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

π-Allylmetal Chemistry. 6.[1] Synthesis and Equilibria of Unusually Stable σ-Allylplatinum(II) and -palladium(II) Complexes Containing Polyhaloaryl Groups

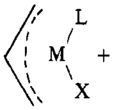
SHIGEAKI NUMATA, ROKURO OKAWARA, and HIDEO KUROSAWA*

Received December 1, 1976 AIC60857E

Unusually stable σ-allyl complexes of the form *trans*-$\mathrm{M(\sigma\text{-allyl})(Ar)L_2}$ (M = Pt, Pd; allyl = $\mathrm{CH_2{=}CHCH_2}$, $\mathrm{MeCH{=}CHCH_2}$, $\mathrm{CH_2{=}CMeCH_2}$; Ar = 2,3,5,6-$\mathrm{C_6HCl_4}$, $\mathrm{C_6F_5}$; L = $\mathrm{PPh_3}$, $\mathrm{PMe_2Ph}$) have been prepared from $\mathrm{M(\pi\text{-allyl})(Ar)(PPh_3)}$ and L. The ease of the formation of these σ-allyl complexes decreases in the order $\mathrm{MeCH{=}CHCH_2} \simeq \mathrm{CH_2{=}CHCH_2} \gg \mathrm{CH_2{=}CMeCH_2}$, $\mathrm{PMe_2Ph} > \mathrm{PPh_3}$, and Pt > Pd ≫ Ni. A variable-temperature ^{1}H NMR spectral study indicated that the occurrence of the trans structure in such σ-allyl complexes is a result of thermodynamic but not necessarily kinetic control. *cis*-σ-Allyl complexes of the form $\mathrm{M(\sigma\text{-}CH_2{=}CHCH_2)(Ar)(diphos)}$ (diphos = $\mathrm{Ph_2PCH_2CH_2PPh_2}$) have also been prepared.

Introduction

Ligand-induced π–σ allyl interconversion in square-planar nickel triad metal complexes has been the subject of many studies[2] (eq 1). In this system, the equilibrium constant and



$$+\ \mathrm{L} \rightleftharpoons \mathrm{M(\sigma\text{-allyl})XL_2} \qquad (1)$$

the rate of the interconversion in both directions and consequently the lifetime of a σ-allylmetal species are expected to depend on the nature of allyl, X, and L. Under conditions of fast chemical exchange of L, the system is called "dynamic allyl" giving rise to dynamic ^{1}H NMR spectra. In most of these studies, however, the extent to which a σ-allyl species really exists and what the actual structure of the σ-allyl species is have remained yet to be answered.[3] This may be explained as due to mainly (i) the lack of sufficiently slow rates of π–σ interconversion to give frozen ^{1}H NMR spectra, (ii) the ready ionization of the halide ligands resulting in the increase in the number of equilibrium species, and/or (iii) difficulty in isolating kinetically inert σ-allyl complexes of the nickel triad metals. Thus, isolated σ-allyl complexes which have a close relation to the π–σ interconversion include $\mathrm{Ni(\pi\text{-}2\text{-}MeC_3H_4)(\sigma\text{-}2\text{-}MeC_3H_4)(PEt_3)}$,[6] $\mathrm{Pd(\sigma\text{-}2\text{-}MeC_3H_4)Cl(PPh_3)_2}$,[7] $\mathrm{Pt(\sigma\text{-}2\text{-}MeC_3H_4)_2(PPh_3)_2}$,[8] $\mathrm{Pt(\sigma\text{-}2\text{-}MeC_3H_4)(diphos)(PPh_2Me)PF_6}$,[9] and $\mathrm{Pt(\sigma\text{-}1\text{-}MeC_3H_4)Cl(PPh_3)_2}$,[10] but most of them were characterized principally through vibrational spectral evidence and gave no unambiguous ^{1}H NMR spectra for the σ-allyl structures. Further, although low-temperature ^{1}H NMR spectra of $\mathrm{Pd(\pi\text{-}2\text{-}MeC_3H_4)(S_2CNMe_2)/PMe_2Ph}$ in $\mathrm{CDCl_3}$ were shown to be consistent with the formation of $\mathrm{Pd(\sigma\text{-}2\text{-}MeC_3H_4)(S_2CNMe_2)(PMe_2Ph)}$, successful isolation of this product could not be carried out.[11]

