Table I summarizes several of the 7-oxanorbornene derivatives successfully polymerized.[12] The choice of catalyst employed is critical. Highly Lewis acidic transition-metal compounds such as WCl_6 or $WOCl_4$ preferentially coordinate to and cationically open the 1,4-bridging epoxide moiety.[13] Tungsten alkylidene catalysts IX and X are also more selective toward olefin metathesis but are still subject to deactivating side reactions. These side reactions are more pronounced by using catalyst IX, as evidenced by the production of only low molecular weight oligomers (Table II). The successful polymerization of monomers containing reactive pendant functionalities (such as alcohols or carbonyl groups) is best achieved by the use of catalysts based on group VIII metals such as ruthenium and osmium.[14] Choice of the appropriate catalyst can potentially offer significant synthetic control over polymer characteristics such as the cis/trans ratios of the metathesized double bonds and the ring diad tacticity[15] (Table II).

Structural characterization of the isomeric constitution of these highly soluble poly(7-oxanorbornene) polymers can be accomplished by use of ^{1}H and ^{13}C NMR data. The cis/trans double bond ratio in these unsaturated polymers can be determined directly from the ^{1}H and ^{13}C NMR spectra[16] (Table II). Assignment of the ring diad tacticity, however, first requires the hydrogenation of the main chain double bonds (eq 2) to generate
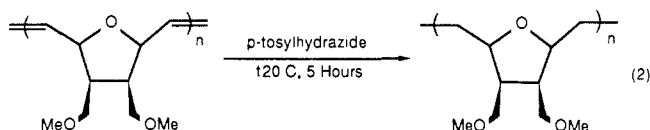
the fully saturated polymer.[17] The ^{13}C NMR spectrum of saturated poly VI shows two sets of resonances which can be unambiguously assigned to the isotactic and syndiotactic diads.[18]

Preliminary liquid/liquid and solid/liquid ion extraction experiments indicate that these poly(7-oxanorbornene) polymers do indeed coordinate various cations. Poly VI will coordinate Na^+, K^+, and Cs^+ (but not Li^+) salts as observed through solid/liquid extractions.[19] Of greater interest, however, is the observation

that the flexible binding cavities formed by poly VI will preferentially complex large polyaromatic cationic dyes such as methylene blue and rhodamine 6G.[20] Poly VI demonstrates high selectivity by complexing only dyes comprised of large organic cations and small anions (Cl^-). Dyes comprised of Na^+ and large aromatic anions are not complexed. This selectivity is exactly opposite to that observed for ion complexation by using 18-crown-6. Further ion complexation studies which will relate the isomeric constitution of a particular polymer to its ion binding efficiency are currently in progress.

In addition to binding ions in solution, these poly(7-oxanorbornene) polymers act as ion permeable membranes.[11] Demonstration of ion transport through these ionophoric materials is obtained by placing solid membranes cast from the poly(7-oxanorbornene) polymers between two ion concentration cells and measuring, by means of two SCE electrodes, the membrane potential resulting from diffusion of ions through the ionophoric membranes.[21] From the measured membrane potentials, cation transport numbers for K^+, Na^+, and Li^+ (all Cl^- salts) were calculated to be 0.84, 0.73, and 0.73, respectively. Current efforts are focusing on systematic structural modifications of the basic poly(7-oxanorbornene) skeletons, in order to enhance both their ion transport and ion selectivity properties.

(12) A typical polymerization procedure is presented here for monomer VI. All manipulations were performed under dry, inert atmosphere. Catalyst IX (87.0 mg, 0.148 mmol) is dissolved in dry benzene (1.0 mL). To this solution is added slowly via cannula olefin VI (680 mg, 3.7 mmol, 25 equiv) dissolved in benzene (1.0 mL). After 24 h at room temperature, methanol (1.0 mL) is added to the reaction, and the resulting solution cannulated into 50 mL of pentane. The polymeric precipitate is isolated and redissolved in the minimum amount of CCl_4, and the insoluble catalyst residue is filtered. The polymer is again precipitated by slow addition to pentane, filtered, and dried under vacuum to yield 0.41 g (59% yield) of poly VI: ^{1}H NMR (90 MHz, $CDCl_3$) 5.72, 5.58, 4.5, 4.22, 3.45, 3.34, 2.25 ppm; IR (thin film) 2090 (s), 1475 (m), 1460 (m), 1390 (m), 1190 (s), 1100 (vs), 1018 (s), 963 (s) cm^{-1}.

