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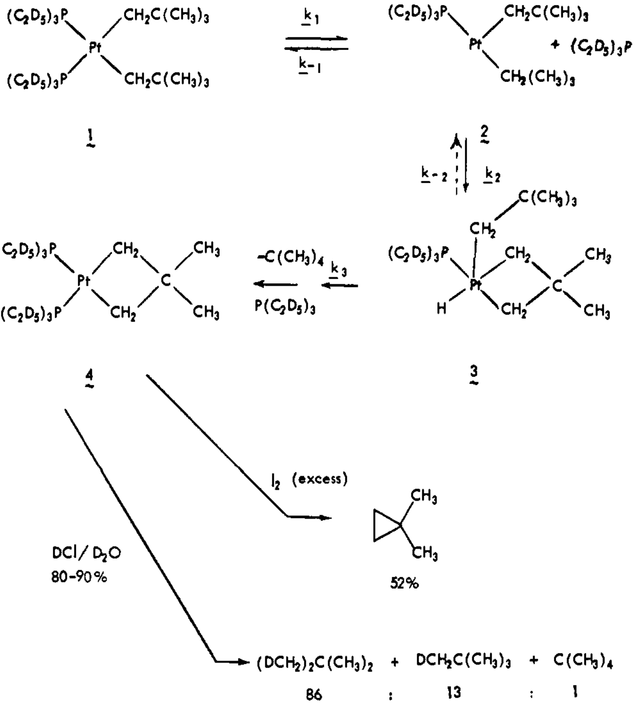
Thermal Generation of Bis(triethylphosphine)-3,3-dimethylplatinacyclobutane from Dineopentylbis(triethylphosphine)platinum(II)[1]

Sir:

Reactions which cleave unactivated aliphatic carbon-hydrogen bonds are important in a range of heterogeneous platinum-catalyzed transformations of hydrocarbons, and a mechanistic understanding of these types of reactions is one objective of current research in catalysis.[2] The mechanisms of heterogeneous reactions are difficult to examine directly. Here we outline the mechanism of a tractable and well-defined solution reaction—the conversion of dineopentylbis(triethylphosphine)platinum(II) (**1**) to bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (**4**)—which involves cleavage of an unactivated C-H bond by intramolecular oxidative addition to a soluble platinum species. This mechanism establishes certain of the structural features which facilitate C-H bond activation in solution and suggests, by analogy, possible characteristics of the heterogeneous reactions.

Heating a solution of **1** (0.08 M, 157 °C, 2.25 h, 0.02 M Et_3P)[3] in cyclohexane results in the disappearance of **1** and the appearance of 1 equiv of neopentane, 0.8 equiv of **4**, and 0.1 equiv of 2,2,5,5-tetramethylhexane. The solution remains homogeneous throughout the decomposition. Compound **4** was isolated as a light yellow oil by removing cyclohexane and titurating with acetonitrile to remove unreacted **1**. **4** showed the following: ^1H NMR (C_6D_6) δ 0.73 (t of t, 4 H, 1:4:1, $J_{Pt-H} = 74$, $J = 12$ Hz, Pt-CH_2), 1.57 (t, 6 H, $J = 3$ Hz, $C(CH_3)_3$; ^{31}P (C_6H_{12}, H_3PO_4 external reference) δ +9 ppm (t, 1:4:1, $J_{Pt-P} = 1862 \pm 8$ Hz). Treatment of **4** with aqueous 38% DCl in D_2O yielded a mixture of deuterated neopentanes.[4] Examination of the cracking pattern of this neopentane indicated that the deuterium was present in CH_2D rather than CHD_2 groups and is consistent with activation of a γ C-H bond and not an α C-H bond.[5] Treatment of **4** with excess iodine generated 1,1-dimethylcyclopropane. The dimethylcyclopropane derived from thermolysis of $[(CH_3)_3CCD_2]_2Pt(PEt_3)_2$ followed by treatment with I_2 was d_2.