In order to both reduce the rate involved in eq 1 and avoid routes to the ionic species, we have introduced, in place of the halide ligand, bulky, and sufficiently electronegative substituents, 2,3,5,6-$\mathrm{C_6HCl_4}$ (abbreviated as $\mathrm{C_6HCl_4}$ hereafter) and $\mathrm{C_6F_5}$, into allylplatinum and palladium complexes. We wish to describe the preparation and the structure of some unusually stable σ-allyl complexes, $\mathrm{M(\sigma\text{-allyl})(Ar)L_2}$ (M = Pt, Pd; allyl = $\mathrm{CH_2{=}CHCH_2}$, $\mathrm{MeCH{=}CHCH_2}$, $\mathrm{CH_2{=}CMeCH_2}$; Ar = $\mathrm{C_6HCl_4}$, $\mathrm{C_6F_5}$; L = $\mathrm{PPh_3}$, $\mathrm{PMe_2Ph}$; $\mathrm{L_2}$ = diphos). ^{1}H NMR spectral evidence for equilibria between π- and σ-allyl species is also given. The present work thus provided more detailed means of understanding the π–σ allyl interconversion in the nickel triad complexes.

Experimental Section

Materials. $\mathrm{Tl(C_6HCl_4)_3}$, $\mathrm{Pt(\pi\text{-}C_3H_5)(C_6HCl_4)(PPh_3)}$, **1**, and $\mathrm{Pd(\pi\text{-}C_3H_5)(C_6HCl_4)(PPh_3)}$, **5**, were prepared as described previously.[12] $\mathrm{Pt(\pi\text{-}2\text{-}MeC_3H_4)Cl(PPh_3)}$ and $\mathrm{Pt(\pi\text{-}1\text{-}MeC_3H_4)Cl(PPh_3)}$ were prepared according to the reported procedures.[10] Most other chemicals and all solvents used were of reagent grade.

Spectra. ^{1}H NMR spectra were obtained on a Japan Electron Optics JNM-PS-100 spectrometer with tetramethylsilane as internal standard. Infrared spectra of the solid compounds were taken on Hitachi 225 (4000–600 cm^{-1}) and Hitachi EPI-2-G (700–200 cm^{-1}) spectrophotometers, both equipped with gratings. Molecular weights were determined using a Mechrolab vapor pressure osmometer, Model 302.

$\mathrm{Pt(\pi\text{-}2\text{-}MeC_3H_4)(C_6HCl_4)(PPh_3)}$, 2, and $\mathrm{Pt(\pi\text{-}1\text{-}MeC_3H_4)(C_6HCl_4)(PPh_3)}$, 3. These complexes were prepared in a manner similar to that[12] for obtaining **1**. **2**: yield 72%; mp 203–204 °C. Anal. Calcd for $\mathrm{C_{28}H_{23}Cl_4PPt}$: C, 46.24; H, 3.19. Found: C, 45.97; H, 3.14. **3**: yield 65%; mp 199–202 °C. Anal. Calcd for $\mathrm{C_{28}H_{23}Cl_4PPt}$: C, 46.24; H, 3.19. Found: C, 46.51; H, 3.16.

$\mathrm{Pt(\pi\text{-}C_3H_5)(C_6F_5)(PPh_3)}$, 4. To a THF solution (8 mL) of pentafluorophenyllithium, which was obtained from pentafluorobenzene (500 mg, 3 mmol) and an equimolar amount of commercial *n*-butyllithium in *n*-hexane, was added dropwise $\mathrm{Pt(\pi\text{-}C_3H_5)Cl(PPh_3)}$ (1066 mg, 2 mmol) in THF (40 mL) under nitrogen at −78 °C. Rapid stirring at this temperature was continued for 1 h. The reaction mixture was allowed to warm to room temperature and the solvent was removed in vacuo. The yellow residue thus obtained was extracted with benzene (10 mL) and purified by chromatography through a short Florisil column. Recrystallization from benzene–methanol gave yellow crystals of **4** (550 mg, 43%), mp 133 °C dec. Anal. Calcd for $\mathrm{C_{27}H_{20}F_5PPt}$: C, 48.73; H, 3.03. Found: C, 49.21; H, 3.31.

