indicates a tetradentate behavior of the ligand in the trans-octahedral chromophore. For this compound the observed spectral features are clearly consistent with C_s symmetry in which the five- and six-membered chelate rings have gauche and chair conformations, respectively. No changes were observed in the NMR spectrum as the pD was lowered which confirms our earlier conclusion that Ni(isocyclam)$^{2+}$ is not involved in acid–base equilibria.

In conclusion, we feel that the available data are only consistent with tetradentate behavior for the isocyclam ligand in its nickel(II) complexes and that there is no basis for the claim that it is tridentate in the diamagnetic species.

Registry No. I, 52877-36-8; [Ni(isocyclam)]$^{2+}$, 46365-93-9; [Ni(isocyclam)(H$_2$O)$_2$]$^{2+}$, 68317-92-0; [Ni(isocyclam)](ClO$_4$)$_2$, 68344-01-4.

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Received October 30, 1980

Electron-Transfer Catalysis of Substitution

Sir:

In describing[1] our results on chiral discrimination in outer-sphere electron-transfer reactions, we neglected an important set of results which are germane to our case. Busch et al.[2] report that when (–)-Co(*d*-PDTA)$^-$ reacts with ethylenediamine, Co(en)$_3^{3+}$ is formed with a large excess of one chiral form over the other. Detailed observations were not given nor do they appear in either of two subsequent papers.[3,4] However, in ref 2 it is stated that in the first experiment (50% en at 25 °C) "complete retention of generic configuration" was observed. Further, that in attempts to reproduce the experiment, random results were obtained. A more detailed account of reaction conditions is given by Irving and Gillard[5] in reporting on the same reaction. In $\sim$25% en in water at 25 °C, reaction was found to be essentially complete in 12 min producing Co(en)$_3^{3+}$ which showed an optical rotatory power ca. 90% that of a pure enantiomer.

The purpose of this communication is to point out that the rapid reaction reported by Irving and Gillard[5] does not correspond to direct substitution but that instead an electron-transfer process carries the reaction.

We find, just as has been reported,[5] that the reaction between en and Co(PDTA)$^-$ is complete in a matter of minutes (our conditions differed from those of I and G only in that we used 50% en in water). The reaction is accelerated by Co^{2+}, but when H$_2$O$_2$ is present, the half-life is longer than 2 h. Reaction does eventually set in, but of course H$_2$O$_2$ is in time consumed by en.

Our interest has extended also to the kinetic data reported by Busch et al.[4] In attempting to reproduce the results of some of their experiments, (pH 10, 35 °C; see Table II of ref 4) we find, as they reported, that the reaction is first order in Co(PDTA)$^-$. However, our values of k_{obsd} are smaller than theirs by almost a factor of 2, and we observe a short induction period in the reaction. Moreover, when S$_2$O$_8^{2-}$ at $\sim 10^{-2}$ M is present, the rates are decreased by a factor of at least 10 and by an even larger factor when H$_2$O$_2$ is added. When argon is passed through the reaction mixture, the rates of reaction are increased. We infer therefore that the kinetics reported[4] apply to the reaction of Co(PDTA)$^-$ with en as catalyzed by Co^{2+}. We infer furthermore that Co^{2+} is not necessarily adventitious but that it is maintained at a steady state, being produced by the reduction of Co(III) by en and scavenged by O$_2$. At any rate, we believe that the intrinsic rate of the direct reaction of en with Co(PDTA)$^-$ was not being studied by Busch et al.[4]

From these observations, we conclude that the results on retention of chirality which have been reported apply to the reaction catalyzed by Co^{2+}; i.e., they speak to chiral discrimination in the reaction of Co(PDTA)$^-$ with Co(en)$_3^{2+}$ and *not* to direct replacement of PDTA by en as has been assumed. It is obvious that the large degree of discrimination has important implications as to the detailed geometry of the activated complex for electron transfer.

