example demonstrates that, even in a complex molecule, the formula works quite well.

The Gaussian damping factor Γ causes a quenching of the magnitude of the recurrence overlaps in the time domain. It physically represents relaxation into other modes, the bath, etc. In the calculations discussed here it can be considered to be a phenomenological line width factor. Γ is usually in the range of 50–200 cm^{-1} for metal complexes in condensed media.

An example of conditions where Γ can have a major effect is given in the table. If $\omega_1 = 203$ cm^{-1} and $\omega_2 = 302$ cm^{-1}, the maximum of the product of the overlaps occurs when $n_1 = 2$ and $n_2 = 3$. These conditions give $\omega_M = 101$ cm^{-1} (Figure 2, middle). However, Γ must be small enough for the overlap at these values of n to be significant. If Γ is larger, these higher recurrences will be damped out and only the first recurrence of each mode will have significant magnitude. In this case, only the product at $n_1 = 1$ and $n_2 = 1$ is important and $\omega_M = 277$ cm^{-1} (Figure 2, top).

It is also important to recognize that Γ cannot be too small. If it is small enough to allow a large number of recurrences to have significant amplitude, no MIME will be observed, but instead a highly resolved spectrum consisting of progressions in all of the displaced modes will be seen (Figure 2, bottom).

The effect of the displacements Δ_k on the MIME frequency is apparent from eq 6. The displacements act as a type of weighting factor on the contributions of the normal modes to the MIME. In some situations, the value of Δ for one mode will be much larger than those for other displaced modes. In this case the MIME frequency will be very close to the frequency of the most highly displaced mode and may be indistinguishable from it in an experimental spectrum. This situation commonly arises in metal complexes where a metal–ligand bond is highly displaced while bond lengths within the ligand itself are only slightly changed. The origin of this effect is readily seen from eq 6. If Δ_k for one mode is much larger than the other Δ's, it will dominate the sums in both the numerator and the denominator and $\omega_M \approx \omega_k$.

The effect of having Δ for one mode much larger than the Δ's for the other modes on the overlaps in the time domain is shown in Figure 1 (bottom). In this example, $\Delta_{500} = 0.5$ while $\Delta_{1100} = 1.7$. The overlap recurrences for the highly displaced high-frequency mode are sharp while those for the low-frequency mode with a small displacement are broad. The total product overlap is thus dominated by the sharp recurrences of the low-frequency mode, and the spectrum in the frequency domain shows a spacing of 1125 cm^{-1}.

Five qualitative features of the simple formula (eq 6) are worth discussing. First, if all of the $n_k = 1$, then the MIME frequency must fall between the highest and the lowest real frequencies. Second, it can happen that ω_M is lower than any of the individual frequencies. (This situation was illustrated above for $\omega_1 = 302$ and $\omega_2 = 203$ where $\omega_M = 101$.) Third, it is not possible for ω_M to be larger than the highest frequency ω_k except for a minor shift due to Γ. Fourth, ω_M may correspond fortuitously to one of the ω_k values, but mode k may not even be displaced! Fifth, it is clear from eq 6 that many combinations of Δ's and ω's can give the same ω_M. Thus, ω_M can not be used to provide a unique determination of the contributing modes nor their displacements.

In several recently reported spectra,[9] clusters of sharp phonon mode features are superimposed on the broader scale MIME frequency bands. These types of features should not be confused with the clusters of intramolecular bands, which, by virtue of the large Γ, are unresolved and form the MIME spacing. The frequencies of the phonon bands will either change or the bands will disappear when the condensed medium is changed from a single crystal to different types of glasses or matrices. The MIME features should not change (or only slightly change if the vibrational frequencies of the molecule are sensitive to the medium.)

In summary, equally spaced vibronic peaks in poorly resolved luminescence spectra of large molecules in condensed media will usually be MIME peaks. They may be indistinguishable from a progression in one mode of the displacement if that mode is much larger than all other displacements. When Γ is small, a highly resolved spectrum containing bands from progressions in all of the displaced modes will be obtained and no MIME will be observed. When the MIME is present, the simple formula for the MIME frequency that was derived above gives a result that is very close to the result from the exact calculation but does not require calculations of overlaps or Fourier transforms.

Acknowledgment. E.J.H. and J.I.Z. gratefully acknowledge the NSF (Grants CHE-85-07138 and CHE-85-09329, respectively) for support of this work.

