$  (Benson, J. W.; Angelici, R. J. *Organometallics* **1992**, *11*, 922). In the latter case, THT binds significantly more strongly than any of the aromatic S-containing ligands studied.

(36) Lugovskoy, S.; Lin, J.; Schultz, R. H. *Dalton Trans.* **2003**, 3103.

(37) The three data points that do not correspond to ligands whose spectra are given in Table 1 are for the ligands 2,5-dihydrofuran ( $k_{\text{CO}}^{\text{trans}} = 15.011 \text{ mdyn } \text{Å}^{-1}$ ), 2,3-dihydrofuran ( $k_{\text{CO}}^{\text{trans}} = 15.027 \text{ mdyn } \text{Å}^{-1}$ ), and 2-methylfuran ( $k_{\text{CO}}^{\text{trans}} = 15.274 \text{ mdyn } \text{Å}^{-1}$ ).

**Table 3. Ligand Polarizabilities**

ligand	polarizability, Å <sup>3</sup>	
	expt <sup>a</sup>	calcd <sup>b</sup>
thiophene	9.00	9.03
THT		10.41
furan	7.23	7.23
2-methylfuran		7.37
2,3-dihydrofuran		7.45
2,5-dihydrofuran		7.75
THF		7.97
pyrrolidine		8.77
pyrrole	7.94	8.06

<sup>a</sup> Experimental values from the compilation in ref 43. <sup>b</sup> Calculated by using Miller's additivity method.<sup>43</sup> The calculated values were used to fit the data to eq 3 only in those cases for which no experimental value was available.

need first to consider why the simple one that only considers  $k_{\text{CO}}^{\text{trans}}$  fails. Since this model only takes into account a property of the product, there is of course no reason a priori that it should have been expected to have worked in the first place. After all, a late transition state implies only that the transition state is *similar* to the products,<sup>42</sup> not that it is identical to them. In the particular case of the reactions under consideration in the present work,  $k_{\text{CO}}^{\text{trans}}$  is a measure of the incoming ligand's ability to donate electron density to the metal only after the reaction is already complete. But the height of the reaction barrier will be determined not only by the ligand's bonding to the W(CO)<sub>5</sub> center in the product but also by its interaction with the W(CO)<sub>5</sub>(CyH) reaction partner as it approaches the intermediate and as the system approaches the transition state. One measure of the ability of the ligand's electron cloud to react to changes in the electronic environment in which it finds itself is its polarizability  $\alpha$ . On this basis, we might expect the significantly more polarizable second-row heterocycles<sup>43</sup> (cf. Table 3) to be more reactive with W(CO)<sub>5</sub>(CyH) than their first-row analogues. Another way of putting this argument is to note that all of the ligands under discussion are expected to be much stronger donors ( $\sigma$  or  $\pi$ ) than acceptors,<sup>44</sup> which means that  $k_{\text{CO}}^{\text{trans}}$  will be primarily related to the

(38) A reviewer has questioned our inclusion of pyrrole in the discussion of reactivity trends, given Harman's observation of  $\eta^2$  (i.e., side-on through a C=C double bond) binding of pyrrole in [Os(NH<sub>3</sub>)<sub>5</sub>(pyrrole)]<sup>2+</sup>. (Pyrrole is also known to bind face-on in such complexes as Cr(CO)<sub>3</sub>( $\eta^2$ -pyrrole).) Our conclusion that in the *kinetic* product of reaction between pyrrole and W(CO)<sub>5</sub>(CyH) the pyrrole is bound  $\eta^1$  is based on several factors. The IR spectrum of W(CO)<sub>5</sub>(pyrrole) has C–O stretches that are much more typical of an  $\eta^1$ -bound heterocycle than of a ligand bound through a double bond (cf. the spectra of W(CO)<sub>5</sub>( $\eta^1$ -2,3-DHF) and W(CO)<sub>5</sub>( $\eta^2$ -2,3-DHF) given in ref 28). We have also performed a DFT calculation that indicates that the  $\eta^1$  structure is an energy minimum of CpMn(CO)<sub>2</sub>(pyrrole); in that case, the pyrrole ring is nonplanar and the N atom binds through the lone pair made available by the loss of aromaticity (Lugovskoy, S.; Schultz, R. H. Work in progress). And, as noted above, in our studies of ligand substitution at M(CO)<sub>5</sub>(CyH) with ambidentate ligands, we have observed that the incoming ligand invariably binds  $\eta^1$  in the kinetic reaction product even when the  $\eta^2$  structure is thermodynamically more stable. We have also found that the loss of additional CO ligands to form a complex with a face-on ring is a thermal process that occurs on a much longer time scale than that of ligand substitution at W(CO)<sub>5</sub>(CyH).

