Contribution from the Department of Petroleum Chemistry,
Osaka University, Yamadakami, Suita, Osaka, Japan

π-Allylmetal Chemistry. I. Synthesis and Decarboxylation of Allyloxycarbonylplatinum(II) Complexes. An Organoplatinum Analog of the Retro-Ene Reactions[1,2]

HIDEO KUROSAWA

Received January 30, 1975 AIC500711

Some allyloxycarbonyl- and *N*-allylcarbamoylplatinum(II) complexes, $Pt(COXCHR^1CR^2{=}CHR^3)ClQ_2$ (X = O or NH; R^1, R^2, R^3 = H or Me; Q = PPh_2Me or PPh_3), have been prepared. Spectroscopic evidence suggests the structure of these complexes as having a square-planar trans configuration without significant interaction between the C=C bond and the platinum atom. The allyloxycarbonyl complexes undergo a ready decarboxylation either by thermal means or on treatment with an equimolar amount of $AgClO_4$, affording the corresponding π-allylplatinum(II) complexes. The reaction of *N*-allylcarbamoyl complex with $AgClO_4$ similarly gives the π-allyl complex. A possible reaction sequence for such decarboxylation involving intermediate π-olefin coordination and a subsequent six-membered transition state has been suggested.

Introduction

The chemistry of π-allylmetal complexes has received much attention in recent years from a variety of points of view including their role in organic synthesis,[3] fluxional behavior in solution,[4,5] and the nature of bonding.[5] The reaction mode in some of the methods of obtaining π-allyl complexes essentially parallels that involved in the preparation of simple alkylmetal counterparts,[6] e.g., metathesis by means of the more reactive organometallic compounds, oxidative addition of organic halides, and insertion of carbon–carbon double bonds into metal–alkyl, –hydrogen, or –halogen bonds. Of greater interest, however, is the fact that some reactions appear to be applicable exclusively to the synthesis of π-allyl complexes. These include conversion of π-olefinmetal to π-allyl complexes by virtue of hydrogen abstraction from an allylic position[6,7] and the reaction of allylic alcohols, ethers, and esters with some nickel and palladium complexes which involves a ready C–O bond cleavage.[6-8] We have undertaken a systematic study of the latter type of reactions in order to develop other routes to π-allyl complexes. Emphasis has been placed upon gaining precise insight into the mechanism of such π-allyl formation as well as of π-allyl-participating organic syntheses. The present paper describes the synthesis of allyloxycarbonylplatinum(II) complexes and their novel decarboxylation which provides another example of a specific and convenient method of preparing π-allyl complexes.

Experimental Section

trans-Crotyl alcohol was prepared from *trans*-crotonaldehyde and $LiAlH_4$. Other allylic alcohols and allylamine were purchased from Nakarai Chemicals Ltd. Silver perchlorate was dried over P_2O_5. Infrared spectra were recorded on a Jasco IR-G spectrophotometer (4000–400 cm^{-1}) and a Hitachi EPI-2G spectrophotometer (700–200 cm^{-1}). ^1H NMR spectra were measured on a Japan Electron Optics JNM-PS-100 spectrometer. Tetramethylsilane was used as internal standard (τ 10.00).

Preparation of Allyloxycarbonylplatinum(II) Complexes, I–VI (See Table I). As essentially the same procedure was employed for the synthesis of all the complexes, only a typical experiment is described below.

Method 1. To a mixture of 3 ml of allyl alcohol and 100 mg of Na_2CO_3 was added a solid sample of $[PtCl(PPh_3)_2(CO)]ClO_4$ (280 mg) which had been obtained from *cis*-$PtCl_2(PPh_3)_2$ and $AgClO_4$ in methylene chloride under a carbon monoxide atmosphere and used without further purification. The mixture was vigorously stirred at room temperature for 2 hr, and the alcohol was evaporated under vacuum. Benzene (10 ml) was added to the residual solids and the solution was filtered. The filtrate was concentrated to a volume of ca. 3 ml under vacuum. To this solution was added diethyl ether (3 ml) and the solution was kept in refrigerator overnight to give colorless fine crystals of III (160 mg; 60%). This sample had the ν(C=O) band at 1640 cm^{-1} and ν(C—O) at 1050 cm^{-1} (Nujol).

Method 2. Complex III was alternatively prepared by the reaction of $Pt(COOMe)Cl(PPh_3)_2$[9] (100 mg) and allyl alcohol (0.5 ml) in methylene chloride (3 ml) at room temperature for 48 hr. Recrystallization by adding diethyl ether (5 ml) to the reaction mixture gave colorless crystals (70 mg; 72%). The infrared spectrum (Nujol) of this sample initially showed ν(C=O) at 1620 and ν(C—O) at 1100 cm^{-1}, but on standing in the solid state these bands were gradually replaced by those exhibited by the spectrum of the sample obtained by method 1. A single band for each of such vibrational modes was observed in the solution spectra (CH_2Cl_2) of the samples prepared by both methods. IV was prepared from 2-methallyl alcohol by methods similar to those for obtaining III. V and VI were prepared in a way similar to method 1 above, using *trans*-crotyl alcohol and 1-butene-3-ol, respectively. I and II were prepared similarly by using $[PtCl(PPh_2Me)_2(CO)]ClO_4$ or $Pt(COOMe)Cl(PPh_2Me)_2$ which had been obtained without purification by methods similar to those for the corresponding triphenylphosphine analogs. Recrystallization of I and II was performed in benzene–*n*-hexane in the refrigerator.