(13) Evidence of the 1,4-epoxide ring opening is obtained by the addition of 1 equiv of VI to a solution containing $WOCl_4$. Upon mixing, the ^{1}H NMR spectrum of VI shows a complete loss of the bridgehead proton signals at 4.3 ppm, accompanied by the appearance of new olefin signals at ca. 5.3 ppm. After 15 min nonspecific decomposition to unidentified products is observed.

(14) Ho, H. T.; Ivin, K. J.; Rooney, J. J. *J. Mol. Catal.* **1982,** *15,* 245.

(15) The ring diad tacticity in these systems is defined as
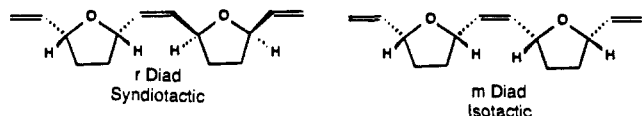
(16) The allylic carbons in the ^{13}C NMR spectrum are the best resolved indicators of the double bond's configuration with the trans and cis signals appearing at 81.8 and 77.3 ppm, respectively.

(17) Hamilton, J. G.; Ivin, K. J.; Rooney, J. J. *J. Mol. Catal.* **1985,** *28,* 255.

(18) The two unique ring carbons and the methylene linker carbons all appear as two sets of resonances in the ^{13}C NMR spectrum of saturated poly VI: the isotactic set at 32.74, 81.16, and 46.2 ppm and the syndiotactic set at 31.90, 80.83, and 45.87 ppm ($CDCl_3$). Absolute assignment of the two sets of resonances as the isotactic and syndiotactic sets required polymerization of the chiral resolved monomer 5-(methylmethoxy)-7-oxanorbornene and subsequent analysis of the resulting chiral polymer's ^{13}C NMR spectrum's head/tail fine structure. Details of this analysis is to be published. For a complete discussion of this method, see: Ivin, K.; Lapienis, G.; Rooney, J. *Polymer* **1980,** *21,* 436.

(19) An efficient 1,3-dinitrobenzene "yes/no" screening test was employed to determine the presence of solubilized hydroxide salts in CCl_4 solutions containing poly(7-oxanorbornene). The formation of the red Meisenheimer hydroxide/dinitrobenzene complex upon addition of the solid hydroxide salt to the CCl_4/polymer solution indicates a positive ion binding result. The appropriate control experiments were run to eliminate the possibility of any spurious complexation results not mediated by the poly(7-oxanorbornene) polymers.

(20) Typical liquid/liquid extraction experiments were performed by extracting standardized aqueous dye solutions with solutions of the poly(7-oxanorbornene) polymers dissolved in either CCl_4 or benzene. Dye concentrations in the aqueous phase before and after the extractions were monitored by UV absorbance measurements.

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Activation of Dihydrogen by Organo-Iridium-Phosphido Complexes. Evidence for α-Hydrogen Abstraction by a Terminal Phosphide Ligand

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The basicity of a terminal phosphido group bound to a transition metal (L_nM-PR_2) is well documented.[1,2] Intermolecular transformations involving metal phosphides and electrophiles such as CH_3I, I_2,[3,4] HX,[5,6] S_8,[5,6] NO,[7] Ph_2PCl,[8] and other metal com-

[†] Fellow of the Alfred P. Sloan Foundation (1984–1987).

