fore must be intramolecular. Rapid *cis–trans* exchange was also observed in deuteriochloroform solutions of (NOR)Rh(S–DBM) to which varying amounts of DMSO were added. Careful line-shape measurements at −36° indicated the rearrangement to be first order in added DMSO. It thus may be concluded that in the presence of the donor molecule DMSO, either as a solvent or added ligand, the intramolecular rearrangement of (diolefin)Rh(S–DBM) complexes proceeds *via* a five-coordinate intermediate. On the basis of the present evidence, however, it is not possible to distinguish among mechanisms 1, 2, and 3 in the solvents which are, at best, poor nucleophiles.

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[24] (a) National Science Foundation Predoctoral Fellow, 1968–present; (b) Alfred P. Sloan Research Fellow, 1968–1970.

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Addition Reactions on Coordinated Olefinic Ligands. III. *trans* Addition of a Nucleophile to a Platinum(II) Coordinated Simple Olefin

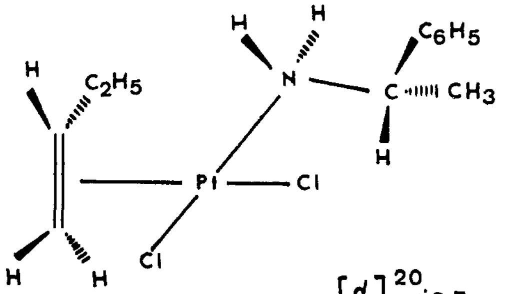
Sir:

It is well known[1] that coordination to platinum-group metals yields simple unsaturated hydrocarbons susceptible to attack by nucleophiles. Studies of the mechanism of this type of reactions have been carried out, mainly on catalytic systems.[2] Noncatalytic processes have also been reported and observations on the mechanism presented[3] in some cases. A double role has been generally attributed to the metal,[4] which is assumed to activate *both* the unsaturated substrate and the nucleophile, *via* coordination.

In fact, kinetic results[5] for the oxidative hydrolysis of simple olefins are consistent with *cis* addition to the unsaturated ligand of a precoordinated nucleophile. Furthermore, the presence of the nucleophile as a ligand in a rearranging intermediate is in accord with the general observation, recently pointed out,[6] that coordination should assist a reaction in which a nucleophilic reagent attacks a ligand.

On the other hand, no coordination of the nucleophile is involved when the reacting substrate is a diene complex: the stereochemical pattern of some of the reactions has been investigated[7] and the *exo* configuration[8] of the reaction products gave unambiguous evidence for a *trans*-addition mechanism. This difference in behavior between diene and simple olefin complexes has been discussed[9,10] on steric grounds.

It has been shown[11,12] in a previous study on the reactivity of coordinated olefins that stable alkyl derivatives are formed upon addition of ammonia and amines to Pd(II) and Pt(II) diene complexes and mono-olefin Pt(II) complexes. It has been found[11] that the reaction of an amine with a diene complex involves a *trans* addition, which utilizes the same steric pathway as the nucleophilic attacks quoted in ref 7. In the present investigation we examined the analogous reaction of diethylamine and ammonia with a resolved diastereoisomeric complex of a prochiral α olefin,[13] *i.e.*, of a substrate in which only one of the two nonsuperimposable faces of the unsaturated ligand is coordinated to the metal.



I $[\alpha]^{20}_{D}$ +2.7
c 0.1,acetone

The complex, (+)-*cis*-dichloro[(*S*)-1-butene][(*S*)-α-methylbenzylamine]platinum(II), $[\alpha]^{20}\text{D}$ +2.7° (*c* 0.1, acetone), was prepared by a procedure similar to that described[13] for the analogous propylene complex and resolved by consecutive fractional crystallization from acetone until constant rotation was obtained.

Anal. Calcd for $C_{12}H_{19}NCl_2Pt$: C, 32.51; N, 3.16; Pt, 44.01. Found: C, 32.72; N, 3.19; Pt, 44.32.

Assignment of the absolute configuration to the coordinated 1-butene has been made on the basis of a previous X-ray analysis[14] on an analogous diastereoisomeric complex and of the CD spectrum of I, which is reported in Figure 1. More precisely the assignment was made on the basis of the sign of the 27,000-cm^{-1} band, which has been correlated[15] to the configuration of the coordinated olefin.[16] The reaction of diethyl-

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[1] See, as early reports (a) J. Smidt, W. Hafner, R. Jira, and J. Sedlmeier, *Angew. Chem.*, **71**, 176 (1959); (b) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **133**, 377 (1960); (c) E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, 370 (1961); (d) J. S. Anderson, *J. Chem. Soc.*, 971 (1934).

[2] See, for a review, J. Halpern, *Advan. Chem. Ser.*, No. **70**, 1 (1968).

