a check on crystal and electronic stability three representive reflections were measured every 30 min. The intensities of these standards remained constant within experimental error throughout data collection for **1a**. Linear corrections for decay were applied as given in Table VII.

Structure Solution and Refinement. Relevent conditions are summarized in Table VII. The structures were solved by either direct or Patterson methods. The structures were refined in full-matrix least-squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, and the weight w is defined as $4F_o^2/s^2(F_o^2)$. The standard deviation on intensities $s^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$ where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, Lp is the Lorentz–polarization factor, and the parameter p (ignorance factor) is a factor introduced to downweight intense reflections. Here p was set to 0.060. Hydrogen atoms were included as fixed atoms in idealized positions.

Scattering factors were taken from Cromer and Waber.[41] Anomalous dispersion effects were included in F_c;[42] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[43] Only the reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement converged with unweighted and weighted agreement factors of according to $R_1 = \sum||F_o| - |F_c|/\sum|F_o$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. The height of the highest peak in the final difference Fourier and the estimated error based on ΔF[44] are given in the Table VII. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin (q/l), and various classes of indices showed no unusual trends for any of the compounds.

Acknowledgment. We acknowledge the technical assistance of E. J. Delawski.

Registry No. 1a, 118376-71-9; **1b**, 118376-74-2; **2a**, 118376-73-1; 3, 53382-61-9; $[Bu_4N^+]_2[C_4(CN)_6^{2-}]$, 118376-69-5; $[Bu_4N^+]_2[C_6(CN)_6^{2-}]$, 58619-43-5; $[(C_6H_3Me_3)_2Fe^{2+}][C_6(CN)_6^{2-}]$, 106865-37-6; $[(C_6Me_6)_2Fe^{2+}][C_6(CN)_6^{2-}]$, 106865-38-7; $[(C_6H_3Me_3)_2Ru^{2+}][C_6(CN)_6^{2-}]$, 106865-39-8; $[(C_6Me_6)_2Ru^{2+}][C_6(CN)_6^{2-}]$, 106865-40-1; $[(C_6Me_6)_2Fe^{2+}][PF_6^-]_2$, 53382-63-1; $[(C_6Me_6)_2Ru^{2+}][BF_4^-]_2$, 71861-31-9.

Supplementary Material Available: X-ray structural reports for **1a**, **2a**, and **3** that contain the following: descriptions of experimental procedures for **1a** and **2a** that include data collection, data reduction, and structure solution and refinement, tables of crystal data, intensity measurements, structure solution and refinement, positional and thermal parameters, general temperature factor expressions (*U*'s), bond distances, bond angles, and torsional angles, root-mean-square (rms) amplitudes of thermal vibrations tables of intermolecular N and H contacts for **1a**, **2a**, and **3**, and least-squares planes for **1a**, and drawings of two cations and a single anion with labeling schemes with 25% probability ellipsoids (64 pages); listings of structure factors for **1a**, **2a**, and **3** (30 pages). Ordering information is given on any current masthead page.

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[41] Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

[42] Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

[43] Cromer, D. J. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

[44] Cruickshank, D. W. J. *Acta Crystallogr.* **1949**, *2*, 154.

Stereoselective Vinylic C–H Activation by a Homogeneous Iridium Catalyst

J. W. Faller* and C. J. Smart

Department of Chemistry, Yale University, New Haven, Connecticut 06520

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Vinylic hydrogen–deuterium exchange between a number of terminal olefins and benzene-d_6 is readily catalyzed by $Ir(i\text{-}Pr_3P)_2H_5$. For mono- and disubstituted 1-alkenes H/D exchange is found to be stereoselective, with a preference for activation of the C–H bond trans to the larger substituent at the β-carbon. The degree of stereoselectivity is found to vary with the bulkiness of the β-carbon substituent. Regio- and stereoselectivity are also observed to be independent of the presence of an allylic proton in the substrate, thus indicating that H/D exchange is effected more readily by direct insertion of the catalyst into the vinyl C–H bond than by either reversible π-allyl complex formation or addition of metal hydride to the double bond followed by β-hydride elimination. In addition, for β,β-disubstituted terminal olefins, it is shown that deuteration of the position cis to the larger β-carbon substituent also can occur via a vinyl C–H activation process as well as indirectly via a metal hydride addition–elimination process.

Introduction

Numerous examples of H/D exchange reactions with arenes are catalyzed by transition-metal complexes in homogeneous systems.[1,2] Although observed less frequently, similar H/D exchanges have also been found between vinylic hydrogens and deuterated solvents.[3] Isomerization catalysts also allow incorporation of deuterium into olefins via metal deuteride intermediates. In all of these cases where an M–H(D) is involved in the reaction path, it is frequently assumed that olefinic H/D exchange occurs either via M–D addition to the double bond followed by β-hydride elimination or via reversible allylic proton abstraction to form an η^3-allyl complex of the metal deuteride. We have found that a third mechanism, namely, reversible insertion of a catalytic species into olefinic C–H bonds, is important in at least one group of catalysts, bis(trialkylphosphine)iridium pentahydrides. The relevance of this process may well extend to other

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[1] (a) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 483. (b) Parshall, G. W. *Catalysis* **1977**, 334. (c) Barefield, E. K.; Parshall, G. W.; Tebbe, F. N. *J. Am. Chem. Soc.* **1970**, *92*, 5234–5. (d) Jones, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1650–1663; **1985**, *107*, 620–631 and references therein. (e) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245–269 and references therein.

[2] By "catalyst" we mean the compound added to the reaction to accelerate its rate. Important intermediates in the catalytic cycle are referred to as "active" species. [Cf. Tolman, C. A.; Faller, J. W. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983, p 14.]

[3] Cramer, R. *J. Am. Chem. Soc.* **1966**, *88*, 2272; *Acc. Chem. Res.* **1968**, *1*, 186–191.

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catalytic systems. In a recent communication, we reported that H/D exchange between benzene-d_6 and 3,3-dimethyl-1-butene (neohexene) was observed to be catalyzed by the Ir(i-Pr$_3$P)$_2$H$_5$ complex.[4] For this substrate, high stereoselectivity of the exchange led to the conclusion that insertion of the metal into the trans vinyl C–H bond was the mechanism leading to the selectively deuterated product and that this process was faster than addition and elimination of M–H across the double bond. Whereas this process is analogous to that described over 20 years ago for arene C–H bond activation,[3] this was the first report of its importance in the homogeneous catalytic activation of alkene substrates.[4] The subsequent isolation of a vinyl hydride complex from the interaction of ethylene with a Cp*Ir derivative in a stoichiometric reaction[5] emphasizes the importance of insertion as a mode of interaction of an active metal species with an olefin. More recently, it has been shown that direct insertion into vinyl C–H bonds is an important feature of the alkene activation chemistry of a group of iron–phosphine complexes.[5]

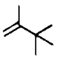
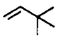
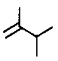
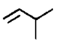
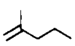
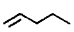
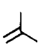
Although neohexene might be considered a special case which shows anomalous reactivity, we now wish to report results which demonstrate that H/D exchange via a process involving insertion into vinyl C–H bonds occurs commonly in a broad range of terminal olefins (including those which possess allylic hydrogens). Facile H/D exchange was observed between benzene-d_6 and most of the terminal olefin substrates studied, including 1-pentene and isobutene.

