t-butyl alcohol was added 2.25 g (0.02 mol) of powdered potassium *t*-butoxide, and the resulting mixture was heated at reflux for 12 hr. After the addition of 100 ml of ether, the solution was washed with two 50-ml portions of water and dried. The solvent was evaporated to give 365 mg (42.5%) of **14**, mp 75–78° (from pentane); $\nu_{max}^{CCl_4}$ 1300, 1165, and 1110 cm^{-1} (–SO$_2$–); $\delta_{TMS}^{CHCl_3}$ 4.10 (multiplet, 1 H, >CHO–), 2.80 (broad absorption, 2 H, >C*H*SO$_2$–), 2.00 (multiplet, 8 H, –CH$_2$–), and 1.18 (singlet, 9 H, *t*-butyl group).

Anal. Calcd for $C_{11}H_{20}O_3S$: C, 56.40; H, 8.95; S, 13.81. Found: C, 56.25; H, 8.54; S, 13.98.

***endo*-2-Hydroxy-8-thiabicyclo[3.2.1]octane 8,8-Dioxide (15).** A 269-mg (1.16 mmol) sample of **14** was refluxed in 10 ml of hydrobromic acid (47–49%) for 10 hr. Work-up in the predescribed manner yielded 104 mg (51%) of **15**, mp 295–297° (from ethyl acetate–pentane); $\nu_{max}^{CHCl_3}$ 3400 (–OH), 1300, 1155, and 1105 cm^{-1} (–SO$_2$–).

Anal. Calcd for $C_7H_{12}O_3S$: C, 47.73; H, 6.81; S, 18.21. Found: C, 47.73; H, 6.88; S, 18.00.

Oxidation of 50 mg of **15** with Jones' reagent as above yielded 39 mg of 2-oxo-8-thiabicyclo[3.2.1]octane 8,8-dioxide (**16**), mp 256–258° (from chloroform–hexane); $\nu_{max}^{CHCl_3}$ 1727 (>C=O), 1320, 1150, and 1110 cm^{-1} (–SO$_2$–).

1-Chlorosulfonyl-9-thiabicyclo[3.3.1]nonane 9,9-Dioxide (20). To a solution of 5.0 g (0.029 mol) of **19**[8a,b] in 200 ml of ether was added dropwise with stirring under nitrogen 28 ml of 1.6 *M* (0.045 mol) *n*-butyllithium in hexane. The yellow solution was stirred at room temperature for 10 min and was then added to 25 ml of sulfuryl chloride cooled to 0°. The resulting mixture was stirred at room temperature for 1 hr and the ether and excess sulfuryl chloride were removed *in vacuo*. Methylene chloride (200 ml) was added and the organic phase was washed with water (two 100-ml portions), dried, and concentrated to a volume of 50 ml. An equal volume of hexane was added and the solution was cooled overnight at 0°. There was obtained 2.3 g (28.4%) of **20** as white crystals, mp 163–165°, from chloroform–hexane; $\nu_{max}^{CHCl_3}$ 1380, 1170 (–SO$_2$Cl), 1325, and 1135 cm^{-1} (–SO$_2$–).

1-Chloro-9-thiabicyclo[3.3.1]nonane 9,9-Dioxide (21). A 1.5-g (7.2 mmol) sample of **20** was placed in a sublimation apparatus and was heated at 160° (0.05 mm). As decomposition occurred, the chloro sulfone (660 mg, 59%) sublimed. Recrystallization of this material from ethyl acetate provided the analytical sample, mp 229–231° (sealed tube); $\nu_{max}^{CHCl_3}$ 1312, 1120, and 1110 cm^{-1} (–SO$_2$–); $\delta_{TMS}^{CDCl_3}$ 3.30 (multiplet, 1 H, >C*H*SO$_2$–) and 2.40 (multiplet, 12 H, –CH$_2$–).

Anal. Calcd for $C_8H_{13}ClO_2S$: C, 46.05; H, 6.23; Cl, 17.00; S, 15.37. Found: C, 45.96; H, 6.27; Cl, 17.04; S, 15.35.

$\Delta^{1,5}$-Bicyclo[3.3.0]octene (27). To a solution of 2.0 g (0.036 mol) of potassium hydroxide in 100 ml of water was added 1.25 g (6.0 mmol) of **21** and the mixture was refluxed for 48 hr. The reaction mixture was cooled, pentane (50 ml) was added, and the precipitate was filtered and dried. There was recovered 310 mg (25%) of **21**. The pentane layer was dried and carefully fractionated to give 490 mg (75%) of **27**, whose spectra were identical with those of an authentic sample.[34]

1-Chlorosulfonyl-8-thiabicyclo[3.2.1]octane 8,8-Dioxide (23). A 5.9-g (0.037 mol) sample of **22** in 200 ml of ether was treated with 30 ml of 1.6 *M n*-butyllithium in hexane and then 35 ml of sulfuryl chloride as previously described. There was obtained 5.8 g (62%) of **23**, mp 133–135° (from ethyl acetate–pentane); $\nu_{max}^{CHCl_3}$ 1380, 1170 (–SO$_2$Cl), 1150, and 1117 cm^{-1} (–SO$_2$–).

