57016-57-6; $[Pt(PPh_3)_3][BF_4]_2$, 57016-59-8; $Pt(PPh_3)_2O_2$, 29894-57-3; $Pt(PPh_3)_2(C_2H_4)$, 12120-15-9; $NOBF_4$, 13826-86-3; HBF_4, 16872-11-0; PPh_3, 603-35-0.

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π-Allylmetal Chemistry. II.[1] A Novel Method to Prepare π-Allylplatinum(II) Complexes from Allylamines[2]

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Received June 5, 1975 AIC50397+

The reactions of several allylic amines with cationic platinum(II) hydrides $[PtH(PPh_3)_2L]ClO_4$ (L = CO, $AsPh_3$, PPh_3) afford the complexes $[Pt(\pi\text{-allyl})(PPh_3)_2]ClO_4$ and the amines in which the allylic group in the parent amines is replaced by hydrogen, in varying yields depending on the structure of the allylic moieties in the amines used: $CH_2CH{=}CH_2 \simeq CH_2CMe{=}CH_2 > CHMeCH{=}CH_2 > CH_2CH{=}CHMe$-*trans*. The reactions of primary allylamines with $PtH(ClO_4)(PPh_3)_2$ in benzene give *trans*-$[PtH(PPh_3)_2(NH_2CHR^3CR^2{=}CHR^1)]ClO_4$ (R^1, R^2, R^3 = H or Me) in which the existence of the Pt–N bonding is indicated by the infrared and ^1H NMR spectra. These amine adducts are converted slowly to the corresponding π-allyl complexes in methylene chloride at room temperature. Such a rearrangement is accelerated by the addition of a catalytic amount of CO, $AsPh_3$, or PPh_3. Different reactivity patterns of the formation of π-allylplatinum(II) complexes from allylamines and alcohols or ethers with cationic platinum(II) hydrides are discussed in terms of the differences in basicities of the nitrogen and oxygen donors toward both platinum and proton.

Introduction

Several allylic compounds have been employed to obtain π-allylmetal complexes depending on the type of metallic reagents used. Allyl halides are probably most frequently used in, e.g., oxidative addition to low-valent metallic compounds, nucleophilic substitution with complex metal anions, and the preparation of the Grignard reagents for metathesis.[3] Allylic alcohols and esters can also be utilized to prepare π-allyl complexes of Ni(II) and Pd(II)[4-6] where a high nucleophilicity of the metal atom in the low oxidation state as in $Ni(CO)_4$ or bis(1,5-cyclooctadiene)nickel may well be a driving force for the C–O bond cleavage by displacing the hydroxyl or carboxyl anions. In other reactions, a different route involving elimination of CO_2 or aldehydes was suggested to be a key step in the formation of π-allylplatinum(II) complexes from allyl alcohols or ethers and carbonyl-[1,7] or hydridoplatinum(II)[8] complexes. However, little is known of the use of allylic amines for formation of π-allyl complexes except in the preparation of 3-allylacetylacetones from allylamines and acetylacetone catalyzed by a palladium complex[9] in which formation of an intermediate π-allyl complex may play an important role. The reason for the lesser utilization of the allylamines as compared to halides or alcohols for the formation of π-allyl complexes is possibly related, in part, to the fact that the amino anions are much less effective leaving groups than the halide and hydroxyl anions. Here we report a facile conversion of various allylamines to π-allylplatinum(II) complexes induced by cationic platinum(II) hydrides with a concomitant substitution of the hydrogen atom for an allylic group in the parent amines, a reaction which appears to be potentially applicable to some organic syntheses.[10]

Experimental Section

Materials. Allylamine and diallylamine were purchased from Nakarai Chemicals Ltd. *trans*-Crotylamine, 2-methylprop-2-enylamine, and 1-methylprop-2-enylamine were prepared from the corresponding allylic chlorides by the Gabriel phthalimide method.[12] *N*-Allylethylamine[13] and *N*-allyldiethylamine[14] were prepared by the literature methods. *N*-Allylacetamide was prepared from allylamine and acetyl chloride. Silver perchlorate was dried over P_2O_5. $[PtH(PPh_3)_2L]ClO_4$, where L = CO (Ia), PPh_3 (Ic), or pyridine, and $PtH(ClO_4)(PPh_3)_2$ (III) were prepared according to the literature methods.[15] The complex $[PtH(PPh_3)_2(AsPh_3)]ClO_4$ (Ib) used in the reactions with allylamines was produced in situ by reacting III with $AsPh_3$ in a 1:1 mol ratio in methylene chloride. The deuteride $PtDCl(PPh_3)_2$ was prepared from $Pt(PPh_3)_4$ and DCl in benzene, and

