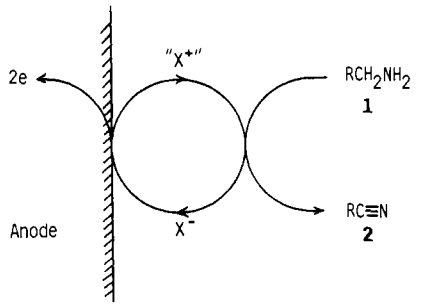
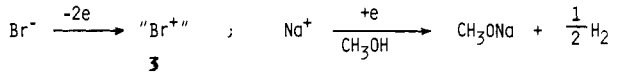
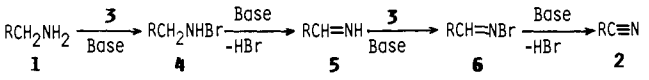
Scheme I



Indirect Electrooxidation

Scheme II





Scheme III

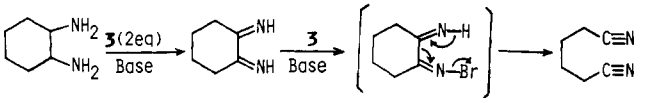
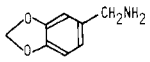
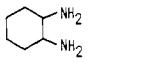


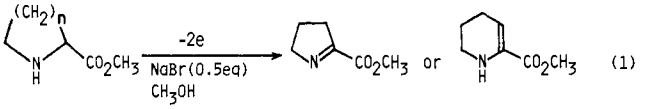
Table I. Electrooxidation of Amines to Nitriles[a]

entry	amines	electricity passed, F/mol	yield of nitriles, %[b]
1	$CH_3(CH_2)_7NH_2$	8.6	80 (95)[c]
2	$CH_3(CH_2)_5NH_2$	8.6	79 (90)[c]
3	$Ph(CH_2)_nNH_2$, n = 1	7.0	50
4	n = 3	8.7	81
5	n = 4	8.7	82
6	p-$CH_3C_6H_4CH_2NH_2$	8.4	64
7		6.4	81
8		8.4	60[d]
9	$PhCH_2C(NH_2)HCO_2H$	5.7	80[e]

[a] CH_3OH (30 mL)-NaBr (6 mmol)-amine (4 mmol). [b] Isolated yield. [c] Determined by GLC. [d] Adiponitrile. [e] Phenylacetonitrile.

are possible; a plausible route is exhibited in Scheme III.

The intermediary formation of imines **5** was supported by the observation that the oxidation of α-amino acid esters **7** and **8** gave the imine derivatives **9**[8] (80%) and **10** (67%), respectively (eq 1).



(1)

7, n=2
8, n=3

9 80 % (after 4 F/mol)

10 67 % (after 5 F/mol)

The electrooxidation of phenylalanine under our reaction conditions gave phenylacetonitrile (80%). Similar results were obtained with the corresponding methyl ester (76% yield of phenylacetonitrile).

Acknowledgment. Thanks the Ministry of Education, Science, and Culture, Japan, for a Grant-in-Aid for Special Project Research (1) (No. 57118003 and 58110003).

(8) Poisel, H.; Schmidt, U. *Chem. Ber.* **1975**, *108*, 2547.

Registry No. octylamine, 111-86-4; hexylamine, 111-26-2; benzenemethanamine, 100-46-9; benzenepropanamine, 2038-57-5; benzenebutanamine, 13214-66-9; 4-methylbenzenemethanamine, 104-84-7; 1,3-benzodioxole-5-methanamine, 2620-50-0; 1,2-cyclohexanediamine, 694-83-7; phenylalanine, 63-91-2; octanenitrile, 124-12-9; hexanenitrile, 628-73-9; benzonitrile, 100-47-0; benzenepropanenitrile, 645-59-0; benzenebutanenitrile, 2046-18-6; 4-methylbenzonitrile, 104-85-8; 1,3-benzodioxole-5-carbonitrile, 4421-09-4; adiponitrile, 111-69-3; phenylacetonitrile, 140-29-4.