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Synthesis, Reactivity, and Variable-Temperature NMR Studies of Transition-Metal Complexes Containing the 2,3-Dihydrothiophene Ligand

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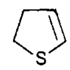
The transition-metal complexes $W(CO)_5(2,3\text{-DHT})$ (**1**), $[Re(CO)_5(2,3\text{-DHT})]SO_3CF_3$ (**3**), $PdCl_2(2,3\text{-DHT})_2$ (**4**), and $Ru(CO)_3Cl_2(2,3\text{-DHT})$ (**5**) containing S-bound 2,3-dihydrothiophene (2,3-DHT), a proposed intermediate in thiophene hydrodesulfurization, have been prepared and characterized. Variable-temperature ^1H NMR studies of complexes **1**, **3**, and **5** establish that the barrier to inversion of the coordinated sulfur increases with the oxidation state of the metal: W(0) < Re(I) < Ru(II). In the series of $W(CO)_5(L)$ complexes, where L = 2,3-DHT, 2,5-DHT, and tetrahydrothiophene (THT), the inversion barriers decrease in the order 2,3-DHT (48.5 kJ/mol) > 2,5-DHT (45.6) > THT (43.9), which is also the order of decreasing ring strain in the sulfur ligands. Thus, the less strained the ligand, the more easily it achieves the planar transition state required for inversion.

Introduction

Hydrogenation of thiophene to 2,3-dihydrothiophene (2,3-DHT) has been proposed as the initial step in the hydrodesulfurization (HDS) of thiophene.[2-4] In order to understand how 2,3-DHT might coordinate to metal ion sites on the HDS catalyst, we have prepared several of its transition-metal complexes. Little is known



2,3-DHT

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of the organometallic chemistry of this reactive vinyl thioether perhaps due to the problems of preparing and purifying 2,3-DHT, which polymerizes upon warming or in the presence of acids, and decomposes slowly upon exposure to air.[5] Only $Mn(CO)_3$-(2,3-DHT)Cl[3a] and the S-bound complex $Cr(CO)_5$(2,3-DHT)[6] have been reported. By preparing transition-metal complexes containing 2,3-DHT as a ligand, we sought to establish its preferred binding modes, i.e., via the sulfur, the olefin, or both the sulfur and the olefin, as well as explore the reactivity of the coordinated ligand from the perspective of modeling HDS reactions. Herein, we describe the facile reaction of 2,3-DHT with transition-metal complexes to give S-bound complexes, the reactivity of the coordinated 2,3-DHT ligand, and variable-temperature ^1H NMR studies of several 2,3-DHT complexes.

Experimental Section

General Procedures. All reactions were carried out under N_2 in reagent grade solvents. Methylene chloride and hexanes were dried over CaH_2 and distilled under N_2. Tetrahydrofuran (THF) was distilled from Na–benzophenone under N_2. Pentane and acetone were dried over molecular sieves. All solvents were purged with N_2 prior to use. ^1H and ^{13}C NMR spectra were obtained on a Nicolet NT-300 spectrometer, and variable-temperature ^1H NMR studies were done on a Bruker WM-300 spectrometer with deuteriated solvents used as internal locks. All ^1H NMR chemical shifts are referenced to $(CH_3)_4Si$. ^2H NMR spectra were taken on the Bruker WM-300 spectrometer with the proton signal of the solvent used as the internal lock and $CDCl_3$ at δ 7.26 ppm as the internal reference. Electron-ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. Fast atom bombardment (FAB) spectra were obtained by using a Kratos MS-50 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc. Infrared spectra were obtained on a Perkin-Elmer 681 spectrophotometer and were calibrated by using the 1944-cm^{-1} peak of polystyrene. $Re(CO)_5OSO_2CF_3$,[7] $[Ru(CO)_3Cl_2]_2$,[8] K_2PdCl_4,[9] and 2,3-DHT[10] were prepared by literature methods.

Pentane Solution of 2,3-DHT. The 2,3-DHT was prepared as described previously.[10] After the 2,3-DHT was filtered through the frit covered with Na_2CO_3, the frit was washed 4 times with 25 mL of pentane to give an approximately 0.5 mM solution of 2,3-DHT in pentane (assuming 100% conversion of 2-acetoxytetrahydrothiophene to 2,3-DHT and 5% loss of 2,3-DHT during workup). Solutions of 2,3-DHT could be stored in a dry ice–2-propanol bath under N_2 for up to 3 weeks. For preparations of the 2,3-DHT metal complexes, 1–3 mL of the pentane solution was used.