Table I. Results of the Reaction of Allylamines with $[PtH(PPh_3)_2L]ClO_4$ in CH_2Cl_2[a]

Amine	Yield[b] of $[Pt(\pi\text{-allyl})(PPh_3)_2]ClO_4$, % (L =) CO	$AsPh_3$
CH_2=$CHCH_2NH_2$	75	78
CH_2=$CHCH_2NHEt$	64	68
CH_2=$CHCH_2NEt_2$	45	75
trans-MeCH=$CHCH_2NH_2$	19	*c*
CH_2=$CMeCH_2NH_2$	70	73
CH_2=$CHCHMeNH_2$	55	30
CH_2=$CHCH_2NHCOMe$	*d*	*e*

[a] Carried out at room temperature for 1 hr (L = CO) and 24 hr (L = $AsPh_3$). Approximate concentration in each reactant 3×10^{-2} to 6×10^{-2} mol/l. [b] Calculated from the amounts obtained after recrystallization. [c] Very small. [d] No π-allyl formation. 65% of $[Pt(CHEtNHCOMe)(PPh_3)_2]ClO_4$ was obtained after 5 hr. [e] Almost no reaction except that only a very small amount of $[Pt(CHEtNHCOMe)(PPh_3)_2]ClO_4$ was formed after 24 hr.

was found to contain only a trace amount of the hydride as confirmed by the infrared spectrum.

Instruments. Infrared spectra were recorded on Hitachi 225 (4000–600 cm^{-1}) and Hitachi EPI-2G (700–200 cm^{-1}) spectrophotometers, both equipped with gratings. ^1H NMR spectra were measured on a Japan Electron Optics JNM-PS-100 spectrometer. Tetramethylsilane was used as internal standard (τ 10.00).

Reactions of Allylamines with Platinum(II) Hydrides (Ia, Ib, and Ic). The products, $[Pt(\pi\text{-allyl})(PPh_3)_2]ClO_4$ (allyl = CH_2CH=CH_2, CH_2CMe=CH_2, and CH_2CH=$CHMe$), were identified by comparing the infrared and ^1H NMR spectra with those of authentic samples.[8] As essentially the same procedure was employed for all the reactions, only a typical experiment is described below. To a methylene chloride solution (3 ml) of Ib (112 mg) was added *N*-allyldiethylamine (11 mg) with stirring, and the solution was kept at room temperature for 24 hr. The ^1H NMR spectrum showed the formation of $[Pt(\pi\text{-}C_3H_5)(PPh_3)_2]ClO_4$ and diethylamine in ca. 90% yields. The volatile materials were distilled under reduced pressure at room temperature, and the distillates were treated with 1 ml of 0.1 *N* aqueous HCl. Methylene chloride was removed from the distillate under reduced pressure, and 40 mg of $NaBPh_4$ in 5 ml of H_2O was added to the aqueous solution to give 24 mg of $[Et_2NH_2]BPh_4$ (61%) which was confirmed by the ^1H NMR spectrum ($CDCl_3$–acetone-d_6). Recrystallization of the solid products obtained after the separation of the volatile materials was carried out in methylene chloride–diethyl ether in a refrigerator to afford fine crystalline compounds of the π-allylplatinum(II) complex (64 mg, 75%). The other reactions of Ia (1 hr) and Ib (24 hr) with allylic amines shown in Table I were performed similarly to give moderate to good yields of the corresponding π-allyl complexes except the reactions with *trans*-crotylamine which afforded only a small amount of the expected π-crotyl complex after fractional recrystallizations several times, together with considerable amounts of some unidentified products. The infrared spectra of the products from the reactions of Ia before recrystallization showed weak bands at 1790, 1800, and 1855 cm^{-1} (Nujol) which could have been due to $Pt_3(CO)_3(PPh_3)_4$.[16] The π-crotyl complex obtained from *trans*-crotylamine and 1-methylprop-2-enylamine was found to consist of mainly the syn-methyl isomer with a slight amount of the anti isomer present as confirmed by the ^1H NMR spectra.[8] The reactions of Ic with allylamine and 2-methylprop-2-enylamine were carried out in a way similar to those for Ib (reaction time 4 hr) to afford the π-allyl (60%) and π-β-methallyl (63%) complexes.

