Intramolecular Reductive Elimination of Alkanes from *cis*-Hydridoalkylbis(phosphine)platinum(II) Complexes

Sir:

Intramolecular reductive elimination of alkanes from *cis*-hydridoalkyl-metal complexes has frequently been postulated as a step in catalytic reactions (e.g., hydrogenation of alkenes),[1] as well as in certain stoichiometric processes.[2-4] However, rarely have such intermediate hydridoalkyl-metal complexes or the postulated intramolecular reductive elimination reactions been *directly* observed and characterized. A few hydridoalkyl complexes have proved sufficiently stable for characterization,[5] notably several of trans configuration, in some cases apparently so constrained by bulky ligands (e.g., *trans*-$NiH(CH_3)[P(cyclohexyl)_3]_2$),[8] and several containing *substituted* alkyl groups with stabilizing substituents (e.g., CH_2CN).[9] Among the few reported examples of simple molecular *cis*-hydridoalkyl complexes are [*cis*-$RuH(CH_3)(Ph_2PCH_2CH_2PPh_2)_2$][10] and [*cis*-$OsH(CH_3)(CO)_4$].[11,6,7] The former has not been reported to undergo reductive elimination, while reductive elimination of CH_4 from the latter compound apparently is a complex process and, at least under certain conditions, *intermolecular*.[6,7] We report here the synthesis and characterization of several *cis*-hydridoalkylbis(tertiary phosphine)platinum(II) compounds and the examination of the kinetics of their reactions to form alkanes by initial, rate-determining, reductive elimination according to eq 1. These represent the first cases, to our knowledge, in which such simple *intramolecular* reductive elimination of alkanes has been directly observed and kinetically characterized. In addition these systems are of importance in that they afford the first opportunity for the quantitative assessment of the influence of varying ligands (PR'_3 and R) on the rates of such reductive elimination reactions.

$$cis\text{-}[PtH(R)(PR'_3)_2] \xrightarrow{k_1} [Pt(PR'_3)_2] + RH \quad (1)$$

Treatment of a toluene solution of *trans*-$[PtHCl(PPh_3)_2]$ with CH_3MgBr (dissolved in ether) at −78 °C was found to yield *cis*-$[PtH(CH_3)(PPh_3)_2]$ (**1**) quantitatively according to eq 2. The resulting solution proved stable for at least several days at temperatures below −50 °C and the compound *cis*-$[PtH(CH_3)(PPh_3)_2]$ was fully characterized by ^1H and ^{31}P NMR spectroscopy as follows (each signal accompanied by ^{195}Pt satellites). ^1H NMR: Pt-H, δ − 2.1 (1 H, dd, J_{Pt-H} = 1216, J_{P_1-H} = 200, J_{P_2-H} = 24 Hz); Pt-CH_3, δ 1.56 (3 H, dd, J_{Pt-H} = 66, J_{P_1-H} = 6.9, J_{P_2-H} = 10.3 Hz). ^{31}P NMR: δ_{P_1} 30.8, δ_{P_2} 27.8 (J_{Pt-P_1} = 1855, J_{Pt-P_2} = 2010, $J_{P_1-P_2}$ = 10 Hz). All NMR measurements were made at −80 °C. The proton-decoupled ^{31}P spectrum is depicted in Figure 1.

$$trans\text{-}[PtHCl(PPh_3)_2] + CH_3MgBr \rightarrow \underset{\mathbf{1}}{cis\text{-}[PtH(CH_3)(PPh_3)_2]} + MgClBr \quad (2)$$

On warming to −25 °C decomposition of **1** occurred at a conveniently measurable rate to yield $[Pt(PPh_3)_3]$ and CH_4 (identified by ^{31}P and ^1H NMR, respectively; CH_4 also identified mass spectrometrically) according to eq 3. In the presence of added ligands (L = PPh_3 or PhC≡CPh) *the rate of decomposition was unaffected* but the stoichiometry was altered to that of eq 4 (quantitatively confirmed by ^{31}P NMR).

$$3\{cis\text{-}[PtH(CH_3)(PPh_3)_2]\} \rightarrow 3CH_4 + 2[Pt(PPh_3)_3] + Pt \quad (3)$$

$$cis\text{-}[PtH(CH_3)(PPh_3)_2] + L \rightarrow CH_4 + [Pt(PPh_3)_2L] \quad (4)$$

Kinetic measurements, in which the concentrations of **1** as well as the product (i.e., $[Pt(PPh_3)_3]$ or $[Pt(PPh_3)_2(PhC{\equiv}CPh)]$) were monitored by ^{31}P NMR, yielded the first-order rate law, eq 5, with $k_1 = (4.5 \pm 0.5) \times 10^{-4}$ s^{-1} at −25 °C. First-order plots for the disappearance of **1** were invariably linear for at least three half-lives. The above value of k_1 was unaffected by variations in the initial concentration of **1** (2×10^{-2} to 4×10^{-2} M), by the nature or concentration of added ligand (up to 0.1 M PPh_3 or PhC≡CPh), by excess CH_3MgBr (up to 2×10^{-2} M) or by addition of up to 0.14 M EtOH to destroy any excess CH_3MgBr.

