Photolysis of Tungsten Complexes

Furans Bound Face-On: Sequential Loss of CO in the Formation of $[W(CO)_4(\eta^4\text{-}2,5\text{-dimethylfuran})]$**

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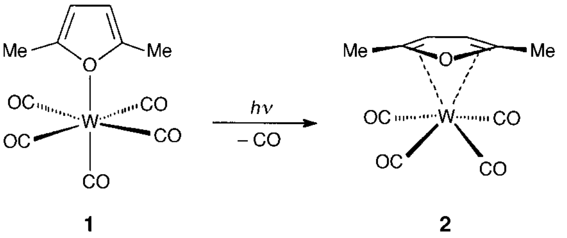
While facially bound aromatic rings C_nH_n are ubiquitous in organometallic chemistry, complexes containing ligands of the type C_nH_nX (X = O or N) bound face-on are much less common. For example, although η^4-thiophene complexes are well-known,[1] and furan is known to bind in an η^4 fashion to surfaces,[2] as a ligand, furan normally prefers to bind in an η^2 fashion through one of its double bonds.[3] In fact, to our knowledge, only one complex containing an η^4-furan ligand has been reported, $[Cp^*Ru(\eta^4\text{-}C_4H_4O)]^+$.[4] We report here the observation of a carbonyl-containing η^4-furan complex, $[W(CO)_4(\eta^4\text{-}Me_2Fur)]$ **2** (Me_2Fur = 2,5-dimethylfuran), and the results of a kinetic study of its formation from $[W(CO)_5(\eta^1\text{-}Me_2Fur)]$ **1** [Eq. (1)].



(1)

It has long been known that photolysis of $[M(CO)_6]$ (M = Cr, Mo, W) in the presence of a bischelating ligand (L_2) produces $[M(CO)_4(L_2)]$.[5] Technological advances made over the past two decades have made it possible to investigate the details of the reaction by means of the techniques of "fast kinetics." Such studies have shown that the reaction proceeds in several steps: first, the pentacarbonyl complex formed by the initial photolysis reacts within tens of picoseconds to form a solvated intermediate $[M(CO)_5(solv)]$ (solv = a molecule of solvent).[6] This solvated intermediate reacts with a molecule of L_2 to produce a monodentate complex $[M(CO)_5(L\text{-}L)]$, which then undergoes a thermally activated intramolecular ligand exchange, on a much slower timescale, to form the bidentate complex $[M(CO)_4(L_2)]$.[7–9]

The majority of the research in which the sequential chelation steps have been observed directly by fast kinetics techniques has concentrated on formation of $[M(CO)_4(\eta^1,\eta^1\text{-}L_2)]$ complexes, where L_2 is a bischelating phosphane or bipyridyl ligand. To our knowledge, the only report in the literature concerning the kinetics of the formation of an $[M(CO)_4(\eta^2,\eta^2\text{-}L_2)]$ complex from $[M(CO)_5(\eta^2\text{-}L\text{-}L)]$, where the ligand is a bischelating diene, is a study of the formation of $[Mo(CO)_4(\eta^2,\eta^2\text{-}NBD)]$ (NBD = norbornadiene) following photolysis of $[Mo(CO)_6]$ solutions containing excess NBD.[10]

We have previously reported[11c] that in the presence of excess Me_2Fur, $[W(CO)_5(CyH)]$ (CyH = cyclohexane) reacts rapidly (second-order rate constant of $2.46 \times 10^6\,L\,mol^{-1}\,s^{-1}$ at 20 °C) to form $[W(CO)_5(Me_2Fur)]$. Based on the similarity of the C–O stretching region of its IR spectrum (two strong stretches at 1927 and 1941 cm^{-1} and a weak one at 2075 cm^{-1}) to those of other $[W(CO)_5L]$ complexes (L = cyclic ether),[11c] we assigned to it the η^1 structure **1**, that is, the ligand is bound to the metal through the lone pair of the O atom. We also determined the activation parameters for the reaction to be $\Delta H^{\ddagger} = 26.4 \pm 1.7\,kJ\,mol^{-1}$ and $\Delta S^{\ddagger} = -41.0 \pm 4.2\,J\,mol^{-1}\,K^{-1}$. $[W(CO)_5(Me_2Fur)]$ is unstable in CyH solution, however. Over the course of a few seconds, its IR absorbtions begin to decay, while simultaneously, new peaks appear in the C–O stretching region of the IR spectrum at 1957, 1991, 2030, and 2097 cm^{-1}. This behavior contrasts with that of the analogous complexes with furan or 2-methylfuran, which are stable for several minutes in a room-temperature CyH solution con-

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taining a moderate excess of free ligand, but then decompose to unidentified products.