Reversible Formal Alkene Insertion into a Chelated Platinum-Alkyl Bond

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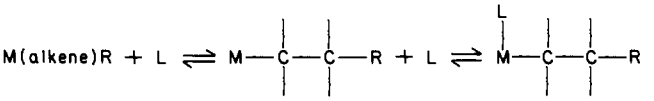
The well-know insertion of alkenes into metal-alkyl bonds is central to many transition-metal-catalyzed reactions. Nevertheless, there are extremely few cases where observation of the key C-C bond-forming step (eq 1) is possible in a structurally and kinetically



(1)

well-defined way. A number of examples of isolable, or at least spectroscopically detectable, $L_nM(alkene)R$ complexes of essentially cis configuration are extant,[1] but in only one highly contrained case[1k] is any insertion[2] reaction observed.[3] In contrast, examples of insertions arising from reaction mixtures whose intermediate components are structurally ill-defined are myriad.[4] The absence of a detailed understanding of this important reaction represents a gap in our knowledge of organometallic reactivity.

We wish to report the preparation and thermal rearrangement of a chelated (2,2-dimethyl-4-penten-1-yl)platinum complex wherein we have been able to observe a reversible alkene insertion into the Pt-alkyl bond. This organic ligand exhibits unusual thermal stability. Still, we believe its chelate complexes are likely to be relatively unstrained and flexible. Thus, it and its structural varients are likely to afford us the opportunity to carry out detailed structure-reactivity studies of the important M(alkene)alkyl insertion-elimination reaction in a variety of metal systems.

Complex **1** (as the BF_4^- salt), a stable solid, is readily prepared by treatment of **2**[5] with $AgBF_4$ in acetone (eq 2).[8] Treatment

(1) (a) Lehmkuhl, H.; et al. *J. Organomet. Chem.* **1982**, *228*, C1-C3. (b) Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 1165-1169. (c) Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27-35. (d) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389-2399. (e) Werner, H.; Werner, R. *J. Organomet. Chem.* **1979**, *174*, C63-C66. (f) Schubert, U.; et al. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 809-810. (g) Clark, H. C.; Jablonski, C. R.; Von Werner, K. *J. Organomet. Chem.* **1974**, *82*, C51-C52. (h) Bennett, M. A.; Chee, H.-K.; Jeffery, J. C. *Inorg. Chem.* **1979**, *18*, 1071-1076. (i) Benn, R. *J. Organomet. Chem.* **1982**, *238*, C27-C30 and references therein. (j) Lehmkuhl, H.; Tsien, Y. L.; Janssen, E.; Mynott, R. *Chem. Ber.* **1983**, *116*, 2425-2436. (k) Coulson, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 200-202.

(2) For simplicity, in this paper we will use the term "insertion" to mean formal insertion, or the formation M-C-C-R from a M(alkene)R complex, regardless of the mechanism.

(3) Probably the best defined example of a reversible alkene insertion is that wherein $(C_5Me_5)_2MMe$ (M = Yb, Lu) is reported to react cleanly with propene to yield the isobutylmetal derivative (Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337-339). Labeling experiments indicate that the insertion is reversible (Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.*, **1982**, *104*, 6471-6473). As expected for a d^0 complex, the presumed M(alkene)R intermediate cannot be observed.

(4) For example: (a) Chien, J. C. W., Ed. "Coordination Polymerization"; Academic Press: New York, 1975. (b) Boor, J. "Ziegler-Natta Catalysis and Polymerizations"; Academic Press: New York, 1979. (c) Heck, R. F. *Adv. Catal.* **1977**, *26*, 323-349.