Experimental Section

General Procedures. The Ir(i-Pr$_3$P)$_2$H$_5$ complex is relatively air-stable in the solid state but rapidly decomposes when its solutions are exposed to air. Thus all handling of solutions containing the catalyst was done by using standard inert atmosphere techniques. In the cases where the progress of the catalytic reactions was followed by NMR, the NMR tubes were sealed under dry nitrogen to provide an inert atmosphere during the course of the reaction. The solvent for all of the reactions was benzene-d_6, which was used as purchased without further purification. Olefins, with the exception of the gaseous substrate isobutene, were freed of peroxide impurities by passage through a short alumina column but were otherwise used as received. The catalyst[6] was prepared by previously established methods.[7] It was found, however, that losses in purification could be avoided by performing recrystallizations at low temperature (−78 °C) from diethyl ether and methanol.

We investigated several analytical methods for the purpose of monitoring the H/D exchange reactions. Among these were ^{13}C NMR, GC–mass spectrometry, ^{1}H NMR, and ^{2}H NMR. Deuterium isotope shifts of the deuterated carbons were observed in the ^{13}C NMR spectra, and without the ability to obtain deuterium-decoupled ^{13}C spectra, this condition allowed unfavorable overlapping of signals of the nondeuterated, monodeuterated, and dideuterated species. While this prevented reliable measurement of the stereoselectivity of the exchange, it was possible to measure regioselectivities from the ^{13}C NMR spectra.

Table I. Stereoselectivity[a] and Regioselectivity[b] Ratios Derived from Integration of Deuterium NMR Spectra of a Range of Olefins

	10% reaction[c]		30% reaction[c]	
substrate	stereo-selectivity	regio-selectivity	stereo-selectivity	regio-selectivity
	100% trans	vinyl only	100% trans	vinyl only
	6:1	8.1:1	4:1	8.3:1
	1.7:1	8:1	1.5:1	9:1
	3:1	3:1	1.6:1	2.1:1
	1.6:1	5:1	1.5:1	3.7:1
	1.5:1	*e*	1.4:1	*e*
		5:1		3:1

[a] Stereoselectivity is reported as trans:cis deuteration of the terminus. [b] Regioselectivity is reported as terminal: internal deuteration in the monosubstituted 1-alkenes and as vinyl:methyl deuteration in the 2-methyl-2-alkyl-1-alkenes. For example, with neohexene as the substrate, ^{2}H NMR integral areas for the trans, cis, and internal vinyl positions (at 10% reaction) were 42, 7, and 6, respectively. [c] The 10% and 30% reactions are defined as the points when 10% and 30% of the combined terminal vinyl sites (cis and trans) are deuterium-substituted. [d] Tabulated results for 2,3,3-trimethyl-1-butene are for experiments where 1 mol equiv of neohexene was added to initiate the catalysis. [e] Due to partial isomerization to *cis*- and *trans*-2-pentene and unfavorable overlap of ^{2}H NMR peaks, the regioselectivity could not be reliably measured.

Mass spectrometry was similarly limited; although accurate measurements of the relative amounts of mono-, di-, and trideuterated olefins in a given reaction mixture were obtained, this information revealed nothing concerning the stereo- or regioselectivity of the H/D exchange.

With few exceptions, both stereo- and regioselectivities could be obtained from the ^{1}H and ^{2}H NMR spectra of all of the substrates studied. The combination of these two complementary techniques was thus held to be the method of choice for monitoring the H/D exchange reactions.

NMR and Mass Spectra. Proton NMR spectra were recorded on Bruker WM250 and WM500 spectrometers, operating at 250 and 500 MHz, respectively, as well as at 90 MHz on a JEOL FX90Q. Deuterium and carbon NMR spectra were recorded on the WM500 spectrometer at 76.8 and 125.7 MHz, respectively. Chemical shifts are reported as parts per million downfield from TMS, using the solvent as the reference. GC–mass spectrometric analyses were performed by using a Kratos MS-80RFA at 20 eV.

The data presented in Table I were obtained by taking deuterium NMR spectra at regular intervals and comparing the integral areas of the deuterio substrate resonances to the area of the deuteriocyclohexane (internal standard) peak in order to obtain concentration values. Alternatively, the proton spectra could be monitored, and relative deuterio to protio substrate ratios could be obtained by measuring the relative areas of the parent and deuterium isotope shifted peaks. The isotope shift was observed to be ca. 0.02 ppm upon geminal deuterium substitution.

Olefin H/D Exchange Reactions. An NMR tube was purged of air with a stream of nitrogen and charged with 15 mg (0.03 mmol) of the Ir(i-Pr$_3$P)$_2$H$_5$ complex. In a separate vial 0.4 mL of benzene-d_6, 0.9 mmol (ca. 0.1 mL) of olefin substrate, and 0.015 mL of cyclohexane-d_{12} were mixed and added to the NMR tube which was then fitted with a septum stopper. Dry nitrogen was

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[4] Faller, J. W.; Felkin, H. *Organometallics* **1985**, *4*, 1488.

[5] (a) (Cp*Ir complex) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581. (b) (CpRe(PMe$_3$)$_2$ complex) Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4856. (c) (Fe complexes) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7434, 7436. (d) (Cp*Sc complexes) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203–219. (e) Suzuki, H.; Omori, H.; Moro-Oka, Y. *Organometallics* **1988**, *7*, 2579–2581. (f) A number of metal insertions into vinyl C–H bonds had been observed previously with bimetallic systems and metal clusters or with olefins containing donor atoms (see references quoted previously[4]). Additionally, a recent report [Burk, M. J.; McGrath, M. P.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 620] has shown vinyl H/D exchange wherein a mechanism of α-hydride elimination–addition has been suggested. This process requires equal deuterium incorporations of cis and trans sites and does not appear to be a significant factor for the reactions with the Ir(i-Pr$_3$P)$_2$H$_5$ described here.

[6] Although the results of this paper were obtained from reactions involving Ir(i-Pr$_3$P)$_2$H$_5$ as the catalyst precursor, stereoselective H/D exchange was also observed when Ir(Et$_3$P)$_2$H$_5$ was used. In the latter case, however, the exchange rate at room temperature was much slower than with the i-Pr$_3$P analogue, fewer catalytic turnovers were obtained, and the selectivity was lower.