Preparation of Other Alkoxycarbonylplatinum(II) Complexes. $Pt(COOR)Cl(PPh_3)_2$ (R = *n*-Pr, *i*-Pr) complexes were prepared in a way similar to method 1 described for the synthesis of III.

Preparation of the *N*-Allylcarbamoylplatinum(II) Complex VII. A benzene solution (10 ml) of $Pt(COOMe)Cl(PPh_3)_2$ (170 mg) and allylamine (0.1 ml) was heated at the refluxing temperature for 4 hr. The solvent was evaporated under vacuum, and the solid products were recrystallized from benzene–diethyl ether to give fine crystalline compounds (100 mg; 57%). The infrared spectrum (Nujol) of this sample showed medium-intensity bands at 1590 and 1560 cm^{-1}. The solution spectrum (CH_2Cl_2) showed a single strong band at 1590 cm^{-1}. VII was also prepared from $[PtCl(PPh_3)_2(CO)]ClO_4$ and allylamine by a method similar to that described for other *N*-alkylcarbamoylplatinum(II) complexes.[10]

Analytical results for all the complexes thus obtained are given in Table I.

Decarboxylation of Allyloxycarbonylplatinum(II) Complexes. (a) Thermal Decarboxylation. $[Pt(\pi\text{-}C_3H_5)(PPh_3)_2]Cl$ was identified by its melting point and ^1H NMR spectrum.[11] The other products from thermal decarboxylation $[Pt(\pi\text{-allyl})Q_2]Cl$ were confirmed by ^1H NMR spectra and by converting the chlorides to the known salts of PF_6 (Q = PPh_2Me)[12] or ClO_4 (Q = PPh_3)[13] anion on treatment with NH_4PF_6 or $NaClO_4$. The π-crotyl complex $[Pt(\pi\text{-}C_4H_7)(PPh_3)_2]ClO_4$ which was obtained this way consisted of only one isomer with the methyl at the syn position[13] when V and VI were used as the starting material. CO_2 formed was confirmed by the infrared spectra of the reaction mixture in the case of the decarboxylation carried out at room temperature. Yields (based on ^1H NMR spectra and the intensity of ν(C=O) band in the recovered reactants) of $[Pt(\pi\text{-allyl})(PPh_3)_2]Cl$ obtained by thermolysis of the allyloxycarbonyl complex (3×10^{-3} *M*) in refluxing benzene are as follows (reaction time in parentheses): III, more than 95% (1 hr); IV, 30% (1 hr) and 90% (3 hr); V, less than 5% (1 hr); VI, more than 95% (1 hr). Thermolyses of V for prolonged periods (5–10 hr) afforded at best a 50% yield of the π-crotyl complex. About 90% yields of $[Pt(\pi\text{-allyl})(PPh_2Me)_2]Cl$ were obtained from thermolyses of I (2 hr) and II (4 hr) in refluxing benzene. The decarboxylation of III (10^{-2} *M*)

Table I. Analytical Data for Some Platinum(II) Complexes

No.	Compd	Dec pt, °C	% C Calcd	% C Found	% H Calcd	% H Found
	$Pt(COOR)Cl(PPh_2Me)_2$					
I	$R = CH_2CH{=}CH_2$	100–105	50.32	50.40	4.36	4.50
II	$R = CH_2CMe{=}CH_2$	108–112	51.00	51.73	4.56	4.67
	$Pt(COOR)Cl(PPh_3)_2$					
III	$R = CH_2CH{=}CH_2$	>180[a]	57.18	56.78	4.20	4.09
IV	$R = CH_2CMe{=}CH_2$	161–164	57.65	57.28	4.37	4.49
V	$R = CH_2CH{=}CHMe$-*trans*	146–148	57.65	57.33	4.37	4.27
VI	$R = CHMeCH{=}CH_2$	>140[a]	57.65	57.55	4.37	4.32
	$R = n$-Pr	211–214	57.04	57.17	4.43	4.43
	$R = i$-Pr	218–220	57.04	57.18	4.43	4.22
VII	$Pt(CONHCH_2CH{=}CH_2)Cl(PPh_3)_2$[b]	186–190	57.25	56.57	4.32	4.24

[a] No definite decomposition point was observed. [b] % N: calcd, 1.67; found, 1.28.