(39) Hodges, L. M.; Gonzalez, J.; Koontz, J. I.; Myers, W. H.; Harman, W. D. *J. Org. Chem.* **1993**, *58*, 4788; **1995**, *60*, 2125.

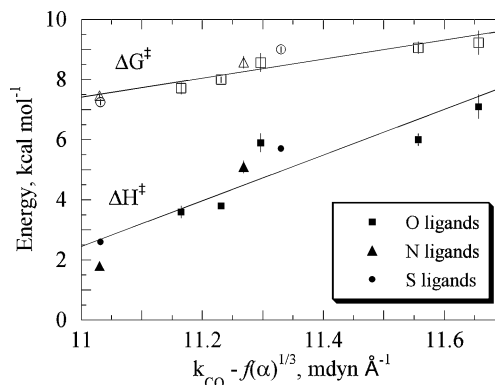
(40) Ofele, K.; Dotzauer, E. *J. Organomet. Chem.* **1971**, *30*, 211.

(41) Krishnan, R.; Gottlieb, H. E.; Schultz, R. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 2179.

(42) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(43) Miller, K. J. *J. Am. Chem. Soc.* **1990**, *112*, 8533.

(44) (a) Sadimenko, A. P. *Adv. Heterocycl. Chem.* **2001**, *78*, 1. (b) Sadimenko, A. P. *Adv. Heterocycl. Chem.* **2001**, *79*, 115.



**Figure 7.**  $\Delta H^\ddagger$  (solid symbols) and  $\Delta G^\ddagger$  at 300 K (open symbols) for ligand substitution at W(CO)<sub>5</sub>(CyH) by L as a function  $k_{\text{CO}}^{\text{trans}} - f\alpha^{1/3}$ , where  $k_{\text{CO}}^{\text{trans}}$  is the stretching force constant of the carbonyl *trans* to L in the product W(CO)<sub>5</sub>L,  $\alpha$  is the polarizability of L, and  $f$  is a normalization factor (for the data shown here,  $f = 1.91$  mdyn Å<sup>2</sup>). Shown are results for five-membered heterocycles containing O (■, □), NH (▲, △), or S (●, ○). The solid lines are least-squares linear fits to the data.

properties of the ligand's HOMO. Clearly, this is the dominant effect, as the data presented in Figure 6 indicate. But a more accurate model needs to take into account interactions involving the ligand's LUMO as well, both because of the involvement of the LUMO in the bonding to the metal center and because the ability of the ligand's electron cloud to distort (i.e., the strength of the induced dipole in the presence of a charge) is related to its HOMO–LUMO gap.

After investigating a number of different functions of  $\alpha$  and combinations of  $\alpha$  and  $k_{\text{CO}}^{\text{trans}}$  (e.g.,  $k_{\text{CO}}^{\text{trans}} + \alpha$ ,  $k_{\text{CO}}^{\text{trans}}/\alpha$ ,  $\alpha^2$ ,  $\alpha^{1/2}$ , etc.), we obtained the best correlation to  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  (indeed, the only reasonable linearization) by adding a term in  $\alpha^{1/3}$ , eq 3, Figure 7.<sup>45</sup>

$$\Delta E^\ddagger = m[k_{\text{CO}}^{\text{trans}} - f\alpha^{1/3}] + b \quad (3)$$

$\Delta E^\ddagger$  is the activation parameter of interest ( $\Delta H^\ddagger$  or  $\Delta G^\ddagger$ ) and  $f$  is a normalization factor. If  $k_{\text{CO}}^{\text{trans}}$  is given in mdyn Å<sup>-1</sup> and  $\alpha$  in Å<sup>3</sup>, the best linearization of  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  was obtained with  $f = 1.91 \pm 0.04$  mdyn Å<sup>-2</sup>. While  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  for ligand exchange do show a general trend of becoming lower as the polarizability of L rises, neither  $\alpha$  nor  $\alpha^{1/3}$  alone provides as strong a correlation with the activation parameters as eq 3 does (cf. Figures S-1 and S-2 of the Supporting Information; Figure S-3, which shows  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  as a function of the dipole moment of L, is given for comparison).