Anal. Calcd for $C_7H_{11}ClO_4S_2$: C, 32.50; H, 4.25. Found: C, 32.32; H, 4.16.

1-Chloro-8-thiabicyclo[3.2.1]octane 8,8-Dioxide (24). A 1.0-g (3.86 mmol) sample of **23** was placed in a sublimation apparatus and was heated at 150° (0.05 mm). The solid rapidly decomposed and **24** sublimed as it was produced. There was obtained 620 mg (85%) of **24**, mp 194–196° (sealed tube) after recrystallization from ethyl acetate; $\nu_{max}^{CHCl_3}$ 1312, 1150, and 1120 (–SO$_2$–); $\delta_{TMS}^{CDCl_3}$ 3.25 (multiplet, 1 H, >C*H*SO$_2$–) and 2.20 (multiplet, 10 H, –CH$_2$–).

Anal. Calcd for $C_7H_{11}ClO_2S$: C, 43.20; H, 5.65; S, 16.48. Found: C, 43.27; H, 5.70; S, 16.49.

Acknowledgment. This work was supported in part by the National Science Foundation, Grant GP-2939. The authors are indebted to Mr. J. C. Philips for his preliminary efforts on this problem and to Dr. E. Block who, prior to the completion of this work, made us aware of a somewhat parallel study he had performed at an earlier data.

[34] E. Block, Ph.D. Thesis, Harvard University, 1967.

Addition Reactions on Coordinated Olefinic Ligands. I. The Reactions of Amines with Diene Complexes of Platinum(II) and Palladium(II)

Rosario Palumbo, Augusto De Renzi, Achille Panunzi, and Gastone Paiaro

Contribution from the Istituto Chimico, Laboratorio di Chimica Generale e Inorganica dell'Università di Napoli, Naples, Italy.

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Abstract: A new nucleophile addition reaction to dienes coordinated to platinum(II) or palladium(II) was studied. Ammonia and aliphatic primary and secondary amines reacted smoothly with the diene π complexes to give derivatives containing carbon–metal σ bonds. The behavior of 1,5-cyclooctadiene, norbornadiene, 1,5-hexadiene, and 4-vinylcyclohexene complexes was investigated. Structural assignments were made on the basis of degradative studies. Data on the stereochemistry of the addition were also obtained.

Growing interest and investigations are centered on reactions involving ligands coordinated to transition metals. In this area, peculiar interest for reactions on unsaturated ligands stems from the importance of several catalytic processes which involve alkenes and polyenes.[1] A well-known reaction, for instance, is the addition of a nucleophilic agent to coordinated dienes in platinum(II)[2] and palladium(II)[3] complexes. Actually

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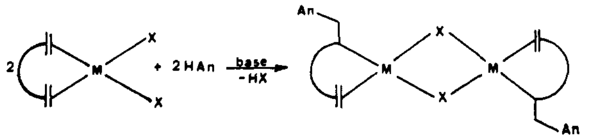
[1] See, for an excellent review on this area: J. P. Candlin, K. A. Taylor, and D. T. Thompson: "Reactions of Transition-Metal Complexes," Elsevier Publishing Co. Amsterdam, 1968.

[2] (a) K. A. Hoffmann and J. V. Narbutt, *Chem. Ber.*, **41**, 1625 (1908); (b) J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 2496 (1957).

[3] J. Chatt, L. M. Vallarino, and L. M. Venanzi, *ibid.*, 3413 (1957).

one of the first reactions studied was the reaction of an alkoxy group with a diene coordinated to platinum(II).[2a] The chemistry of this reaction was subsequently clarified by Chatt, *et al.*, [2b] who proved the reaction products to be binuclear metal alkyl derivatives.

Nmr and X-ray investigations[4] led to elucidation of the stereochemistry of several addition products obtained from *endo*-dicyclopentadiene, 1,5-cyclooctadiene, dipentene, and norbornadiene complexes. On the ground of these stereochemical data, the mechanism of reaction of the alkoxy group was interpreted[4a] as a *trans* addition across the double bond. The mechanism pattern has been recently examined[5] in a brief comparative study of diene and simple olefin complexes. The studies on the subject were extended to other nucleophiles and reactions of diene complexes with silver acetate and species producing carbanions were reported.[6] In each case, indicating as HAn such species, the general reaction scheme was of the type represented by the schematic eq A.



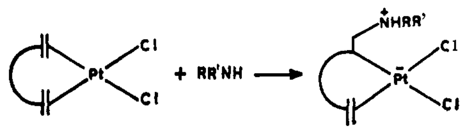
(A)

In a preliminary account[7] from this laboratory it was reported that addition can also take place when the attacking nucleophile is a neutral molecule, *i.e.*, an amine. The present work is an extension of our previous investigations[8] on the relationship between simple and stable molecular models and the homogeneous catalytic processes involving unsaturated substrates.

In this paper we describe a detailed investigation of the reaction of diene complexes of platinum(II) with primary aliphatic amines. Data on the reactions with ammonia and secondary and tertiary amines are also reported. The behavior of diene palladium(II) complexes is preliminarily examined.