Reaction of *N*-Allylacetamide with Ia and Ib. A methylene chloride solution (2 ml) containing Ia (100 mg) and CH_2=$CHCH_2NHCOMe$ (20 μl) was allowed to stand at room temperature for 5 hr. The solvent was evaporated under reduced pressure, and the residual solids were washed by *n*-hexane. The solid products were recrystallized from methylene chloride–diethyl ether to give crystalline compounds formulated as $[Pt(CHEtNHCOMe)(PPh_3)_2]ClO_4$ (II) whose identification was based on comparison of melting point, infrared, and ^1H NMR spectra with those of an authentic sample[8] (yield 70 mg, 65%). An analogous reaction of Ib with the amide afforded only a small amount of the same product after 24 hr as found by the infrared spectrum.

Preparation of Hydrido(amine)platinum(II) Complexes (See Table II). In a typical preparation, allylamine (15 mg) was added to a benzene solution (10 ml) of III (150 mg) at room temperature, when precipitation of white crystals began to occur gradually. *n*-Hexane (20 ml) was added to the reaction mixture after 10 min, and recrystallization of the solid products from methylene chloride–diethyl ether afforded fine crystalline $[PtH(PPh_3)_2(NH_2CH_2CH$=$CH_2)]ClO_4$ (IVa) (148 mg, 92%). IVb, IVc, IVd, and V shown in Table II were prepared in the same way. A similar treatment of III with diallylamine in benzene at 5° followed by the addition of *n*-hexane gave only the π-allyl complex in ca. 90% yield.

Reaction of Allylamine with III in Acetone. Allylamine (30 mg) was added to III (435 mg) in dry acetone (100 ml), and the solution was kept at room temperature for 1 hr. The solvent was evaporated under reduced pressure, and the solid products were dissolved in 5 ml of methylene chloride. Diethyl ether (8 ml) was added, and the solution was kept in a refrigerator overnight to give crystalline $[Pt(\pi\text{-}C_3H_5)(PPh_3)_2]ClO_4$ (205 mg, 45%). After filtering off the π-allyl complex, the filtrates were again evaporated under reduced pressure, and the remaining solids were repeatedly recrystallized from methylene chloride–diethyl ether to afford fine crystalline $[PtH(PPh_3)_2(C_3H_5N$=$CMe_2)]ClO_4$ (VI) (150 mg, 31%).

Conversion of IV to π-Allyl Complexes. (a) Noncatalytic Conversion. In a typical experiment, a methylene chloride solution (3 ml) containing 90 mg of IVc was allowed to stand at room temperature for 4 days. The ^1H NMR spectrum showed the formation of ca. 70% yield of $[Pt(\pi\text{-}C_4H_7)(PPh_3)_2]ClO_4$ together with weak, unassignable peaks at ca. τ 9.0. Diethyl ether (20 ml) was added to give white powdery products which were further recrystallized from methylene chloride–diethyl ether in a refrigerator to afford 50 mg (59%) of the π-β-methallyl complex. IVa gave a similar amount of the π-allyl complex. IVb and IVd afforded 29 and 45% yields of mainly the syn isomer of the π-crotyl complex after repeated recrystallizations, together with some unidentified products.

(b) Catalytic Conversion. $AsPh_3$ (3 mg) was added to a methylene chloride solution (3 ml) containing 90 mg of IVc, and the solution was allowed to stand at room temperature for 2 days. Diethyl ether (3 ml) was added to this solution to give 61 mg (73%) of the π-β-methallyl complex. Addition of PPh_3 (3 mg) (2 days) or passage of CO gas (20 min) to the solution of IVc similarly gave the π-β-methallyl complex. Treatment of IVa and IVd with $AsPh_3$ similarly gave the π-allyl (85%) and syn-π-crotyl (48%) complexes. IVb and a catalytic amount of $AsPh_3$ afforded only 22% of the π-crotyl complex after 2 days.