[7] Clerici, M. G.; DiGioacchino, S.; Maspero, F.; Perrotti, E.; Zanobi, A. *J. Organomet. Chem.* **1975**, *84*, 379.

bubbled through the solution via a syringe needle to rid the sample of dissolved oxygen as well as to provide an inert atmosphere within the tube. The sample was then frozen in liquid nitrogen and the tube sealed with a torch.

After thawing, the catalytic solution was colorless during an induction period of between 5 and 20 min depending upon the substrate. The solution then developed a yellow to orange color with simultaneous observation (by NMR) of significant vinylic H/D exchange. By the time the observable exchange reaction had slowed to a negligible rate (usually several hours), the color had darkened to a deep red-orange.

The rate of the reaction and the product distribution were unaffected by the presence or absence of ambient light, indicating that the H/D catalyst initiation and H/D exchange reactions do not depend on a photochemical process. The results shown in Table I were obtained in the absence of light; i.e., the samples were not removed from the capped NMR probe for the duration of the experiment.

Sample Preparation for GC–Mass Spectrometric Analysis. For the case of neohexene, deuterium incorporation was also monitored by GC–MS. GC–MS samples were prepared by stirring 31 mg (0.06 mmol) of $Ir(i\text{-}Pr_3P)_2H_5$ with 0.25 mL (2.0 mmol) of neohexene in 2.0 mL of benzene-d_6. The product mixture was monitored for deuterium incorporation by NMR until ca. 25% of the total available vinyl protons had been exchanged. The reaction was then terminated by exposure to air, and the volatile components (solvent and products) were vacuum transferred to a separate flask.

Effect of Added Phosphine on H/D Exchange. To a vial containing 0.8 mL of benzene-d_6, 0.2 mL (1.55 mmol) of neohexene, and 0.03 mL of cyclohexane-d_{12} (internal integration reference) was added 0.030 g (0.058 mmol) of $Ir(i\text{-}Pr_3P)_2H_5$. This solution was divided into two equal volumes, and to one was added 0.08 mL (0.51 mmol) of neat $i\text{-}Pr_3P$ immediately. Both samples were then sealed and monitored for H/D exchange by ^1H and ^2H NMR. H/D exchange in the control tube (without added phosphine) was observed 20 min after the sample had been prepared; H/D exchange in the other sample was not observed after 2 days.

Competition Studies. In an effort to ascertain the origin of the observed stereoselectivity of the vinylic H/D exchange, the relative rates of reaction of several of the substrates were studied. **Neohexene versus 2,3,3-trimethyl-1-butene**: 0.05 mL of neohexene (0.39 mmol) and 0.05 mL of 2,3,3-trimethyl-1-butene (0.36 mmol) were mixed with 0.01 mL of cyclohexane-d_{12} and 0.4 mL of benzene-d_6 and added to an NMR tube containing 13 mg (0.025 mmol) of $Ir(i\text{-}Pr_3P)_2H_5$. Dry nitrogen was passed through the solution for 1 min, and the tube was sealed. **Neohexene versus isobutylene**: 0.025 mL (0.20 mmol) of neohexene and 0.01 mL of cyclohexane-d_{12} were added to 0.5 mL of a saturated solution of isobutylene in benzene-d_6. This solution was then added to an NMR tube containing 15 mg (0.029 mmol) of $Ir(i\text{-}Pr_3P)_2H_5$. Dry nitrogen was passed through this solution for several seconds, and the tube was sealed. Both competition reactions were monitored by ^2H NMR.

Test for Homogeneity. The vinyl H/D exchange process in the presence of $Ir(i\text{-}Pr_3P)_2H_5$ appeared to be homogeneous, with no sign of deposition of solid during the reaction, even after several days. In addition, neither the rate nor the selectivity of the exchange was affected by the presence of elemental mercury, indicating that a colloidal iridium species was not present.[8]

Results and Discussion

Although homogeneous catalytic C–H bond activation of alkanes[2] and arenes[1,3] and the involvement of metal hydrides in the process are now well-known, the most commonly studied processes involving metal hydrides and carbon–carbon double bonds have been catalytic hydrogenation[9,10] and double-bond isomerization.[10] For these two processes, the mechanisms most often implicated have been: (a) η^2-coordination of the olefin to the metal center followed by reversible allylic H transfer to form an η^3-allyl complex and (b) M–H addition across the double bond followed by β-hydride elimination to generate either starting material or isomerized product.[10,11] In cases where H/D exchange between deuterio solvents and substrate was observed,[10,11] the deuterated byproducts were attributed to these same two processes, involving a deuterated catalyst, which in turn would have been generated by catalytic activation of the C–D bonds of the deuterated solvent.

Catalyst Initiation and the Catalytic Cycle. Isotopic exchange with solvent and with ligands has been observed for a number of metal complexes[12] and in our case provides a path for generating a continuing supply of M–D in a catalytically active species. In order to provide an open ligand site for substrate coordination, the first step in the initiation sequence of the 18-electron $Ir(i\text{-}Pr_3P)_2H_5$ species is presumably a dissociative process. An attractive possibility for the first step is reversible dissociation of a phosphine ligand. Consistent with this as the first step was the observation that the catalytic H/D exchange was inhibited when the reaction was carried out in the presence of free phosphine. Furthermore, formation of some mixed-phosphine complex $Ir(i\text{-}Pr_3)(PEt_3)H_5$ but no tris(phosphine) complex was observed in the presence of PEt_3.

In all of the H/D exchange reactions studied, a short induction period was noted, during which a small amount of olefin substrate was reduced to alkane. Vinyl H/D exchange was *not* observed *prior* to this alkane formation. This suggests that the second step in the initiation sequence is coordination of olefin substrate followed by eventual reduction to the analogous alkane by a net addition of two hydride ligands to the double bond. At this point the iridium trihydride species may recoordinate the free phosphine to generate a 16-electron bis(phosphine) compound; alternatively, the 14-electron species could be responsible for the next step in the catalytic cycle. See Scheme I for one plausible pathway.

Either of these ligand-deficient compounds could participate in the remainder of the catalyst initiation, namely, reversible insertion into the C–D bonds of the solvent to produce Ar–H and metal deuteride. It is this deuterated catalytic intermediate that is ultimately responsible for deuteration of the substrate by reversible insertion into vinyl C–H bonds (vide infra). Interestingly, the hydride resonance (δ −10.9 (t)) of *the* $Ir(i\text{-}Pr_3)_2H_5$ *species was present* (albeit in ever decreasing concentrations) *at all times during the catalysis*.[13] There was a slow disappearance of this precursor and conversion to the active catalyst with time, even in the presence of excess (here, ca. 30-fold) olefin. In the ^2H NMR spectrum, no metal deuteride analogue of the pentahydride bisphosphine nor of any other metal deuteride was observed during the reaction. Thus, $Ir(i\text{-}Pr_3P)_2H_5$ acts as a reservoir for producing small amounts of a very active species over a fairly long period and throughout the reaction time.[14] This

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[8] Tests for homogeneity of catalytic reactions have been discussed by: Crabtree, R. H.; Anton, D. R. *Organometallics* **1983**, *2*, 855–859.