It is probably *not* intuitively obvious why, of all of the possible ways of treating the data, the best results should have been obtained by the addition of a term in  $\alpha^{1/3}$  rather than some other function of  $\alpha$ . There is, however, justification for the use of  $\alpha^{1/3}$  as something more than a purely empirical correction factor: various theoretical treatments have shown that an atom or molecule's softness (which is of course directly related to the HOMO–LUMO gap) is better expressed by the cube root of its polarizability than by the polarizability

(45) The ligands shown in the figure are, in increasing order of  $k_{\text{CO}}^{\text{trans}} - f\alpha^{1/3}$  (given in parentheses), pyrrolidine (11.030), THT (11.032), THF (11.165), 2,5-DHF (11.231), pyrrole (11.269), 2,3-DHF (11.297), thiophene (11.330), 2-methylfuran (11.557), furan (11.657).

itself.<sup>46</sup> This observation of a correlation between the ligand's reactivity with  $W(CO)_5(\text{CyH})$  and its softness is consistent with our conclusion that reactions 1 and 2 go through an  $I_a$  mechanism. In such a mechanism, the incipient  $W-L$  bond is already partially formed at the transition state, and so the major factor determining the reactivity is the ligand's ability to donate electron density to the metal center. But since the bond is *only* partially formed, the reactivity must also be determined in part by the ability of the ligand's electron cloud to distort and, hence, interact with the frontier orbitals of the  $W(CO)_5$  fragment, while the  $W-L$  distance is still larger than its equilibrium value. The possibility that the LUMO interaction involved is back-donation from the metal seems less likely, since none of the ligands discussed here is a particularly strong  $\pi$ -acceptor, and in thiophene complexes, a tilt angle of  $140^\circ$  is typical of a complex with minimal  $\pi$ -back-bonding.<sup>12b,d</sup> While we have shown that the ligand's softness appears to be important in controlling its reactivity toward the metal center, preliminary results from our laboratory indicate that the facile conclusion that this reactivity trend is a reflection of the proverbial preference of soft acids for soft bases<sup>47</sup> is probably *not* correct. We have observed that at room temperature  $Cr(CO)_5(\text{CyH})$ —a harder Lewis acid than  $W(CO)_5(\text{CyH})$ —reacts more rapidly with thiophene than with furan, and more rapidly with THT than with THF.<sup>48</sup>

Finally, in addition to the more general discussion of the reactivity of thiophene and THT in the context of all of the ligands studied, we turn to trends in families of ligands (aromatic ligands of the form  $C_4H_4E$  on one hand and saturated ligands of the form  $C_4H_8E$  on the other). In our previous studies of O- and N-containing heterocycles, we observed a linear correlation between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for ligand exchange at  $W(CO)_5(\text{CyH})$ . A plot of  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  that includes results for reactions 1 and 2 (cf. Figure S-4 of the Supporting Information) reveals that the linear relationship is maintained even when the S ligands are included. This observation is consistent with our conclusion that the correlation between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for ligand substitution at an alkane-solvated transition-metal intermediate depends more on the solvent than on the particular ligands or complex under study. It also means that "relative reactivity" in the sense of the relative magnitudes of the second-order rate constant  $k_a$  will be temperature-dependent, as illustrated in the Eyring analyses presented in Figures S-5 and S-6 of the Supporting Information.

Comparison of  $\Delta H^\ddagger$  for the two sets of ligands reveals that in both cases  $\Delta H^\ddagger$  for reaction with  $C_4H_nE$  as a function of E increases in the order  $NH < S < O$ . For the aromatic ligands (pyrrole, thiophene, and furan), this ordering is consistent with the relative magnitudes of  $k_{CO}^{trans}$  in  $W(CO)_5L$ . For the aliphatic ligands, once

again, THT appears to be the odd man out, as  $\Delta H^\ddagger$  for reaction 2 is lower than that for the analogous reaction with THF even though  $k_{CO}^{trans}$  is higher in  $W(CO)_5(\text{THT})$ . In addition, THF is a stronger Lewis base than THT, at least in the condensed phase.<sup>49</sup> Although the trends in  $\Delta H^\ddagger$  for the two families of ligands do follow the trends in gas-phase basicity and proton affinity,<sup>50</sup> it is not clear that there is, or ought to be, any fundamental connection between a ligand's gas-phase reactivity toward proton transfer and its reactivity in condensed phase toward a transition metal. For instance, not only is the gas-phase  $Li^+$  affinity of THF higher than that of THT,<sup>51</sup> but the aromatic ligands tend to protonate at a C atom rather than at the heteroatom.<sup>52</sup>

Thus, it appears that the reactivity order  $N < S < O$  reflects a fundamental *kinetic* preference innate to the elements (or rather, to the relative electronic properties of the compounds that they form). This kinetic preference does not appear to be directly related to any simple physical or thermodynamic property. Further studies are underway to see if these trends hold in the reactions of small heterocycles with other alkane-solvated transition-metal intermediates.