$\mathrm{Pd(\pi\text{-}C_3H_5)(C_6F_5)(PPh_3)}$, 6. The complex was prepared in a manner similar to that for **4**; yield 42%, mp 142 °C dec. Anal. Calcd for $\mathrm{C_{27}H_{20}F_5PPd}$: C, 56.22; H, 3.50. Found: C, 56.16; H, 3.44.

$\mathrm{Pt(\sigma\text{-}CH_2CH{=}CH_2)(C_6HCl_4)(PPh_3)_2}$, 8. Triphenylphosphine (87 mg, 0.33 mmol) was added to a dichloromethane solution (3 mL) of **1** (238 mg, 0.33 mmol). A 3-mL amount of *n*-hexane was added and the solution was cooled in the refrigerator whereupon colorless crystals formed slowly (306 mg, 91%). Molecular weights found by vapor pressure osmometry in benzene at 25 °C were 562, 630, 759, and 804 at concentrations 0.022, 0.053, 0.19, and 0.31 mol %; calcd for the monomer 976.

$\mathrm{Pt(\sigma\text{-}CH_2CH{=}CHMe)(C_6HCl_4)(PPh_3)_2}$, 9, and $\mathrm{Pt(\sigma\text{-}CH_2CH{=}CH_2)(C_6F_5)(PPh_3)_2}$, 10. These were prepared from $\mathrm{PPh_3}$ and **3** or **4** in a similar way to that for obtaining **8**: **9**, yield 89%, colorless prisms; **10**, yield 85%, pale yellow prisms.

$\mathrm{Pt(\sigma\text{-}CH_2CH{=}CH_2)(C_6HCl_4)(PMe_2Ph)_2}$, 11. Dimethylphenylphosphine (73 mg, 0.53 mmol) was added to a chloroform solution (2 mL) of **1** (151 mg, 0.21 mmol). Removal of the solvent left a pale yellow solid which was purified by chromatography through a short Florisil column eluted with chloroform. Addition of methanol to the eluent and concentration to a small volume gave 100 mg (67%) of colorless crystals.

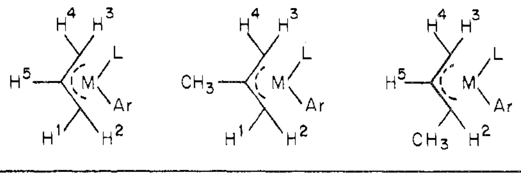
$\mathrm{Pt(\sigma\text{-}CH_2CMe{=}CH_2)(C_6HCl_4)(PMe_2Ph)_2}$, 12, and $\mathrm{Pd(\sigma\text{-}CH_2CH{=}CH_2)(C_6HCl_4)(PMe_2Ph)_2}$, 13. These complexes were prepared from $\mathrm{PMe_2Ph}$ and **2** or **5** (2:1 ratio) in an essentially similar manner to that described above: **12**, yield 78%, colorless needles; **13**, recrystallized from diethyl ether–*n*-hexane, yield 50%, yellow crystals. Although the ^{1}H NMR spectrum at room temperature of an *o*-dichlorobenzene solution containing **5** (40 mg) and an equimolar

Table I. Analytical, Physical, and Infrared Data for σ-Allyl Complexes of Pt(II) and Pd(II)

Complex	No.	Mp,[a] °C	% C		% H		ν(C=C),[b] cm^{-1}
			Calcd	Found	Calcd	Found	
Pt(σ-$CH_2CH=CH_2$)(C_6HCl_4)($(PPh_3)_2$	8	182–183	55.40	55.12	3.72	3.58	1611
Pt(σ-$CH_2CH=CHMe$)(C_6HCl_4)(PPh_3)$_2$	9	198–199	55.83	55.66	3.88	3.96	
Pt(σ-$CH_2CH=CH_2$)(C_6F_5)(PPh_3)$_2$	10	194–195	58.26	58.57	3.80	3.92	1610
Pt(σ-$CH_2CH=CH_2$)(C_6HCl_4)(PMe_2Ph)$_2$	11	135–136	41.28	41.46	3.88	3.99	1601
Pt(σ-$CH_2CMe=CH_2$)(C_6HCl_4)(PMe_2Ph)$_2$	12	133–134	42.12	42.06	4.08	4.17	1611
Pd(σ-$CH_2CH=CH_2$)(C_6HCl_4)(PMe_2Ph)$_2$	13	107–108	47.02	46.96	4.42	4.45	1599
Pt(σ-$CH_2CH=CH_2$)(C_6HCl_4)(diphos)	14	184–185	49.49	49.27	3.56	3.44	1603
Pd(σ-$CH_2CH=CH_2$)(C_6HCl_4)(diphos)	15	145–147	55.26	55.40	3.98	3.88	1607
Pd(σ-$CH_2CH=CH_2$)(C_6F_5)(diphos)	16	156–159	58.96	59.47	4.10	4.36	1600