[9] (a) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711. (b) Crabtree, R. H.; et al. *J. Am. Chem. Soc.* **1982**, *104*, 6994.

[10] Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134.

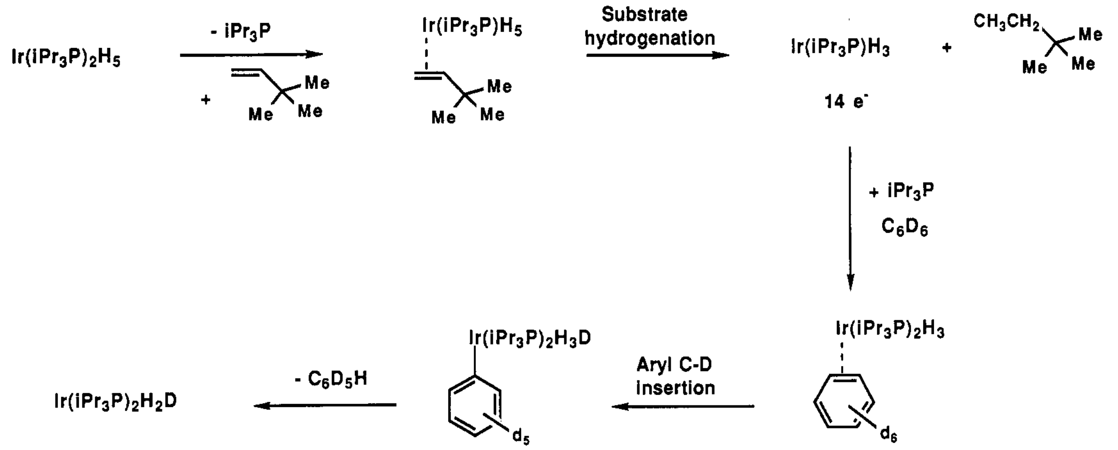
[11] Masters, C. *Homogeneous Transition-Metal Catalysis, A Gentle Art*, Chapman and Hall, London, 1981, especially pp 73–81 and pp 243–247.

[12] (a) Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* **1969**, 1963–1972. (b) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240–2. (c) Morris, R. H.; Shiralian, M. *J. Organomet. Chem.* **1984**, *260*, C47–C51.

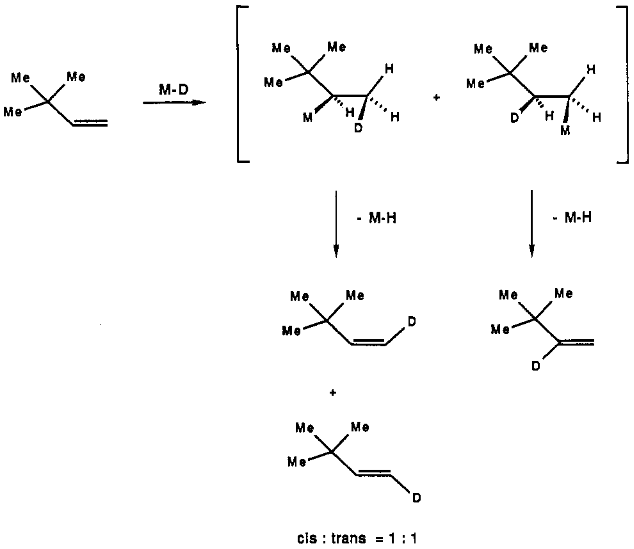
[13] After several hours, H/D exchange was no longer observable; however, this was found to be due to inavailability of *undeuterated* vinyl positions rather than to inactivity of the remaining catalyst. Upon addition of a second charge of undeuterated substrate, the H/D exchange reaction resumed with the same selectivity observed initially.

[14] Jones, W. D.; Fan, M. *Organometallics* **1986**, *5*, 1057.

Scheme I



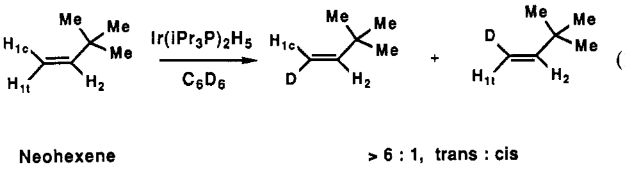
Scheme II



conflicts with the perception that all of the pentahydride is converted rapidly into an active species at an early phase of the reaction.

Trans Selectivity in the Deuteration of 1-Alkenes. Earlier work has shown[4] that vinyl H-D exchange occurs rapidly in some terminal olefins in the presence of Ir(i-$Pr_3P)_2H_5$ in a deuterated aromatic solvent. The remarkable stereoselectivity of the exchange indicates that the M-H addition-β-hydride elimination reactions are *not* a major factor in the H-D exchange process. For example, with the neohexene substrate, one would predict a 1:1 cis versus trans deuteration of the terminus, according to Scheme II.

The NMR spectra in Figure 1, however, illustrate that the H/D exchange products obtained with neohexene show a marked preference for terminal versus internal deuteration (~8:1) and that among the deuterium that appears in the terminus, there is a preference (~6:1) in favor of deuteration of the position trans to the *tert*-butyl group.[15] Neither of these results is consistent with the predictions based on Scheme II. In particular, one would have expected the intermediate formed by anti-Markovnikov addition of M-D to the double bond to be favored, which should result in more facile exchange of the *internal* vinyl proton. Furthermore, β-hydride elimination from the Markovnikov-addition intermediate would be expected to yield equal amounts of cis and trans deuterium substitution at the terminus. Consequently, it was postulated that reversible insertion of the metal into the vinyl C-H bond was facile and was at least 6 times faster[16] than the addition-elimination process[17] (see eq 1).



(1)

Consideration of the data summarized in Table I indicates a clear preference for exchange of the vinyl proton trans to the larger substituent. This implies that *the vinyl insertion phenomenon* discussed above for the Ir(i-$Pr_3P)_2H_5$-catalyzed exchange in neohexene *is not restricted to olefins substituted with bulky alkyl groups.* Although the degree of stereoselectivity appears to be governed in large part by the steric bulk of alkyl substituents at the β-carbon of the terminal alkene substrates, stereoselective H/D exchange was observed for even the relatively less hindered cases, such as 1-pentene and 3-methyl-1-butene, which show the usual preference for exchanging the proton trans to the alkyl group.