Results and Discussion

Reactions of Platinum(II) Complexes of 1,5-Hexadiene and 4-Vinylcyclohexene. The type of products obtainable by reaction between equimolar amounts of amine and of a complex of general formula dichloro-(diene)platinum(II) is related to the type of coordinated diene. A common behavior was shown by the complexes of an open-chain diene (1,5-hexadiene) and of a diene containing only one endocyclic double bond and a vinyl bond (4-vinylcyclohexene). In both cases the reaction went to substantial completion to give a product containing an amine unit per metal atom. The process is schematically represented by the following equation, when a primary or secondary amine or ammonia is used.



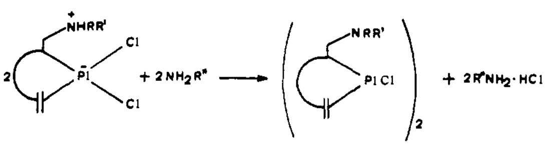
(B)

I II

IIa–d, diene = 1,5-hexadiene
IIe–h, diene = 4-vinylcyclohexane
IIa, e, R = H; R' = H
IIb, f, R = H; R' = C_2H_5
IIc, g, R = H; R' = $C_6H_5(CH_3)CH$
IId, h, R = C_2H_5; R' = C_2H_5

The reaction of dichloro(1,5-hexadiene)platinum(II) with an equimolar amount of triethylamine was also examined, but no conclusive evidence of addition was obtained.

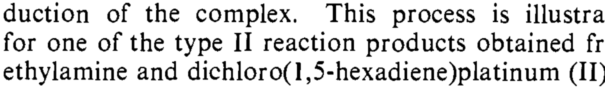
When a primary or a secondary amine is used, product II can further react in the presence of base (*e.g.*, an alkali carbonate) with loss of hydrochloric acid. An equimolar amount of the same (or a different) amine can be used as the dehydrohalogenating agent. A binuclear product is formed according to the schematic eq C.



(C)

II III

Molecular Structure of the Type II Alkyl Derivatives. Type II products contain a carbon–platinum σ bond, formed upon addition of amine to one coordinated double bond. No precipitation reactions with heavy anions as $PtCl_4^{2-}$, $[Pt(C_2H_4)Cl_3]^-$, and $B(C_6H_5)_4^-$ could be obtained from the complexes. Chemical evidence for the above-reported formulation can be achieved by destructive reduction of the complexes in THF solution with hydrogen or $NaBH_4$. The corresponding substituted amine is formed. For instance, the type II product formed by reaction of equimolar amounts of ethylamine and dichloro(4-vinylcyclohexene)platinum(II) gave, on reduction, N-ethyl-2-cyclohexylethylamine as reported below.



(D)

It was also found that boiling a type II product with 37% HCl and successive treatment (of the obtained water-soluble complex) with cyanide ion gave a substituted amine, still containing a double bond, which on reduction gave the same amine obtained by direct reduction of the complex. This process is illustrated for one of the type II reaction products obtained from ethylamine and dichloro(1,5-hexadiene)platinum (II).

It is interesting to compare the platinum(II) complexes of unsaturated amines described by Venanzi, *et al.*,[9] with species II and III. In particular, it is worth mentioning that electronic spectra for the type II complexes and the quoted monomeric species containing a quaternary ammonium group are similar. Furthermore, the infrared spectra of the complexes support the

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(4) (a) J. K. Stille and R. A. Morgan, *J. Am. 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 L. M. Venanzi, *Chem. Commun.*, 310 (1966).

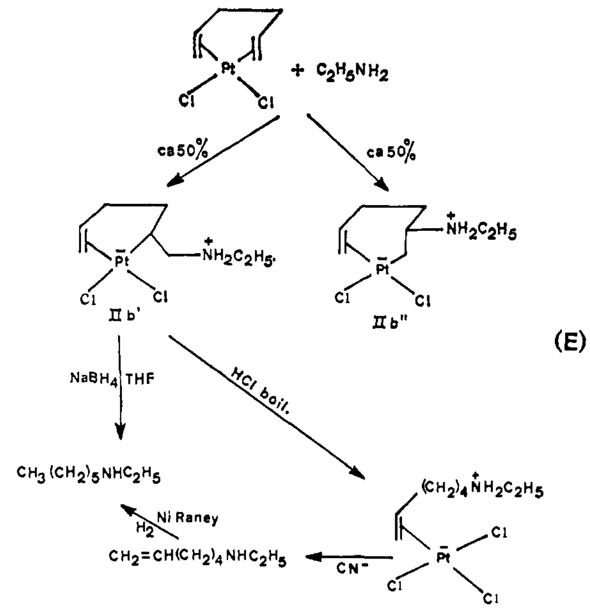
(5) B. L. Shaw, *ibid.*, 464 (1968).

(6) (a) C. B. Anderson and B. J. Burreson, *J. Organometal. Chem.* (Amsterdam), **7**, 181 (1967); (b) H. Takahashi and J. Tsuji, *J. Am. Chem. Soc.*, **90**, 2387 (1968); (c) B. F. G. Johnson, J. Lewis, and M. S. Subramanian, *Chem. Commun.*, 117 (1966).