Acknowledgment. Support of this work by National Science Foundation Grant No. CHE79-08633 is gratefully acknowledged.

Registry No. (–)-Co(*d*-PDTA)$^-$, 78854-20-3; en, 107-15-3.

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(1) Geselowitz, D. A.; Taube, H. *J. Am. Chem. Soc.* **1980**, *102*, 4525.

(2) Busch D. H.; Cooke, D. W.; Swaminathan, K.; Im, Y. A. "Advances in the Chemistry of Coordination Compounds"; Macmillan: New York, 1961; p 139.

(3) Busch, D. H.; Swaminathan, K. *J. Inorg. Nucl. Chem.* **1961**, *23*, 150.

(4) Busch, D. H.; Swaminathan, K.; Cooke, D. W. *Inorg. Chem.* **1962**, *1*, 260.

(5) Irving, H.; Gillard, R. D. *J. Chem. Soc.* **1961**, 2249.

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Catalytic Isomerization of Alkenes by Palladium(II) Compounds. An Alternative Mechanistic View

Sir:

The catalytic isomerization of alkenes by Pd(II) compounds, especially Pd(PhCN)$_2$Cl$_2$ (**1**), has been the subject of a number of mechanistic studies.[1] The commonly postulated mechanism involves the oxidative addition of an allylic C–H bond to the Pd(II) catalyst to produce a palladium(IV) allyl hydride species, **2**, as outlined in Scheme I(A). However, Pd(IV) constitutes a rare and unstable oxidation state for palladium,[2] and in view of the pronounced electrophilicity of Pd(II) compounds which lack strongly basic ligands (e.g., PR$_3$),[3] such an oxidative addition step appears unlikely. Moreover, we have observed that the catalytic isomerization of alkenes proceeds

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(1) (a) Harrod, J. F.; Chalk, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 3491. (b) Cramer, R.; Lindsey, R. V. *Ibid.* **1966**, *88*, 3534. (c) Bingham, D.; Hudson, B.; Webster, D. E.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* **1974**, 1521.

(2) Hartley, F. R. "The Chemistry of Platinum and Palladium"; Wiley: New York, 1973.

(3) For numerous examples attesting to the electrophilicity of Pd(II) compounds, see: Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer-Verlag: New York, 1980.