[a] Uncorrected. [b] Nujol mulls.

Table II. ^1H NMR Data[a] for M(π-allyl)(Ar)L in $CDCl_3$



No.	Complex				H^1	H^2	H^3	H^4	H^5	CH_3	C_6HCl_4
	M	Allyl	Ar	L							
1	Pt	C_3H_5	C_6HCl_4	PPh_3	3.96 dt $J_5 = 6$ $J_4 = 2$ $J_P = 6$	2.64 dd $J_5 = 13$ $J_P = 10$ $J_{Pt} = 56$	2.34 d $J_5 = 13$ $J_{Pt} = 40$	3.64 dd $J_5 = 7$ $J_1 = 2$	4.80 m		6.92 s
2	Pt	2-MeC_3H_4	C_6HCl_4	PPh_3	3.70 dd $J_4 = 2$ $J_P = 6$	2.62 d $J_P = 9$ $J_{Pt} = 56$	2.32 s $J_{Pt} = 40$	3.38 d $J_1 = 2$		2.04 s $J_{Pt} = 55$	6.96 s
3	Pt	1-MeC_3H_4	C_6HCl_4	PPh_3		3.60 m	2.07 d $J_5 = 12$ $J_{Pt} = 41$	3.32 d $J_5 = 7$	4.70 dt $J_2 = 12$ $J_3 = 12$ $J_4 = 7$	1.68 t $J_2 = 6$ $J_P = 6$ $J_{Pt} = 20$	6.92 s
4	Pt	C_3H_5	C_6F_5	PPh_3	4.03 dt $J_5 = 5$ $J_4 = 2$ $J_P = 5$	2.56 dd $J_5 = 12$ $J_P = 10$ $J_{Pt} = 49$	2.30 d $J_5 = 13$ $J_{Pt} = 44$	3.80 dd $J_5 = 6$ $J_1 = 2$	4.80 m		
6	Pd	C_3H_5	C_6F_5	PPh_3	4.18 dt $J_5 = 6$ $J_4 = 2$ $J_P = 6$	3.05 dd $J_5 = 13$ $J_P = 9$	2.69 d $J_5 = 13$	3.96 dd $J_5 = 7$ $J_1 = 2$	5.40 m		
7[b]	Pd	C_3H_5	C_6HCl_4	PMe_2Ph	3.88 t $J_5 = 5$ $J_P = 5$	2.92 dd $J_5 = 13$ $J_P = 9$	2.44 d $J_5 = 12$	3.44 d $J_5 = 6$	5.40 m		

[a] Chemical shift in ppm downfield from TMS, J in Hz; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet; J_x = coupling constants with proton numbered x, J_P = coupling constants with ^{31}P, J_{Pt} = coupling constants with ^{195}Pt. [b] In o-dichlorobenzene δ(P–CH_3) 1.36 (d), $J_P = 8$ Hz, and 1.42 (d) $J_P = 8$ Hz.

amount of PMe_2Ph shows the complete formation of Pd(π-C_3H_5)(C_6HCl_4)(PMe_2Ph), **7** (see Table II, Figure 1d), attempts to isolate this compound were unsuccessful.

Pt(σ-$CH_2CH=CH_2$)(C_6HCl_4)($Ph_2PCH_2CH_2PPh_2$), 14. Bis(diphenylphosphino)ethane (diphos) (81 mg, 0.21 mmol) was added to a dichloromethane solution (2 mL) of **1** (144 mg, 0.2 mmol). A 2-mL amount of n-hexane was added and the solution was kept in the refrigerator. Colorless crystals formed slowly; yield 51%.