Table II. Infrared[a] and ^1H NMR[b] Data for the Platinum(II) Complexes *trans*-$Pt(COXCHR^1CR^2{=}CHR^3)ClQ_2$

Compound						Stretching, cm^{-1}			Chemical shifts, τ					
No.	Q	X	R^1	R^2	R^3	C=O	C–O	Pt–Cl	XCH	R^1	R^2	C*H*R^3	R^3	PMe
I	PPh_2Me	O	H	H	H	1635	1060	280	6.59 d ($J_{HH} = 5$) ($J_{PtH} \leqslant 8$)		4.5–5.2 m			7.81 t ($J_{PtH} = 33$) ($J_{PH} = 7.5$)
II	PPh_2Me	O	H	Me	H	1638	1040	280	6.69 s ($J_{PtH} \leqslant 8$)		8.64 s	5.48 s 5.42 s		7.87 t ($J_{PtH} = 33$) ($J_{PH} = 7.5$)
III	PPh_3	O	H	H	H	1640[c]	1063[c]	280 295	6.92 d ($J_{HH} = 5$) ($J_{PtH} \leqslant 8$)		4.6–5.3 m			
IV	PPh_3	O	H	Me	H	1640[c]	1052[c]	270	6.97 s ($J_{PtH} \leqslant 8$)		8.67 s	5.50 s 5.42 s		
V	PPh_3	O	H	H	Me	1640[c]	1060[c]	285	6.95 d ($J_{HH} = 5.5$) ($J_{PtH} \leqslant 8$)		5.2 m 4.8 m		8.48 d ($J_{HH} = 6$)	
VI	PPh_3	O	Me	H	H	1638[c]	1035[c]	285	5.96 q ($J_{HH} = 5$)	9.73 d ($J_{HH} = 5$)	4.9–5.5 m			
VII[d]	PPh_3	NH	H	H	H			283	7.38 t ($J_{HH} = 5$)		4.9–5.5 m			

[a] In Nujol mulls except as noted. [b] In $CDCl_3$. τ in ppm; *J* in Hz. Key: s, singlet; d, doublet; t, triplet; q, quintet; m, complex multiplet. [c] In CH_2Cl_2. [d] τ(NH) hidden under 4.9–5.5.

in the presence of $SnCl_2$ or Me_2SnCl_2 (10^{-3} *M*) was carried out in methylene chloride at room temperature, affording ca. 70% yield of $[Pt(\pi\text{-}C_3H_5)(PPh_3)_2]Cl$ after 24 hr in the former and 5 hr in the latter catalyst system.

(b) Decarboxylation with the Aid of $AgClO_4$. The reactions of all the allyloxycarbonyl complexes with $AgClO_4$ were performed in essentially the same way, and only a typical procedure is therefore given below. To a methylene chloride solution (3 ml) of III (162 mg; 0.2 mmol) was added $AgClO_4$ (41 mg; 0.2 mmol) in acetone (1 ml) with stirring. AgCl immediately precipitated was filtered off, and the filtrate was kept at room temperature for 1 hr. The solvents were evaporated under vacuum. The residual solids were recrystallized from methylene chloride–diethyl ether to give colorless fine crystalline $[Pt(\pi\text{-}C_3H_5)(PPh_3)_2]ClO_4$ (150 mg; 87%). When the same reaction was carried out in 20 ml of benzene, solid products were gradually precipitated on keeping the reaction mixture at room temperature after AgCl had been removed by filtration. After 5 hr, benzene was decanted off, and recrystallization from methylene chloride–diethyl ether gave 90% yield of the same product. The reactions of I and II with $AgClO_4$ were carried out similarly in methylene chloride–acetone mixed solvents; yields (based on ^1H NMR spectra) of $[Pt(\pi\text{-allyl})(PPh_2Me)_2]ClO_4$ were 70% (2 hr) and 75% (24 hr), respectively. The reaction of IV, V, or VI with $AgClO_4$ was performed in a way similar to that of III in benzene with the reaction period 48 hr; yields of the π-allyl complexes were 60%, 68%, and 62%, respectively. The product from V and $AgClO_4$ consisted of only the isomer with the syn methyl substituent in the π-crotyl ligand. On the other hand, the π-crotyl complex with 65% syn and 35% anti methyl isomers was obtained from an analogous reaction of VI as confirmed by ^1H NMR spectra.[13]

Reaction of VII with $AgClO_4$. The reaction of VII (160 mg) with $AgClO_4$ (40 mg) in methylene chloride (4 ml) and acetone (2 ml) was carried out in a manner similar to that for the reaction of III with $AgClO_4$. The color of the solution gradually became deep brown when the reaction mixture kept at room temperature after AgCl had been removed. After 5 hr, the solvents were evaporated under vacuum, and repeated recrystallization of the residual solids from methylene chloride–diethyl ether gave 70 mg (41%) of $[Pt(\pi\text{-}C_3H_5)(PPh_3)_2]ClO_4$.

Results and Discussion

Preparation and Structure of Allyloxycarbonyl- and *N*-Allylcarbamoylplatinum(II) Complexes. The reaction of cationic carbonylplatinum(II) complexes with alcohols is known[9,14] to afford alkoxycarbonylplatinum(II) complexes as shown in eq 1 (Q = tertiary phosphine or arsine, R = Me, Et).