## Summary and Conclusions

$W(CO)_5(\text{CyH})$  reacts with thiophene and THT to form a more stable complex,  $W(CO)_5(C_4H_7S)$ . THT is considerably more reactive than thiophene, consistent with our previous observations that a stronger electron donor will have a lower enthalpic barrier to ligand substitution at  $W(CO)_5(\text{CyH})$ . Measurements of the kinetics of these reactions via time-resolved IR absorption spectroscopy enable us to calculate  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ . The low enthalpic barriers of these reactions relative to the  $(CO)_5W-CyH$  bond dissociation energy, the negative enthalpies of activation, and strong dependence of the kinetics on the properties of the ligand are all evidence that the reaction proceeds via an associative interchange mechanism.

THT is found to be significantly more reactive than would have been predicted based on its electron-donating ability alone. We have shown, however, that the exceptional reactivity of THT can be explained by its high polarizability: the higher ability of its electron cloud to distort relative to that of other ligands studied enhances its ability to stabilize an electron-poor transition state even before the  $W-L$  distance in the incipient product complex has reached its equilibrium value. Furthermore, we have found that  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  correlate well with a function that explicitly takes into account the ligand's polarizability in addition to its electron-donating ability in  $W(CO)_5L$ . This model also accounts for the higher than expected reactivity of pyrrolidine.

(46) (a) Roy, R. K.; Chandra, A. K.; Pal, S. *J. Mol. Struct. (THEOCHEM)* **1995**, *331*, 261. (b) Pal, S.; Chandra, A. K. *J. Phys. Chem.* **1995**, *99*, 13865. (c) Ghanty, T. K.; Ghosh, S. K. *J. Phys. Chem.* **1996**, *100*, 12295. (d) Chattaraj, P. K.; Poddar, A. *J. Phys. Chem. A* **1998**, *102*, 9944. (e) Hohm, U. *J. Phys. Chem. A* **2000**, *104*, 8418.

(47) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561. (c) Pearson, R. G. *Inorg. Chim. Acta* **1995**, *240*, 93. (d) Ayers, R. W.; Parr, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 2010.

(48) Bar-Moshe, M.; Biber, L.; Gavish, S.; Moshe, H.; Revzin, T.; Waichman, S.; Schultz, R. H. Work in progress.

(49) (a) Wirth, H. E.; Slick, P. I. *J. Phys. Chem.* **1962**, *66*, 2277. (b) Abboud, J.-L. M.; Roussel, C.; Gentric, E.; Sraidi, K.; Lauransan, J.; Guilhéneuf, G.; Kamlet, M. J.; Taft, R. W. *J. Org. Chem.* **1988**, *53*, 1545.

(50) Hunter, E. P.; Lias, S. G. *J. Phys. Chem. Ref. Dat.* **1998**, *27*, 413.

(51) Burk, P.; Koppel, I. A.; Koppel, I.; Kurg, R.; Gal, J.-F.; Maria, P.-C.; Herreros, M.; Notario, R.; Abboud, J.-L. M.; Anvia, F.; Taft, R. W. *J. Phys. Chem. A* **2000**, *104*, 2824.

(52) (a) Carmody, M. P.; Cook, M. J.; Dassanayake, N. L.; Katritzky, A. R.; Linda, P.; Tack, R. D. *Tetrahedron* **1976**, *32*, 1767. (b) Houriet, R.; Schwarz, H.; Zummack, W.; Andrade, J. G.; Schleyer, P. v. R. *Nouv. J. Chim.* **1981**, *5*, 505. (c) Joule, J. A.; Mills, K.; Smith, G. F. *Heterocyclic Chemistry*, 3d ed.; Chapman and Hall: London, 1995.

**Acknowledgment.** This work was supported by the Israel Science Foundation, founded by the Israel Academy of Arts and Sciences. The author would also like to thank Prof. R. J. Angelici (Iowa State University) for bringing ref 21 to his attention, Dr. P. Aped and Prof. H. Basch (Bar-Ilan University) for assistance with the DFT calculations, and Dr. H. Schultz for useful discussions regarding the statistical analysis of the raw data.

**Supporting Information Available:** Tables S-1 and S-2, which list the pseudo-first-order rate constants for the reaction of  $W(CO)_5(CyH)$  with THT and with thiophene, and Figures S-1 through S-6. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM049588Z