Preparation of $W(CO)_5$(2,3-DHT) (1). $W(CO)_6$ (0.500 g, 1.42 mmol) was dissolved in freshly distilled, degassed THF (40 mL) in a quartz photolysis tube equipped with an N_2 bubbler. The resulting solution was photolyzed with a 450 W, 366-nm lamp for 7 h under N_2 or until no $W(CO)_6$ was apparent by IR spectroscopy. The pentane solution of 2,3-DHT (0.134 g, 1.56 mmol), was added by syringe. The reaction mixture was stirred for 1 h, and the solvent was removed in vacuo. The resulting yellow-brown residue was extracted into pentane (3 × 30 mL). The solution was filtered and the pentane removed in vacuo to give a bright yellow powder; yield 0.472 g (1.15 mmol, 81%). Anal. Calcd for $C_9H_6O_5WS$: C, 26.34; H, 1.48. Found: C, 26.18; H, 1.39. ^1H NMR ($CDCl_3$): δ 6.19 (1 H, dt, J_{4-5} = 5.70 Hz, J_{3-5} = 2.22 Hz, H_5), 5.87 (1 H, dt, J_{3-4} = 2.87 Hz, H_4), 3.53 (2 H, t, J_{2-3} = 7.97, H_2), 2.96 (2 H, tt, H_3). ^{13}C NMR (THF-d_8): δ 35.4 (C_3), 43.5 (C_2), 127.6 (C_4), 129.6 (C_5), 192.4 (equatorial CO), 198.0 (axial CO). IR (hexanes): 2070 (w), 1940 (s), 1930 (m) cm^{-1}. EIMS (70 ev) (*m/e*): M^+ (410), $M^+ - CO$ (382), $M^+ - 5CO$ (270), $M^+ - 2CO -$ DHT (268, base peak).

Preparation of $W(CO)_5$(THT) (2). Compound **2** was prepared by the same method as **1**, from $W(CO)_6$ (0.500 g, 1.42 mmol) and tetrahydrothiophene (THT) (0.125 g, 0.135 mL, 1.51 mmol). It was isolated as a yellow-green powder; yield 0.509 g (1.24 mmol, 87%). This complex has been previously prepared by Strohmeier et al.[11] ^1H NMR (CD_2Cl_2): δ 3.91 (2 H, m, $H_{2,5}$), 2.07 (2 H, m, $H_{3,4}$). ^{13}C NMR (CD_2Cl_2): δ 31.05 ($C_{3,4}$), 45.37 ($C_{2,5}$). IR (pentane): 2078 (w), 1939 (s), 1919 (m) cm^{-1}. EIMS (70 eV) (*m/e*): M^+ (412), $M^+ - CO$ (384), $M^+ - 2CO$ (356), $M^+ - 3CO$ (328).

Preparation of $[Re(CO)_5(2,3\text{-DHT})]SO_3CF_3$ (3). To a solution of $Re(CO)_5OSO_2CF_3$[7] (0.644 g, 1.36 mmol) in acetone (20 mL) was added 2,3-DHT, (0.129 g, 1.50 mmol) in pentane by syringe. After the mixture was stirred for 9 h under N_2, the acetone was removed in vacuo to give a white oil. Prepared in this manner, **3** contained small amounts of impurities. Attempts to recrystallize it, however, were unsuccessful, and an elemental analysis was not obtained. Yield: 0.641 g (1.14 mmol, 84%). ^1H NMR (acetone-d_6): δ 6.63 (1 H, dt, J_{4-5} = 5.67 Hz, J_{3-5} = 2.30 Hz, H_5), 6.35 (1 H, dt, J_{3-4} = 2.83 Hz, H_4), 4.20–4.0 (2 H, br, s, H_2), 3.3–3.2 (2 H, br, s, H_3). ^{13}C NMR (acetone-d_6): δ 36.00 (C_3), 42.95 (C_2), 123.85 (C_4), 136.23 (C_5), 177.08 (axial CO), 179.38 (equatorial CO). IR (acetone): 2155 (w), 2057 (s), 2022 (m) cm^{-1}. MS (FAB, glycerol) (*m/e*): M^+ (413), $M^+ - CO$ (385), $M^+ - 2CO$ (357), $M^+ -$ DHT (327).

Preparation of $PdCl_2(2,3\text{-DHT})_2$ (4). To a slurry of K_2PdCl_4 (0.110 g, 0.337 mmol) in acetone (50 mL) was added 2,3-DHT (0.0585 g, 0.680 mmol) in pentane by syringe. The mixture was allowed to stir for 24 h, resulting in a clear reddish orange solution with no solid K_2PdCl_4 remaining. The acetone was removed in vacuo, and the resultant red-orange solid was recrystallized by dissolving it in a minimum of hot acetone (50 °C) and cooling the solution slowly to −20 °C. Yield: 0.696 g (0.199 mmol, 59%). Anal. Calcd for $C_8H_{12}Cl_2S_2Pd$: C, 27.48; H, 3.46. Found: C, 27.14; H, 3.41. ^1H NMR (acetone-d_6): δ 6.39 (1 H, dt, J_{4-5} = 6.0 Hz, J_{3-5} = 2.70 Hz, H_5), 6.24 (1 H, dt, J_{3-4} = 2.0 Hz, H_4), 2.95 (2 H, br, s, H_2), 2.79 (2 H, br, s, H_3). ^{13}C ($CDCl_3$): δ 132.92 (C_5), 122.65 (C_4), 35.60 (C_2), 34.10 (C_3).

