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Communications

Observation of Linkage Isomerization in $W(CO)_5$(2,5-Dihydrofuran)

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Summary: UV photolysis of a cyclohexane solution of $W(CO)_6$ *in the presence of 2,5-dihydrofuran (DHF) yields* $W(CO)_5(\eta^1(O)\text{-DHF})$ *with a bimolecular rate constant on the order of* 10^7 *L mol*$^{-1}$ *s*$^{-1}$*. Time-resolved IR (TRIR) absorption spectroscopy is used to monitor the consequent intramolecular isomerization to* $W(CO)_5(\eta^2\text{-}(C,C)\text{-DHF})$*, which occurs with a rate constant on the order of 1−10 s*$^{-1}$ *at 20−60 °C; activation parameters for the isomerization are determined to be* $\Delta H^{\ddagger} = 17.3 \pm 0.3$ *kcal/mol and* $\Delta S^{\ddagger} = 0.9 \pm 0.9$ *eu.*

2,5-Dihydrofuran (2,5-DHF) is an interesting ligand because it has the potential to bind in two very different ways: as a σ-donor by binding η^1 through the oxygen atom or as a π-acceptor by binding η^2 through the double bond. While the coordination chemistry of this ligand has not been extensively explored, those complexes that have been fully characterized thus far have shown η^2 binding.[1] In our laboratory, we have been using time-resolved infrared absorption spectroscopy (TRIR) to investigate the behavior of alkane-solvated organometallic reaction intermediates. Specifically, we have studied some of the ligand exchange reactions of the cyclohexane (CyH) solvate complex $W(CO)_5(CyH)$ with a variety of small heterocycles L to form complexes $W(CO)_5(L)$.[2,3] In the case of reaction with 2,5-dihydrofuran (2,5-DHF), reaction 1, formation of the product

$$W(CO)_5(CyH) + 2,5\text{-DHF} \rightarrow W(CO)_5(2,5\text{-DHF}) \qquad (1)$$

was observed to occur with a second-order rate constant on the order of 10^7 L mol^{-1} s^{-1} ($\Delta H^{\ddagger} = 15.9 \pm 0.8$ kJ mol $^{-1}$, $\Delta S^{\ddagger} = -59 \pm 15$ J mol^{-1} K^{-1}).[2] This product, stable on the microsecond to millisecond time scale, was assigned the structure of the η^1-(*O*)-bound isomer, based on the similarity of its IR spectrum to that of $W(CO)_5$(THF) and on the similarity of the activation parameters of reaction 1 to those for the formation of $W(CO)_5$(THF) from $W(CO)_5(CyH)$.[2]

Figure 1 shows three IR spectra taken at different times following photolysis of a CyH solution containing 5×10^{-4} mol L^{-1} $W(CO)_6$ and 0.016 mol L^{-1} 2,5-DHF. Spectra obtained by using time-resolved step-scan FTIR (S^2FTIR) reveal formation of $W(CO)_5(CyH)$, with C−O stretching frequencies at 1954 and 1928 cm^{-1} immediately[4] upon photolysis. A new complex with C−O stretching frequencies at 1934 and 1913 cm^{-1} is formed over the course of tens of microseconds. Several minutes

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[1] McGrath, D. V.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 3611. Balavoine, G. G. A.; Boyer, T.; Livage, C. *Organometallics* **1992**, *11*, 456.

[2] (a) Krav-Ami, S.; Schultz, R. H. *J. Chem. Soc., Dalton Trans.* **1999**, 115. (b) Lugovskoy, A.; Paur-Afshari, R.; Schultz, R. H. *J. Phys. Chem. A*, submitted for publication.

[3] Paur-Afshari, R.; Lin, J.; Schultz, R. H. *Organometallics* **2000**, *19*, 1682−1691.

[4] "Immediately" in our experiments is consistent with the solvation rate of "naked" $W(CO)_5$ of ca. 10^{11} s^{-1} (Lee, M.; Harris, C. B. *J. Am. Chem. Soc.* **1989**, *111*, 8963).