$$-d[PtH(CH_3)(PPh_3)_2]/dt = k_1[PtH(CH_3)(PPh_3)_2] \quad (5)$$

These observations are most plausibly interpreted in terms of the mechanistic scheme encompassing the rate-determining step (1), where R = CH_3 and R′ = Ph, followed by

$$[Pt(PPh_3)_2] + L \xrightarrow{fast} [Pt(PPh_3)_2L] \quad (6)$$

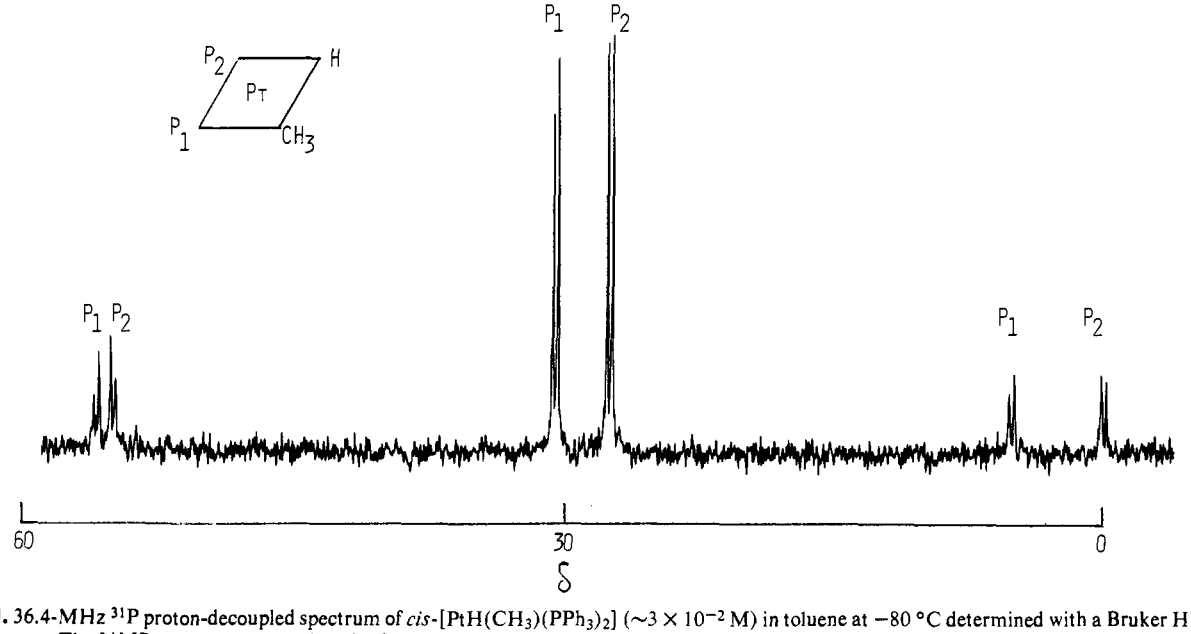

Figure 1. 36.4-MHz ^{31}P proton-decoupled spectrum of *cis*-$[PtH(CH_3)(PPh_3)_2]$ (~3×10^{-2} M) in toluene at −80 °C determined with a Bruker HFX-90 spectrometer. The NMR parameters are given in the text.

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or, in the absence of added ligand,

$$3[Pt(PPh_3)_2] \xrightarrow{fast} 2[Pt(PPh_3)_3] + Pt \quad (7)$$

Further support for this interpretation is provided by the following observations. (1) Deuterium-labeling experiments using various isotopic mixtures demonstrated conclusively that the reductive elimination is *intramolecular*. Thus, complete decomposition of an equimolar mixture of $[PtH(CH_3)(PPh_3)_2]$ and $[PtD(CD_3)(PPh_3)_2]$ yielded predominantly CD_4 and CH_4 ($[CD_4]:[CD_3H] \gtrsim 20:1$, determined mass spectrometrically); similarly an equimolar mixture of $[PtH(CD_3)(PPh_3)_2]$ and $[PtD(CH_3)(PPh_3)_2]$ yielded predominantly CH_3D and CD_3H ($[CD_3H]:[CD_4] \gtrsim 25:1$). (2) Comparison of the rates of decomposition of $[PtH(CH_3)(PPh_3)_2]$ and $[PtD(CH_3)(PPh_3)_2]$ revealed an appreciable normal primary isotope effect, i.e., $k_1^H/k_1^D = 3.3 \pm 0.3$.

