mobile with respect to that interface and that this mobility, by burying or exposing polar functional groups, can strongly influence macroscopic properties of the interface such as wettability. The high hydrophobicity of **2** at low pH reemphasizes the effectiveness with which small, nonpolar organic groups at an interface can shield underlying polar functionality from contact with water.[10]

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Comparison of Migratory Aptitudes of Hydride and Alkyl Groups in β-Migratory Insertion Reactions of $Cp^*(P(OMe)_3)Rh(C_2H_4)R^+$ (R = H, CH_2CH_3)

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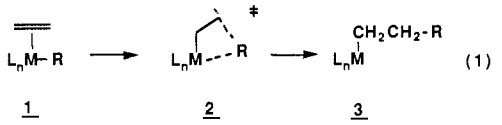
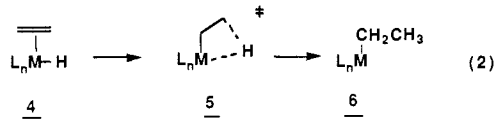
Received July 25, 1988

The β-migratory insertion reaction (eq 1) of metal alkyl olefin complexes is thought to be the key step in Ziegler–Natta olefin polymerization reactions and related oligomerizations and dimerizations.[1,2] However, such migratory insertion reactions have rarely been observed for stable complexes of type **1**.[3]

The structure and dynamics of the often more accessible hydride systems (eq 2) should prove useful in predicting the rates of alkyl

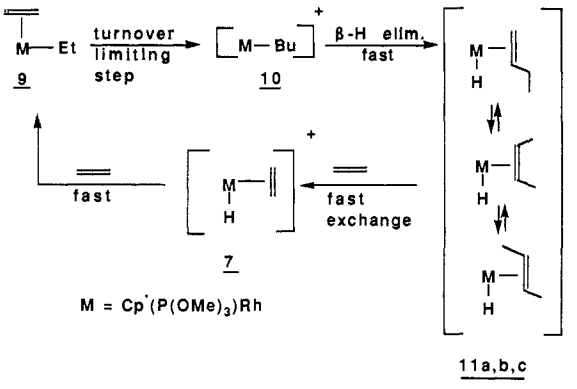




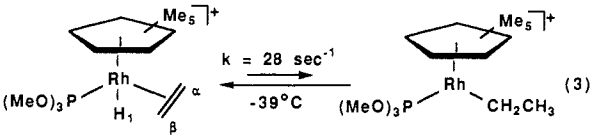
migrations in ethylene alkyl complexes (eq 1). Earlier[4] we suggested that when the stable form of the hydride complex is the agostic structure **5** (as compared to the terminal structure **4**) the barrier to alkyl migration in the alkyl analogues of these systems should be lower relative to alkyl analogues of terminal hydride systems, **4**. That is, the same factors which favor a bridging over a terminal hydride structure should dictate a smaller energy difference between **1** and **2**. This proposal has been verified in the case of agostic Co(III) systems of the type $Cp^*(L)Co\text{-}CH_2\text{-}CH_2\text{-}\mu\text{-}H^+$.[4]

No quantitative data are currently available regarding relative rates of hydride and alkyl migrations in terminal hydride systems **4** and their alkyl analogues.[5,6] We report here a study of $Cp^*(P(OMe)_3)Rh(H)(C_2H_4)^+$ and the ethyl analogue $Cp^*(P(OMe)_3)Rh(C_2H_5)(C_2H_4)^+$ which establishes migratory aptitudes for -H versus $-CH_2CH_3$ groups in these systems.

Scheme I



Protonation of $Cp^*(P(OMe)_3)Rh(C_2H_4)$[7] with $HBF_4\cdot Me_2O$ in CD_2Cl_2 at −30 °C yields the stable orange-yellow salt $Cp^*(P(OMe)_3)Rh(H)(C_2H_4)^+$, **7**.[7-9] The hydride is terminal and not



agostic as indicated by lack of coupling between the rhodium hydride and $^{13}C_\alpha$ or $^{13}C_\beta$ (<4 Hz) and the large values of J_{Rh-H} (18 Hz) and J_{P-H} (18 Hz). Complex **7** exhibits two dynamic processes. Ethylene rotation is rapid, and from line shape analysis a rotational barrier of ca. 9.6 ± 0.4 kcal/mol at −60 °C can be estimated. At higher temperatures the hydride signal at −9.95 ppm broadens and averages with the ^1H signals of the ethylene ligand due to a reversible migratory insertion reaction shown in

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(6) Activation barriers may be crudely estimated for the migratory insertion reactions of $CpNi(C_2H_4)R$,[3a] $CpCo(C_2H_4)(CH_3)_2$,[3b] and $Cp^*Co(C_2H_4)(CH_3)_2$;[3c] but in each case the hydride analogue is unknown, and thus a comparison of hydride and alkyl migration barriers is not possible.