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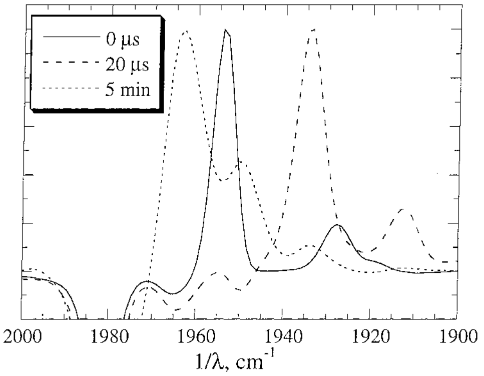
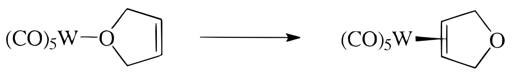


Figure 1. FTIR absorption spectra (1900−2000 cm^{-1}, 4 cm^{-1} resolution) at various times after the flash photolysis of a CyH solution containing 5×10^{-4} mol L^{-1} $W(CO)_6$ and 0.016 mol L^{-1} 2,5-DHF. Shown are S^2FTIR spectra of the solution 0.2 μs and 20 μs after the initial photolysis pulse, and an IR spectrum obtained several minutes after the solution had been exposed to approximately 100 laser shots.

later, however, the IR peaks corresponding to this species have all but disappeared, while new ones, at 1963 and 1952 cm^{-1}, have grown in. We attribute these spectral changes to formation of $W(CO)_5(\eta^1$-(*O*)-2,5-DHF) (**1*O***) as the kinetic product followed by linkage isomerization to the thermodynamic product, $W(CO)_5$-(η^2-(*C*,*C*)-2,5-DHF) (***1C***),[5] reaction 2:[6]



(2)

1*O* **1*C***

We found this result to be intriguing for several reasons. While the dynamics of linkage isomerization has received considerable study,[7] with only rare exceptions,[8] detailed investigation has been limited to systems in which the isomerization occurs between structurally and chemically similar (or identical) sites. Furthermore, the *dynamics* of linkage isomerization has generally only been studied for transformations among structures of nearly equal stabilities,[7] or for very fast ($>10^3$ s^{-1})[9] or very slow ($<10^{-3}$ s^{-1})[7] processes. The dynamics of a linkage isomerization reaction in which complex is formed on a very rapid time scale but isomerizes much more slowly seems not to have been considered in detail previously. Presumably, under the usual experimental conditions of such studies, either a kinetic product such as **1*O*** is not sufficiently long-lived to be detectable or it is sufficiently long-lived relative to the rate of its formation that the kinetics of its subsequent reactions are not conveniently measured on a "fast-kinetics" experimental apparatus.[10]

The experiments discussed here were performed on the TRIR spectrometer in our laboratory, which has been described in detail previously.[3] Briefly, a CyH solution containing $<10^{-3}$ mol L^{-1} $W(CO)_6$ and excess 2,5-DHF is photolyzed by the pulsed (ca. 20 ns, 40−80 mJ/pulse) output of a XeCl excimer laser (308 nm). A CW beam of IR light from a Pb-salt diode laser tuned to 1934 cm^{-1} (corresponding to one of the C−O stretching absorbances of the kinetic product,[2] Figure 1) passes through the sample cell, and the time dependence of the signal reaching the detector following the photolysis flash is monitored. The time-dependent signal is then converted to absorbance, and the first-order rate constant for the isomerization is then calculated as the rate of the exponential decay of this absorbance. While the growth in the absorbance at 1963 cm^{-1} (corresponding to formation of **1*C***) was not used to determine the isomerization rate constant, for those cases where it was monitored, its time dependence was consistent within experimental error of those determined from the decay of the absorbance at 1934 cm^{-1}.

Typical kinetic traces are shown in Figure 2, showing a fast bimolecular reaction of $W(CO)_5$(CyH) to form **1*O*** followed by a slow decay to **1*C***. The time-dependent absorbance at 1934 cm^{-1} does not return to its baseline, indicating that some **1*O*** remains in the solution even after the reaction has gone to completion; small peaks corresponding to the CO stretches of this product can be seen in the IR spectrum shown in Figure 1 as well. We estimate, on the basis of the relative integrations of the IR absorbances shown in Figure 1 and the ratio of $\Delta A_0/\Delta A_\infty$ of the time-dependent absorptions at 1934 cm^{-1}, that the equilibrium amount of **1*O*** present in the solution is on the order of a few percent of the amount of **1*C***.

The rate of the isomerization (k_{obs}) was monitored over the temperature range 20−60 °C. To within experimental error, it is independent of [$W(CO)_6$] (which was varied by a factor of 2 in different experimental runs) or of [2,5-DHF] (which was varied by a factor of 10), indicating that the isomerization is intramolecular and the back-reaction (either from equilibration between the isomers or from exchange with 2,5-DHF in the solution) occurs slowly enough not to interfere with the observed kinetics.[11] Note that the two possible mechanisms for the formation of **1*O*** are kinetically indistinguishable; in both cases, k_{obs} will be the sum of the rate constant for isomerization of **1*O*** to **1*C*** and the rate constant for the reappearance of **1*O*** either from isomerization or exchange. Since the formation of **1*O*** from **1*C*** (by

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[5] The ^{1}H NMR spectrum of complex **1*C*** (600 MHz, C_6D_{12}): δ 4.75 (s, 2H); δ 4.54 and 4.59 (AB q, $J = 9.5$ Hz, 2H each) is consistent with the proposed η^2-*C,C* geometry. The diastereotopic methylene protons imply that the ring is bound face-on to the metal.

