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Ethylene Rotation in Chiral Octahedral Rhenium(I) Complexes

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Summary: A series of complexes of the type [TpRe(CO)-(L_D)(η^2-ethylene)] has been synthesized, where L_D is ^{t}BuNC, PMe_3, pyridine, 1-methylimidazole, or NH_3 (increasing in electron-donating ability of L_D). The rates of the propeller-like rotation of ethylene about the ethylene−rhenium bond have been determined using spin saturation transfer experiments at low temperatures (−85 to −60 °C). It was found that the $\Delta G^\ddagger$ values correlate with both the C≡O stretching frequencies and Re(II/I) reduction potentials for these complexes, indicating that the barrier to rotation is primarily electronic in nature.

Introduction

Olefin complexes are typically dynamic in nature.[1−15] The propeller-like rotation of bound ethylene about the metal−olefin bond was first clearly demonstrated in 1972.[6] Free energies of activation for this process have been reported from 7 to 19 kcal/mol, depending on the type of bound olefin, metal center, and ligand set involved.[2] In addition to the abundance of experimental work, theoretical treatments of this subject have been published.[16,17]

Our interest in the dynamic behavior of olefin complexes stems from a recent study from our group concerning the linkage isomerization of aromatic ligands bound to Re(I).[18] Complexes of the type [TpRe(CO)(L_D)-(η^2-L_{Ar})] {Tp = hydridotris(pyrazolyl)borate, L_D is a (primarily) electron-donating ligand (vide infra), and L_{Ar} is an aromatic ligand} were found to undergo both inter- and intrafacial linkage isomerizations in which the metal migrated from one C=C bond face either to the opposite face or to another double bond on the same face. Unfortunately, the specific rates for these processes were on the same time scale as those reported for olefin rotations for other systems. To clearly differentiate these dynamic processes, we set out to measure the rotation rates of a series of octahedral ethylene complexes of Re(I) in which the electron density of the metal could be systematically varied by adjusting the ligand set. Thus, a new series of octahedral complexes of the type [TpRe(CO)(L_D)(η^2-ethylene)] was prepared, where L_D is ^{t}BuNC (**1**), PMe_3 (**2**), pyridine (**3**), 1-methylimidazole (**4**), or NH_3 (**5**). The ligands chosen for L_D provide a range of CO stretching frequencies from 1832 to 1767 cm^{-1} and reduction potentials from 0.46 to −0.03 V (NHE). With these complexes in hand, we set out to measure the rates of ethylene rotation and to correlate them with the electronic properties of the metal.

Results and Discussion

Complexes of the type [TpRe(CO)(L_D)(η^2-ethylene)] were synthesized from their parent cyclohexene, naphthalene, or benzene precursors either by direct substitution with ethylene (as with [TpRe(CO)(1-methylimidazole)(η^2-benzene)]) or by an oxidation/reduction sequence (as with [TpRe(CO)(PMe_3)(η^2-cyclohexene)]). At 20 °C, the ^{t}BuNC (**1**) and PMe_3 (**2**) complexes exhibited two sharp peaks in their ^{1}H NMR spectra corresponding to the protons of the ethylene ligand. When a solution of the PMe_3 complex (**2**) was cooled to −85 °C, four well-resolved resonances could be observed in the range of 0.8−2.6 ppm. However, the ethylene peaks for the ^{t}BuNC complex (**1**) were still severely broadened at this temperature, indicating a significantly lower barrier to rotation than observed for the phosphine analogue (**2**). At 20 °C, ^{1}H NMR spectra (Table 2) for the pyridine (**3**), 1-methylimidazole (**4**), and NH_3 (**5**) complexes were also broadened, but upon cooling to temperatures near −65 °C, all showed well-resolved spectra. Proton assignments were made on the basis of comparison with other olefin complexes[18−21] and NOE, COSY, and spin

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saturation data (vide infra). The $^1H-^1H$ coupling constants of the ethylene protons agree well with those observed for other dihapto-coordinated complexes of ethylene (see Experimental Section for details).[5,22] At the temperatures where spin saturation data were recorded, interfacial isomerization and substitution of the ethylene ligand could be ruled out; thus rotation was assumed to be the dynamic process responsible for exchanging the protons (vide infra).