(7) G. Paiaro, A. De Renzi, and R. Palumbo, *ibid.*, 1150 (1967).

(8) (a) G. Paiaro and A. Panunzi, *J. Am. Chem. Soc.*, **86**, 5148 (1964); (b) A. Panunzi and G. Paiaro, *ibid.*, **88**, 4843 (1966); (c) A. Panunzi, A. De Renzi, and G. Paiaro, *Inorg. Chim. Acta*, **1**, 475 (1967).

(9) (a) R. G. Denning and L. M. Venanzi, *J. Chem. Soc.*, 3241 (1963); (b) D. V. Claridge and L. M. Venanzi, *ibid.*, 3419 (1964).



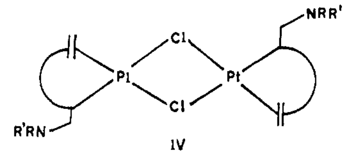
(E)

presence of a quaternary ammonium group, showing in the 3300–2400-cm.$^{-1}$ region the complex band structure which has been reported for the unsaturated amine complexes.

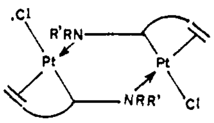
As reported below, the behavior of the addition products upon reaction with bases is also in agreement with a type II structure.

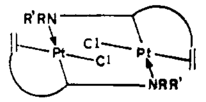
Molecular Structure of the Dimeric Derivatives of Type III. As noted previously, a loss of hydrochloric acid by complex II led, in the case of the less rigid dienes, to binuclear species. A destructive reduction of the binuclear type complex afforded the same higher substituted amine, which could be obtained from the corresponding type II derivative.

On the ground of analyses and molecular weights, structures IV, V, and VI are possible in principle. It is understood that the following molecular models are only schematic.



IV





V VI

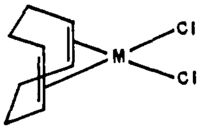
The binuclear species reacted readily at room temperature with methanolic hydrochloric acid to give the type II species, but the uptake of HCl was not immediate, as it should be for IV. The complexes did not react by splitting with *p*-toluidine in chloroform at room temperature. This reaction is described[2b] as a distinctive one for chlorine-bridged platinum(II) binuclear species. Furthermore, the NH stretching frequencies for a noncoordinated secondary amine group (as present in IV) are generally observed[9b] around 3290 cm^{-1}. The coordination to the metal is reported to shift this band about 80 cm^{-1} toward lower energies. Infrared spectra of the binuclear species show NH stretching around 3215 cm^{-1}.

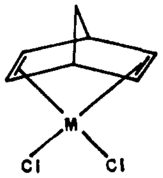
A choice between the two possible amine-bridged structures can be made on the basis of quoted observations[4d] on the relative effectiveness of a σ carbon–platinum bond and a π-coordinated double bond as *trans*-labilizing ligands. Structure VI is favored on this ground, owing to the stronger *trans* effect claimed for the σ bond.

Electronic spectra of the binuclear species deriving from either 1,5-hexadiene or 4-vinylcyclohexene complexes show an intense (ϵ 8000–10,000) absorption peak at about 380 and 345 mμ. This band is a charge-transfer band, which by comparison with the spectral properties of *cis*- and *trans*-dichloro(olefin)(amine)platinum(II) complexes and of the quoted[9] unsaturated amine complexes, can be attributed to a strong platinum–platinum interaction. It is worth mentioning that molecular models show that such an interaction is possible only for a type VI structure. This type of structure appears to be sterically hindered when the attacking amine is diethylamine; actually the diethylamine derivative of the 4-vinylcyclohexene complex did not show a comparable band down to 250 mμ.

We wish finally to comment on the behavior of ethylamine derivatives of 1,5-hexadiene complex. As reported in reaction scheme E, two type II complexes are formed in an about 1:1 ratio, two different addition directions being involved. No binuclear species could be obtained by IIb'', while it was found that alkali removed hydrochloric acid from this product giving an unidentified material markedly different from a type III species. Treatment with alkali carbonate of the IIb' and IIb'' mixture led to a binuclear product which was originated only by IIb'. In fact, this product gave IIb' when treated with HCl. The binuclear derivative gave N-ethylhexylamine, as IIb' did, by destructive reduction. When the reduction was carried out on the IIb' and IIb'' mixture, both N-ethylhexylamine and N-ethyl-1-methylpentylamine formed. It should also be pointed out that no binuclear species could be obtained from the ammonia derivative in which the same addition direction as in IIb'' is involved. All these observations are consistent with a type VI structure for dimeric species. It is easy to see that in all cases in which binuclear species could not be obtained, type VI structures would be characterized by Pt–Pt distances of the same order of C–N distances.

Reaction of Platinum(II) and Palladium(II) Complexes of 1,5-Cyclooctadiene and Norbornadiene. The behavior of complexes of a diene containing the two double bonds either in a fused ring structure (norbornadiene) or in the same ring (1,5-cyclooctadiene) was also examined. The reaction products of these complexes are different from those given by complexes of less rigid dienes (*vide supra*).