Attempted Deuterium–Hydrogen Exchange in $[PtD(PPh_3)_2(NH_2$-*n*-Bu$)]ClO_4$. *trans*-$[PtD(PPh_3)_2(NH_2$-*n*-Bu$)]ClO_4$ (Vd) was prepared from *trans*-$PtDCl(PPh_3)_2$, $AgClO_4$ and *n*-butylamine in benzene in a manner essentially similar to that for V. The infrared

Table II. Analytical Data for Some Platinum(II) Hydrides ($[PtH(PPh_3)_2L]ClO_4$)

Compd No.	L	Dec point, °C	%C Calcd	%C Found	%H Calcd	%H Found	%N Calcd	%N Found
IVa	CH_2=$CHCH_2NH_2$	*a*	53.46	53.25	4.26	4.42	1.60	1.76
IVb	MeCH=$CHCH_2NH_2$	137–140	53.90	53.82	4.53	4.46	1.57	1.52
IVc	CH_2=$CMeCH_2NH_2$[b]	*a*	52.15	51.98	4.32	4.47	1.50	1.62
IVd	CH_2=$CHCHMeNH_2$	*a*	53.90	53.78	4.53	4.61	1.57	1.59
V	*n*-$BuNH_2$	147–150	53.78	53.49	4.74	4.72	1.57	1.68
VI	CH_2=$CHCH_2N$=CMe_2	152–155	55.05	54.97	4.51	4.60	1.53	1.50

[a] Gradually decomposed above 150°. [b] The compound contains 0.5 mol of CH_2Cl_2 per 1 atom of Pt, which was also confirmed by the ^1H NMR spectrum in $CDCl_3$.

Table III. Infrared[a] and ^{1}H NMR[b] Data for Platinum(II) Hydrides (*trans*-[PtH(PPh_3)$_2$L]ClO_4)

Compd No.	L	ν(Pt-H), cm^{-1}	τ(PtH),[c] ppm	$^1J_{PtH}$, Hz	Others (τ)
IVa	CH_2=$CHCH_2NH_2$	2200	26.45	1040	7.64 (br, CH_2N), 7.2 (br, NH_2), 4.8-5.6 (m, CH=CH_2)
IVb	*trans*-MeCH=$CHCH_2NH_2$	2195	26.7	1055	8.62 (d, J_{HH} = 6 Hz, Me), 7.68 (br, CH_2N), 7.3 (br, NH_2), 5.0-5.55 (m, -CH=CH-)
IVc	CH_2=$CMeCH_2NH_2$	2200	26.45	1035	8.98 (s, Me), 7.65 (br, CH_2N), 7.2 (br, NH_2), 5.96 (s) and 5.60 (s) (=CH_2)
IVd	CH_2=$CHCHMeNH_2$	2195	26.4	1030	9.44 (d, J_{HH} = 7 Hz, Me), 7.76 (br, CHN), 7.05 (br, NH_2), 4.85-5.5 (m, CH=CH_2)
V	*n*-$BuNH_2$	2180 2195	26.8[d]	1060[d]	9.46 (m, $CH_2CH_2CH_3$), 8.24 (br, CH_2N), 7.6 (br, NH_2)
VI	CH_2=$CHCH_2N$=CMe_2	2205	26.75	1000	8.52 (s) and 8.12 (s) (=CMe_2), 6.88 (d, J_{HH} = 6 Hz, CH_2N), 5.2 (m, =CH_2), 4.3 (m, CH=)
	Pyridine	2203[e]	27.0	1020	

[a] In Nujol mulls. [b] In $CDCl_3$ except as noted. s = singlet, d = doublet, m = multiplet, br = broad. [c] Triplet with $^2J_{PtH} \simeq 13$ Hz. [d] In CH_2Cl_2. [e] Reference 15.

spectrum of a methylene chloride solution of Vd (10 mg/1 ml) showed a δ(Pt-D) band at 588 cm^{-1}, although the ν(Pt-D) band was apparently overlapped by the strong bands at ca. 1580 cm^{-1} due to $\delta(NH_2)$. The intensity of the δ(Pt-D) band relative to that of one of the ClO_4^- vibrations at 627 cm^{-1} remained virtually unchanged during the periods of more than 2 days. Further, the spectrum of the sample recovered after evaporating the solvent did not show any increase in the intensity of the band at ca. 2200 cm^{-1} due to the residual hydride contained in the original sample of Vd.