[3] (a) E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, 370 (1961); (b) E. W. Stern, *ibid.*, 111 (1963); (c) J. Tsuji and K. Ohno, *Advan. Chem. Ser.*, No. 70, 155 (1968), and references therein; for hydride attack on an iron π complex, see M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, 1, 58 (1963).

[4] This is certainly the case in the reactions which involve a *cis* ligand insertion mechanism, see P. Cossee, *Recl. Trav. Chim. Pays-Bas*, **85**, 1151 (1966).

[5] For a review, see P. M. Henry, *Advan. Chem. Ser.*, No. **70**, 126 (1968).

[6] M. M. Jones, "Ligand Reactivity and Catalysis," Academic Press, New York, N. Y., 1968, pp 84–85.

[7] (a) J. K. Stille and R. A. Morgan, *J. Amer. Chem. Soc.*, **88**, 5135 (1966); (b) M. Green and R. I. Hancock, *J. Chem. Soc. A*, 2054 (1967); (c) L. I. Dahl and W. Oberhansli, *Inorg. Chem.*, 4, 629 (1965); (d) W. A. Whitla, H. M. Powell, and M. L. Venanzi, *Chem. Commun.*, 310 (1966); (e) J. K. Stille and D. B. Fox, *Inorg. Nucl. Chem. Lett.*, **5**, 157 (1969).

[8] Only in one case has a *cis* addition been reported, see C. B. Anderson and B. J. Burreson, *Chem. Ind.* (London), 620 (1967).

[9] B. L. Shaw, *Chem. Commun.*, 464 (1968).

[10] F. R. Hartley, *Nature*, **223**, 615 (1969).

[11] R. Palumbo, A. De Renzi, A. Panunzi, and G. Paiaro, *J. Amer. Chem. Soc.*, **91**, 3874 (1969), part I in the series.

[12] A. Panunzi, A. De Renzi, R. Palumbo, and G. Paiaro, *ibid.*, **91**, 3879 (1969), part II in the series.

[13] A. Panunzi and G. Paiaro, *ibid.*, **88**, 4843 (1966), and literature cited therein.

[14] E. Benedetti, P. Corradini, and C. Pedone, *J. Organometal. Chem.*, **18**, 203 (1969).

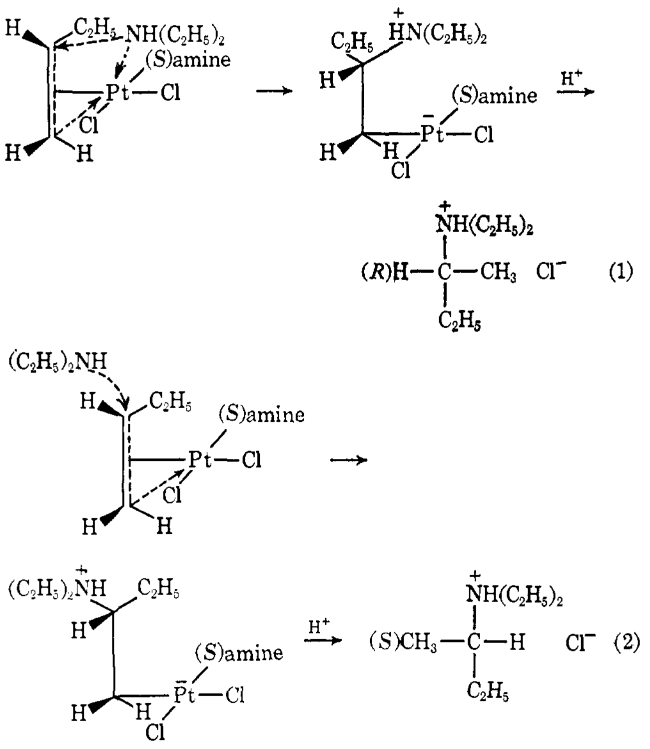
[15] (a) P. Corradini, G. Paiaro, A. Panunzi, S. F. Mason, and G. H. Searle, *J. Amer. Chem. Soc.*, **88**, 2863 (1966); (b) E. Premuzic and A. I. Scott, *Chem. Commun.*, 1078 (1967); (c) A. D. Wrixon, E. Premuzic, and A. I. Scott, *ibid.*, 639 (1968); (d) A. I. Scott and A. D. Wrixon, *ibid.*, 1184 (1969).

[16] Data from a X-ray analysis on the complex I confirm the absolute

amine with I has been obtained by adding the amine (0.731 g, 0.01 mol) as a 0.2 *M* acetone solution to a stirred ice-cold solution of the complex (4.433 g, 0.01 mol) in the same solvent. The crude alkyl derivative[17] obtained after removal of the solvent was stirred with 37% HCl at room temperature for about 3 hr. The acid hydrolysis gave N,N′-diethyl-*sec*-butylamine hydrochloride in 40% yield, calculated on the starting π complex. The free amine was obtained by means of alkali treatment and purified by gas-chromatographic preparative methods: the identification was made on the basis both of the retention time and of the ir spectrum, compared with those of an authentic sample.