Preparation of $Ru(CO)_3Cl_2$(2,3-DHT) (5). $[Ru(CO)_3Cl_2]_2$[8] (0.0800 g, 0.156 mmol) was dissolved in 25 mL of dry degassed $CHCl_3$. 2,3-DHT (0.030 g, 0.35 mmol) in pentane was added by syringe, and the mixture was stirred for 4 h. Removal of the solvent in vacuo gave a white powder, which was recrystallized from CH_2Cl_2 and hexanes. Yield: 0.078 g (0.114 mmol, 73%). Anal. Calcd for $RuC_7H_6O_3Cl_2S$: C, 24.57; H, 1.77. Found: C, 24.93; H, 2.04. ^1H NMR (CD_2Cl_2): δ 6.39 (1 H, dt, J_{4-5} = 5.72 Hz, J_{3-5} = 2.84 Hz, H_5), 6.25 (1 H, dt, J_{3-4} = 2.35 Hz, H_4), 4.20 and 3.45 (2 H, br, m, H_2), 3.20 and 2.9 (2 H, br, m, H_3). ^{13}C (CD_2Cl_2): δ 188.4 (1 CO), 182.1 (2 CO), 136.08 (C_5), 129.71 (C_4), 35.86, 35.65 ($C_{2,3}$). IR ($CHCl_3$): 2138 (s), 2079 (s), 2055 (m) cm^{-1}. EIMS (70 eV) (*m/e*): M^+ (344), $M^+ - HCl$ (306), $M^+ - 2HCl$ (270).

Reaction of $W(CO)_5$(2,3-DHT) with HCl. $W(CO)_5$(2,3-DHT) (**1**) (0.200 g, 0.488 mmol) was dissolved in dry, degassed hexanes (20 mL) in a 50-mL round-bottom flask sealed under N_2 with a septum. Gaseous HCl (0.82 mmol) was injected into the solution with a gastight syringe. The solution was stirred vigorously for 2 h, and the solvent was removed in vacuo. The resultant blue-green solid was extracted with dry, degassed pentane, giving a green solution and leaving an insoluble blue solid. The pentane was removed from the solution in vacuo, giving a green-yellow powder. Yield: 0.0541 g (27%). The ^1H and ^{13}C NMR and mass spectra were the same as those of $W(CO)_5$(THT) (**2**).

Results and Discussion

Preparation of Transition-Metal Complexes with Sulfur-Bound 2,3-DHT. The syntheses described in this section demonstrate that 2,3-DHT forms transition-metal complexes by coordinating through its sulfur atom as is typical of simple thioethers.[12] While 2,3-DHT itself is not very stable, polymerizing upon heating and slowly decomposing on exposure to air,[5,10] the complexes **1**, **3**, **4**, and **5** containing the S-bound 2,3-DHT are not air or moisture sensitive. They have been stored in air for months without decomposition. In addition, the 2,3-DHT is strongly bound in these complexes, the 2,3-DHT in **1** being displaced only slowly (over 3 h) by a 10 fold excess of *t*-BuNC. This is in contrast to thiophene, which is aromatic and coordinates only weakly through its sulfur. Only three complexes of S-bound thiophene have been reported, and in all of them, the thiophene can be readily displaced

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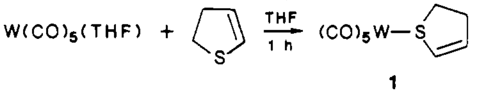
by weakly coordinating solvents.[13]

Substitution of the labile THF ligand in $W(CO)_5(THF)$ with 2,3-DHT leads to the S-bound 2,3-DHT complex **1**, in 81% yield (eq 1). The ^1H and ^{13}C NMR chemical shifts of the 2,3-DHT

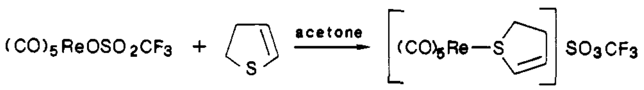


(1)

1

in **1** support sulfur coordination of the ligand; all resonances are at lower field in the complexed ligand (^1H NMR ($CDCl_3$): δ 6.19, 5.87, 3.53, 2.96) than in the free ligand (δ 6.14, 5.59, 3.21, 2.74).[10] If, on the other hand, olefin coordination had occurred, the olefinic resonances for H_4 and H_5 would be expected to shift to higher field.[14] For example, in (1,6-bis(diphenylphosphino)-*trans*-hex-3-ene)tricarbonyltungsten the two olefinic protons shift from 5.5 to 4.34 ppm upon coordination.[14c]