The only other $[W(CO)_5(\eta^1\text{-L})]$ (L = cyclic ether) complexes that we had previously observed to be unstable on a time scale of seconds are those in which the ligand also contains a double bond.[12] Following their initial formation from $[W(CO)_5(CyH)]$, these complexes undergo an intramolecular linkage isomerization to yield $[W(CO)_5(\eta^2\text{-L})]$, in which the ligand is bound to the metal by means of its double bond. Although η^2 binding is normally seen in furan complexes,[3] this kind of linkage isomerization cannot account for the behavior of $[W(CO)_5(Me_2Fur)]$, since the observed IR spectrum, which contains four C–O stretches, is inconsistent with a $[W(CO)_5L]$ structure. Rather, the IR spectrum is typical of that of a *cis*-$[M(CO)_4L_2]$ complex.[10,13] We assign this new complex the structure $[W(CO)_4(\eta^4\text{-}Me_2Fur)]$ **2**, produced by an intramolecular replacement of a second CO ligand and rearrangement of the Me_2Fur ligand from O-bound to π-bound at the ring face [Eq. (1)].

This structural assignment is supported by ^{1}H NMR spectroscopy. When a CyH solution containing $2\times 10^{-3}\,\text{mol}\,\text{L}^{-1}$ $[W(CO)_6]$ and $0.15\,\text{mol}\,\text{L}^{-1}$ Me_2Fur is placed in a quartz NMR tube and exposed to the output of a XeCl excimer laser (308 nm), two new peaks appear in the ^{1}H NMR spectrum. The intensities of these peaks grow with additional photolysis, and the relative integrations are consistent with those of Me_2Fur, indicating that they arise from a photolysis product that contains Me_2Fur. In this product, the peak corresponding to that of the ring protons has shifted upfield relative to free Me_2Fur, from $\delta = 5.68$ to $\delta = 4.49$, while that corresponding to the methyl protons has shifted downfield, from $\delta = 2.15$ to $\delta = 2.36$. Upfield shifts in ring proton resonances but downfield shifts in methyl proton resonances upon complexation are typical for a facially bound methyl-substituted aromatic ligand, e.g., η^6-mesitylene.[14] Although the NMR data indicate that approximately 20% conversion of $[W(CO)_6]$ to this product had taken place, and the complex is stable for hours in CyH solution, we have not yet succeeded in isolating it. $[Cp^*Ru(\eta^4\text{-}C_4H_4O)]^+$ has also been reported to be stable only in solution.[4]

In order better to understand what is occurring in our system, we performed a kinetic study in which we used time-resolved IR absorption spectroscopy to monitor the conversion of $[W(CO)_5(\eta^1\text{-}Me_2Fur)]$ **1** to the final product. We observed that under the conditions of our experiment, the conversion occurs with clean first-order kinetics, and the rate of the decay of the intensities of the peaks corresponding to $[W(CO)_5(\eta^1\text{-}Me_2Fur)]$ **1** is equal, to within experimental error, to that of the growth of the product.[15] Furthermore, to within experimental error, the observed first-order rate constant is independent of $[Me_2Fur]$ and of $[W(CO)_6]$ in the initial solution. The independence of the rate on the reactant concentrations is clear evidence of an intramolecular process, consistent with our assigment of the structure $[W(CO)_4(\eta^4\text{-}Me_2Fur)]$ **2** to the product of the reaction. It also precludes the two other structures for the complex that might explain the spectral data: *cis*-$[W(CO)_4(Me_2Fur)_2]$, which would also have four IR-active CO stretches, or a dimeric complex in which a molecule of Me_2Fur bridges two $W(CO)_x$ fragments, which is consistent with the ^{1}H NMR spectrum. Since those two species would necessarily be formed in bimolecular reactions, the reaction rate constant for their formation would depend on the concentrations of the reactants. We also note that, to within experimental error, the reaction rate constant for formation of $[W(CO)_4(\eta^4\text{-}Me_2Fur)]$ **2** is the same whether the reaction takes place under Ar or in a CO-saturated solution under 1 atm of CO, implying that the reaction is irreversible under our experimental conditions.

Figure 1 shows an Eyring analysis of the temperature dependence of the rate constants that yields activation parameters of $\Delta H^{\neq} = 61.9 \pm 1.3\,\text{kJ}\,\text{mol}^{-1}$ and $\Delta S^{\neq} = -33.5 \pm 4.6\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$. These activation parameters are similar to those of chelate ring closure in $[W(CO)_5(\text{L-L})]$, where L_2 is a bischelating N donor such as a bipyridyl, phenanthroline, or diazabutane ligand.[9] The low value of $\Delta H^{\neq}$ relative to the [W]–CO bond dissociation energy[16] and the negative $\Delta S^{\neq}$ indicate that the second CO replacement, like the first, is associative,[11] in which the Me_2Fur rearrangement and CO loss are concerted. Once again, this behavior is typical of intramolecular chelate ring closure.