(7) (a) Prepared by the reaction of $Cp^*Rh(C_2H_4)_2$ with $P(OMe)_3$ in analogy with the preparation of $Cp^*Rh(C_2H_4)(PMe_3)$: Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, *23*, 2376. (b) ^1H NMR (25 °C, C_6D_6) δ 3.29 (d, J_{P-H} = 12.8 Hz, $P(OMe)_3$), δ 1.87 (d, J_{P-H} = 3 Hz, C_5Me_5), δ 2.21, 1.7 (multiplets, C_2H_4). Anal. Found: (Calcd): C, 45.94 (46.16); H, 6.99 (7.23).

(8) ^1H NMR parameters for **7** are similar to those for $Cp(PMe_3)Rh(C_2H_4)(H)^+BF_4^-$ reported by Werner.[5b,c]

(9) **7**: ^1H NMR (−94 °C, CD_2Cl_2), δ −9.95 (t, $J_{P-H} = J_{Rh-H}$ = 18 Hz, H_1), δ 2.5, 2.6, 2.9, 3.0 (multiplets, four inequivalent protons of C_2H_4), δ 1.85 (d, J_{P-H} = 4 Hz, C_5Me_5), δ 3.5 (d, J_{P-H} = 13 Hz, $P(OMe)_3$); ^{13}C NMR (−94 °C, CD_2Cl_2), δ 104 (s, C_5Me_5), δ 52.7 (dq, J_{P-C} = 3.3 Hz, J_{C-H} = 149 Hz, $P(OMe)_3$), δ 9.98 (q, J_{C-H} = 129 Hz, C_5Me_5). Ethylene signals are obscured by CD_2Cl_2 but are visible in acetone-d_6 at −94 °C: δ 53.4 (t, J_{C-H} = 161 Hz, C_α or C_β), δ 54.6 (t, J_{C-H} = 161 Hz, C_α or C_β).

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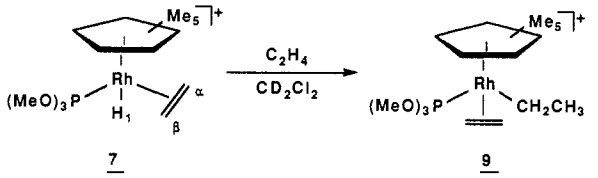
eq 3. By using standard spin saturation transfer techniques the rate constant for hydride migration was determined to be 28 s^{-1} at −39 °C which corresponds to $\Delta G^{\ddagger}$ = 12.0 kcal/mol.

Treatment of **7** in CD_2Cl_2 at −80 °C with 20–50 equiv of ethylene results in rapid trapping of **8** and formation of the ethyl ethylene complex **9**.[10,11] Warming **9** to 23 °C in the presence



7 **9**

of excess ethylene results in the catalytic dimerization of ethylene by **9** to butenes (1-butene:*cis*-2-butene:*trans*-2-butene = 7:1:1)[12] with *no change* in the spectral intensity of **9**. The rate of production of butenes is linear over more than 30 turnovers with a turnover rate of 1 equiv of C_2H_4/**9**/42 min.

The proposed mechanism for butene formation is shown in Scheme I. Migratory insertion of **9** generates the unsaturated rhodium–butyl complex **10** which, upon β-elimination, must give initially the 1-butene complex **11a**. The 2-butene isomers must arise by the well-established mechanism of migratory insertion of **11a** to the Rh-*sec*-butyl complex followed by reelimination. Whether equilibrium is established among isomers **11a–c** prior to butene displacement by ethylene is unknown. Since no other species are detectable in significant quantities[13] the turnover limiting step must be the migratory insertion reaction **9** → **10**. From the rate of production of butenes at 23 °C the rate constant for migratory insertion of **9** is calculated to be 2×10^{-4} s^{-1}, $\Delta G^{\ddagger}$ = 22.3 kcal/mol.

These experiments establish for the first time a quantitative measure of the relative migratory aptitudes of hydride and alkyl groups in the β-migratory insertion reaction. The difference in free energies of activation ($\Delta G^{\ddagger}_{Et\ mig} - \Delta G^{\ddagger}_{H\ mig}$) is 10.3 kcal/mol which corresponds to a rate ratio of $k_{H\ mig}/k_{Et\ mig}$ of ca. 10^7–10^8 at 25 °C.[14] This value is somewhat smaller than that observed for the relative rates of -H and -CH_3 α-migration in $Cp^*_2Ta(CH_2)(H)$ and $Cp^*_2Ta(CH_2)(CH_3)$ of (k_H/k_{Me} = 10^{10}) at 50 °C.[2d] The large difference in activation barriers for hydride versus alkyl migrations is consistent with the fact that alkyl migrations are unobserved in ethylene alkyl complexes where the analogous terminal hydride systems show barriers for migration of greater than 17–18 kcal/mol.[2d,5] Relative migratory aptitudes of hydride and alkyl groups may vary significantly from system to system. We are probing this point by examining other pairs of isoelectronic complexes, $L_nM(C_2H_4)H/L_nM(C_2H_4)R$.

Acknowledgment is made to the National Science Foundation (Grant No. CHE-8705534) for support of this research.