Reaction of 2,3-DHT with $Re(CO)_5OSO_2CF_3$ in acetone leads to substitution of the triflate anion by 2,3-DHT (eq 2). When

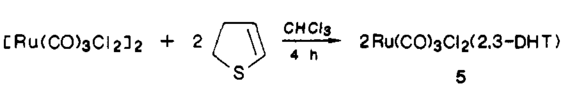


3

(2)

other less polar solvents such as CH_2Cl_2 or $CHCl_3$ were used for this reaction, **3** did form, but in lower yields. In addition, the time required for reaction was longer and some decomposition of the 2,3-DHT occurred. When the reaction was followed by ^1H NMR in acetone-d_6, however, the reaction went cleanly to produce **3**. For the reaction in acetone, the solvent was removed, giving **3** as a white oil. Attempts to recrystallize **3** from CH_2Cl_2 with nonpolar solvents such as diethylether or hexanes led to decomposition, giving $Re(CO)_5OSO_2CF_3$ and free 2,3-DHT. Because of this, the compound was not obtained analytically pure. It was characterized by its IR, ^1H and ^{13}C NMR, and FAB mass spectra.

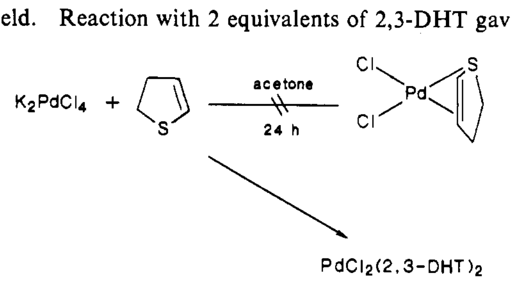
Reactions of 2,3-DHT with K_2PdCl_4 and $[Ru(CO)_3Cl_2]_2$, which have been shown to react with donor ligands,[15] also give complexes in which the ^1H NMR indicates that the 2,3-DHT is coordinated only through the S atom. In the Pd(II) salt $[CpPd(PPh_3)(H_2C{=}CH_2)]ClO_4$, the ethylene shifts to higher field by 1.33 ppm upon coordination.[16] Complexes of the formula $[CpRu(PMe_3)_2(acrylonitrile)]PF_6$ have been isolated where the acrylonitrile coordinates either through the nitrogen or the olefin.[17] The olefinic hydrogens of the olefin-coordinated isomer are 2.5 ppm upfield from those in the nitrogen-coordinated complex. Since the ^1H NMR olefinic resonances in **4** and **5** shift to lower rather



(3)

5

than higher field, we assign these complexes as S-bound. When K_2PdCl_4 was reacted in a 1:1 ratio of Pd:2,3-DHT in an attempt to prepare a complex in which both the sulfur and olefin were coordinated, the bis(2,3-DHT) complex **4** was obtained but in only 37% yield. Reaction with 2 equivalents of 2,3-DHT gave **4** in



(4)

4

59% yield after recrystallization from warm acetone. The product is presumed to have the trans structure as is typical of other bis(thioether)palladium complexes.[18]

Several other attempts to obtain complexes of S- and olefin-bound 2,3-DHT were also unsuccessful. Photolytic and thermal removal of CO from **1** and **3**, which would open a site for olefin coordination, led only to decomposition of the complexes. Similarly, when $PdCl_2(2,3\text{-DHT})_2$ was treated with $AgBF_4$, only decomposition of the complex was observed by ^1H NMR.

Reactivity of Coordinated 2,3-DHT Complexes. A freshly prepared yellow solution of **1** in $CDCl_3$ turns green within 4 min. Examination of the ^1H NMR spectrum of the solution after approximately 10 min shows two new resonances at δ 3.16 (m) and 2.49 (m) that grow larger as the resonances for the coordinated 2,3-DHT disappear. After 3 h, a green solid is isolated in relatively low yield (~10%) after evaporation of the solvent and is identified by ^1H and ^{13}C NMR, IR, and mass spectroscopy as $W(CO)_5(THT)$ (**2**).[11] This complex can also be prepared by reaction of $W(CO)_5(THF)$ with tetrahydrothiophene, THT. This surprising conversion of coordinated 2,3-DHT to THT was of considerable interest because the hydrogenation of 2,3-DHT to THT is also observed over Re and Mo HDS catalysts supported on γ-Al_2O_3 at 300 °C.[4b,c] Potentially, the conversion of the 2,3-DHT in **1** was initiated by small amounts of HCl present in $CDCl_3$. Indeed, passing the $CDCl_3$ through basic alumina prior to dissolving **1** greatly decreased the rate of formation of **2**, $W(CO)_5(THT)$. To investigate the possibility that the reaction was initiated by acid, we undertook the reaction of **1** with HCl. When a solution of **1** in hexanes was treated with 1.7 equiv of HCl, the yellow solution turned green immediately, and **2** was isolated as a yellow-green powder in 27% yield. In an effort to establish the hydrogen source for the conversion of 2,3-DHT to THT, **1** was also reacted with DCl gas in $CDCl_3$.[19] No deuterium incorporation was seen by integration of the ^1H NMR spectrum of **2** at either position of the THT ligand or by ^2H NMR. Therefore, neither HCl nor the solvent $CHCl_3$ is the source of hydrogen for the formation of the THT ligand. The hydrogen apparently comes from the 2,3-DHT itself. The low yield (27%) of **2** in the reaction of **1** with HCl is consistent with this possibility. None of the other side products of this reaction could be identified.