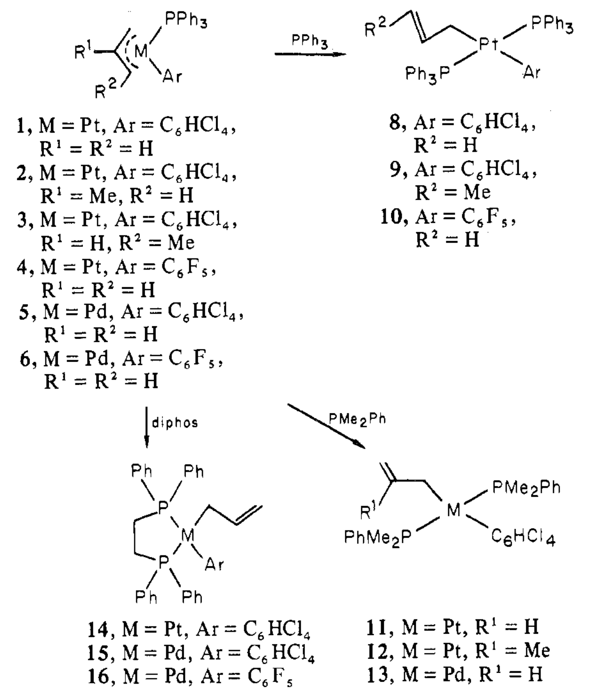
Pd(σ-$CH_2CH=CH_2$)(C_6HCl_4)($Ph_2PCH_2CH_2PPh_2$), 15, and Pd(σ-$CH_2CH=CH_2$)(C_6F_5)($Ph_2PCH_2CH_2PPh_2$), 16. These were prepared in an essentially similar way to that described above for **14**: **15**, recrystallized from diethyl ether, yield 65%, yellow crystals; **16**, recrystallized from diethyl ether, yield 95%, pale yellow crystals. Analytical data of σ-allyl complexes of Pt(II) and Pd(II), **8–16**, are summarized in Table I.

Results and Discussion

^1H NMR Spectra of π-Allylplatinum(II) Complexes. Examination of ^1H NMR spectra[13] of **1–4** indicates a static π-allyl bonding of platinum (cf. Table II) rather than dynamic allyls. The ^1H NMR spectra of **1** and **2** in o-dichlorobenzene were temperature independent in the range 23–160 °C, indicating the maintenance of the rigid π-allyl structure even at high temperatures. We previously reported similar nonfluxionality of **5**[1,12] in the ^1H NMR spectra. Assignments of the spectra were mainly based on the preferential coupling of ^{31}P with allylic protons trans to the phosphorus atom,[4] thus leading to the location of the methyl in **3** trans to the phosphine. The spectra of **3** showed no resonances attributable to the anti-methyl isomer. The J_{Pt-H^2} values of **1** and **2** are larger than the J_{Pt-H^3} values. This suggests a stronger NMR trans influence[14] of the C_6HCl_4 group compared to that of PPh_3. The NMR trans influence of the C_6F_5 group may be comparable to that of PPh_3, judging from the value of J_{Pt-H^2} and J_{Pt-H^3} in **4**.

Synthesis and Characterization of σ-Allyl Complexes of Pt(II) and Pd(II). Upon addition of tertiary phosphines, π-allyl complexes **1–6** gave air-stable σ-allylplatinum(II) and -palladium(II) complexes **8–16** as shown in Scheme I. The ^1H NMR spectra[15] at room temperature of **8–16** except for