$$[PtClQ_2(CO)]^+ + ROH \rightarrow Pt(COOR)ClQ_2 + H^+ \qquad (1)$$

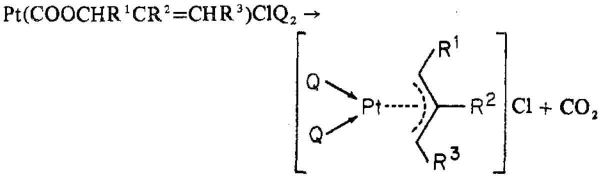
This reaction could readily be applied to the synthesis of allyloxycarbonyl analogs (Q = PPh_2Me or PPh_3, R = $CH_2CH{=}CH_2$, $CH_2CMe{=}CH_2$, $CH_2CH{=}CHMe$-*trans*, and $CHMeCH{=}CH_2$). In the reactions of the last two alcohols, no positional isomerization with respect to the C=C bond was observed, in agreement with the mechanism expected[15] for reaction 1. Some of the complexes could also be obtained by an indirect method involving transesterification of $Pt(COOMe)ClQ_2$ with allylic alcohols. The carbamoyl complex $Pt(CONHCH_2CH{=}CH_2)Cl(PPh_3)_2$ was prepared similarly from $Pt(COOMe)Cl(PPh_3)_2$ or $[PtCl(PPh_3)_2(CO)]ClO_4$ and allylamine.

The relevant infrared and ^1H NMR spectral data for the complexes investigated here are shown in Table II. The infrared spectra of I–VI showed two intense bands around 1640 and 1050 cm^{-1} associated with ν(C=O) and ν(C—O) modes, respectively. The band at 1590 cm^{-1} observed in the solution spectrum of VII may be due to the ν(C=O) plus δ(NH) mode.

We believe all the complexes have a planar configuration without any significant interaction between the C=C bond and the platinum atom in the ground state for the following reasons. In the ^{1}H NMR spectra of I–VI, the chemical shifts[16] for the olefinic protons are observed in the range much lower than those in some allyloxycarbonyliridium(I) complexes[17] which have been shown to involve an intramolecular C=C coordination to iridium. Further, at least those olefinic proton signals which could be well resolved in the present complexes showed no couplings with ^{31}P and ^{195}Pt nuclei of spin $^1/_2$. Equivalence of two allylic methylene proton resonances observed in I–V and VII is also in accord with the absence of an asymmetric center in the molecule. A rigid coordination of the C=C bond to platinum would have made such allylic protons a diastereotopic pair. It was unfortunately difficult to assign an infrared band due to the stretching of the free C=C bond because of the appearance of the very intense ν(C=O) band in the region where the former is expected to occur.

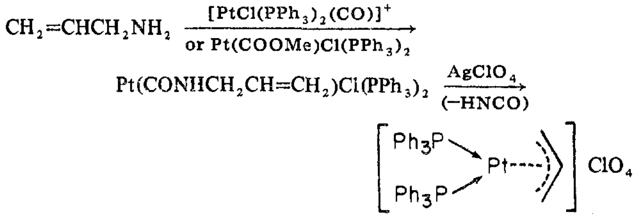
That two phosphine ligands are located mutually trans may be deduced from the appearance of the phosphine methyl proton resonances as 1:2:1 triplets in the ^{1}H NMR spectra of I and II owing to the large ^{31}P–^{31}P coupling.[18] The geometry of $\mathrm{Pt(COOMe)Cl(PPh_3)_2}$ has previously been suggested to be trans on the basis of the use of the intensity of an infrared absorption band at 550 ± 5 cm^{-1} in many bis(triphenylphosphine)platinum(II) complexes;[19] only the cis complexes have a strong band in this region. The same conclusion may be drawn concerning the stereochemistry of III–VII. The absorption bands of medium intensity around 280 cm^{-1} in the spectra of I–VII can consequently be assigned to the stretching of the Pt–Cl bond trans to the allyloxycarbonyl or *N*-allylcarbamoyl groups. Comparison of these values with those associated with the Pt–Cl bonds trans to other ligands[20] suggests that the COXR ligands (X = O or NH) are among those of relatively high trans influence, comparable to the alkyl ligands.

Decarboxylation of Allyloxycarbonylplatinum(II) Complexes. The complexes I–VI are stable in methylene chloride and benzene at room temperature. I and III are fairly stable in freshly purified chloroform at room temperature, but they do decompose rapidly when dissolved in aged chloroform to afford the π-allylplatinum(II) complexes and $\mathrm{CO_2}$ (eq 2, Q = PPh$_2$Me and PPh$_3$, R^1 = R^2 = R^3 = H). We cannot explain this behavior in chloroform at the moment. In refluxing benzene, all the allyloxycarbonyl complexes underwent similar decarboxylation to give moderate to high yields of the π-allyl complexes depending on the structure of the allylic moiety (eq 2, Q = PPh$_2$Me or PPh$_3$, R^1 = R^2 = R^3 = H, R^1 = R^3 = H and R^2 = Me, R^1 = R^2 = H and R^3 = Me, R^1 = Me and R^2 = R^3 = H). The order of the reactivities in a series of the triphenylphosphine complexes was qualitatively found to be the following (see Experimental Section): III ≃ VI > IV >> V. Only one isomer of the π-crotyl complex with the methyl at the syn position was obtained from V and VI (vide infra). It is notable that analogous complexes $\mathrm{Pt(COOR)Cl(PPh_3)_2}$ (R = Me, *n*-Pr, *i*-Pr) were found to be quite inert with regard to a similar decarboxylation even in refluxing benzene for prolonged periods. Complex VII was also found to be much more stable under similar conditions.