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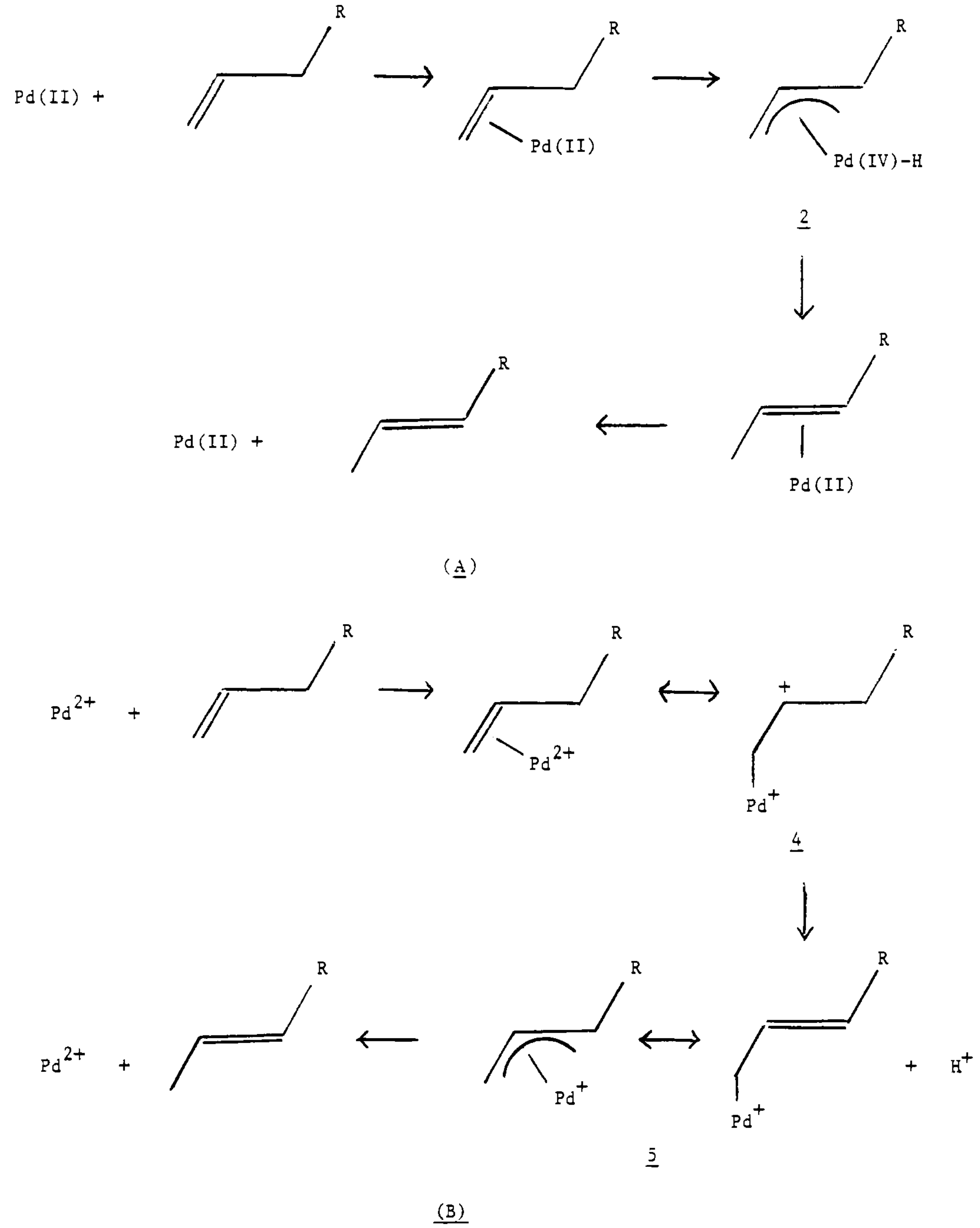
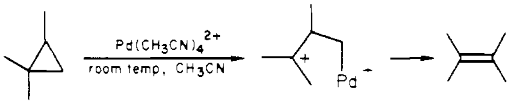
Scheme I



faster with the more electrophilic compound $[Pd(CH_3CN)_4](BF_4)_2$ (**3**) compared to **1**. Therefore, for reasons discussed below, we believe that the alternative mechanism outlined in Scheme I(B) is more consistent with the observed chemistry of Pd(II) compounds which do not have strongly basic ligands.

The key intermediate in the second mechanism is the incipient carbonium ion, **4**, generated through the interaction of the alkene with Pd(II) center. Loss of H^+ from **4** would yield **5**, the proton then cleaving the Pd–C bond in a well-precedented step[4] to produce the isomerized alkene and regenerating the catalyst. The formation of **5** and H^+ from alkene and Pd(II) may be visualized as a heterolytic cleavage of C–H bond by Pd(II). The formation of products arising out of the rearrangement of carbonium ions generated by the heterolytic cleavage of C–C bonds of strained ring compounds by **1** is of course well-known.[5,6] Furthermore, if incipient carbonium ions are formed through the interaction of Pd(II) with alkenes, then electrophilic Pd(II) species should be capable of catalyzing the carbonium ion induced migration reactions of suitably substituted olefins. Indeed, **3** was found to catalyze the rearrangement of *tert*-butylethylene → tetramethylethylene at room temperature, in acetonitrile (Scheme II).[7] Tetramethylethylene was also the major product in the reaction of 1,1,2-trimethylcyclopropane with **3** (eq 1).[7]



(1)

Because of the dissociation of H^+, the mechanism outlined

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(4) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 243.