Results and Discussion

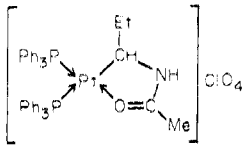
Reactions of Allylamines with Platinum(II) Hydrides. The reaction of several allylamines with [PtH(PPh_3)$_2$L]ClO_4 I (Ia, L = CO; Ib, L = $AsPh_3$) in methylene chloride at room temperature afforded varying yields of the corresponding π-allyl complexes [Pt(π-allyl)(PPh_3)$_2$]ClO_4 (allyl = CH_2CH=CH_2, CH_2CMe=CH_2, CH_2CH=CHMe) depending on the structure of the allylic moieties in the amines used (eq 1, Table I). In each reaction with Ia, the formation

$$[PtH(PPh_3)_2L]ClO_4 + CHR^1{=}CR^2CHR^3N< \xrightarrow{-L} \left[\begin{array}{c} Ph_3P \\ Ph_3P \end{array}\!\!>\!Pt\!<\!\begin{array}{c} R^1 \\ R^2 \\ R^3 \end{array}\right] ClO_4 + HN< \quad (1)$$

L = CO, $AsPh_3$, PPh_3; R^1, R^2, R^3 = H or Me; N< = NH_2, NHEt, NEt_2

of a small amount of $Pt_3(CO)_3(PPh_3)_4$[16] was confirmed by the infrared spectra. Ammonia, ethylamine, and diethylamine were also formed in quantities similar to those of [Pt-π-C_3H_5)(PPh_3)$_2$]ClO_4 from the reactions of allyl-, *N*-allylethyl- and *N*-allyldiethylamine, respectively. Analogous reactions of Ic (L = PPh_3) with allyl- and 2-methylprop-2-enylamine under similar conditions also gave the π-allyl and π-β-methallyl complexes in ca. 60% yields.

It is notable in Table I that the reaction of Ia with *N*-allylacetamide gave no π-allyl complex but a product (II)



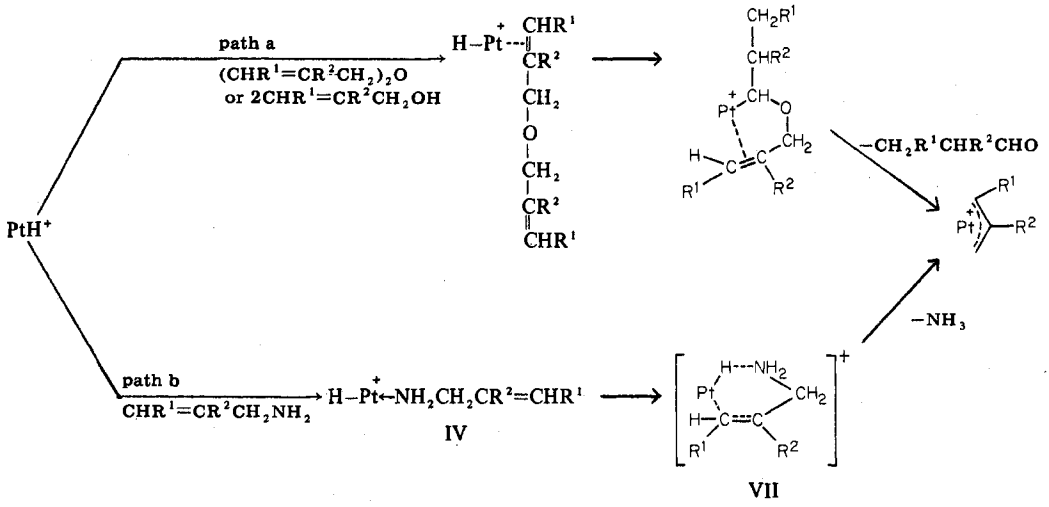
II

resulting from the addition of the Pt-H bond across the C=C bond in MeCH=CHNHCOMe, a supposed isomerization product of the parent amide. It was suggested previously[8] that such C=C bond migration and insertion of the allylic derivatives are the consequences of the initial coordination of olefins to platinum, a process which is readily attained especially in those platinum(II) hydrides which contain very weakly bound ligands such as acetone, nitrate, or perchlorate anion trans to the hydridic hydrogen. Hence, the reactions of the allylic amines with potentially cationic PtH(ClO_4)(PPh_3)$_2$ (III) have also been investigated. The addition of the primary allylamines to a benzene solution of III at room temperature resulted in a rapid precipitation of a cationic amine adduct, *trans*-[PtH(PPh_3)$_2$($NH_2CHR^3CR^2$=CHR^1)]ClO_4 (IV) (IVa, R^1 = R^2 = R^3 = H; IVb, R^1 = Me, R^2 = R^3 = H; IVc, R^1 = R^3 = H, R^2 = Me; IVd, R^1 = R^2 = H, R^3 = Me), in almost quantitative yields. A similar reaction of diallylamine with III did not give an analogous amine complex even at 5° but the π-allyl complex was produced in a very high yield.