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Communications to the Editor

plexes M′L$_n$[2,9] provide convincing evidence that the lone pair on a pyramidal phosphido donor is chemically active. Although not an electrophile, dihydrogen can be polarized by interaction with a metal and a coordinated ligand that contains a lone pair of electrons resulting in protonation of the basic ligand. Our interest[10] in the activation of dihydrogen by metal complexes containing basic ligands compelled us to examine this mode of reactivity for complexes containing terminal phosphide ligands. What was uncovered was an unusual intramolecular transformation involving the basic phosphide moiety abstracting an α-hydrogen from a coordinated methyl group. In this paper, we document (i) the first example of intramolecular proton transfer from an alkyl ligand to a coordinated phosphido group and (ii) the apparent heterolytic splitting of H$_2$ by a metal phosphide complex.[11]
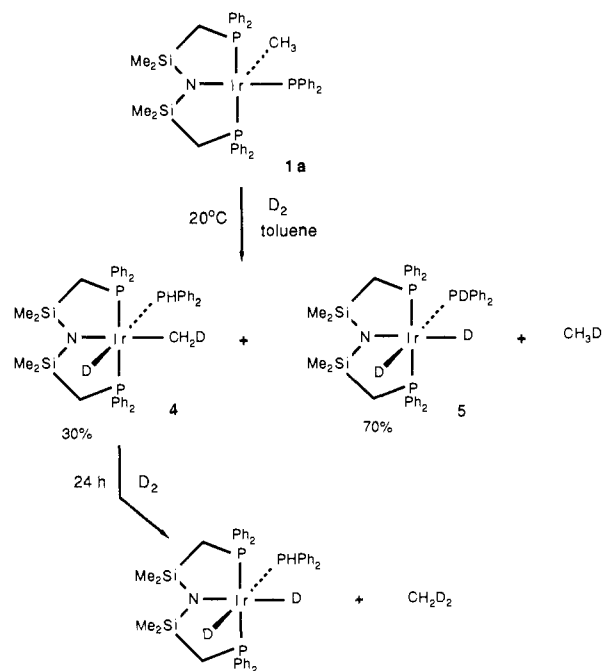
The dark purple iridium(III) methyl phosphido complexes, Ir(CH$_3$)(PR$_2$)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (**1a**, R = phenyl; **1b**, R = *m*-tolyl), were synthesized by treatment of the previously reported square pyramidal iridium(III) methyl iodide derivative, Ir-(CH$_3$)(I)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$],[12] with stoichiometric amounts of the corresponding lithium diarylphosphides. On the basis of previous work from our laboratory with octahedral and five-coordinate iridium amides[13] and NOEDIFF experiments, the solution stereochemistry of the five-coordinate phosphide derivative is not easily distinguishable between square pyramidal and trigonal bipyramidal;[14] for the purpose of this work square-pyramidal geometry is assumed.

The reaction of a toluene solution of **1a** with 1 atm of H$_2$ produces a mixture of the methyl hydride **2** and the dihydride **3** in the ratio of 30:70 by ^{1}H NMR spectroscopy (eq 1). Upon stirring the mixture of **2** and **3** under excess dihydrogen for an additional 24 h, the methyl hydride complex **2** is converted to the dihydride complex **3**.
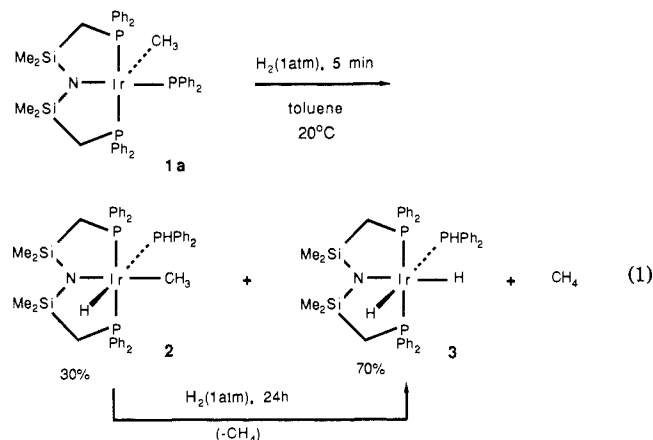

In order to obtain some information on the mechanism involved in the formation of these hydride complexes, the analogous reaction with D$_2$ was carried out (Scheme I). Some very intriguing results were revealed. The ^{1}H NMR for the reaction of **1a** and 1 atm of D$_2$ still showed P*H*Ph$_2$ resonance of the methyl hydride; fur-