Similar results were obtained for the corresponding complexes of several para-substituted triarylphosphines, $[PtH(CH_3)(PR'_3)_2]$, where $R' = p\text{-}XC_6H_4$. The rates of reaction ($10^4 k_1$, s^{-1}, at -25 °C) decreased along the sequence $R' = p\text{-}ClC_6H_4$ (9.2) > C_6H_5 (4.5) > $p\text{-}CH_3C_6H_4$ (1.4) > $p\text{-}CH_3OC_6H_4$ (0.47). This sequence is consistent with the expected increasing tendency of electron-withdrawing substituents on the phosphine ligands to stabilize platinum(0) and, hence, to increase the driving force for the reductive elimination reaction 1.

Similar experiments on $[PtH(C_2H_5)(PPh_3)_2]$ demonstrated the analogous reductive elimination of C_2H_6, with $k_1 = 9 \times 10^{-4}$ s^{-1} at -25 °C (i.e., ca. twice the corresponding rate for the methyl compound). Preliminary rate measurements on several other $[PtH(R)(PPh_3)_2]$ compounds revealed the qualitative sequence of decreasing reactivity: $R = C_6H_5 > C_2H_5 > CH_3 > CH_2CH{=}CH_2$.

The initial product of the reductive elimination reaction 1, i.e., $[Pt(PPh_3)_2]$, has previously been identified as an intermediate in the substitution and oxidative addition reactions of platinum(0) complexes,[12-14] e.g.,

$$[Pt(PPh_3)_3] \overset{-PPh_3}{\rightleftharpoons} [Pt(PPh_3)_2] \overset{RC\equiv CR}{\rightleftharpoons} [Pt(PPh_3)_2(RC{\equiv}CR)] \quad (8)$$

The facile intramolecular reductive elimination of CH_4 from $[PtH(CH_3)(PPh_3)_2]$ at temperatures as low as -25 °C clearly demonstrates not only that the process is thermodynamically favorable but that the kinetic barrier is low. The reverse process, i.e., the oxidative addition of CH_4 to $[Pt(PPh_3)_2]$ (or to $[Pt(PPh_3)_3]$ via $[Pt(PPh_3)_2]$ which is readily derived thereform by dissociation) *must, accordingly, be precluded on thermodynamic rather than on kinetic grounds*. This conclusion is of some significance in the context of the widespread current interest in the catalytic activation of saturated hydrocarbons and suggests that oxidative addition (at least with such mononuclear complexes) is not a promising approach.

Further studies along these lines, including extensions to other hydridoalkylplatinum(II) complexes as well as to corresponding complexes of other metals, notably palladium(II) and nickel(II), are in progress.

Acknowledgments. Support of this research through a grant from the National Science Foundation is gratefully acknowledged. One of us (L.A.) thanks Montedison Co. for a leave of absence.

References and Notes

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(14) The isolation of solid "$[Pt(PPh_3)_2]$", prepared through a route related to that of reactions 2 and 1 has previously been claimed.[15] All subsequent attempts to prepare this compound in monomeric form under conditions where it is sufficiently stable for direct detection and characterization, either in solution or as a solid, appear to have failed. Related monomeric platinum(0) complexes of other (more bulky) phosphines, e.g., $[Pt\{P(cyclohexyl)_3\}_2]$ and $[Pt\{P(i\text{-}Pr)_3\}_2]$ have, however, been isolated and unequivocally characterized.[16]
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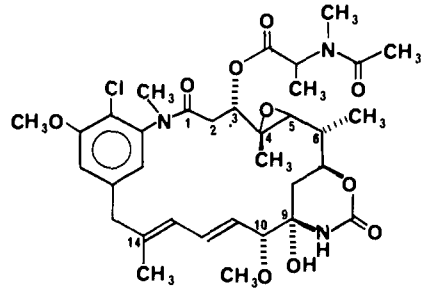
Received December 27, 1977

Total Synthesis of (±)-*N*-Methylmaysenine[1]

Sir:

Maytansine (**1**) is a promising antitumor agent which is now in phase II of clinical studies with human patients. The isola-



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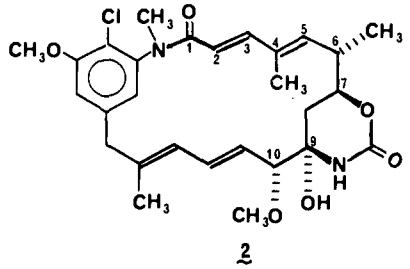
tion and determination of structure of this interesting substance by Kupchan et al.[2,3] are among the most notable of recent developments in the field of organic natural products. Because of the extreme scarcity of maytansine and its congenors (e.g., *N*-methylmaysenine (**2**), or maysine which is the 4,5-oxide of



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N-methylmaysenine), and the therapeutic promise of maytansine, there has been considerable interest in maytansenoid synthesis; a number of groups have reported initial studies and good progress in this area.[4] This communication describes the

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