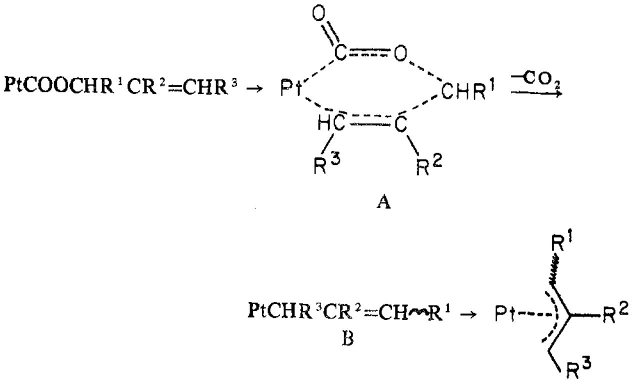


(2)

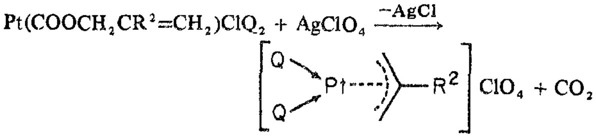
Scheme I



Scheme II



A more facile decarboxylation of the allyloxycarbonyl complexes could be performed by treating these with an equimolar amount of AgClO$_4$ to remove the chloride ligand. Thus, for example, the reactions of I–III with AgClO$_4$ in either methylene chloride–acetone or benzene at room temperature resulted in the formation of the cationic π-allyl complexes in very high yields (eq 3, Q = PPh$_2$Me or PPh$_3$, R^2 = H or Me).



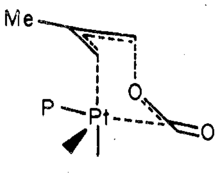
(3)

Similar reactions of the other allyloxycarbonyl complexes with AgClO$_4$ in benzene afforded moderate yields of the corresponding π-allyl complexes. The π-crotyl complex which was obtained from V in this way consisted of only the syn methyl isomer, while the same complex from VI was shown to be a mixture of the syn (65%) and anti (35%) isomers (vide infra).

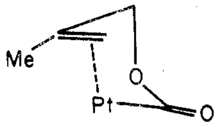
The reaction of VII with AgClO$_4$ in methylene chloride–acetone at room temperature also gave the π-allyl complex in ca. 40% yields, thus adding another example to the relatively rare utilization of allylamines for π-allyl formation[21] (Scheme I).

Although decarbonylation of acylmetal complexes[22] and decarboxylation of metal carboxylates[23] have been known to produce alkylmetal complexes, rather few studies have been reported of decarboxylation of alkoxycarbonyl complexes which affords alkylmetal complexes. For example, Otsuka et al. recently reported[24] that thermolysis of several alkoxycarbonyl complexes of Ni(II) and Pd(II) fails to give any evidence to support the formation of a metal–alkyl bond. Thus, the present reactions 2 and 3 provide the first example of a ready metal–carbon bond formation through decarboxylation of alkoxycarbonyl complexes.[25]

A few mechanistic implications for such a facile decarboxylation of I–VI can be derived from currently available evidence. The specific formation of the platinum–carbon bonds through reactions 2 and 3 in comparison to the failure of $\mathrm{Pt(COOR)Cl(PPh_3)_2}$ (R = Me, *n*-Pr, *i*-Pr) to afford alkylplatinum(II) complexes under similar conditions may suggest a concerted process in the former case, in a way similar to those advanced in the retro-ene reactions[27] or the Cope and Claisen rearrangements[28] (Scheme II). The σ-allyl intermediate **B** formed this way is most likely to rearrange rapidly to the π-allyl form under the conditions employed.[11] Preference for a chair-like transition state over a boat-like alternative in the Cope and Claisen rearrangements has already been well evidenced.[28] It is difficult, however, to determine definitely whether the platinum atom becomes five-coordinate or whether either the chloride or the phosphine ligand dissociates in the transition state A in the case of the thermal decarboxylation. In any case, that V is much more reluctant to undergo reaction 2 than are III, IV, and VI is presumably due to the greater steric interaction between the terminal methyl and the phosphine or the chloride ligand in A. On the other hand, the reason for the slower rates of both the thermal and the silver-assisted decarboxylations of IV than of III seems rather less clear. Molecular models for A derived from IV indicated very little steric constraint around the 2-methyl substituent in several conceivable configurations around the platinum atom except one with the phosphine lying closest to the methyl, namely



However, this model is apparently not appropriate for the decarboxylation proceeding through the cationic four-coordinate platinum. No information is available concerning the electronic effect of the 2-methyl on the energy levels of A. One possible explanation for the relative reactivity of IV vs. III in question would be that A is preceded by occurrence of an intermediate complex involving intramolecular coordination of the C=C bond to platinum (structure C), with