[6] C−O stretches for $W(CO)_5$(THF) appear at 1933 and 1911 cm^{-1}, while those for $W(CO)_5$(cyclopentene) appear at 1960 and 1943 cm^{-1}.[2] Symmetry requires that a third C−O stretch be present; we have identified this very weak absorbance (1−5% of the intensity of the strongest peak) for **1*O*** (2075 cm^{-1}),[2b] **1*C*** (2083 cm^{-1}), $W(CO)_5$(THF) (2074 cm^{-1}),[3] and $W(CO)_5$CyH (2087 cm^{-1}).[3]

[7] (a) Balahura, R. J.; Lewis, N. A. *Coord. Chem. Rev.* **1976**, *20*, 109. (b) Jackson, W. G.; Sargeson, A. M. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, p 336. (c) Orell, K. G. *Mech. Inorg. Organomet. React.* **1989**, *6*, 337. (d) Buckingham, D. A. *Coord. Chem. Rev.* **1994**, *135/136*, 587. (e) Keiter, R. L.; Benson, J. W.; Keiter, E. A.; Lin, W.; Jia, Z.; Olson, D. M.; Brandt, D. E.; Wheeler, J. E. *Organometallics* **1998**, *17*, 4291. (f) Cole, S.; Dulaney, K. E.; Bengali, A. A. *J. Organomet. Chem.* **1998**, *560*, 55.

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[9] (a) Xie, X.; Simon, J. D. *J. Phys. Chem.* **1989**, *93*, 4401. (b) Ladogana, S.; Nayak, S. K.; Smit, J. P.; Dobson, G. R. *Inorg. Chem.* **1997**, *36*, 650.

[10] For example, in a study of the reaction of $W(CO)_5$(CyH) with 4-acetylpyridine (Dobson, G. R.; Spradling, M. D. *Inorg. Chem.* **1990**, *29*, 880), it was observed that the kinetic product is O-bound, while the thermodynamic product is N-bound, but the kinetics of the isomerization were on a much slower time scale than was of interest to the authors of that study.

[11] The lack of significant broadening of the peaks in the ^{1}H NMR spectrum of **1*C*** also indicates that any exchange or isomerization that would make the methylene H atoms equivalent must be slow at room temperature.

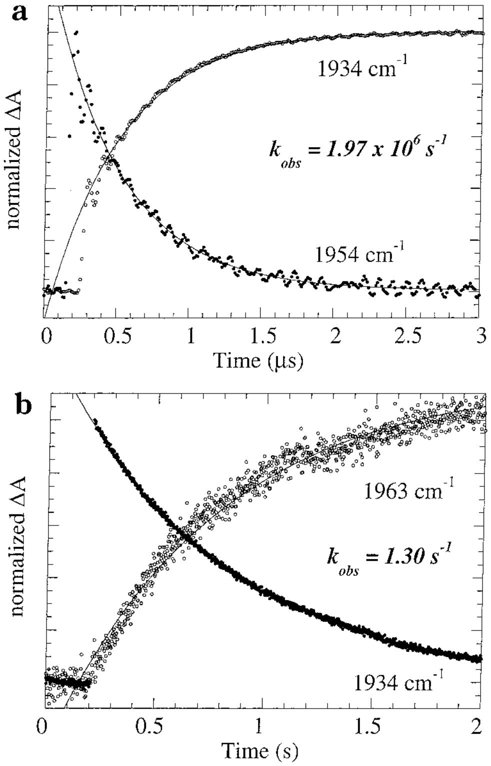

Figure 2. Time-dependent IR absorptions (normalized to $\Delta A_{max} = 1$ for each transient) following photolysis of a room-temperature CyH solution containing 5×10^{-4} mol L^{-1} W(CO)$_6$ and 0.222 mol L^{-1} 2,5-DHF. (a) Decay of the absorption by W(CO)$_5$(CyH) at 1954 cm^{-1} and the growth of the absorption by **1*O*** at 1934 cm^{-1} (the nonzero absorption at $t = 0$ is due to overlap from a W(CO)$_5$(CyH) absorption at 1928 cm^{-1}). (b) Decay of the absorption by **1*O*** of at 1934 cm^{-1} and the growth of the **1*C*** absorption at 1963 cm^{-1}. Note that the two graphs are on different time scales. The solid lines indicate exponential fits to the observed time-dependent absorptions (a, $k_{obs} = 1.97 \times 10^6$ s^{-1}; b, $k_{obs} = 1.3$ s^{-1}).