Another reaction of 2,3-DHT observed over HDS catalysts is dehydrogenation to give thiophene.[4b,c] The mass spectrum of $Ru(CO)_3Cl_2(2,3\text{-DHT})$, shows loss of two HCl molecules giving a $Ru(CO)_3(thiophene)^+$ ion, presumably containing a thiophene ligand. We sought to promote on a larger scale the elimination of HCl from **5** giving a thiophene complex or free thiophene. When **5** was heated in $CDCl_3$ in an NMR tube for 1 h at 50°, no formation of thiophene or a thiophene-containing complex was observed by ^1H NMR. Likewise, complete thermal decomposition of a small solid sample of **5** at 120 °C in a sealed NMR tube under vacuum did not result in HCl elimination to give thiophene. Similar reactions were also attempted with $PdCl_2(2,3\text{-DHT})_2$ **4**; however, they again gave no evidence for the formation of thiophene.

Inversion of Sulfur in Complexes Containing 2,3-DHT. An interesting feature of the 2,3-DHT complexes is the change in

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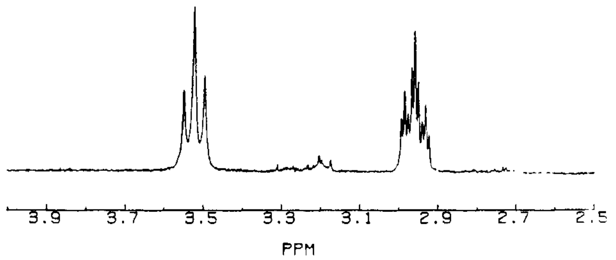


Figure 1. Room-temperature ^{1}H NMR spectrum of the methylene region of W(CO)$_5$(2,3-DHT) (1) in CDCl$_3$.

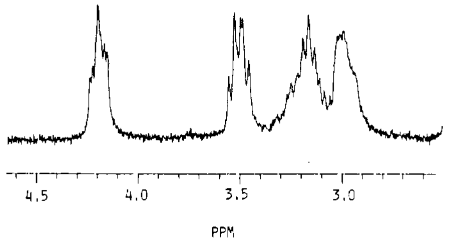
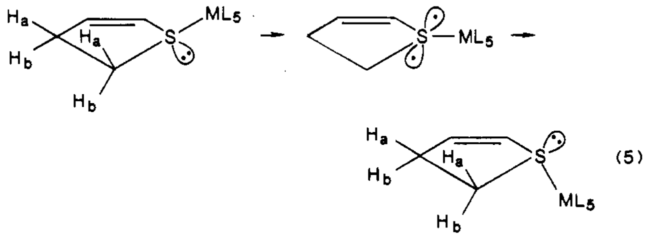


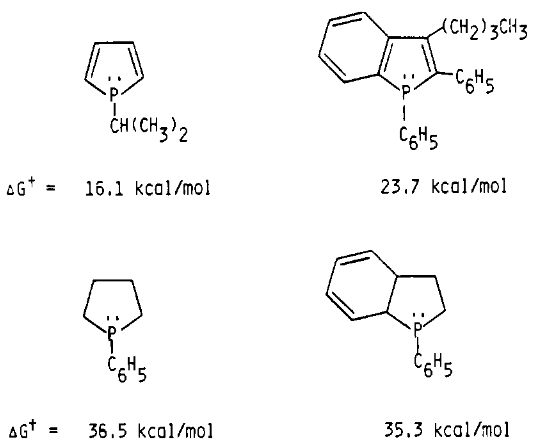
Figure 2. Room-temperature ^{1}H NMR spectrum of the methylene region of Ru(CO)$_3$Cl$_2$(2,3-DHT) (5) in CDCl$_3$.