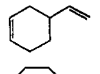
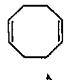
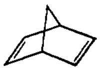




VII VIII

VII, VIII a M = Pt
VII, VIII b M = Pd

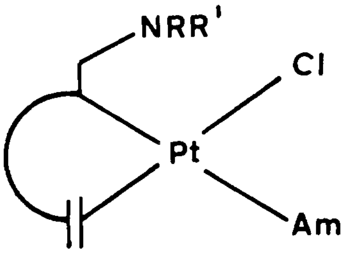
Table I. Higher Amines from the Reductive Destruction of the Addition Products[a]

Diene in the substrate	Amine used in the attack			
	NH_3	$C_2H_5NH_2$	$(C_2H_5)_2NH$	$C_6H_5CH(CH_3)NH_2$
	$CH_3(CH_2)_3CH(CH_3)NH_2$, 93%	$CH_3(CH_2)_3CH(CH_3)NHC_2H_5$, 45% $CH_3(CH_2)_5NHC_2H_5$, 48%	$CH_3(CH_2)_5N(C_2H_5)_2$, 92%	$CH_3(CH_2)_5NHCH(CH_3)C_6H_5$, 88%
	$C_6H_{11}(CH_2)_2NH_2$, 85%	$C_6H_{11}(CH_2)_2NHC_2H_5$, 92%	$C_6H_{11}(CH_2)_2N(C_2H_5)_2$, 90%	$C_6H_{11}(CH_2)_2NHCH(CH_3)C_6H_5$, 87%
	$C_8H_{15}NH_2$, 57%[b]	$C_8H_{15}NHC_2H_5$, 62%[b]	$C_8H_{15}N(C_2H_5)_2$, 53%[b]	$C_8H_{15}NHCH(CH_3)C_6H_5$, 60%[b]
				*exo*-$C_7H_{11}NHCH(CH_3)C_6H_5$, 45%[b]

[a] Results are referred to type II products for the less rigid dienes. [b] Yield is calculated on starting diene complex.

No mononuclear product of type II could be isolated by reaction of equimolar amounts of dichloro(1,5-cyclooctadiene)platinum(II) or dichloro(norbornadiene)platinum(II) and a primary amine. While unequivocal evidence of amine addition to the coordinated diene was obtained, the initially formed species (likely of type II) appeared to react, by elimination of HCl, with the amine faster than the starting diene complex. An equimolar amount of amine was actually not sufficient for the complete reaction of the diene complex, an excess of an equivalent being necessary. It must be noted that only about one-third of the excess amine was recovered, on washing the crude reaction product, as the hydrochloride. By the destructive reduction of the washed reaction product, together with the original amine, a new one was obtained which derives from the addition to the coordinated diene. For instance, by reducing the products of the reaction between diethylamine and VIIa, both diethylamine and N,N-diethylcyclooctylamine were obtained.

On the ground of the behavior of the less rigid diene complexes, a binuclear species should have formed in the presence of excess amine. Molecular models show that such a species in the case of rigid dienes is very likely an halogen bridged one (type IV). It is therefore expected that the excess of the amine is consumed in the fission of chlorine bridges of IV and partially is competitive with the amino groups of IV in neutralizing the eliminated hydrochloric acid. Mononuclear species of type IX appeared then conceivably to have formed.



IX

A question arises about the reason why a type II mononuclear species, which is isolated in the case of less rigid dienes, could not be obtained for the more rigid ones. This behavior can be rationalized by examining the molecular models, on the ground of the *exo* configuration proved for a norbornadiene derivative. Models show that only for less rigid dienes intramolecular interaction between the ammonium grouping and the platinum atom is possible. Such an interaction should involve a hydrogen of the ammonium grouping and the nonbonding electron density of the metal and it is likely to be responsible for the higher stability of type II derivatives of the less rigid dienes.

The 1,5-cyclooctadiene and the norbornadienepalladium(II) complexes, differently from the palladium(II) complexes of less rigid dienes, were sufficiently stable in the presence of amine to allow isolation of the addition products. The nature of these products appeared to be of the same type as the platinum(II) complexes. The addition of amine to one of the two coordinated double bonds was proved, as reported below for the platinum derivatives.

We notice finally that the described chemical behavior does not rule out the possibility that π-allylic structures might be involved in one or more of all prepared addition products. It must be noted however that the results[4a] of structural investigations on the related alkoxide addition products point against this possibility. A thorough nmr investigation was precluded by the lack of solubility of the type II species and the complexity of the spectra of the type III products.

Stereochemistry of the Addition. The stereochemistry of the addition to each of the four studied diene complexes was investigated by comparison between authentic samples and the substituted amines obtained by destructive reduction (as shown in reaction scheme D) of the addition products.

In Table I amines obtained from derivatives of the four diene complexes are listed. It can be seen that the diene structure as well as the substitution degree of the attacking amine are responsible for the addition direction. The addition of ammonia on the less rigid diene complex occurred on the second carbon atom of the vinyl group, thus indicating that only electronic effects were involved in that case. It is worth noticing that the configuration of the amine obtained from the derivative formed upon α-methylbenzylamine attack of the norbornadiene complex is of the same type reported[4a] for the alkoxy addition of the same complex.