At −85 °C, the spectrum of 2 showed four broadened, yet distinct, resonances, each corresponding to one of the four ethylene protons (see Experimental Section for details). Spin saturation transfer experiments at −85 °C using the Forsén−Hoffman method[23−25] indicated a specific rate of rotation of 10.3 s^{-1}, corresponding to a $\Delta G^{\ddagger}$ of 10.0 kcal/mol. Note that this rate corresponds to a 180° rotation about the rhenium−ethylene bond. Cooling of the ^{t}BuNC system to our experimental limit of −85 °C still resulted in resonances too broad to perform spin saturation experiments. Due to complexity of the proton spectrum, a coalescence temperature could not be confidently assigned. However, the specific rate at this temperature could be estimated to be ~2000 s^{-1} by comparing line broadening with the other [TpRe(CO)(L$_D$)(η^2-ethylene)] systems. Assuming that $\Delta S^{\ddagger}$ was negligible for this process, a free energy of activation could be calculated for −85 °C of 8.0 ± 0.5 kcal/mol. The other complexes (**3**−**5**) showed four well-resolved resonances (ethylene protons) at temperatures as high as −65 °C. Thus, spin saturation transfer experiments were performed at this temperature for the pyridine (**3**), 1-methylimidazole (**4**), and NH_3 (**5**) complexes. At −65 °C, the ethylene ligand of the pyridine complex was found to rotate at a specific rate of 0.68 s^{-1}, corresponding to a $\Delta G^{\ddagger}$ of 12.2 kcal/mol. At −68 °C, the ethylene ligand of the 1-methylimidazole complex rotated with a specific rate of 0.19 s^{-1}, corresponding to a $\Delta G^{\ddagger}$ of 12.5 kcal/mol. Finally, at −60 °C, the ammonia complex underwent ethylene rotation with a specific rate of 0.44 s^{-1}, indicating a $\Delta G^{\ddagger}$ of 12.7 kcal/mol. These results are summarized in Table 1. In all cases, irradiation of one proton of the ethylene ligand resulted in saturation transfer with only one partner, which we assigned to have a trans/vicinal relationship to the proton that was irradiated.

Table 1. Electrochemical, Infrared, and Activation Energy Data for Ethylene Rotation in the Complexes TpRe(CO)(L$_D$)(η^2-ethylene)

L$_D$	$\nu_{C\equiv O}$ (cm^{-1})	$E_{1/2}$ (V)[a]	specific rate (s^{-1})[b,c]	$\Delta G^{\ddagger}$ (kcal/mol)
^{t}BuNC	1836	0.46[e]	2 × 10^3 (−85 °C)[d]	8.0 ± 0.5
PMe$_3$	1810	0.31[f]	10.3 (−85 °C)	10.0 ± 0.3
Py	1793	0.14[e]	0.68 (−65 °C)	12.2 ± 0.3
1-MeIm	1785	−0.03[e]	0.19 (−68 °C)	12.5 ± 0.3
NH$_3$	1767	0.21[f,g]	0.44 (−60 °C)	12.7 ± 0.3

[a] All electrochemical half-cell potentials were recorded at ambient temperature, are referenced to NHE, and were found to be reversible, unless otherwise noted (100 mV/s; TBAH). [b] The rotation rate refers to the rate at which the ethylene ligand rotates through an angle of 180° relative to the metal complex. [c] All rotation rates are ±5%. [d] Rotation rate estimate based on line broadening. [e] Recorded in DMA. [f] Recorded in CH_3CN. [g] Value reported is $E_{p,a}$ at 100 mV/s.

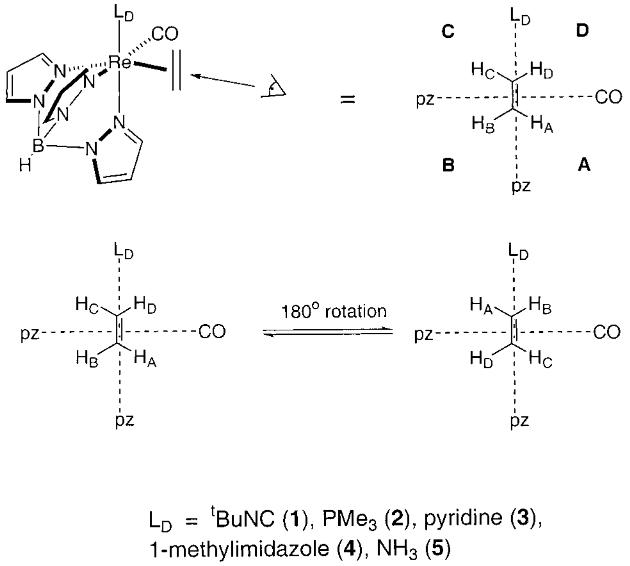

Figure 1. Projection of ethylene complexes of the type TpRe(CO)(L$_D$)(η^2-ethylene) showing the designation of ethylene protons.