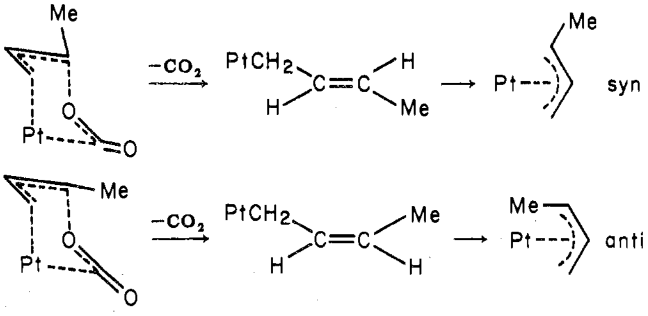


C

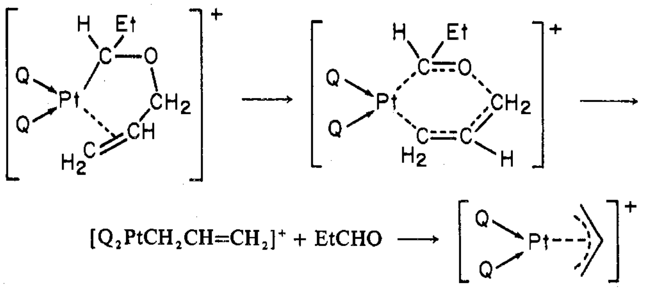
the stability of such an intermediate derived from IV being less than that from III. This is in agreement with the fact that introducing more alkyl substituents at the olefinic carbons results in marked decrease in the stability of the π-olefinplatinum complexes on both electronic and steric grounds;[29] the stability of $PtCl_3(ol)^-$ (ol = $CH_2{=}CHCH_2NH_3^+$) is ca. 300 times as high as that for ol = $CH_2{=}CMeCH_2NH_3^+$ and ca. 5 times as high as that for ol = *trans*-$MeCH{=}CHCH_2NH_3^+$. Furthermore, such π-bond formation as in C is expected to be greatly favored by removing the chloride ligand with a silver ion to vacate one coordination site, in view of the ready coordination of numerous olefins as well as acetylenes to platinum in the cationic hydrido and alkylplatinum(II) complexes;[12,30] this has indeed been realized in the more facile decarboxylation 3 than 2. Thus, the stabilities of both A and C may well affect the overall rate of the decarboxylation, the former effect probably being more important than the latter.

A choice of the formation of two isomeric π-crotyl complexes $[Pt(\pi\text{-}C_4H_7)(PPh_3)_2]ClO_4$ from the reaction of VI with $AgClO_4$ has possibly been determined by the relative stabilities of the two forms of the transition state A as shown in Scheme III, since no interconversion of the two isomers was observed[13] to occur under the conditions employed here. In the transition state derived from VI, the methyl group syn to the 2 hydrogen presumably suffers less steric constraint than at the anti position, thus giving a higher amount of the syn product. In the case of the analogous reaction of V, the more stable syn product[13] may well have been obtained preferentially from an intermediate complex B involving a $PtCHMeCH{=}CH_2$ moiety. On the other hand, the formation of only the syn form of the π-crotyl complex $[Pt(\pi\text{-}C_4H_7)(PPh_3)_2]Cl$ from thermolysis of VI must certainly be a consequence of rapid anti–syn isomerization under the conditions employed, for it has been shown previously[13] that the anti form of the complex $[Pt(\pi\text{-}C_4H_7)(PPh_3)_2]ClO_4$ can readily be converted to the syn form on treatment with the free chloride or bromide anion owing to the role of the halide ligands in stabilizing a σ-allyl intermediate.

Scheme III



Scheme IV



We have also suggested previously[2] that a ready decarboxylation of III in the presence of $SnCl_2$ as catalyst is likewise attributed to π-olefinplatinum complexation stabilized by $SnCl_3^-$. However, the precise role of $SnCl_2$ in catalyzing reaction 2 should be reconsidered with care, since the same reaction was also catalyzed by several tin compounds[31] including Me_2SnCl_2, the mechanism of such apparently acid-catalyzed decarboxylation remaining to be fully elucidated.

Finally, it seems of interest to note a similarity in the reaction patterns of the decarboxylation above and of the formation of π-allylplatinum(II) complexes and aldehydes from cationic platinum(II) hydrides and diallyl ether.[13] In the latter reaction, the importance of intramolecular C=C coordination has already been suggested, and we now further propose that such a π-olefinplatinum intermediate is followed by a transition state in a way similar to that described in the former reaction (Scheme IV).

Acknowledgment. Partial support of this work by the Hattori Hokokai is acknowledged. Thanks are also due to Professors R. Okawara and S. Murai of this department for helpful discussions.

Registry No. I, 53224-24-1; II, 53224-25-2; III, 53224-22-9; IV, 53224-23-0; V, 55493-59-9; VI, 55493-60-2; VII, 55493-61-3; $Pt(COO\text{-}n\text{-}Pr)Cl(PPh_3)_2$, 55493-40-8; $Pt(COO\text{-}i\text{-}Pr)Cl(PPh_3)_2$, 55493-41-9; $[PtCl(PPh_3)_2(CO)]ClO_4$, 53203-81-9; $Pt(COOMe)Cl(PPh_3)_2$, 20524-02-1; allyl alcohol, 107-18-6; allylamine, 107-11-9; $AgClO_4$, 7783-93-9.