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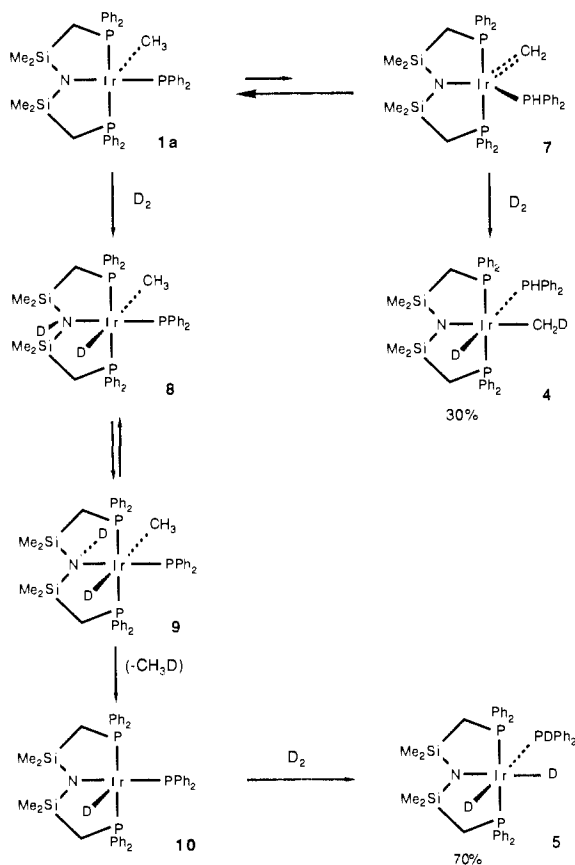
(11) For an authentic example of heterolytic cleavage of a metal-phosphide bond by H$_2$, see: Roddick, D. M.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 4670.

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(14) NOEDIFF results shows a very small enhancement of the IrCH$_3$ resonance upon irradiation of the ligand methylene (PCH$_2$Si) protons which is consistent[12,13] with a geometry between square pyramidal and trigonal bipyramidal.

Scheme I

thermore the protons on the iridium—methyl were a broadened peak instead of the quartet observed for the previous reaction with H$_2$. The ^{2}H NMR was also completely consistent with the structures **4** and **5** shown in Scheme I. The gaseous products evolved in this reaction are CH$_3$D and CH$_2$D$_2$, as confirmed by mass spectrometry. The corresponding reaction of **1a**-d_3, Ir-(CD$_3$)(PPh$_2$)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], with H$_2$ gives the complementary result as shown in eq 2. The minor isomer is now the isotopomer with no P*H*Ph$_2$ resonance in the ^{1}H NMR spectrum. Interestingly, the ratio of isomers is changed to 20:80 for the methyl hydride-d_2 **6**, to the dihydride **3**, indicative of a significant isotope effect.
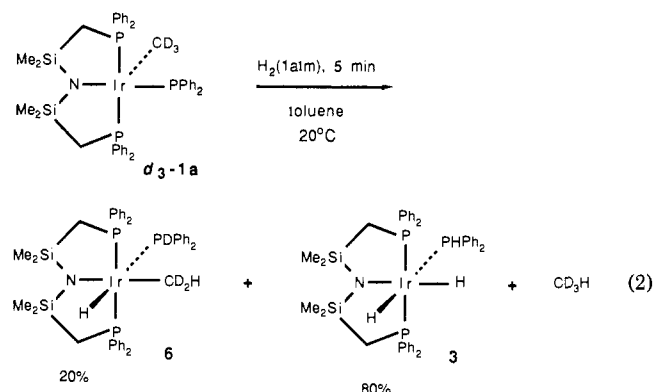
The reaction of **1a** with D$_2$ was also followed by variable temperature ^{1}H NMR. From −70 °C to +10 °C, only the starting phosphide was detected, but as the reaction mixture was warmed to 20 °C, the complexes **4** and **5** appeared almost simultaneously in their respective yields of 30% and 70%. This experiment along with the deuterium-labeling study indicates that the methyl hydride is not an intermediate in the formation of the dihydride, even though it is ultimately converted to the dihydride upon being stirred under excess H$_2$ for 24 h.