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[15] The portion of the spectrum of neohexene in Figure 1 is readily assigned to the following: the inner proton, H_2 (δ 5.88 ($J_{2\text{-}1c}$ = 16.8, $J_{2\text{-}1t}$ = 9.7 Hz)); the trans terminal proton, H_{1t} (δ 4.94 (J = 9.7 Hz)); and the cis terminal proton, H_{1c} (δ 5.00 (J = 16.8 Hz)). The exchange principally of H_{1t} is indicated by the decrease in the intensity of the resonance and the change in the coupling pattern to a doublet of triplets ($J_{2\text{-}1c}$ = 16.8, $J_{2\text{-}1t}$ = 1.6 Hz) owing to the reduction of the cis vinyl coupling upon deuterium substitution. H_{1c} shows a small upfield intrinsic isotope shift of 0.02 ppm upon substitution by D_{1t}.

[16] The trans:cis selectivity for the deuteration of neohexene was originally reported[4] to be nearly 91% using ^{1}H NMR. With subsequent availability of higher field NMR spectrometers and the use of the (more reliable) integral values from deuterium NMR spectra, the value was found to be slightly greater than 86% (~6:1). Deuteration of H_{1c} is underestimated in ^{1}H NMR since this product is rapidly converted to D_2C=CH-t-Bu and D_2C=CD-t-Bu by trans vinyl activation and addition-elimination reactions (see Scheme V).

[17] Only processes which replace H by D can be observed; hence, insertion into terminal vinylic C-H or addition-elimination actually occur at a rate which is faster than the observed H/D exchange rate and which depends upon the statistics and the magnitude of kinetic isotope effects. The key feature is that significant deuteration at C-2 is not observed to a significant extent early in the reaction. This process does, however, provide a route for equilibrating cis and trans terminal vinyl positions. Thus, cis addition of Ir-D to *trans*-CHD=CH-t-Bu via Scheme II would yield *erythro*-MCHDCHD-t-Bu. Upon elimination this product would either revert to *trans*-CHD=CH-t-Bu or yield *trans*-CHD=CD-t-Bu,[18] which in turn would undergo rapid exchange to yield CD_2=CD-t-Bu. Note that in *trans*-CHD=CH-t-Bu, deuterium at the terminus is trans to the t-Bu group; in *trans*-CHD=CD-t-Bu, the terminal hydrogen is trans to the t-Bu group.

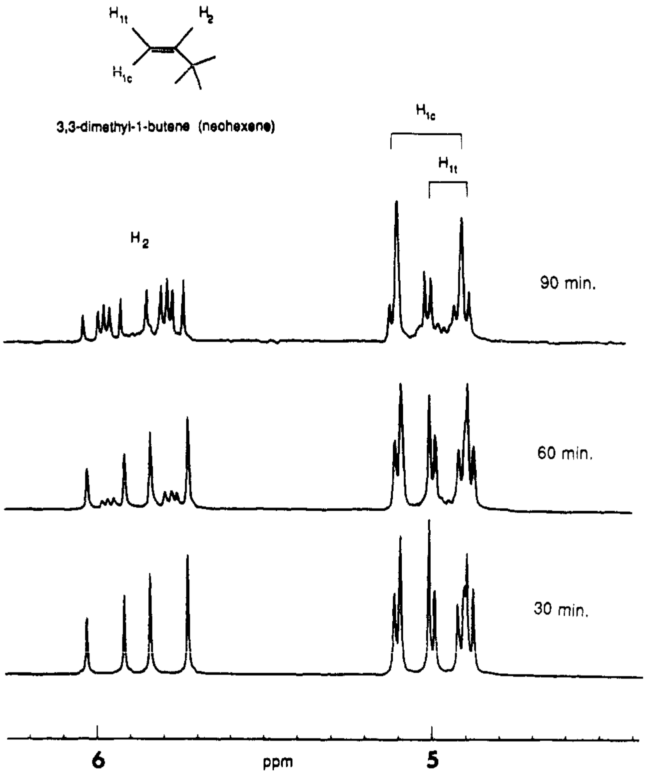


Figure 1. The 90-MHz ^{1}H NMR of neohexene in benzene-d_6 at 30 °C in the presence of 3 mol % Ir(i-Pr$_3$P)$_2$H$_5$. The spectra were taken after 30, 60, and 90 min after the temperature was raised from −78 °C.

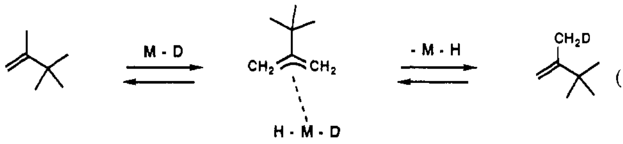
Cis Deuteration by the Vinyl Insertion Process. On the basis of the neohexene results, it was assumed initially that the insertion mechanism was primarily responsible for the H/D exchange only at the trans position of the olefin. Deuteration of the cis and (where applicable) internal positions was presumed to arise from participation of some slower and less selective mechanism or isomerization.[17] However, when the relative deuterium ratios were determined with greater accuracy by using ^{2}H NMR, it was clear that in some cases deuterium incorporation into the cis position of the alkene terminus must also result partially from direct vinylic C–H activation by the process of insertion of the metal into the C–H bond.

This is illustrated by the case of 2,3-dimethyl-1-butene where the extent of deuterium exchange with the proton cis to the isopropyl group exceeded the deuterium incorporation into the methyl group of the β-carbon during the entire course of the reaction. As depicted in Scheme III, the cis deuterated product may be formed by the Markovnikov addition of M–H to the double bond and subsequent β-hydride elimination. However, if the source of the β-hydrogen is one of the methyl groups, one would expect equal amounts of methyl-deuterated product **2** and vinyl-deuterated products *trans*-**1** and *cis*-**1**. This is tantamount to the prediction that methyl deuteration by the addition–elimination mechanism would not be slower but rather twice as fast as deuterium exchange with the cis vinyl proton. Further evidence indicating that this pathway is not important in the overall deuteration reaction is the fact that hydrogen elimination from the isopropyl group, yielding the tetrasubstituted olefin **3** is not observed at all.

A second route to *cis*-deuterio-2,3-dimethyl-1-butene proceeds via the π-allyl intermediates shown in Scheme IV. However, cis deuterium incorporation by this process depends on the reactivation of the methyl-deuterated products **5** and **6**; hence it, too, fails in providing an adequate explanation for the observation of more cis vinyl deuteration than methyl group deuteration. Additionally, the other expected deuterated byproduct of the reaction sequence, **4**, is not observed.