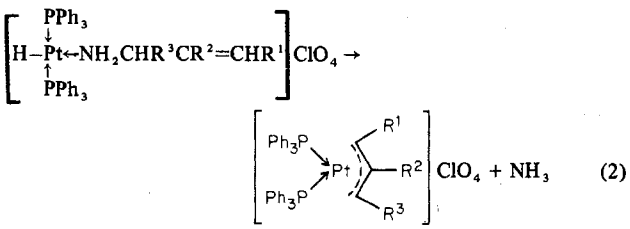
That the amine ligand in IV coordinates to platinum through the nitrogen atom but not the C=C was deduced from spectroscopic evidence. The infrared spectra (Nujol) of IVc and IVd showed very weak bands at 1650 and 1640 cm^{-1}, respectively, possibly attributed to ν(C=C). In the ^{1}H NMR spectrum of IVc, the olefinic proton resonances showed no couplings with ^{31}P and ^{195}Pt nuclei, although the corresponding resonances[17] in the other complexes were too complex to resolve well. The hydridic hydrogen resonances in the spectra of IV all appeared as 1:2:1 triplets due to the coupling with two equivalent ^{31}P nuclei, indicating a trans configuration. The values of $^1J_{PtH}$, τ(PtH), and ν(Pt-H) are known to depend on the nature of the ligand trans to the hydrogen.[18] Thus, these values observed for the present complexes IV are very close to the corresponding values of *trans*-[PtH(PPh_3)$_2$-(NH_2-*n*-Bu)]ClO_4 (V), respectively (Table III), while quite different values of τ(PtH) (16.3-17.2) were reported previously for *trans*-[PtH(PR_3)$_2$(C_2H_4)]$^+$ (PR_3 = PPh_2Me,[19] PEt_3[20]). Although the olefinic ligands are higher in the NMR trans influence order than the nitrogen donor in the amines, the preferential coordination of a ligand of the lower trans influence over that of the higher counterpart as was found in IV also occurred in some cationic methylplatinum(II) complexes.[21] It is also notable in Table III that the values of $^1J_{PtH}$, τ(PtH), and ν(Pt-H) in *trans*-[PtH(PPh_3)$_2$L]ClO_4 do not vary greatly when the donor atom in L is changed from an sp^2 nitrogen as in pyridine and N(C_3H_5)=CMe_2 (see later) to an sp^3 nitrogen as in the amines. Similarly, a very small variation in the values of $^2J_{PtCH_3}$ and ν(Pt-CH_3) is evidently seen in some methylplatinum(IV) complexes containing the nitrogen donor ligands.[22]

Complexes IV are reasonably stable in methylene chloride at room temperature for at least a day, but they do decompose slowly in this solvent to afford ca. 60-30% yields of the corresponding π-allyl complexes after 4 days (eq 2). When a catalytic amount (10-15 mol %) of $AsPh_3$ or PPh_3 was added to the methylene chloride solution of IV, the formation of the π-allyl complexes occurred more rapidly. Passage of carbon

Scheme I



(R¹, R² = H or Me)



(2)

R¹, R², R³ = H or Me

monoxide gas through the same solution similarly resulted in the facile rearrangement to the π-allyl complexes, while the addition of pyridine was not effective in this respect.

The π-allyl formation from allylamine and III was also rapid in acetone, but in this case the reaction suffered from the formation of a by-product, *trans*-[PtH(PPh_3)$_2$(CH_2=$CHCH_2N$=CMe_2)]ClO_4 (VI) in a yield comparable to that of the π-allyl complex. For reasons similar to those given for IV above, VI was indicated to have Pt–N bonding (see Table III). VI does not rearrange to the π-allyl complex in acetone for prolonged periods, suggesting that the formation of the π-allyl complex and VI occurs independently.