To account for the observed distribution of deuterium, and equilibrium between the methyl diphenylphosphide complex **1a** and the methylidene diphenylphosphine species **7** is proposed as shown in Scheme II. Such an intramolecular proton transfer from a hydrocarbyl ligand to a phosphido donor is extremely rare.[15]

(15) To our knowledge, this is the first example of intramolecular proton abstraction from an alkyl group by a phosphide moiety.

Scheme II

Although we have no evidence for **7** at the present, reaction of D₂ across the iridium–carbon double bond does generate **4**, the correct methyl hydride isotopomer. The sequence of reactions to convert **1a** to the dideuteride **5** is speculative but draws on earlier observations of ancillary ligand involvement in the activation of dihydrogen and aromatic C–H bonds.[16] In particular, addition of D₂ produces the amine deuteride **8** which can rearrange to the isomer **9** by amine dissociation, inversion at nitrogen, and reassociation; elimination of CH₃D from **9** to give the phosphido deuteride **10** followed by addition of D₂ generates the observed major product **5**.

Some preliminary mechanistic studies have been done. It can be shown that the proposed phosphido deuteride **10** does not reductively eliminate to the iridium(I) diphenylphosphine complex Ir(PDPh₂)[N(SiMe₂CH₂PPh₂)₂] prior to D₂ addition since reaction of the perprotio complex Ir(PHPh₂)[N(SiMe₂CH₂PPh₂)₂][17] with H₂ does not yield the *mer*-dihydride **3** but rather *fac*-Ir-(H)₂(PHPh₂)[N(SiMe₂CH₂PPh₂)₂] irreversibly. The attempts to prepare the proposed intermediate **7** by either the addition of 1 equiv of PHPh₂ to the previously reported methylidene complex, Ir(=CH₂)[N(SiMe₂CH₂PPh₂)₂],[18] or by the reaction of CH₂N₂[19] with Ir(PHPh₂)[N(SiMe₂CH₂PPh₂)₂] have been unsuccessful; in the former reaction, a complex mixture results, while, in the latter, the iridium(I) derivative Ir(PMePh₂)[N(SiMe₂CH₂PPh₂)₂] is the only product. Clearly, neither of these procedures is kinetically feasible for accessing the proposed equilibrium in Scheme II. Further studies are underway to provide additional evidence for the reversible intramolecular proton transfer from an alkyl to a terminal phosphide ligand.

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(17) The complex Ir(PHPh₂)[N(SiMe₂CH₂PPh₂)₂] was prepared by addition of PHPh₂ to Ir(n²-C₈H₁₄)[N(SiMe₂CH₂PPh₂)₂][12] (C₈H₁₄ = cyclooctene).

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Positive Evidence for Tetrahedral R′C(OR)₃H⁺ Intermediates in the Gas Phase

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Most acyl-transfer reactions occur in solution via an addition–elimination pathway, involving a tetrahedral intermediate under both acid and base catalysis.[1,2] So far, the role of tetrahedral intermediates has not found a comparable recognition in the gas phase where parallel reactions at the carbonyl group seem to take a different course,[3–5] as shown by ion cyclotron resonance (ICR) spectrometry. The discrepancy between the mechanistic patterns prevailing in solution and in the low-pressure gaseous environment typical of ICR studies poses the question of whether a bridge between such extremes can be found in reaction media of intermediate molecular density. To this purpose, alcoholysis of esters has been examined in the gas phase at atmospheric pressure, exploiting a radiolytic technique which has proved useful in similar problems.[6] The results now reveal close analogies with the addition–elimination pathway prevailing in solution. Furthermore, a suitable choice of reactants has allowed me to quench the ester alcoholysis reaction and to actually obtain orthoesters as neutral end products, thus achieving unequivocal characterization of cationic tetrahedral species as the charged reaction intermediates.

Table I illustrates typical experiments where carboxylic esters have been methylated by the gaseous Me₂F⁺ Lewis acid[7] in the presence of an alcohol and occasionally of basic additives. In general, the carbonyl oxygen of esters is the thermodynamically favored site for electrophilic attack, in particular for protonation,[8] although intermediates protonated at the ether oxygen are seen to play a kinetic role.[4,9] The present results, especially the detection of ortho esters, require that a significant fraction of electrophilic methylation occurs at the carbonyl oxygen, either

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