The N,N′-diethyl-*sec*-butylamine obtained by the reaction was the dextrorotatory enantiomer, which has the *S* configuration,[18] with a high optical purity ($[\alpha]^{15}\text{D}$ +85.1°, lit.[19] $[\alpha]^{15}\text{D}$ +89.3°). Scheme I shows a *cis* (eq 1) and a *trans* addition (eq 2) as possible steric paths for the nucleophilic attack. In eq 1 the precoordination of the nucleophile is simply shown as the formation of a pentacoordinated intermediate: it is obvious that the reaction of *any* intermediate containing the nucleophile in *any* given coordination site will yield the same stereochemical result, *i.e.*, the (−)-(*R*)-N,-N′-diethyl-*sec*-butylamine. A *trans* addition will ultimately lead, on the other hand, to the dextrorotatory enantiomer, as has been found.

Scheme I



The reaction of I with ammonia was performed under the same experimental conditions described for the diethylamine reaction. Ammonia, however, was introduced as a gas in the reaction vessel containing the acetone solution of I. Hydrolysis of the reaction product gave in this case *sec*-butylamine as the main product as well as small amounts of other butylamines.[20] The *sec*-butylamine was isolated through preparative gas chromatography and appeared to be the positive enantiomer, $[\alpha]^{15}\text{D}$ +7.56° (lit.[19] $[\alpha]^{15}\text{D}$ +7.80°). This enantiomer has the *S* configuration.[18]

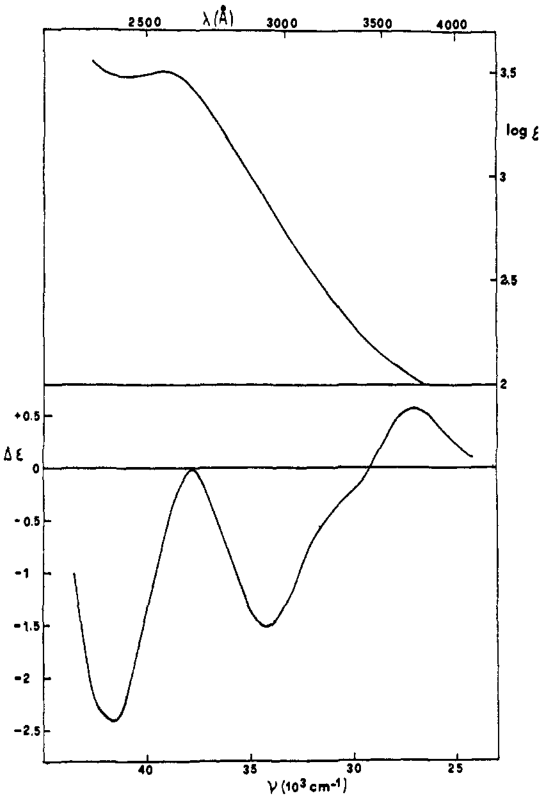


Figure 1. The electron absorption and circular dichroism spectra of complex I in ethanol solution.

These results give straightforward and unambiguous evidence that in the case reported the attack does *not* involve intramolecular rearrangement of an intermediate containing the attacking nucleophile as a coordinated ligand: only the unsaturated substrate has been activated *via* coordination on the metal.

Acknowledgment. This work was performed with the financial support of the Italian Consiglio Nazionale delle Ricerche (CNR).

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configurational assignment: C. Pedone and E. Benedetti, private communication.

[17] The subsequent demolition reaction indicates that the addition product appears of the same type as those obtained in addition reactions of amines with complexes containing α olefins and phosphine donors (see ref 12). It is worth mentioning that in this case stabilizing π ligands are not present. Furthermore the attack direction is different in the two cases. In fact, attack of diethylamine on *cis*-dichloro(1-butene)(tri-*n*-butylphosphine)platinum(II) leads to an equimolecular mixture of N,N′-diethyl-*n*-butylamine and N,N′-diethyl-*sec*-butylamine.

[18] A. Kjaer and S. H. Hanson, *Acta Chem. Scand.*, **11**, 898 (1957).

[19] W. Leithe, *Ber.*, **63**, 804 (1930).

[20] The multiple alkylation of ammonia in the presence of coordinated olefins has been discussed in a previous paper,[12] where analogous addition reactions with phosphine-containing complexes were reported.

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Preparation and Structure of a Novel Tetracyanoethylene Complex of Iridium

Sir:

Whereas the reactions of a number of activated olefins with the hydrido complexes $IrH(CO)(PPh_3)_3$,[1]