(10) **9**: ^1H NMR (−117 °C, CD_2Cl_2) δ 3.75 (d, $J_{P-H} \approx$ 11.2 Hz, P(OMe)3), δ 1.69 (d, J_{P-H} = 4.4 Hz, C_5Me_5), δ 1.17 (t, J_{C-H} = 7.2 Hz, CH_2CH_3), δ 2.4, 2.7, 2.8, 3.5 (multiplets, four inequivalent protons of C_2H_4). The CH_2 signal is obscured by the C_5Me_5 signal but was located by decoupling experiments: ^{13}C NMR (−108 °C, CD_2Cl_2), δ 104.3 (s, C_5Me_5), δ 8.4 (q, J_{C-H} = 129 Hz, C_5Me_5), δ 55.1 (dq, J_{P-C} = 10 Hz, J_{C-H} = 148 Hz, $P(OMe)_3$), δ 55.1 (br, C_1 or C_2), δ 65.0 (br, C_1 or C_2), δ 18.9 (q, J_{C-H} = 127 Hz, CH_2CH_3), δ 16.2 (tdd, J_{C-H} = 144 Hz, J_{Rh-C} and J_{P-C} are either 10 and 15 Hz or 15 and 10 Hz, respectively, CH_2CH_3). From line shape analysis of the ^1H NMR spectrum an approximate barrier for olefin rotation of 7 kcal/mol at −110 °C can be calculated.

(11) An analogous reaction of $Cp(PMe_3)Rh(C_2H_4)(H)^+$ with C_2H_4 has been reported by Werner,[5b,c] but no further insertions of the alkyl species were observed.

(12) The equilibrium ratio of *trans*-2-butene:*cis*-2-butene:1-butene at 25 °C is 100:30:4. When **9** is exposed to a limited amount of ethylene, butenes are isomerized after ethylene dimerization has occurred.

(13) Two very low intensity doublets (<5%) in the pentamethylcyclopentadienyl region grow in rapidly when butene production begins after which their intensity remains constant throughout the dimerization reaction. It is likely that these are butene-hydride species (**11a–c**); experiments are in progress to identify them.

(14) In calculating this relative rate difference at 25 °C we have assumed that the free energy of activation for hydride migration is temperature independent. It is likely that for both intramolecular processes $\Delta S^{\ddagger}$ values are small and $\Delta G^{\ddagger}$ values will be nearly independent of temperature.

Chiral Lithium: Conformation and Dynamic Behavior of Monomeric Neopentyllithium–*N,N,N′,N′,N″*-Pentamethyldiethylenetriamine Complex

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Received August 26, 1988

Organolithium[1] compounds exhibit an astonishing variety of structures[2-4] which undergo fast equilibrium carbon lithium[4-7] and lithium ligand bond exchange, respectively, as well as rapid conformational interconversions including inversions at C_αLi.[8] These processes are often fast enough even at very low temperature as to obviate the utility of NMR studies of RLi structure and dynamic effects. In this communication we report that neopentyllithium, **1**, monomer complexed to *N,N,N′,N′,N″*-pentamethyldiethylenetriamine, PMDTA, in diethyl ether, is a system in which the above exchange processes are slow enough at 160 K to provide unusually detailed information on its structure. Then, above 160 K NMR line shape analysis[9] enabled us to disentangle the different fast dynamic processes—internal rotation, N–Li coordination exchange, and monomer–dimer[7] interconversion.

Neopentyllithium, **1**, was prepared by cleavage of the mercury compound with ^6Li shavings in cyclopentane at 297 K over 7 days. This material was identical in all respects with material prepared by reaction of neopentyl chloride with lithium metal.[10]

In diethyl ether at all temperatures **1** consists entirely of dimers as evidenced by the $^{13}C_\alpha$ NMR multiplicity of 1:2:3:2:1 with $J(^{13}C_\alpha,^6Li)$ of 8.9 Hz and C_α shift at 34.4 δ.

A sample of **1**, 0.5 M with PMDTA, 0.30 M in diethyl ether at 166 K consists of monomeric **1** complexed to PMDTA as evidenced by $^{13}C_\alpha$ at 34.4 δ, 1:1:1, with $J(^{13}C_\alpha,^6Li)$ = 14.7 Hz[11] and a second species which exhibits the same ^{13}C NMR parameters just described for the dimeric etherate. There is no detectable free triamine in this solution up to 300 K. With PMDTA in excess of **1** free triamine is resolved from complexed triamine. The monomer–dimer ratio does not change significantly between 160 and 300 K.

Most interestingly at 146 K *all* but *two carbons* (methylenes) of complexed PMDTA are magnetically nonequivalent, see Figure 1. We can assume that the structure of **1**·PMDTA qualitatively resembles those of other RLi·PMDTA monomers studied crystallographically in the past, i.e., that Li is tridentately coordinated to PMDTA.[12] Then the NMR data at 146 K imply that our species, **1**·PMDTA, is conformationally locked about the C–Li internuclear axis, in the form of *one rotamer* within which the *tert*-butyl group is disymmetrically sited with respect to the tri-

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