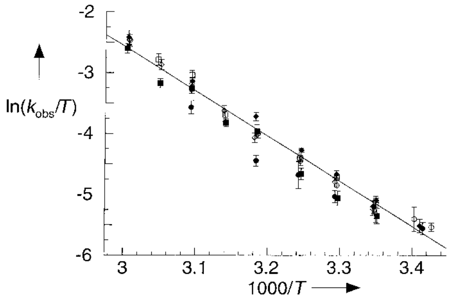

Figure 1. Eyring plot for the conversion of $[W(CO)_5(\eta^1\text{-}Me_2Fur)]$ **1** to $[W(CO)_4(\eta^4\text{-}Me_2Fur)]$ **2**. Shown are experimentally measured first-order rate constants with 1 σ uncertainties. Different symbols represent measurements made at different concentrations of Me_2Fur and $[W(CO)_6]$. The solid line is a weighted least-squares linear fit to the data corresponding to $\Delta H^{\neq} = 61.9\,\text{kJ}\,\text{mol}^{-1}$, $\Delta S^{\neq} = -33.5\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$.

As mentioned above, neither furan nor 2-methylfuran produces $[W(CO)_4(\eta^4\text{-L})]$ under the experimental conditions that yield $[W(CO)_4(Me_2Fur)]$ **2** within several seconds of the initial photolysis. We have previously noted that more strongly electron-donating ligands tend to react more rapidly with $[W(CO)_5(CyH)]$ because they can more readily stabilize the transition state for the ligand exchange.[11b,c] Presumably, similar considerations are at work in the present case. Me_2Fur, being more electron rich than furan or MeFur, can better stabilize a complex with electron-withdrawing ligands. Thus, the $[W(CO)_5(\eta^1\text{-}Me_2Fur)]$ complex **1** will be the most thermodynamically stable of the three, making competition from dissociation less significant than in the other two cases. Not only that, but for the same reason, formation of $[W(CO)_4(\eta^4\text{-L})]$ from $[W(CO)_5(\eta^1\text{-L})]$ should have the lowest activation barrier for L = Me_2Fur, which can best stabilize a transition state in which a bond is being broken. Hence, it is not surprising that $[W(CO)_4(Me_2Fur)]$ is much

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more readily formed and observed than the analogous furan and MeFur complexes.

Further studies are underway to isolate [W(CO)$_4$(η^4-Me$_2$Fur)] **2**, to elucidate the kinetics of the analogous furan and MeFur systems, and to produce and identify [M(CO)$_4$(η^4-L)] complexes with these ligands as well.

Experimental Section

The spectrometer with which the kinetic experiments were performed has been described in detail previously.[11a] An Ar-degassed CyH solution containing 0.5–1 × 10^{-3} mol L^{-1} [W(CO)$_6$] and a large excess of Me$_2$Fur was prepared. The solution flowed through a temperature-controlled (± 0.8 °C) CaF$_2$ IR cell (pathlength 0.5 mm), where it was exposed to a pulse (~20 ns, typically 60–80 mJ/pulse) of 308-nm light emanating from a XeCl excimer laser. The flow was maintained to ensure that each laser pulse irradiates fresh solution. The reaction kinetics were determined from the time dependence of the change of the absorption of the output of a Pb-salt diode laser. For these experiments, the laser was tuned to 1957 cm^{-1}, corresponding to a C–O stretch of the product complex **2**. Measurements were also made of the decay of the C–O stretch of [W(CO)$_5$(η^1-Me$_2$Fur)] **1** at λ = 1942 cm^{-1}, and were consistent with those obtained from the growth of the product. Because the output of our laser is not as strong at λ = 1942 cm^{-1}, these transients were of lower quality and were not used for the kinetic analysis. The raw transients were converted to ΔA (A = absorbance). First-order rate constants were obtained by fitting the time dependence of ΔA to a single exponential and by linear fits to $\ln|\Delta A_t - \Delta A_\infty|$. The reported rate constants (see Supporting Information) are the averages of several independent fits to the data, and are given with 1 σ uncertainties to the fits.

Static IR spectra of reaction products were obtained by photolyzing a [W(CO)$_6$]/Me$_2$Fur solution with 1–100 laser shots, taking an aliquot of the solution, and measuring its IR spectrum in a Bruker Equinox 55 FTIR spectrometer. NMR spectra were obtained on a Bruker DPX-300 instrument with presaturation of the resonance of the C$_6$H$_{12}$ solvent protons. The chemical shift of the protons in neat CyH was measured in a separate experiment and found to be δ = 1.443 relative to the TMS internal standard.

CyH was obtained in spectrophotometric- or HPLC-grade purity and distilled from Na/benzophenone to remove remaining H$_2$O. [W(CO)$_6$] was obtained in 98 % purity from Strem Chemicals and used without further purification. Me$_2$Fur was obtained from Aldrich in > 99 % purity (confirmed by NMR), distilled from a drying agent, and stored over KOH.

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