Experimental Section

In the preparation and isolation procedures, all operations were carried out in nitrogen. Infrared spectra were determined in

Nujol and hexachlorobutadiene mulls on a Beckman IR-9 instrument. Electronic spectra were recorded on a Beckman DK2 spectrophotometer. Molecular weights were determined in chloroform solution with a Hitachi-Perkin-Elmer Model 115 apparatus. Melting points are uncorrected. Gas chromatographic analyses were carried out on a Fractovap GV chromatograph, using a 3-ft column packed with SE 30 on Chromosorb. Some of the elemental analyses were performed in this laboratory and others by Mikroanalitisches Laboratorium of the Max-Planck Institut für Köhlenforschung, Mülheim.

Materials. All solvents were distilled through a fractionation column after treatment with suitable drying agent and stored and handled in nitrogen. The other chemicals used were of Analar grade.

Diolefin Complexes. Dichloro(1,5-cyclooctadiene)platinum(II) and dichloro(norbornadiene)platinum(II) were obtained by the known method.[4a] Dichloro(4-vinylcyclohexene)platinum(II) was prepared by the Kuljian and Frye procedure.[10] Dichloro(1,5-hexadiene)platinum(II) was prepared by the Jensen[11] procedure. Dichloro(1,5-cyclooctadiene)palladium(II)[3] and dichloro(norbornadiene)palladium(II)[12] were prepared according to known methods.

Authentic Samples of Higher Substituted Amines. Cyclooctylamine could be purchased by Schuchardt. Authentic samples of the following amines were prepared by known procedures: 1-methylpentylamine,[13] 2-cyclohexylethylamine,[14] N-ethyl-2-cyclohexylethylamine,[15] N,N-diethyl-2-cyclohexylethylamine,[16] and N-ethyl- and N,N-diethylhexylamines.[17]

N-Ethyl-1-methylpentylamine was obtained as the hydrobromide by reaction at room temperature of ethylamine and 2-bromohexane in a closed tube. In similar way, N-ethyl- and N,N-diethylcyclooctylamine hydrobromides were obtained from cyclooctyl bromide and the corresponding simpler amine. The N-α-methylbenzylcyclooctylamine hydrobromide was obtained by reaction between cyclooctylamine and α-methylbenzyl bromide at 120° for 6 hr. N-*exo*-Norbornyl-α-methylbenzylamine, N-hexyl-α-methylbenzylamine, and N-α-methylbenzyl-2-cyclohexylethylamine were obtained as the hydrobromides by reactions of α-methylbenzylamine and the corresponding bromide at temperatures ranging between 90 and 120° (reaction periods: 2–4 hr).

Preparation of the Complexes IIa and IIe. To a stirred ice-cold solution of 3.0 g of dichloro(1,5-hexadiene)platinum (II) (0.0086 mol) in 40 ml of methylene chloride, gaseous ammonia (0.0086 mol) was added slowly from a gas buret. The precipitate was separated by filtration, washed with methylene chloride, and dried *in vacuo* to give IIa (2.8 g, yield, 89%). Recrystallization from boiling methanol gave 2.5 g of white crystals, mp 180–190° dec.

Anal. Calcd for $C_6H_{13}NCl_2Pt$: Pt, 53.4; C, 19.7; H, 3.55; N, 3.85. Found: Pt, 53.3; C, 19.5; H, 3.5; N, 3.7.

A similar procedure was used for the preparation of IIe (yield, 92%): white crystals, mp 185–195° dec.

Anal. Calcd for $C_8H_{15}NCl_2Pt$: Pt, 49.9; C, 24.5; H, 3.85; N, 3.6. Found: Pt, 49.5; C, 24.2; H, 3.7; N, 3.5.

Preparation of the Complexes IIb–d and IIf–h. To a stirred ice-cold solution of dichloro(4-vinylcyclohexene)platinum(II) (4.5 g, 0.012 mol) in 30 ml of methylene chloride, a cold solution of 0.54 g of ethylamine (0.012 mol) in 5 ml of the same solvent was added dropwise. The precipitate was collected by filtration, washed with methylene chloride, and dried *in vacuo* to give IIf (4.4 g, 87%). Recrystallization from boiling methanol gave 4.1 g of white crystals, mp 165–175° dec.

Anal. Calcd for $C_{10}H_{19}NCl_2Pt$: Pt, 46.5; C, 28.6; H, 4.55; N, 3.35. Found: Pt, 46.6; C, 28.5; H, 4.5; N, 3.2.

Similar procedures were used for the preparation of IIb′ and IIb″ mixture: white crystals (yield, 88%).

Anal. Calcd for $C_8H_{17}NCl_2Pt$: Pt, 49.6; C, 24.4; H, 4.35; N, 3.55. Found: Pt, 49.5; C, 24.2; H, 4.3; N, 3.4.

IIc: white crystals, mp 155–165° dec (yield, 85%).

Anal. Calcd for $C_{14}H_{21}NCl_2Pt$: Pt, 41.6; C, 35.8; H, 4.5; N, 2.95. Found: Pt, 41.6; C, 35.7; H, 4.4; N, 2.8.