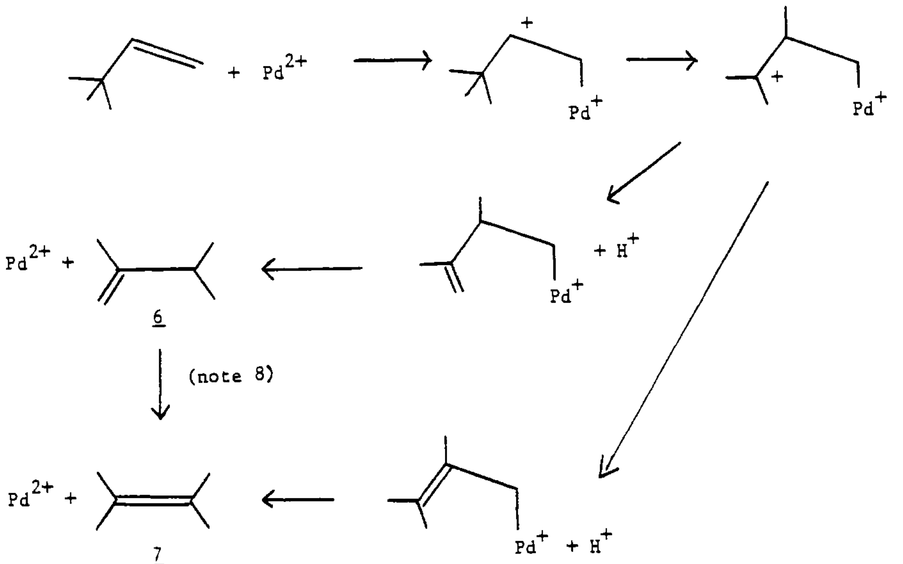
(5) Reference 3; Chapter IV, section 14.

(6) Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 6366.

(7) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627.

(8) In a separate experiment, **3** in acetonitrile was found to catalyze the rapid isomerization of 2,3-dimethyl-1-butene (**6**) to tetramethylethylene (**7**).

Scheme II



in Scheme I(B) should lead to the formation of significant amounts of crossover products, especially in polar solvents. On the other hand, no crossover products are expected if the catalytic isomerization proceeds through a palladium(IV) allyl hydride mechanism (Scheme I(A)). Now, it has been reported[1c] that in the **1**-catalyzed isomerization of pent-1-ene to pent-2-enes, significant amounts (>15%) of pent-2-ene-d_1 and pent-2-ene-d_3 were formed, starting with pent-1-ene-*1,2*-d_2 *even though the reaction was carried out in benzene.* Similar amounts of crossover products were also observed[1a] when a 1:1 mixture of pent-1-ene and hept-1-ene-*3,3*-d_2 was isomerized in the presence of **1** in benzene. These observations would seem to support the mechanism involving heterolytic cleavage of a C–H bond of the olefin (Scheme I(B)).[9]

In conclusion, it appears that incipient carbonium ions may be generated by the interaction of olefins with electrophilic transition-metal centers, and such species may play an important role in transition-metal-catalyzed isomerization of olefins.

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[9] We have now succeeded in isolating a cationic Pd(II) allyl compound of the type **5**, formed by the heterolytic cleavage of the allylic C–H bond of the olefin by **3**, as postulated in Scheme I(B).

Additions and Corrections

1981, Volume 20

Henry W. Choi and E. L. Muetterties*: Catalytic Carbon Monoxide Hydrogenation with $Os_3(CO)_{12}$ and Boron Tribromide.

Page 2664. In the right column, sixth line from the bottom, $Os_2(CO)_6Br$ should read $Os_2(CO)_6Br_4$.

Page 2665. In Table I, for C_2H_6, the last column entry of 0 should read 12.—Henry W. Choi