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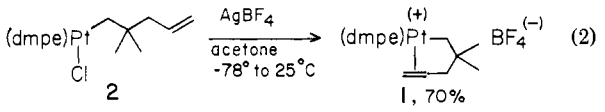
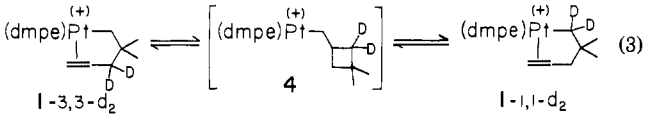


2 1, 70% (2)

of **1** with KI in acetone generates PtI(dmpe)($CH_2C(Me)_2CH_2CH{=}CH_2$) (**3**), and with KCN in ethanol Pt(CN)(dmpe)($CH_2C(Me)_2CH_2CH{=}CH_2$) is formed. Complex **1** has the unusual property (compared to [Pt(diars)($CH_2{=}CH_2$)Et]$^+$, for example[1g]) that it is rather stable at higher temperature; heating of **1** at 125 °C in CD_3NO_2 for 14 h results in only ca. 15% decomposition with no deuterium incorporation from solvent.[9]

Of most interest to us was the potential for observation of reversible formal β-alkyl insertion-elimination in **1**. Formation of a (cyclopentyl)platinum intermediate by direct insertion in **1** is not geometrically possible, but (cyclobutylcarbinyl)platinum **4** formation is.[10,11] One can test for the presence of this equilibrium by the labeling experiment shown in eq 3. Within 8 h



1-3,3-d_2 4 1-1,1-d_2 (3)

of heating **1**-*3,3*-d_2 at 125 °C in CD_3NO_2 a 50:50 mixture of **1**-*3,3*-d_2 and **1**-*1,1*-d_2 had formed. In a preliminary kinetics study, the rearrangement at 125 °C for about one half-life exhibited kinetics which were consistent with a reversible first-order reaction, with $k_{forward} = k_{reverse} = 3.5 \times 10^{-5}$ s^{-1}. The system behaves very cleanly with regard to the position of the deuterium label; both ^1H and ^2H NMR of both **1** and the iodide **3** derived from **1** indicate that deuterium resides only in the 1- and 3-positions—none has been incorporated into the olefinic or methyl groups or into dmpe.

The overall reaction of eq 1 is anticipated to possess a heat of reaction of ca. -20 kcal/mol (C=C π-bond energy - C—C σ-bond energy) when L is alkene, but the first step will be less favorable by the amount of the M(alkene) bond strength. A partial explanation for the lack of examples of M(alkene)R insertions may lie in the relative strengths of M(alkene) bonding. If the bond is too strong, the first step of eq 1 is rendered unfavorable. In the present case, the M(alkene) bond in **1** is kinetically stabilized by chelation, and β-hydride elimination is not possible because of the two β-methyl groups. These attributes of the complex apparently inhibit other paths of reaction so that heating the sample leads to observable insertion-elimination. The ΔH for the insertion step in eq 3 would be ca. -20 + 26(ring strain) + ΔH(Pt(alkene)) kcal/mol. We are not aware of any data on Pt(alkene) bond energies; however, our observation of rapidly reversible insertion suggests that the inherent barrier to alkene insertion may be low for **1**.

This observation of the reversible formal β-alkyl insertion in a M(alkene)R complex is, to our knowledge, the best-defined extant example for a transition metal. Detailed kinetic, activation parameter, conformational, and other mechanistic investigations are under way. Most important, we are in a position to thoroughly probe for substituent and electronic effects on the reaction in other metal and ancillary ligand systems. We are particularly interested in those systems that exhibit Ziegler polymerization activity in the presence of aluminum reagents.

Acknowledgment. This reaction was supported by National Science Foundation Grant CHE 8016573.

Registry No. 1, 91898-44-1; **1**-*1,1*-d_2, 91898-48-5; **1**-*3,3*-d_2, 91898-46-3; **2**, 91898-49-6; **2**-*3,3*-d_2, 91898-50-9; **3**, 91898-51-0; **3**-*1,1*-d_2, 91898-52-1; **3**-*3,3*-d_2, 91898-53-2; Pt(CN)(dmpe)($CH_2C(Me)_2CH_2CH{=}CH_2$), 91898-54-3; 4,4-dimethyl-1-pentene, 762-62-9.