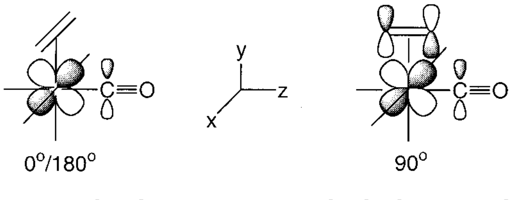

Figure 2. Orbital interactions in both the ground state and transition state for ethylene rotation in TpRe(CO)(L$_D$)(η^2-ethylene).

Table 2. Chemical Shifts (in ppm) of the Bound Protons of TpRe(CO)(L$_D$)(η^2-ethylene) Complexes

L$_D$	H$_A$	H$_B$	H$_C$	H$_D$
PMe$_3$	2.54	0.82	2.05	2.23
Py	3.14	1.60	2.41	2.69
1-MeIm	2.80	1.32	1.95	2.66
NH$_3$	2.63	1.23	1.92	2.76

Crystallographic data for several olefinic and aromatic complexes of the type [TpRe(CO)(L$_D$)(η^2-alkene)] indicate that the bound C═C bond always lies perpendicular to the Re−CO bond, as shown in Figure 1, provided that L$_D$ is not also CO. In this orientation, it is able to interact with the d_{xy} orbital which is orthogonal to the powerful π acid CO. Theoretical studies by Hoffmann suggest that the bound olefin bond may deviate from perpendicular by a few degrees.[17] However, a 90° rotation of the olefin forms a conformer in which the olefin must compete with the CO to back-bond to the metal d_{yz} orbital (Figure 2), thus giving rise to a rotational barrier. In similar systems of the form [CpM(CO)$_2$(η^2-ethylene)] (e.g., M = Mn or Mo), barriers to rotation of 8−10 kcal/mol have been observed.[26]

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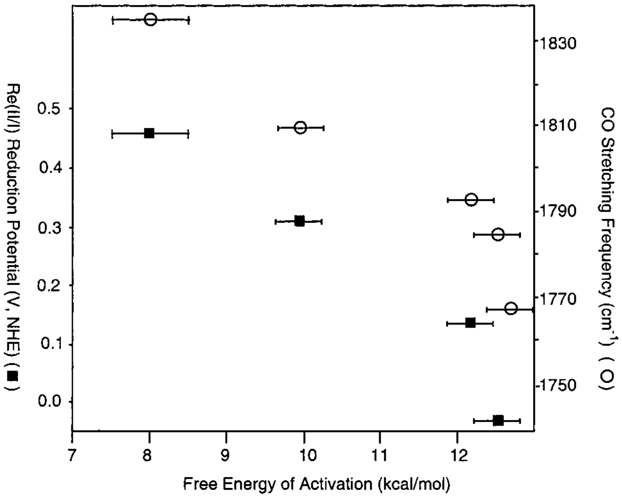

Figure 3. Correlation of free energies of activation for ethylene rotation versus electron density of the metal (as indicated by reduction potential and CO stretching frequency).

As L_D becomes a weaker π acid, the free energy of activation for rotation should increase, assuming that the entropic contribution is negligible. Indeed, free energies of rotation correlate with the carbonyl stretching frequencies (Figure 3). This trend supports the notion that the rotational barrier is due to electronic rather than steric factors.[14,27-29] The absence of significant steric contributions is further supported by MM2 calculations. Free energies of activation for ethylene rotation also correlate with the Re(II/I) reduction potentials for these systems (Figure 3).

Gladysz and co-workers have previously reported that the complex $[CpRe(NO)(PPh_3)(\eta^2\text{-ethylene})]^+$ shows dynamic behavior at ambient temperatures.[30] Using the technique of ^{13}C NMR coalescence, a $\Delta G^\ddagger$ of 16.4 kcal/mol at 96.2 °C was determined for ethylene rotation. The discrepancy between the relatively high $\Delta G^\ddagger$ value seen by Gladysz and the $\Delta G^\ddagger$ values observed in this study warrants some mention due to the similarities between $[CpRe(NO)(PPh_3)(\eta^2\text{-ethylene})]^+$ and $[TpRe(CO)(L_D)(\eta^2\text{-ethylene})]$. In accord with the discussion above, $\Delta G^\ddagger$ for rotation should depend on the *difference* in the relative π acidities between the strong π acid (CO versus NO^+) and the "donor ligand" cis to it (L_D versus PPh_3).[31,32] Since CO is a weaker π acid than NO^+, and the donor ligands can be comparable in the amount of electron density donated to the metal center (PPh_3 versus PMe_3, for example), the difference between the ground state and transition state energies with the nitrosyl system is expected to be larger than in the CO systems studied herein.