whichever mechanism) occurs slowly relative to reaction 2, we did not further consider the back reaction in our analysis of the kinetics. From an Eyring analysis of the temperature dependence of k_{obs}, Figure 3, we determine the following activation parameters for the isomerization: $\Delta H^{\ddagger} = 72.3 \pm 1.4$ kJ mol^{-1} (17.3 ± 0.3 kcal mol^{-1}) and $\Delta S^{\ddagger} = 3.7 \pm 3.8$ J mol^{-1} K^{-1} (0.9 ± 0.9 eu).

It is not difficult to provide a rationale for the relative kinetic and thermodynamic preferences of the interaction of W(CO)$_5$(CyH) with 2,5-DHF. The initial formation of W(CO)$_5$(2,5-DHF) from the transient solvated complex follows an essentially associative pathway in which the CyH molecule has not yet dissociated at the transition state.[2] The presence of the solvent molecule would be expected to create considerable steric interference that makes formation of **1*C*** *kinetically* unfavorable. Indeed, W(CO)$_5$(CyH) is known to react much more slowly with alkenes than it does with ligands that bind through a single atom,[2a,12] presumably for this reason. On the other hand, the tungsten center is a soft Lewis acid that would be expected to have a thermodynamic preference for the softer alkene end of the 2,5-DHF molecule.[13] Furthermore, a "ring-slip" isomerization mechanism (formally similar to inversion of the O atom of DHF) to **1*C*** in which the ring is bound face-on to the metal[5] would be expected to have a low activation energy and a near-zero $\Delta S^{\ddagger}$. We also note that since **1*O*** has a lifetime of only about 2 s at room temperature, it is not surprising that this binding mode for 2,5-DHF has not previously been observed.

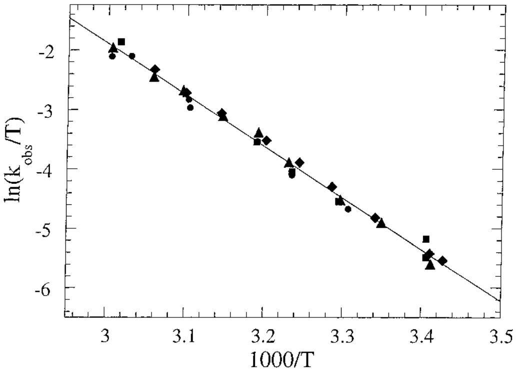

Figure 3. Eyring analysis of the intramolecular isomerization of **1*O***. Shown are ln(k_{obs}/T) (k_{obs} = the first-order rate constant for the isomerization, determined as described in the text) as a function of 1000/T for CyH solutions containing 5×10^{-4} mol L^{-1} W(CO)$_6$ + 0.042 mol L^{-1} 2,5-DHF (●); 5×10^{-4} mol L^{-1} W(CO)$_6$ + 0.021 mol L^{-1} 2,5-DHF (■); 5×10^{-4} mol L^{-1} W(CO)$_6$ + 0.222 mol L^{-1} 2,5-DHF (◆); and 2×10^{-4} mol L^{-1} W(CO)$_6$ + 0.022 mol L^{-1} 2,5-DHF (▲). The solid line is a linear fit through all of the data points, corresponding to $\Delta H^{\ddagger} = 72.3$ kJ mol^{-1} (17.3 kcal mol^{-1}), $\Delta S^{\ddagger} = 3.7$ J mol^{-1} K^{-1} (0.9 eu).

Further studies are currently underway in order to characterize more fully **1*O*** and **1*C***, to more accurately measure the equilibrium constant between them, and to compare the behavior of reaction 2 with the analogous reactions of 2,3-DHF and of Cr and Mo.

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Supporting Information Available: Table of first-order rate constants. This information is available free of charge via the Internet at http://pubs.acs.org.

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(12) Dobson, G. R.; Asali, K. J.; Cate, C. D.; Cate, C. W. *Inorg. Chem.* **1991**, *30*, 4471.

(13) W(CO)$_5$(2,5-dihydrothiophene) has been characterized and binds η^1-*S*, in keeping with the hard/soft acid concepts discussed here: Choi, M.-G.; Daniels, L. M.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 3647.