IId: white crystals, mp 170–178° dec (yield, 90%).

Anal. Calcd for $C_{10}H_{21}NCl_2Pt$: Pt, 46.3; C, 28.5; H, 5.0; N, 3.3. Found: Pt, 46.0; C, 28.6; H, 4.9; N, 3.1.

IIg: white crystals, mp 160–170° dec (yield, 85%).

Anal. Calcd for $C_{16}H_{23}NCl_2Pt$: Pt, 39.4; C, 38.8; H, 4.65; N, 2.8. Found: Pt, 39.4; C, 38.9; H, 4.6; N, 2.6.

IIh: white crystals, mp 165–175° dec (yield, 82%).

Anal. Calcd for $C_{12}H_{23}NCl_2Pt$: Pt, 43.6; C, 32.2; H, 5.15; N, 3.15. Found: Pt, 43.5; C, 32.0; H, 5.1; N, 3.0.

Preparation of the Complexes IIIb–d.[18] The complex IIc (1.0 g, 0.0021 mol) was suspended in methanol (30 ml) with anhydrous sodium carbonate (0.5 g, 0.005 mol). The mixture was stirred at room temperature for 0.5 hr. The resulting yellow solution was filtered and the solvent evaporated *in vacuo*. The residue was crystallized from chloroform–petroleum ether (bp 30–60°) to give 0.8 g of yellow crystals (yield, 87%), mp 150–155° dec.

Anal. Calcd for $C_{28}H_{40}N_2Cl_2Pt_2$: Pt, 45.1; Cl, 8.2; N, 3.25; mol wt, 865.6. Found: Pt, 45.0; Cl, 8.4; N, 3.2; mol wt, 858.

When the reaction was made on the complex IId, using the same procedure above described, the crude product could not be recrystallized owing to extensive decomposition. In the case of the complex IIb only about one half of the used amount (2.0 g, 0.005 mol) dissolved. By concentration of the mother liquor and recrystallization of the residue from ethanol, IIIb (0.5 g, yield, 27.5%) was obtained as yellow crystals, mp 140–170° dec.

Anal. Calcd for $C_{16}H_{32}N_2Cl_2Pt_2$: Pt, 54.7; Cl, 9.9; N, 3.9; mol wt, 713.4. Found: Pt, 54.5; Cl, 10.1; N, 3.8; mol wt, 702.

Preparation of the Complexes IIIf–h. The procedure was similar to that used for the IIId complex except that the reaction was carried out at reflux for about 10 min, until complete dissolution of the starting complex occurred. The complexes were recrystallized from chloroform–petroleum ether.

IIIf: ivory-white crystals, mp 145–150° dec (yield, 74%).

Anal. Calcd for $C_{20}H_{36}N_2Cl_2Pt_2$: Pt, 51.0; Cl, 9.3; N, 3.65; mol wt, 765.6. Found: Pt, 50.8; Cl, 9.4; N, 3.5; mol wt, 752.

IIIg: cream crystals, mp 180–190° dec (yield, 68%).

Anal. Calcd for $C_{32}H_{44}N_2Cl_2Pt_2$: Pt, 42.5; Cl, 7.75; N, 3.05; mol wt, 917.8. Found: Pt, 41.9; Cl, 7.8; N, 3.0; mol wt, 905.

IIIh: white crystals, mp 112–114° dec (yield, 62%).

Anal. Calcd for $C_{24}H_{44}N_2Cl_2Pt_2$: Pt, 47.5; Cl, 8.65; N, 3.40; mol wt, 821.6. Found: Pt, 47.4; Cl, 8.7; N, 3.3; mol wt, 804.

Type II complexes were obtained by dissolving the corresponding type III derivatives in excess of methanolic HCl. The products precipitated after 3 hr. The identification was obtained by ir spectra.

Amine Addition to the Complexes VIIa,b and VIIIa,b. To a stirred ice-cold suspension of 2.0 g (0.0053 mol) of VIIa in 20 ml of methylene chloride was added 1.296 g (0.0107 mol) of α-methylbenzylamine in 5 ml of the same solvent dropwise. A solution was obtained when about the entire amount of amine was added. The solvent was removed *in vacuo* and the residue was thoroughly washed with ether and water and dried. Concentration of the collected washing afforded 0.28 g (0.00175 mol) of α-methylbenzylamine hydrochloride. The elemental analyses on this material showed a Cl:Pt ratio of about 1.6. The crude product could not be crystallized and was used as such in the degradative reduction.

Similar procedures were applied for the reactions of the complex VIIa with ammonia and ethylamine, and for the reactions of VIIb, VIIIa, and VIIIb with α-methylbenzylamine. The crude products were used in all cases in the degradative reduction.

Reaction of Dichloro(1,5-hexadiene)platinum(II) with Triethylamine. The reaction was carried out as described for the preparation of IIf but no precipitate was obtained upon amine addition. To the reaction solution an equal volume of toluene was added and the mixture was kept in the cold for 2 hr. The white crystalline precipitate was collected on a filter, washed with ether, and dried *in vacuo* (mp 130–150° dec, yield, 78%).