Scheme I. Mechanism of Conversion of **1** into **4**. No Stereochemistry Is Implied by **3**



The origin of the hydrogen atom consumed in conversion of a neopentyl group of **1** to neopentane was established as a methyl group of a second neopentyl group by deuterium labeling experiments:

$$[(CH_3)_3CCH_2]_2Pt[P(C_2D_5)_3]_2 \xrightarrow[157\ ^\circ C]{C_6D_{12}} (CH_3)_3CCH_2H\ (97\%\ d_0,\ 3\%\ d_1) \quad (1a)$$

$$[(CH_3)_3CCD_2]_2Pt[P(C_2D_5)_3]_2 \xrightarrow[157\ ^\circ C]{C_6D_{12}} (CH_3)_2CCD_2H\ (93\%\ d_2,\ 7\%\ d_3) \quad (1b)$$

The decomposition of $[(CH_3)_3CCH_2]_2Pt[P(C_2D_5)_3]_2$ in solutions of C_6D_{12} containing added $P(C_2D_5)_3$ (0.02-0.3 M) was followed by NMR spectroscopy. These decompositions obeyed the empirical rate equation

$$d[\mathbf{1}]/dt = k_{obsd}[\mathbf{1}][P(C_2D_5)_3]^{-1} \quad (2)$$

The observed rate equation is compatible with the formal rate expression

$$d[\mathbf{1}]/dt = k_1k_2[\mathbf{1}]/(k_2 + k_{-1}[P(C_2D_5)_3]) \quad (3)$$

derived for a preequilibrium dissociation of phosphine followed by rate-limiting C-H addition, and with an analogous expression for a scheme in which C-H reductive elimination (k_3) is rate limiting (Scheme I). Analysis of the temperature dependence for decomposition of **1** over the range 118-157 °C yielded these values for the Arrhenius activation parameters: $E_a = 49 \pm 4$ kcal mol^{-1}, $A = 10^{20\pm2}$ s^{-1}. The exchange of $(CH_3CH_2)_3P$ into $[(CD_3CD_2)_3P]_2Pt[CH_2C(CH_3)_3]_2$ was followed by ^{31}P NMR spectroscopy. This exchange was complete at 100 °C in 1.0 h with no detectable decomposition of **1**. The rate of this exchange was independent of added Et_3P concentration from 0.1 to 1.7 M and indicated that exchange occurred by an S_N1 process. This observation is consistent with the preequilibrium dissociation of Et_3P implied in Scheme I.[6]

The solubility of **1** in solutions of cyclohexane containing triethylphosphine established that the decrease in rate of decomposition of **1** observed on adding triethylphosphine could

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not be rationalized by assuming an associative equilibrium forming $[(CH_3)_3CCH_2]_2Pt(PEt_3)_3$: a quantity of triethylphosphine which decreased the rate of decomposition of **1** by a factor of 15 increased its solubility by only 16%.[7] Examination of the ^{31}P NMR spectrum of **1** in the presence of triethylphosphine also showed no evidence of formation of a species containing three triethylphosphine moieties under conditions (0.08 M **1**, 0.3 M Et_3P,) in which 93% of **1** would have necessarily been converted into such a species to rationalize the observed decrease in k_{obsd}.

The observation of a significant kinetic isotope effect in the decomposition of **1** indicates that C-H bond breaking or bond forming occurs in or before the rate-limiting step. The rates of decomposition of **1**-d_0 and $[(CD_3)_3CCD_2]_2Pt[P(C_2D_5)_3]_2$ (**5**) were determined by comparing the yields of neopentane as a function of time. After correction for isotopic impurities, analysis of these data yielded $k_1/k_5 = k_H/k_D = 3.0\text{-}3.5$.

The most important conclusion from this work is that the cleavage of an unactivated C-H bond which takes place during the conversion of **1** into **4** proceeds by an oxidative addition to the platinum atom of a reactive (trialkylphosphine)dialkylplatinum(II) moiety. We are currently studying a number of other examples of related, unactivated C-H bond cleavage reactions involving additions to platinum:[8] most appear to involve a $LPtR_2$ moiety as the reactive intermediate, and thus to require a vacant coordination site on (formally) three-coordinate platinum(II). The available evidence is not sufficient to distinguish between oxidative addition of a C-H bond to platinum(II) (k_2) or reductive elimination of a C-H bond from platinum(IV) (k_3) as the overall rate-limiting step.[9]

Activation of C-H bonds by surface atoms of platinum metal occurs readily.[10] We note that a prominent feature of a metal surface is the availability of vacant coordination sites and suggest that explicit comparisons of the reactivity of vacant sites on soluble complexes and on metal surfaces should be one of the most useful and direct methods of establishing parallels between homogeneous and heterogeneous catalysts. The activation energy determined for the transformation **1** → **4** described here ($E_a \simeq 49$ kcal mol^{-1}) cannot be directly compared with the lower values ($E_a \simeq 10$ kcal mol^{-1}) characterizing C-H bond cleavage during surface reactions,[10] since the former is composed of contributions from the energy of dissociation of a phosphine ligand, the energy (or the energy of activation) of addition of the C-H bond to platinum, the strain energy involved in forming the platinacyclobutane ring, and (possibly) the energy of activation for reductive elimination of neopentane from **3**. Studies of other C-H oxidative additions to platinum and of systems designed to provide comparable thermodynamic parameters for homogeneous and heterogeneous activation of C-H bonds by platinum will be reported as they are completed.