their ^{1}H NMR spectra with temperature. These changes result from exchange of the methylene hydrogens on the same carbon caused by inversion of the pyramidal sulfur (eq 5).[20] This inversion process, which has been examined in other transition-metal-thioether complexes,[20] was conveniently monitored by ^{1}H NMR for several of the 2,3-DHT complexes. Both the influence of the formal oxidation state of the metal and the presence of the olefin on the barrier to inversion were examined.[20,21]



The ^{1}H NMR spectrum of 1, W(CO)$_5$(2,3-DHT), at room temperature is shown in Figure 1. Two resonances are seen for the two sets of methylene hydrogens at δ 3.53 and 2.96. If no inversion of sulfur were occurring or if it were very slow on the NMR time scale, four resonances, one for each of the inequivalent methylene hydrogens, would be observed. The fact that only one resonance is observed for each set of methylene hydrogens reflects rapid inversion at sulfur on the NMR time scale.[22] In contrast, the room-temperature ^{1}H NMR spectrum of 3, [Re(CO)$_5$(2,3-DHT)]SO$_3$CF$_3$, shows two broad signals for the methylene protons. The exchange process is occurring at a rate comparable to that of the NMR time scale. Figure 2 shows the room temperature spectrum of 5, Ru(CO)$_3$Cl$_2$(2,3-DHT), where inversion is slow enough that four separate methylene resonances are observed. On the basis of these qualitative observations, 1, 3, and 5 follow a trend of increasing barrier to inversion with increasing formal oxidation state of the metal: W(0) < Re(I) < Ru(II). A similar trend was observed previously where the $\Delta G^{\ddagger}$ for inversion was greater for Pt(IV) than Pt(II) in the complexes: [PtXMe(MeSCH$_2$CH$_2$SMe)] vs. PtXMe$_3$(MeSCH$_2$CH$_2$SMe)][23] and PtX$_2$(MeSCH$_2$CH$_2$SMe) vs. PtX$_4$(MeSCH$_2$CH$_2$SMe).[24]

Chart I. Barriers to Inversion of Phosphorus

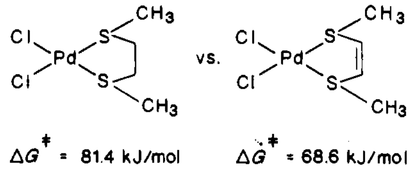


For 1 and 3, the barriers to inversion were low enough so that we were able to examine the exchange process from the slow to the fast exchange limits. From the coalescence temperature, the barriers to inversion in these complexes were estimated by using eq 6,[25] where T_c is the coalescence temperature and $\delta\nu$ is the

$$\Delta G^{\ddagger} = 1.92T_c[9.97 + \log (T_c/\delta\nu)] \qquad (6)$$

frequency difference in hertz between sites in the exchanging system. Coalescence temperatures were determined to ±2 °C. Since $\delta\nu$ was taken simply as the separation between the coalescing multiplets, the error in $\Delta G^{\ddagger}$ is estimated to be ±2 kJ/mol. Using this method, we obtained $\Delta G^{\ddagger}$ values of 48.5 kJ/mol (T_c = 233 K) and 62.7 kJ/mol (T_c = 310 K) for 1 and 3, respectively. While the majority of the Re(I) complexes previously examined have chelating sulfur ligands, as in ReCl(CO)$_3${MeS(CH$_2$)$_2$SMe}, $\Delta G^{\ddagger}$ = 65.1 kJ/mol, and ReI(CO)$_3$(MeS(CH$_2$)$_2$SMe), $\Delta G^{\ddagger}$ = 66.7 kJ/mol, these values[26] are quite similar to our estimate of 62.7 kJ/mol for 3. The value obtained for W(CO)$_5$(2,3-DHT) is similar to those for related complexes: W(CO)$_5$(SCH$_2$SCH$_2$SCH$_2$), $\Delta G^{\ddagger}$ = 53.0 kJ/mol;[27] W(CO)$_5${MeSCH$_2$SCH$_2$SMe}, $\Delta G^{\ddagger}$ = 42.5 kJ/mol.[20]

Eekhof et al.[28] reported on inversion barrier of 45.6 kJ/mol for W(CO)$_5$(2,5-DHT), where 2,5-DHT is the isomer of 2,3-DHT with the double bond between the 3 and 4 carbons. Thus, the inversion barrier for W(CO)$_5$(2,5-DHT) is lower than that (48.5 kJ/mol) for W(CO)$_5$(2,3-DHT) (1). Thus, olefin conjugation with the sulfur in 1 does not lower the inversion barrier. Such a lowering might be expected since the lone pair of electrons on the sulfur in the planar transition state should be stabilized by conjugation with the olefin. This lowering of the inversion barrier by conjugation has been observed in a number of transition metal complexes with chelating sulfide ligands, e.g.:[20,23]