References and Notes

(1) A preliminary note has been published: H. Kurosawa and R. Okawara, *J. Organomet. Chem.*, **71**, C35 (1974).
(2) Presented in part at the Japan–U.S. joint seminar on the Prospects in Organo(transition metal) Chemistry, Honolulu, Hawaii, 1974.
(3) See, e.g., R. Baker, *Chem. Rev.*, **73**, 487 (1973).
(4) K. Vrieze, H. C. Volger, and P. W. N. M. van Leeuwen, *Inorg. Chim.*

Acta, Rev., **3**, 109 (1969); J. W. Faller and M. T. Tully, *J. Am. Chem. Soc.*, **94**, 2676 (1972); J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 1839 (1967).

(5) H. L. Clarke, *J. Organomet. Chem.*, **80**, 155 (1974).

(6) M. L. H. Green, "Organometallic Compounds", Vol. 2, M. L. H. Green, and K. Wade, Ed., Methuen, London, 1968.

(7) F. R. Hartley, "The Chemistry of Platinum and Palladium", Applied Science, London, 1973, p 418.

(8) N. L. Bauld, *Tetrahedron Lett.*, 859 (1962); W. Hafner, H. Prigge, and J. Smidt, *Justus Liebigs Ann. Chem.*, **693**, 109 (1966).

(9) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Am. Chem. Soc.*, **91**, 1346 (1969).

(10) C. R. Green and R. J. Angelici, *Inorg. Chem.*, **11**, 2095 (1972).

(11) H. C. Volger and K. Vrieze, *J. Organomet. Chem.*, **9**, 527 (1967).

(12) H. C. Clark and H. Kurosawa, *Inorg. Chem.*, **11**, 1275 (1972).

(13) H. C. Clark and H. Kurosawa, *Inorg. Chem.*, **12**, 357 (1973).

(14) W. J. Cherwinski and H. C. Clark, *Can. J. Chem.*, **47**, 2665 (1969).

(15) J. E. Byrd and J. Halpern, *J. Am. Chem. Soc.*, **93**, 1634 (1971).

(16) A uniform upfield shift of the resonances due to the olefinic protons as well as the allylic and some methyl protons in I–VII by ca. 0.5–1 ppm in comparison to those of the parent allyl alcohols and allylamine is presumably attributed to magnetic anisotropy of the phenyl rings of the phosphines.

(17) P. J. Fraser, W. R. Roper, and F. G. A. Stone, *J. Organomet. Chem.*, **66**, 155 (1974).

(18) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

(19) S. H. Mastin, *Inorg. Chem.*, **13**, 1003 (1974).

(20) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973); see p 359.

(21) H. Kurosawa and R. Okawara, *J. Organomet. Chem.*, **81**, C31 (1974).

(22) A. Wojcicki, *Adv. Organomet. Chem.*, **11**, 87 (1973).

(23) P. G. Cookson and G. B. Deacon, *Aust. J. Chem.*, **25**, 2095 (1972); T. Tsuda, T. Nakatsuka, T. Hirayama, and T. Saegusa, *J. Chem. Soc., Chem. Commun.*, 557 (1974).

(24) S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto, and K. Ataka, *J. Am. Chem. Soc.*, **95**, 3180 (1973).

(25) A metallocarboxylic acid intermediate has been postulated in the reaction of alkoxycarbonyl complexes with H_2O to give a metal hydride and CO_2.[26]

(26) R. J. Angelici, *Acc. Chem. Res.*, **5**, 335 (1972).

(27) P. Vitins and K. W. Egger, *J. Chem. Soc., Perkin Trans. 2*, 1292 (1974), and references cited therein.

(28) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., Germany, 1971, p 148; G. Frater, A. Habich, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **52**, 335 (1969).

(29) R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc. A*, 328 (1967).

(30) M. H. Chisholm and H. C. Clark, *Acc. Chem. Res.*, **6**, 202 (1973).

(31) H. Kurosawa, unpublished results.

Contribution from the Fachbereich Biologie Universität Konstanz, Konstanz, West Germany,
and the Fondation Curie-Institut du Radium, Section de Biologie, Orsay, France

Flavoquinone–Metal Complexes. I. Structure and Properties

J. LAUTERWEIN, P. HEMMERICH,* and J.-M. LHOSTE

Received October 15, 1974 AIC40715P

Dark red flavoquinone–metal complexes have been detected by proton magnetic resonance and optical absorption in aprotic solvents. The stoichiometry and the formation constants of the complexes were measured by metal ion titration in acetone with the relative order of stability $\mathrm{Cu^I} > \mathrm{Ni^{II}} > \mathrm{Ag^I}$, $\mathrm{Co^{II}} > \mathrm{Cu^{II}} > \mathrm{Zn^{II}} > \mathrm{Cd^{II}} > \mathrm{Fe^{II}} \gg \mathrm{Mn^{II}}$, $\mathrm{Mg^{II}}$, $\mathrm{Fe^{III}}$ for the tris, bis, or mono complexes obtained in the presence of an excess of flavine. Stable bidentate chelates at O(4α)–N(5) were observed, corresponding to octahedral tris complexes ($\mathrm{Zn^{II}}$, $\mathrm{Cd^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, and $\mathrm{Fe^{II}}$) and tetrahedral ($\mathrm{Ag^I}$ and $\mathrm{Cu^I}$) or square-planar ($\mathrm{Cu^{II}}$) bis complexes. Labile complexes corresponding to weak monodentate binding at the keto groups of the flavine were observed with $\mathrm{Mg^{II}}$, $\mathrm{Mn^{II}}$, and $\mathrm{Fe^{III}}$. They were also observed with the former ions as secondary sites of coordination. The nature—though not the kinetics—of the binding was found to be largely independent of the metal among the bidentate complexes, either with diamagnetic or with paramagnetic ions, excluding extensive charge transfer from the metal toward the electron-deficient flavoquinone ligand.