(5) The preparations of close analogues of **1** have been reported[6] and are based on the HCl cleavage (Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, *705-716*) of $Pt(PR_3)_2R_2$ complexes prepared as previously reported (ref 7 and Bockmann et al.: Bochmann, M.; Wilkinson, G.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1980**, 1879-1887). The synthesis of the organic ligands is based on the alkylation of the anion of the *tert*-butyl imine of isobutyraldehyde (House, H. O.; Liang, W. C.; Weeks, P. D. *J. Org. Chem.* **1974**, *39*, 3102-3107).

(6) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 0000.

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(8) Complex **2**: ^1H NMR (CD_3NO_2, 270 MHz) δ 1.16 (s, CCH_3), 1.24 (s, CCH_3), 1.68 (dtd, $\Delta\delta$ = 38, J_{PtH} = 16, J_{PH} = 10 Hz, $P(CH_3)_2$), 1.77 (dtd, $\Delta\delta$ = 16, J_{PtH} = 18, J_{PH} = 13 Hz, $P(CH_3)_2$), 2.08 (br, PCH_2CH_2P), 2.63 (br td, J_{PtH} = 50, J_{PH} = 11 Hz, one allylic CH), 4.05 (br td, J_{PtH} = 42, J_{HH} = 16 Hz, C=CH_2, cis H), 5.39 (tdddd, J_{PtH} = 42, J_{PH} = 12, J_{PH} = 3, $J_{HH_{cis}}$ = 9, $J_{HH_{gem}}$ = 3 Hz, C=CH_2, trans H), 5.72 (m, =CH), $PtCH_2$ and the second allylic H are obscured by dmpe resonances. partial $^{13}C\{^1H\}$ NMR (acetone-d_6, 67.9 MHz) δ 84 (td, J_{PtC} = 50, J_{PC} = 12 Hz, =CH_2), 121 (td, J_{PtC} = 50, J_{PC} = 10 Hz =CH). $^2H\{^1H\}$ NMR of **2**-*3,3*-d_2 (CH_3NO_2, 41.4 MHz) δ 1.83 (br), 2.56 (br), small intensity at ca. 4.0 and 5.4 (small % of $CH_2CH{=}CD_2$ from preparative route).

(9) The reaction is carried out in a sealed NMR tube, and monitored by ^1H and ^2H NMR. There is considerable darkening and loss of clarity of the solution, but the resonances of **2** remain sharp and diminish only slightly in intensity. The only obvious side product detected by ^1H NMR is 4,4-dimethyl-1-pentene, formed in ca. 15% yield in 14 hrs.

(10) The reported [Atkins, M. P.; Golding, B. T.; Bury, A.; Johnson, M. D.; Sellars, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 3630-3632] reversible acid-catalyzed rearrangement of (3-buten-1-yl)[Co] to (cyclopropylcarbinyl)[Co] ([Co] = (dimethylglyoximato)$_2$(pyridine)cobalt(III)) is formally similar to the rearrangement reported herein, which may be regarded as a pent-4-enyl/cyclobutylcarbinyl rearrangement.

(11) Confidence in the intermediacy of **4** is enhanced by our extensive direct study of [(1-methylcyclobutyl)methyl]PtCl(PMe_3)$_2$ and {[(1-methylcyclobutyl)methyl]Pt(PMe_3)$_2$(acetone)}$^+$ which indicates that the barrier to ring opening is indeed low.[6] Thus, an unsaturated (cyclobutylcarbinyl)platinum species is a "kinetically competent" intermediate.

Automated Solid-Phase Synthesis, Separation, and Stereochemistry of Phosphorothioate Analogues of Oligodeoxyribonucleotides

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Phosphorothioate (PS) analogues of nucleotides are useful substrates for studying phosphorolytic and phosphoryl-transfer enzymes.[2] These analogues are also employed in the stereospecific synthesis of P-chiral nucleoside phosphates in which chirality at phosphorus exists by virtue of the isotopes of oxygen.[3,4] Chemical methods for the synthesis of PS analogues of oligonucleotides have dealt primarily with dimers;[5-9] however, their elaboration to longer

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