Mechanism of Formation of π-Allyl Complexes. It seems of interest to note marked differences between the reactivity patterns in the formation of the π-allylplatinum(II) complexes from allylamines described above on one hand, and allyl alcohols or ethers[8] on the other, both being induced by the cationic platinum(II) hydrides: (1) the presence of CO, $AsPh_3$, or PPh_3 accelerates the former reactions, but retards or inhibits the latter, (2) the order of the relative ease of the formation of π-allyl complex as a function of the structure of the allylic moieties is $-CH_2CH$=CH_2 ≃ $-CH_2CMe$=CH_2 > $-CH_2CH$=$CHMe$-*trans* for the former, and $-CH_2CH$=CH_2 > $-CH_2CH$=$CHMe$-*trans* ≫ $-CH_2CMe$=CH_2 for the latter. These facts may most satisfactorily be explained by assuming that the differences in basicities of the nitrogen and oxygen donors toward both platinum and proton affect the course of the whole reactions. Thus, in the reactions of the alcohols or ethers, the coordination of the C=C bond to platinum becomes more important than that of the oxygen atom, thereby facilitating the C=C bond migration and insertion to the Pt–H bond which are required for the formation of the π-allyl complexes and aldehydes to occur (Scheme I, path a). The reason for the inhibitory effect of the added ligands can be ascribed to their ability to prevent the olefin coordination. Furthermore, the observed order of the ease of the reactions of the different alcohols or ethers is the same as that expected on the basis of the relative stabilities of the π-olefinplatinum(II) complexes as a function of the structure of the allyl groups.[23]

On the other hand, the preferred coordination of the nitrogen atom in IV as shown before apparently suppresses the addition of the Pt–H bond across the C=C bond, and we suggest an important step involved in the rearrangement of IV to the π-allyl complexes to be a somewhat nucleophilic attack of the nitrogen atom toward the hydrogen atom attached to platinum, followed by the liberation of ammonia. In agreement with this suggestion is the observation that the compounds bearing the nitrogen–allyl bond whose proton affinities are lower than those of the allylic amines do not rearrange to the π-allyl complexes under similar conditions as exemplified by CH_2=$CHCH_2N$=CMe_2 and CH_2=$CHCH_2NHCOMe$. The latter behaved rather differently toward Ia (Table I) and III[8] to result in the isomerization and insertion of the C=C bond affording II in a way essentially similar to that involved in path a above. Further, the role of CO, $AsPh_3$, and PPh_3 in reaction 1 as well as 2 in their presence is assumed to render, through coordination, the hydrogen atom more susceptible to such nucleophilic attack by nitrogen; when Ia was treated with Et_3N in methylene chloride deprotonation occurred rapidly to afford moderate yield of $Pt_3(CO)_3(PPh_3)_4$ as deduced from infrared spectra, and treatment of Ic with KOH was reported to give $Pt(PPh_3)_3$.[24]

Interestingly, such cleavage of the Pt–H bond through the attack by the nitrogen atom as suggested in reaction 2 appears to take place with particular ease by the use of the allylic amines in comparison to other amines, for the *n*-butylamine complex V was far more stable than IV under similar conditions and no significant H–D exchange between the Pt–D and N–H of *trans*-[PtD(PPh_3)$_2$(NH_2-*n*-Bu)]ClO_4 (Vd) could be observed when Vd was kept in methylene chloride at room temperature for more than 2 days. An occurrence of the Pt–D bond cleavage would have resulted in scrambling of the hydrogen and the deuterium in Vd. These facts may lead to a suggestion that as far as the noncatalytic rearrangement of IV to the π-allyl complexes is concerned, the C=C bond also plays some role in facilitating the Pt–H bond fission. Although currently available evidence cannot allow any conclusive discussion, one possible mode of the C=C bond participation in the deprotonation step would be development of the Pt–C bond formation at the terminal position as shown in VII in Scheme I, this model presumably being compatible with the fact that *trans*-crotylamine gave the lowest yields of the π-allyl complex of several allylic amines examined due to the largest

steric constraint in VII.

Acknowledgment. Thanks are due to Professor R. Okawara of this Department for encouragement and valuable discussions.