Conclusion

We have synthesized a family of complexes of the type $[TpRe(CO)(L_D)(\eta^2\text{-ethylene})]$ (L_D = ^{t}BuNC, PMe_3, pyridine, 1-methylimidazole, or NH_3). These complexes are dynamic in ambient solution, resulting from rapid rotation of the ethylene ligand about the ethylene–rhenium bond. The rates and corresponding free energies of activation for the propeller-like rotation of ethylene in these complexes have been determined. The $\Delta G^\ddagger$ values generally correlate with both the carbonyl stretching frequencies and $E_{1/2}$ values of the complexes, demonstrating that the origins of this barrier to rotation are primarily due to the differing π acidities of the L_D ligands.

Experimental Section

$[TpRe(CO)(PMe_3)(\eta^2\text{-ethylene})]$ (2). To a solution of $[TpRe(CO)(PMe_3)(\eta^2\text{-cyclohexene})]$ (0.219 g, 0.374 mmol) in 8 mL of DME in a glovebox was added AgOTf (0.096 g, 0.374 mmol, 1 equiv) in approximately 7 mL of DME. After stirring for 30 min, the solution was filtered through a fine frit. Hexanes (30 mL) were added, and the resulting greenish-yellow precipitate was isolated by filtration though a coarse frit. The solid was refluxed in 50 mL of DME for 30 min. The solution was cooled under vacuum and reduced to a volume of approximately 25 mL, after which it was transferred to a pressure tube. Sodium amalgam (0.859 g of 1.1%, 0.411 mmol, 1.5 equiv) was added, and the tube was pressurized with ethylene (~30 psi) and stirred. After 2 h and 20 min, the tube was allowed to reach atmospheric pressure. The solution was filtered through a fine frit and concentrated by rotary evaporation. The oil was dissolved in a minimal amount of CH_2Cl_2 and loaded on a small deactivated alumina (activity grade V) column. The complex was eluted with ~500 mL of 1:1 Et_2O/hexanes and rotary evaporated to dryness. The fine powder was dissolved in methanol (10 mL) and precipitated by the dropwise addition of aqueous NH_4PF_6. The greenish solid was washed with 30 mL of water and dried in vacuo. Yield: 103 mg, 52%. ^1H NMR (d_6-acetone, 20 °C): δ 8.09 (1H, d, $J = 1.3$ Hz, TpH), 7.98 (1H, br d, TpH), 7.85 (1H, d, $J = 2.2$ Hz, TpH), 7.78 (1H, d, $J = 2.0$ Hz, TpH), 7.63 (1H, d, $J = 2.2$ Hz, TpH), 7.42 (1H, d, $J = 1.1$ Hz, TpH), 6.27 (1H, t, $J = 2.2$ Hz, TpH), 6.21 (1H, t, $J = 2.0$ Hz, TpH), 6.16 (1H, t, $J = 2.2$ Hz, TpH), 2.29 (2H, dd, $J = 8.4$, 2.1 Hz, H_A and H_C), 1.64 (2H, d, $J = 5.3$ Hz, H_B and H_D), 1.37 ppm (9H, d, $J = 8.4$ Hz, $P(CH_3)_3$). ^{13}C NMR (d_6-acetone, 20 °C): δ 148.7, 145.7, 139.8, 136.7, 135.9, 134.6 (Tp 3 and 5 positions), 106.5, 106.2, 105.9 (Tp 4 positions), 37.6 (2C, d, $J = 4.4$ Hz), 16.9 ppm (d, $J = 33.7$, $P(CH_3)_3$), C≡O not seen. ^1H NMR (d_6-acetone, −85 °C): δ 8.19 (1H, d, $J = 1.7$ Hz, TpH), 8.05 (1H, br d, TpH), 8.00 (1H, d, $J = 2.0$ Hz, TpH), 7.92 (1H, d, $J = 2.4$ Hz, TpH), 7.78 (1H, d, $J = 2.0$ Hz, TpH), 7.55 (1H, d, $J = 1.7$ Hz, TpH), 6.31 (1H, t, $J = 2.0$ Hz, TpH), 6.25 (1H, t, $J = 1.7$ Hz, TpH), 6.22 (1H, t, $J = 2.0$ Hz, TpH), 2.54 (1H, br dd, $J = 9.4$, 9.4 Hz, H_A), 2.23 (1H, br dd, $J = 10.4$, 15.4 Hz, H_D), 2.05 (1H, br dd, $J = 18.6$, 9.3 Hz, H_C), 1.37 (9H, d, $J = 8.4$ Hz, $P(CH_3)_3$), 0.82 ppm (1H, br dd, $J = 11.4$, 8.4 Hz, H_B). ^{13}C NMR (d_6-acetone, −85 °C): δ 197.6 (C≡O), 148.9, 145.6, 139.8, 136.7, 136.0, 134.6 (Tp 3 and 5 positions), 106.3 (2C), 105.8 (Tp 4 positions), 37.9 (br d, CH_2), 36.4 (CH_2), 16.1 ppm (d, $J = 32.6$ Hz, $P(CH_3)_3$). IR (HATR): 2480 (ν_{BH}), 1810 cm^{-1} ($\nu_{C\equiv O}$). $E_{1/2} = 0.31$ V (NHE).