Introduction

Previous studies of the interaction of flavines and flavocoenzymes with metal ions,[1-4] as reviewed extensively by Hemmerich and Lauterwein,[5] have led to the distinction of three different types of flavine–metal complexes.

(1) Flavines in their oxidized state ("flavoquinone", $\mathrm{HFl_{ox}}$) do not form stable metal chelates in dilute aqueous solution except with the exceedingly "soft"[6] metal ions $\mathrm{Ag^+}$ and $\mathrm{Cu^+}$.[1,2] These ions are the only ones capable of coordinating the flavoquinone *anion* ($\mathrm{Fl_{ox}^-}$) more strongly than $\mathrm{OH^-}$, according to eq 1. In the case of the biologically relevant donor–acceptor

$$\mathrm{HFl_{ox}} + (\mathrm{Ag^I}, \mathrm{Cu^I})^+ \xrightleftharpoons{\mathrm{pH}>7} (\mathrm{Ag^I}, \mathrm{Cu^I})\mathrm{Fl_{ox}} + \mathrm{H^+} \tag{1}$$

ions of iron and molybdenum,[3] initial complex formation in the lower valence (donor) states $\mathrm{Fe^{II}}$ and $\mathrm{Mo^V}$ is followed by rapid hydrolysis in the upper metal valence states according to eq 2. These complexes of metal donor states with flavoquinone anion have been termed "*charge transfer chelates*". The more stable binary tetrahedral $\mathrm{Ag^I}$ and $\mathrm{Cu^I}$ chelates can only serve as models of distinct but limited relevance for the octahedral $\mathrm{Fe^{II}}$ and $\mathrm{Mo^V}$ chelates, whose stability is largely determined by ternary ligands (other than solvent). It should be emphasized that nothing can be inferred as to their electron and spin distribution at present.

$$\begin{array}{r} \mathrm{HFl_{ox}} + (\mathrm{Fe^{II}}, \mathrm{Mo^V}) \rightleftarrows [\mathrm{Fe^{II}}, \mathrm{Mo^V})\mathrm{Fl_{ox}} \leftrightarrow (\mathrm{Fe^{III}}, \mathrm{Mo^{VI}})\dot{\mathrm{F}}\mathrm{l}] + \mathrm{H^+} \\ \mathrm{H_2O}\big\downarrow\!\uparrow \qquad\qquad \\ (\mathrm{Fe^{III}}, \mathrm{Mo^{VI}})\mathrm{OH} + \mathrm{H\dot{F}lH} \qquad \end{array} \tag{2}$$

(2) General flavine–metal affinity in dilute aqueous solution is only observed[4] for the radical state according to eq 3. In

$$\mathrm{HFl_{ox}} + \mathrm{HFl_{red}H_2} \rightleftarrows 2\mathrm{H\dot{F}lH} \xrightleftharpoons{\mathrm{M^{2+}}} 2\mathrm{MH\dot{F}l^+} + 2\mathrm{H^+} \tag{3}$$

all partly reduced flavine systems, therefore, semiquinone disproportionation is overcome at neutral to slightly alkaline pH by formation of "*radical chelates*" with the flavosemiquinone anion $\mathrm{H\dot{F}l^-}$.

(3) Metal complexes made up from *neutral* flavoquinone and redox-inactive metal ions can, however, be observed in aprotic solvents for low water content. The present detailed study is devoted to those "*flavoquinone chelates*", which contain $\mathrm{RFl_{ox}}$ as ligand (R = H or alkyl substituent at N(3)) in contrast to the first mentioned "charge-transfer chelates". The more polarizable monovalent or divalent ions, either diamagnetic such as $\mathrm{Cu^I}$, $\mathrm{Ag^I}$, $\mathrm{Zn^{II}}$, and $\mathrm{Cd^{II}}$ or paramagnetic such as $\mathrm{Fe^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, and $\mathrm{Cu^{II}}$, will be shown to chelate at the N(5)–O(4α) site according to eq 4. The less polarizable

$$n\mathrm{RFl_{ox}} + \mathrm{M}^{m+} \rightleftarrows \mathrm{M(RFl_{ox})}_n{}^{m+} \tag{4}$$

ions such as $\mathrm{Mg^{II}}$, $\mathrm{Mn^{II}}$, or $\mathrm{Fe^{III}}$ form only *monodentate* complexes very weakly bound at the carbonyl oxygen atoms of the flavine nucleus.

---

* To whom correspondence should be addressed at the Fachbereich Biologie Universität Konstanz.