Anal. Calcd for $C_{12}H_{25}NCl_2Pt$: Pt, 43.4; C, 32.0; H, 5.6; N, 3.1. Found: Pt, 43.1; C, 31.7; H, 5.5; N, 3.0.

General Procedure for Reductive Degradation of Type II and III Products. 1. Treatment with Sodium Borohydride. To a suspension of the complex (0.001 mol) in 10 ml of THF, sodium borohydride (0.004 mol) was added slowly under stirring at room temperature. When after disconnection of the stirrer a clear solution appeared against the metal black, the reaction mixture was filtered

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and to the solution an excess of methanolic HCl was added. Removing of the solvent *in vacuo* gave the crude amine hydrochloride.

2. Treatment with Activated Hydrogen. A suspension of 0.001 mol of the complex and a little amount of 10% palladium on carbon in 10 ml of tetrahydrofuran was shaken in a hydrogenation apparatus at 20 psi. The reaction was stopped when hydrogen absorption ceased (generally after about 1.5 hr). The crude amine hydrochloride was isolated as above.

3. Treatment with Sodium Borohydride in the Presence of Elemental Sulfur. When the above-described reduction was applied to a cyclooctadiene or a norbornadiene derivative a mixture of several amines was obtained, owing to the fission of the higher amine that the reduction should have afforded. This inconvenience could be overcome by following procedure 1, except that a small amount of sulfur was added. In this condition the higher amine was the main product of the reduction.

Degradation of Complex IIb by Hydrolysis and Treatment with Cyanide. Complex IIb (2.0 g) was boiled with 10 ml of 37% HCl until a yellow solution was obtained. After cooling and filtering the solution was concentrated *in vacuo*. The residue was suspended in 2 ml of water and excess sodium cyanide was added. The solution was extracted twice with ether and after washing with water, the ethereal solution was acidified with methanolic HCl. Concentration *in vacuo* gave the crude amine hydrochloride.

An absorption band (1.640 cm^{-1}) of this product indicated that an unsaturated bond was present. This material was hydrogenated with hydrogen activated on Raney nickel before gas chromatographic analysis.

General Procedure of Amine Identification. The crude hydrochloride obtained by reductive degradation of the complexes was dissolved in a minimum amount of water, and after addition of excess sodium hydroxide, the free amine was extracted with a known amount of ether. Glpc analysis was carried out both on this solution and an ether solution containing the authentic sample. Peak areas were measured by means of a planimeter.

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Addition Reactions on Coordinated Olefinic Ligands. II. The Reaction between Amines and Monoolefins Coordinated in *cis*-Dichloro(olefin)(*t*-phosphine)platinum(II) Complexes

Achille Panunzi, Augusto De Renzi, Rosario Palumbo, and Gastone Paiaro

Contribution from the Istituto Chimico, Laboratorio di Chimica
Generale e Inorganica dell'Università di Napoli, Naples, Italy.
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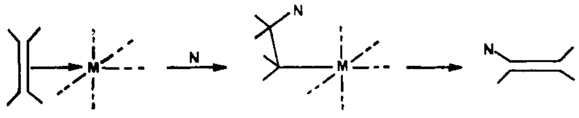
Abstract: Treatment with amines of olefin complexes of the type *cis*-$PtCl_2(Ol)(PR_3)$, in which Ol = ethylene, propene, and 1-butene and R = *n*-butyl and phenyl, led to isolable carbon–platinum σ-bonded derivatives. Dimethyl-, diethyl-, and dibutylamines were mainly used as the attacking nucleophiles. The behavior of ammonia, ethylamine, and triethylamine in the attack was also examined. The addition of the amine to the coordinated double bond was proved by degradative studies. Data on the stereochemistry of the addition of secondary amines to the tri-*n*-butylphosphine complexes were obtained.

The formation of stable alkyl derivatives of transition metals has been related[1] to the energy gap between the highest energy occupied orbital and the lowest energy vacant one associated with the metal. On this basis it is possible to explain why the stability of platinum(II) and palladium(II) alkyls depends on the presence of π-bonding ligands.[2] The role played by such ligands involves the modification of the energy of non-σ-bonding orbitals which increases the cited energy gap. As shown in reaction scheme A a σ-bonded derivative is assumed to be the intermediate in the reaction between a nucleophile, N, and a coordinated monoolefin. In the absence of π-bonding ligands such a compound should not be stable. In fact only a vinyl monomer is generally isolated,[3] according to the last step of reaction scheme A. On the other hand many other metals, or even Pt(IV), form stable alkyl derivatives but do not form stable olefin π complexes. For example, no stable π complexes are known to form by interaction of mercury salts with olefins, the alkyl derivatives being the isolable reaction products.[4] A known case in the transition-metal chemistry in which the first step of eq A is an actual process and both the starting olefin π complex and the alkyl derivative are sufficiently stable and isolable is the one involving the attack of a hydride to an olefin coordinated in a metal carbonyl.[5] It must be pointed out that analogous reactions, which are known to occur with related compounds, show substantial differences. Typical examples are the addition of nucleophiles to one of the two double bonds of a coordinated diene which leads to stable σ-bonded derivatives,[6] and the halogen addition[7] to the double



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