The likely alternative explanation is that in the 2,3-dimethyl-1-butene molecule, while approach of the catalyst to the substrate terminus is certainly biased toward the side trans to the isopropyl group, approach from the cis side is occasionally successful, resulting in the insertion of the metal into the cis vinyl C–H bond. The same argument and conclusion may be applied to (at least) the other disubstituted olefins studied, namely, 2,3,3-trimethyl-1-butene and 2-methyl-1-pentene. These are also observed to incorporate deuterium more rapidly into the cis vinyl position than into the methyl substituent at the β-carbon.

Vinyl Activation versus η^3-Allyl Isomerization. In several of the experiments listed in Table I, stereo- and regioselective results are reported for olefins that contain allylic hydrogen atoms. *These results are especially significant in that they indicate that the vinyl insertion process is not only more rapid than the addition–elimination process but also faster than the reversible η^3-allyl complex formation.* For example, in the case of 2,3,3-trimethyl-1-butene, the regioselectivity observed in the H/D exchange was 100% vinyl (versus methyl). H/D exchange via the reversible η^3-allyl complex process would have predicted the opposite result, namely, initial predominance of the deuterated methyl species, as shown in eq 2.



(2)

Deuteration at Internal Positions. Returning our attention to the deuteration of neohexene, we note that the regioselectivity of the exchange is 8:1, favoring deuteration of the terminus over the β-carbon; it is worthwhile to investigate the origin of this internal deuterium incorporation. When the rates of deuteration of the cis position and the internal position are compared, it is found that they differ only slightly. The rate of cis deuteration is faster, leading to a 1.2:1 ratio of cis:internal deuterium levels when the reaction is 10% complete. Internal deuteration can be attributed to an addition–elimination process. This reaction also provides a path for incorporation of deuterium into the cis terminal position when it occurs with the *trans*-deuterioneohexene (see Scheme V). Late in the reaction, when most of the neohexene has been deuterated in the trans position via the trans vinyl insertion mechanism, the addition–elimination shown in Scheme V would lead to the prediction of equal rates of deuteration of the internal and cis sites. However, early in the reaction, before the trans position is extensively deuterated, the process depicted in Scheme V would lead to an cis:internal deuteration ratio of less than 1.0:1, the opposite of what is observed. Accordingly, cis vinyl insertion (see above) is implicated as a second mode of cis deuterium incorporation, thus accounting for the 1.2:1 cis:internal deuterium ratio.[19] Hence the observed 6:1

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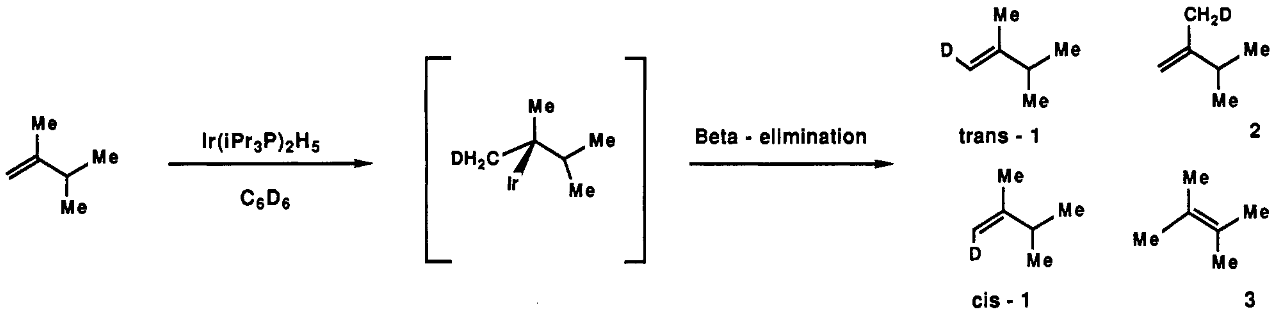
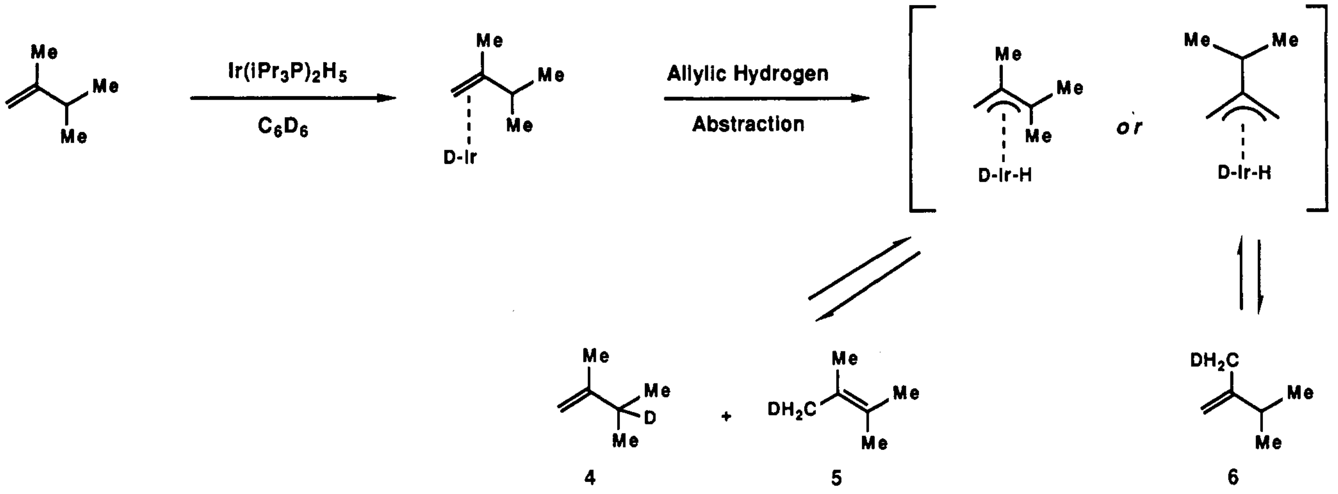
(18) Cis addition of the metal hydride is expected and β-hydride elimination requires coplanarity of the metal and the hydride [cf. McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521].