$[TpRe(CO)(1\text{-methylimidazole})(\eta^2\text{-ethylene})]$ (4). In a glovebox, $[TpRe(CO)(1\text{-methylimidazole})(\eta^2\text{-benzene})]$ (0.082 g, 0.14 mmol) was dissolved in 10 mL of THF. Outside the glovebox, the solution was stirred under slow ethylene purge for 16 h. The solution was brought back into a glovebox, and the solvent was removed in vacuo. The crude precipitate was redissolved in a minimal amount of benzene, and the solution

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was passed through a small silica plug using ether as the eluent. The ethereal solution was concentrated, and the product was isolated by precipitation with hexanes, filtering, and drying in vacuo, resulting in a pale yellow powder. Yield: 60 mg, 80%. ^{1}H NMR (d_6-acetone, 20 °C): δ 7.84 (1H, dd, J = 2.4, 0.6 Hz, TpH), 7.83 (1H, d, J = 1.5 Hz, TpH), 7.78 (1H, dd, J = 1.5, 0.6 Hz, TpH), 7.68 (1H, dd, J = 2.4, 0.6 Hz, TpH), 7.49 (1H, br t, ImH), 7.37 (1H, d, J = 1.8 Hz, TpH), 7.31 (1H, d, J = 1.8 Hz, TpH), 6.96 (1H, t, J = 1.5 Hz, ImH), 6.43 (1H, t, J = 1.5 Hz, ImH), 6.24 (1H, t, J = 2.3 Hz, TpH), 6.16 (1H, t, J = 2.3 Hz, TpH), 6.12 (1H, t, J = 2.3 Hz, TpH), 3.76 (3H, s, NMe), 2.41 (2H, br s, H_A and H_C), 2.05 ppm (2H, br s, H_B and H_D). ^{1}H NMR (d_6-acetone, −65 °C): δ 7.94 (1H, d, J = 2.5 Hz, TpH), 7.89 (1H, d, J = 2.0 Hz, TpH), 7.84 (1H, d, J = 2.0 Hz, TpH), 7.79 (1H, d, J = 2.5 Hz, TpH), 7.64 (1H, br t, ImH), 7.42 (1H, d, J = 2.0 Hz, TpH), 7.30 (1H, d, J = 1.5 Hz, TpH), 7.05 (1H, br t, ImH), 6.30 (1H, br t, ImH), 6.29 (1H, t, J = 2.3 Hz, TpH), 6.21 (1H, t, J = 2.3 Hz, TpH), 6.17 (1H, t, J = 2.0 Hz, TpH), 3.78 (3H, s, NMe), 2.80 (1H, dd, J = 9.5, 9.0 Hz, H_A), 2.66 (1H, dd, J = 9.5, 9.0 Hz, H_D), 1.95 (1H, dd, J = 9.5, 9.0 Hz, H_C), 1.32 ppm (1H, dd, J = 9.5, 9.0 Hz, H_B). ^{13}C NMR (d_6-acetone, −60 °C): δ 146.8, 143.7, 142.4, 138.9, 135.7, 135.2, 135.0, 131.8 (Tp 3 and 5 positions, Im), 106.6, 106.5, 106.2 (Tp 4 positions), 121.8 (Im), 46.9 (CH_2), 45.9 ppm (CH_2). IR: 2480 (ν_{BH}), 1786 cm^{-1} ($\nu_{C\equiv O}$). $E_{1/2}$ = −0.03 V (NHE). Anal. Calcd for $ReC_{16}H_{20}N_8BO$: C, 35.76; H, 3.75; N, 20.85. Found: C, 35.24; H, 3.36; N, 20.48.

The syntheses of compounds **1**, **3**, and **5** are reported in the Supporting Information.

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Supporting Information Available: Synthetic procedures, full characterization, and ^{1}H NMR data for all complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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