References and Notes

(1) Supported by the National Science Foundation (MPS 74-20956 and 7711282CHE).

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(4) All isotopic analyses were obtained using a Hewlett-Packard Model 5990 A GC/MS. The accuracy of these determinations varied with the sample, but should be considered to be precise to ±2% for neopentane. For example, treatment of 1 with aqueous DCl yields neopentane (99% d_1, 1% d_0). The 13% d_1 neopentane obtained on reaction of 4 with DCl is well outside experimental error and seems to represent a real (if presently unexplained) side reaction.

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(6) In principle, a plot of $(k_{obsd})^{-1}$ vs. $[P(C_2D_5)_3]$ can be used to estimate values of k_1 and k_{-1}/k_2. In practice, the uncertainty in these rate constants is so large that they are of only qualitative significance.

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(9) The neopentyl methyl and methylene groups of $(Et_3P)_2Pt[CD_2C(CH_3)_3]_2$ do not interchange. This observation does not guarantee the irreversibility of the step **2** → **3**, since we do not know that the methylene groups of **3** are equivalent.

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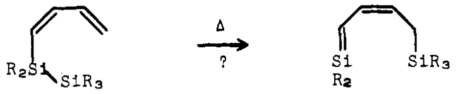
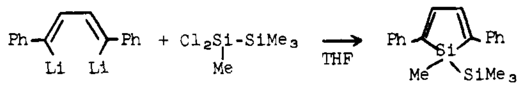
Silicon-Carbon Double-Bond Formation via 1,5-Sigmatropic Migration of Trimethylsilyl from Silicon to Carbon

Sir:

It is well established that a trimethylsilyl group will undergo 1,5 migration on a cyclopentadiene ring far more easily than will hydrogen.[1] Thus, we hoped to utilize this enhanced migratory aptitude in an attempt to observe an unprecedented 1,5 thermal migration of silicon from silicon to carbon in order to generate a 5-silyl-1-sila-1,3-butadiene.



The initial test molecule, 1-methyl-1-trimethylsilyl-2,5-diphenylsilole (**1**), was conveniently prepared in 51% yield from the cyclization of 1,4-dilithio-1,4-diphenylbutadiene and 1,1-dichloro-1,2,2,2-tetramethyldisilane. Silole **1** is a bright



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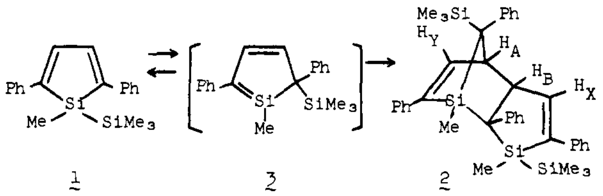
yellow solid: mp 95-96.5 °C; NMR (CCl_4) δ 0.0 (s, 9 H, $SiMe_3$), 0.68 (s, 3 H, SiMe), 7.1-7.6 (m, 12 H, ArH + vinyl); mass spectrum calculated for $C_{20}H_{24}Si_2$ 320.14166, observed *m/e* 320.14006.

Heating silole **1** in an evacuated, sealed tube at 150 °C for 9 h produced a clean mixture of **1** and a white, crystalline product **2** in a 1.1:1.0 ratio, respectively. Product **2** (mp 186.5-188 °C) was assigned the dimer structure shown on the basis of its spectra: NMR (CCl_4) δ −0.78 (s, 9 H, $SiMe_3$), −0.24 (s, 9 H, $SiMe_3$), 0.03 (s, 3 H, SiMe), 1.18 (s, 3 H, SiMe!), 4.02 (t, overlapped d of d, H_B, $J_{AB} = J_{BX} = 5$ Hz), 4.35 (d of d, H_A, $J_{AY} = 2.5$ Hz, $h\nu$ at 6.59 collapses to d), 5.90-7.35 (m, 22 H, ArH + H_X + H_Y); mass spectrum calculated for $C_{40}H_{48}Si_4$ 640.28333, observed *m/e* 640.28233 (2.3% of base peak at *m/e* 320).



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