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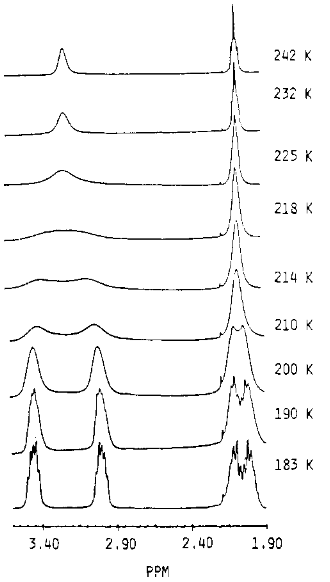

Figure 3. Temperature-dependent ^{1}H NMR spectra of W(CO)$_5$(THT) (**2**) in CDCl$_3$.

Typically, a decrease in $\Delta G^{\ddagger}$ of 10–12 kJ/mol is observed in the conjugated systems. Evidence for π-conjugation effects are also seen in inversion barriers from examination of phospholes,[29] Chart I. In compounds where the phosphorus lone pair can delocalize in an aromatic ring, inversion barriers are substantially lower than for other systems. The increase in the barrier to inversion in the saturated ring systems (C and D in Chart I) reflects the disruption of the "aromaticity" of the phospholene ring. In order to probe further the effect of the olefinic bond in **1** and W(CO)$_5$(2,5-DHT) on the inversion barrier, we undertook a variable-temperature ^{1}H NMR study (Figure 3) of **2**, W(CO)$_5$(THT), with the saturated tetrahydrothiophene ligand. The free energy barrier calculated by using eq 6 is 43.9 kJ/mol (T_c = 218 K). Thus, the trend in inversion barriers for **1**, W(CO)$_5$(2,5-DHT), and **2**, is 48.5, 45.6, and 43.9 kJ/mol, respectively, and can be explained by considering the effect of ring strain. For the series of Pd(II) complexes, $\textit{trans}\text{-PdCl}_2[\overline{\text{S(CH}_2)_x\text{C}}\text{H}_2]_2$, where x = 2, 3, or 4, the barrier to inversion increases with increasing ring strain. The decrease in ring size (i.e., the C–S–C bond angle) presumably constrains access to the planar transition state required for inversion.[20] The ring strain energies for 2,3-DHT, 2,5-DHT, and THT are 18.0, 15.8, and 8.3 kJ/mol,[30] exactly the trend observed for the inversion barriers in the analogous W(CO)$_5$L complexes. It therefore appears that ring strain is the most important factor determining the rates of inversion in the W(CO)$_5$L complexes of 2,3-DHT, 2,5-DHT, and THT.

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Large Positive Activation Volume (+38 cm^3 mol^{-1}) for the Intramolecular Electron-Transfer Reaction from Iron(II) to Cobalt(III) in (μ-Pyrazine-*N*,*N'*)(pentaamminecobalt(III))pentacyanoiron(II) in Aqueous Solution

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The title reaction gave an activation volume ($\Delta V^{\ddagger}$) of +38 ± 1 cm^3 mol^{-1} (pH 5.0 (0.015 M phosphate buffer), I = 0.10 M (NaClO$_4$), 25 °C, 0.1–70 MPa), which is among the largest positive activation volumes ever observed for electron-transfer reactions of metal complexes. While the first-order rate constants differ appreciably on changing added electrolytes (4.9×10^{-2}, 4.1×10^{-2}, and 8.9×10^{-2} s^{-1} for 0.1 M NaClO$_4$, NaCl, and (C$_2$H$_5$)$_4$NClO$_4$, respectively), $\Delta V^{\ddagger}$, as well as $\Delta H^{\ddagger}$ (ca. 130 kJ mol^{-1}), and $\Delta S^{\ddagger}$ (ca. +165 J K^{-1} mol^{-1}), is essentially unchanged. The large positive activation volume cannot be accounted for by the sum of the intrinsic volume change (theoretical estimation, <20 cm^3 mol^{-1}) and the solvational volume change due to the change in electrostriction (<6.51 cm^3 mol^{-1}). The hydrogen-bonding interactions between the ligands and the solvent water molecules may play a significant role in determining the activation volume. The salt effect, which is not great enough to affect the activation parameters, may be explained by the difference in the extent of stabilization between the initial and the transition state.

Introduction

It is increasingly realized that activation volume ($\Delta V^{\ddagger}$) is one of the most useful tools in elucidating the transition state of electron-transfer reactions of metal complexes in solution.[2–11] It is a measure of the volume difference between the initial and the transition state and involves contributions from both the solvation sphere and the reactants themselves.[12] Outer-sphere electron-transfer reactions proceed through encounter complex formation (formation constant, K_{OS}) and net electron-transfer within it (rate

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