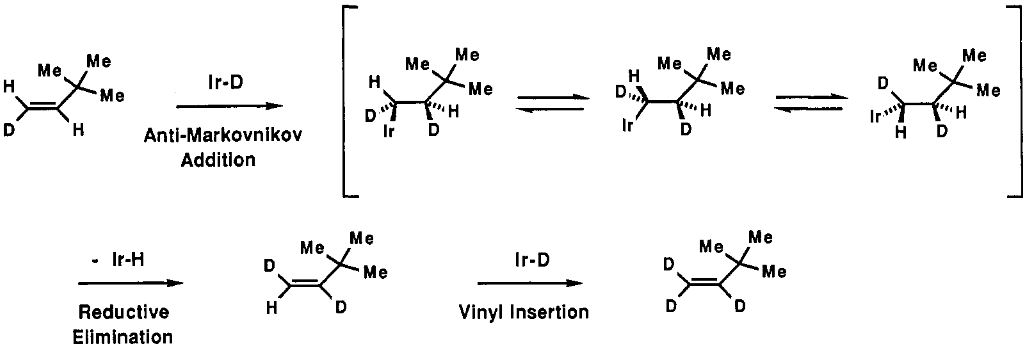
Scheme III



Scheme IV



Scheme V



stereoselectivity of exchange at the terminus is not indicative of the probability of trans versus cis vinyl insertion; it reflects only the total stereoselectivity of all reactions leading to H/D exchange. The actual preference for direct vinyl activation of trans C–H versus cis C–H is much higher than 6:1.

We are now in a position to understand the high stereoselectivity of the 2,3,3-trimethyl-1-butene substrate. On the basis of the hypothesis that it is the *difference* in steric bulk between the two substituents of the β-carbon which gives rise to the stereoselectivity of the H/D exchange at the terminus, it would seem that the trans versus cis selectivity should be higher for neohexene than for 2,3,3-trimethyl-1-butene. However, participation of the latter substrate in the anti-Markovnikov M–D addition process analogous to eq 5 is unobservable, since β-elimination in the next step necessarily regenerates the starting material without scrambling the deuterium already incorporated in the terminus. Thus, the only method of deuteration of the cis terminal position in 2,3,3-trimethyl-1-butene is by the vinyl insertion process, in which activation of the trans position is highly favored (see above).

Steric Limitations on the Olefin in Autoinitiation of Catalysis. Measured by the degree of stereoselectivity, the most successful exchange reactions studied were those employing 2,3,3-trimethyl-1-butene as the substrate. For this substrate, deuteration of the cis position was observable only after deuteration of the trans position reached >90% completion. However, in the absence of 1 mol equiv (based on catalyst molarity) of neohexene, the H/D exchange was extremely slow (induction period >8 h) and proceeded with neither stereo- nor regioselectivity. Figure 2 compares the NMR spectra of this reaction with and without added neohexene after 60 min.

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[19] This implies that late in the reaction the product mixture should contain more CD_2=CH-*t*-Bu than CHD=CD-*t*-Bu and CD_2=CD-*t*-Bu (i.e. internally deuterated products) combined. This prediction is supported by integration of the ^1H-coupled ^{13}C spectrum. Equivalent relaxation rates of the two-carbon nuclei in question was achieved by use 0.1 M $Cr(acac)_3$ as a relaxation reagent.

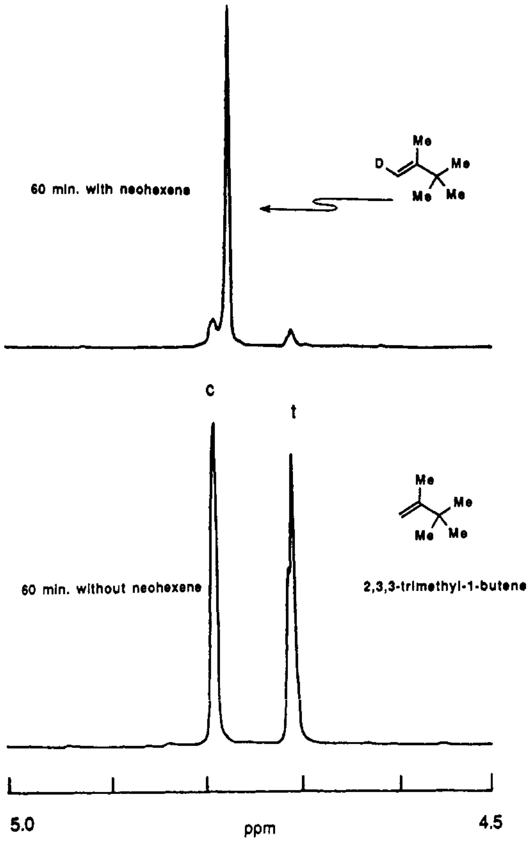

Figure 2. The effect of added neohexene on H/D exchange in 2,3,3-trimethyl-1-butene. These 500-MHz ^{1}H NMR spectra are shown after 60-min reaction time with (upper) and without (lower) neohexene. The lower spectrum is that of 2,3,3-trimethyl-1-butene, indicating essentially no H/D exchange. In the upper spectrum, the original undeuterated substrate peaks are greatly diminished and the isotope shifted peak due to the cis proton of the trans deuterio product has appeared.

During the long induction period, no reduced substrate was observed. When the catalysis was performed in the presence of neohexene, within minutes reduction of the neohexene to 2,2-dimethylbutane was observed with concomitant, rapid exchange of the trans proton of 2,3,3-trimethyl-1-butene. These observations, along with the fact that with all of the less bulky substrates, a small amount of olefin reduction was noted during the induction period, suggest that while 2,3,3-trimethyl-1-butene is an excellent substrate for the H/D exchange reaction with the (electron-deficient) active catalytic species, it is too bulky to interact with the $Ir(i\text{-}Pr_3P)_mH_n$ moiety to produce alkane and the active form of the catalyst (see Scheme I).

Competition Studies. Several competitive H/D exchange reactions were performed for the purpose of probing the substrate properties that have the strongest governing influence on the stereoselective vinylic H/D bond activation. From consideration of the steric environment during the insertion, it seems reasonable to assume that the size of the substituent cis to the C–H bond being activated will be an important factor. To test this hypothesis, competition reactions were designed such that H/D exchange of β-methyl terminal olefins could be directly compared to that of neohexene.

In the competition study with 2,3,3-trimethyl-1-butene versus neohexene, vinylic H/D exchange of the trans terminal position in the latter was observed to be 3.2 times greater than that for the β-methyl-substituted compound. The rate of exchange of the trans terminal position of neohexene was also observed to be 3.1 times faster than exchange of the vinyl positions in isobutylene. The agreement of these results gives us confidence that the ability of the catalyst to activate vinyl C–H bonds is indeed a function of the size of the substituent cis to the position being activated. Additionally, the fact that the rates of trans vinyl H/D exchange of isobutylene and 2,3,3-trimethyl-1-butene are essentially the same suggests that π-complexation of the olefin does not necessarily precede vinyl C–H bond activation. If prior π-complex formation were involved in the rate-determining reaction sequence, one would expect to see a difference in the reaction rates of isobutylene and 2,3,3-trimethyl-1-butene, on the basis of the overall steric bulk at the β-carbon (namely, two methyl groups in the case of isobutylene versus a methyl and a *tert*-butyl group in the case of 2,3,3-trimethyl-1-butene).