Registry No. $[Pt(CH_2CH{=}CH_2)(PPh_3)_2]ClO_4$, 36484-05-6; $[Pt(CH_2CH{=}CHMe)(PPh_3)_2]ClO_4$, 56994-03-7; $[Pt(CH_2CMe{=}CH_2)(PPh_3)_2]ClO_4$, 37036-84-3; IVa, 55031-61-3; IVb, 56930-27-9; IVc, 55031-63-5; IVd, 56930-29-1; V, 56930-31-5; VI, 55031-65-7; $[PtH(PPh_3)_2CO]ClO_4$, 55057-91-5; $[PtH(PPh_3)_3]ClO_4$, 19568-66-2; $[PtH(PPh_3)_2(AsPh_3)]ClO_4$, 55031-67-9; Vd, 56930-33-7; *trans*-$PtDCl(PPh_3)_2$, 22899-18-9; III, 32109-29-8; II, 37383-70-3; $CH_2{=}CHCH_2NH_2$, 107-11-9; $CH_2{=}CHCH_2NHEt$, 2424-02-4; $CH_2{=}CHCH_2NEt_2$, 5666-17-1; *trans*-$MeCH{=}CHCH_2NH_2$, 56930-04-2; $CH_2{=}CMeCH_2NH_2$, 2878-14-0; $CH_2{=}CHCHMeNH_2$, 34375-90-1; $CH_2{=}CHCH_2NHCOMe$, 692-33-1.

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Reactions of (4,9-Dimethyl-5,8-diazadodeca-4,8-diene-2,11-dione)copper(II), (Cu(baen)) with Isocyanates[1]

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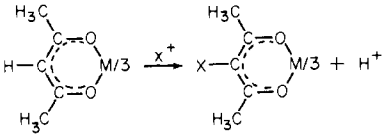
Received July 3, 1975 AIC50469X

The complex (4,9-dimethyl-5,8-diazadodeca-4,8-diene-2,11-dione)copper(II), Cu(baen), reacts quickly and quantitatively in dry benzene solution at the methine position with isocyanates, RN=C=O, where R = 1-naphthyl, C_6H_5, C_2H_5, CH_3, *i*-C_3H_7, and *t*-C_4H_9, in a stepwise manner to yield mono- and diamides of Cu(baen). The rates of these reactions have been qualitatively determined and found to be dependent upon the R group in the order: 1-naphthyl > C_6H_5 > CH_3 > C_2H_5 > *i*-C_3H_7 > *t*-C_4H_9. They are also metal dependent with Cu(baen) reacting much faster than Ni(baen). The complexes have been characterized by elemental analyses, melting points, and electronic and infrared spectra. The ligands have been displaced intact from the complexes with H_2S in benzene or chloroform and characterized by elemental analyses, melting points, and infrared, nuclear magnetic resonance, and mass spectrometry. Sulfuric acid degradation of the complexes in methanol produces N-substituted acetoacetamides. These have been characterized by melting points, infrared, nuclear magnetic resonance, and mass spectrometry and in some cases by their 2,4-dinitrophenylhydrazone derivatives. It is concluded from the data presented that these reactions are essentially electrophilic aromatic substitution reactions.

Introduction

Reactions of coordinated ligands[3,4] have been shown to be potentially very useful, not only for their synthetic applications[5] to organic chemistry and homogeneous catalysis,[6] but also for their relations to life processes. Numerous β-diketone complexes have been studied, and it has been noted that these complexes undergo reactions characteristic of aromatic systems.[7] The methine hydrogen on these chelate rings can be replaced by several groups under electrophilic conditions as illustrated in reaction 1.



(1)

M = Co, Rh, Cr; X = I, Br, Cl, SCN, SAr, SA, NO_2, CH_2Cl, $CH_2N(CH_3)_2$, COR, CHO

Due to the acid lability of these complexes, selective reagents must be employed in order to minimize degradation of the chelate rings.[7] Complexes of Schiff base condensation products of 2,4-pentanedione and diamines such as I, abbreviated M(baen), are even more susceptible to acid hydrolysis.[8] It is probably for this reason that similar reactions of these complexes have not been as extensively investigated. Prior to our initial report[9] few reactions of complexes such as I had been reported.[10-16]

During the course of our studies with compounds I we discovered[9] that these complexes react quickly and quantitatively (reaction 2) with isocyanates to form compounds II and III. These reactions are described in detail herein.

Experimental Section

The starting ligands and their complexes were synthesized according to published procedures,[8] recrystallized from dry benzene–cyclohexane, and dried under vacuum at 60°C. Benzene was distilled, purified by azeotropic distillation, and finally dried over Linde 3Å molecular