Mass Spectrometric Analyses. In order to confirm the conclusions made about the extent of deuteration, mass spectrometric analyses of the product mixture of the H/D exchange reaction with neohexene were undertaken. Early in the exchange reaction (when ca. 25% of the total available trans positions had been exchanged), the relative ratios (corrected for ^{13}C) of the m, m + 1, m + 2, and m + 3 peaks were 100, 57, 12, and 0, respectively. Thus, of the total amount of substrate present, 59% had not undergone H/D exchange at all, 34% had been deuterated once, and 7% had been dideuterated. Essentially no trideuterated material was observed at this stage of the reaction. Although this data reflects neither the stereo- nor regioselectivity of the deuterium incorporation, it supports the deuterium incorporation levels which can be predicted on the basis of the data in Table I.

Specifically, the 10% reaction data in Table I reflect the relative rates of deuterium incorporation into the trans, cis, and internal positions of neohexene of 7.0, 1.1, and 1.0, respectively. Since the rate of trans H/D exchange is much faster, the predominant reaction is trans deuterium substitution. Making the approximation that the reaction only occurs with undeuterated neohexene substrate early in the reaction, one expects that when trans deuteration reaches 25%, deuterium levels in the cis and internal positions should be 4% and 3%, respectively. However, as deuteration of the trans position approaches 25% completion, there are more (~7%) substrate molecules which have been already deuterated in the cis or internal positions, and trans H/D exchange of these (to form dideuterated products) becomes more likely. Furthermore, when the trans position is 25% exchanged, one in four of the substrate molecules activated for trans exchange results in an unproductive exchange of trans deuterium for another deuterium, which effectively slows the production of *trans*-t-BuC_2H_2D and allows more dideuteration via the cis or internal activation paths. Thus, observation of only a 1:5 ratio of dideuterated to monodeuterated product after 41% of the neohexene has incorporated at least one deuterium is consistent with our primary premise that H/D exchanges are sequential and direct paths from t-BuC_2H_3 to t-BuC_2HD_2 are not important.

Conclusions

It has been shown that direct insertion into vinyl C–H bonds is a facile process for the iridium bis(phosphine) pentahydride catalysts. Via this process stereoselective H–D exchange of terminal olefins is observed. The process favors activation of the trans C–H bond, and the selectivity is partially dependent on the bulk of the β-carbon substituent. Our results indicate that the bulk of the substituent cis to the position being activated has a dominant effect on the rate of exchange of that position and hence on the overall selectivity.

Although the best stereoselectivities were observed for those substrates with very bulky β-carbon substituents, it is significant that the vinyl insertion process is still several times faster than M-H addition-β-hydride elimination even for those substrates with relatively small β-carbon substituents. Additionally, vinyl insertion is the primary mode of reaction regardless of the presence of allylic protons.

Normally, a small fraction of the substrate was consumed during the autoinitiation sequence for generation of the vinyl insertion catalyst. However, in the case of the bulkiest of the substrates studied it was shown that addition of a small amount of a smaller olefin was necessary to generate the vinyl insertion catalyst.

We anticipate that this process, analogous to the well-known aryl C-H bond insertion reaction, will continue to be an important consideration in future discussions of transition-metal-catalyzed activation of C-H bonds in olefins.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. $Ir(i\text{-}Pr_3P)_2H_5$, 53470-70-5; $Ir(Et_3P)_2H_5$, 32490-60-1; C_6H_6, 71-43-2; $H_2C{=}C(Me)CMe_3$, 594-56-9; $H_2C{=}CHCMe_3$, 558-37-2; $H_2C{=}C(Me)CHMe_2$, 563-78-0; $H_2C{=}CHCHMe_2$, 563-45-1; $H_2C{=}CMe(CH_2)_2Me$, 763-29-1; $H_2C{=}CH(CH_2)_2Me$, 109-67-1; $H_2C{=}CMe_2$, 115-11-7.

A Mononuclear Oxosulfidomolybdenum(VI) Complex and Other Oxo, Sulfido, and η^2-S_2O Derivatives of (Pentamethylcyclopentadienyl)molybdenum and -tungsten

J. W. Faller* and Yinong Ma

Department of Chemistry, Yale University, New Haven, Connecticut 06520

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The reactions between hydrogen sulfide and $Cp^*W({=}O)_2R$ ($Cp^* = \eta^5\text{-}C_5Me_5$, R = methyl (Me) or Me_3SiCH_2) gave $Cp^*W({=}O)({=}S)R$ (**1a**, R = Me; **1b**, R = Me_3SiCH_2). Similarly, $Cp^*Mo({=}O)_2(CH_2SiMe_3)$ gave $Cp^*Mo({=}O)({=}S)(CH_2SiMe_3)$ (**2**). However, on reaction with H_2S, $Cp^*Mo({=}O)_2Me$ gave an air-sensitive red compound, characterized as the disulfide $Cp^*Mo({=}O)(\eta^2\text{-}S_2)Me$, which is readily oxidized to form a stable compound, $Cp^*Mo({=}O)(\eta^2\text{-}S_2O)Me$ (**3**). The crystal structure of $Cp^*Mo({=}O)(\eta^2\text{-}S_2O)Me$ is reported in detail. The compound crystallizes in the orthorhombic space group *Pbca* (No. 61) with $Z = 8$, $a = 25.134$ (9), $b = 10.000$ (6), and $c = 11.009$ (7) Å, and $V = 2767$ Å^3. Anisotropic refinement of all non-hydrogen atoms and inclusion of hydrogen atoms at calculated positions converged to the residuals $R_1 = 0.038$ and $R_2 = 0.045$.

Introduction

Mononuclear Mo and W complexes containing both oxo and sulfido ligands are extremely rare,[1] owing in part to the propensity of the M=S linkage to dimerize via μ-sulfido bridges and form polynuclear complexes of molybdenum and tungsten.[2] The widespread interest in simple oxosulfidomolybdenum complexes and their tungsten counterparts arises in large measure from their potential use as models for biological systems (for example, the molybdenum sites of xanthine reductase, xanthine oxidase, aldehyde oxidase).[3] The structure and reactivity of this type of model system may provide more insight into both the biological environment and activity of pertinent molybdoenzymatic systems such as xanthine oxidase. This prompted us to investigate the syntheses and reactivities of mononuclear oxosulfidomolybdenum and -tungsten complexes. Both theoretical[4] and experimental studies have shown that the transformation of dioxometal species to monoxometal species is a thermodynamically favorable process.[5,6] Taking advantage of the remarkable stability of the M-C bond in dioxometal system $(\eta^5\text{-}C_5Me_5)M({=}O)_2R$ (M = Mo and W), our approach to the syntheses of oxosulfido complexes has centered about the replacement of one of the oxo ligands with a sulfido ligand by exchange with H_2S.

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