Scheme I



1, M = Pt, Ar = C_6HCl_4, $R^1 = R^2 = H$

2, M = Pt, Ar = C_6HCl_4, R^1 = Me, R^2 = H

3, M = Pt, Ar = C_6HCl_4, R^1 = H, R^2 = Me

4, M = Pt, Ar = C_6F_5, $R^1 = R^2 = H$

5, M = Pd, Ar = C_6HCl_4, $R^1 = R^2 = H$

6, M = Pd, Ar = C_6F_5, $R^1 = R^2 = H$

8, Ar = C_6HCl_4, R^2 = H

9, Ar = C_6HCl_4, R^2 = Me

10, Ar = C_6F_5, R^2 = H

14, M = Pt, Ar = C_6HCl_4

15, M = Pd, Ar = C_6HCl_4

16, M = Pd, Ar = C_6F_5

11, M = Pt, R^1 = H

12, M = Pt, R^1 = Me

13, M = Pd, R^1 = H

13 (see later) confirm a rigid σ-allyl structure, rather than dynamic allyls. The stereochemistry of the crotyl moiety in **9** was assigned trans on the basis of the value of $J_{H^2-H^5}$ = 16 Hz. Mutually trans phosphine structures in **8**–**13** are obvious from the following ^1H NMR and IR data. The use of the intensity of a band at 550 ± 5 cm^{-1} in the infrared spectra has been reported[16] to be useful for the assignments of the stereochemistry for $Pt(PPh_3)_2XY$ type compounds. According to this criterion, the appearance of only very weak bands at 550 cm^{-1} in **8**–**10** suggests trans configuration of the two PPh_3 groups. The phosphine methyl resonances of **11**–**13** (at −50 °C; see later) appear as 1:2:1 triplets due to strong $^{31}P-^{31}P$ coupling in the mutually trans phosphines. Finally, we note that the magnitudes of J_{Pt-CH_2} in **8**, **9**, **11**, and **12** with the trans-phosphine configuration are all smaller than that of the *cis*-σ-allyl complex, **14**. This result can be again interpreted in terms of the stronger NMR trans influence of the C_6HCl_4 group than of the phosphines.

π–σ Allyl Equilibrium. Though the ^1H NMR spectrum of **8** in $CDCl_3$ (concentration in the range 5–10 mol %) at room temperature showed no sign of dynamic behaviors, molecular weight measurements of **8** in benzene (concentration in the range 0.02–0.3 mol %) at 25 °C indicated dissociation of PPh_3 to some extent (see Experimental Section). It was found that the equilibrium between **1** and **8** or **3** and **9** is highly temperature dependent and lies well in favor of the π-allyl complexes at higher temperatures. Thus, the ^1H NMR spectrum of **8** in *o*-dichlorobenzene at 90 °C gave sharp resonances due to the π-allyl complex **1** solely with the complete dissociation of PPh_3. At 60 °C, two separate sets of resonances due to **1** and **8** were observable with the approximate mole ratio π:σ = 2:1. This indicates the slow rate of the π–σ interconversion on the NMR time scale even at higher temperatures. The ^1H NMR spectrum of **9** at 90 °C in *o*-dichlorobenzene similarly showed the presence of only the π-crotyl species, **3**. Inactiveness of **2** to form a σ-2-methylallyl species on addition of excess PPh_3 is consistent with the general trend[2] in the ease of σ-allyl formation, allyl ≫ 2-methylallyl, though the actual cause of such inactiveness may or may not involve other factors such as kinetic inhibition of steric origin.

The ^1H NMR spectra of **11** and **12** in *o*-dichlorobenzene at 90 °C displayed a sharp 1:2:1 triplet for the phosphine methyl resonances as well as clear σ-allyl resonances, indicating nondissociation of PMe_2Ph even at higher temperatures. On the contrary, extensive dissociation of PMe_2Ph from **13** was observed at higher temperatures (see later). It has been reported[17] that attempts to prepare $Ni(\sigma\text{-}C_3H_5)(C_6Cl_5)(PMe_2Ph)_2$ from $Ni(C_6Cl_5)Cl(PMe_2Ph)_2$ and the allyl Grignard reagent lead to isolation of $Ni(\pi\text{-}C_3H_5)(C_6Cl_5)(PMe_2Ph)$, and treatment of this with a large excess of PMe_2Ph gives no ^1H NMR evidence for the σ-allyl formation. From these facts, together with the failure of $Pd(\pi\text{-}C_3H_5)(C_6HCl_4)(PPh_3)$ to form a σ-allyl complex on adding excess PPh_3,[12] it is clear that the relative preference of metals and ligands to form σ-allyl complexes decreases in the order Pt > Pd ≫ Ni and PMe_2Ph > PPh_3. This is probably the first case where the most direct comparison of the trend of π–σ allyl interconversion between the nickel triad metals is made.

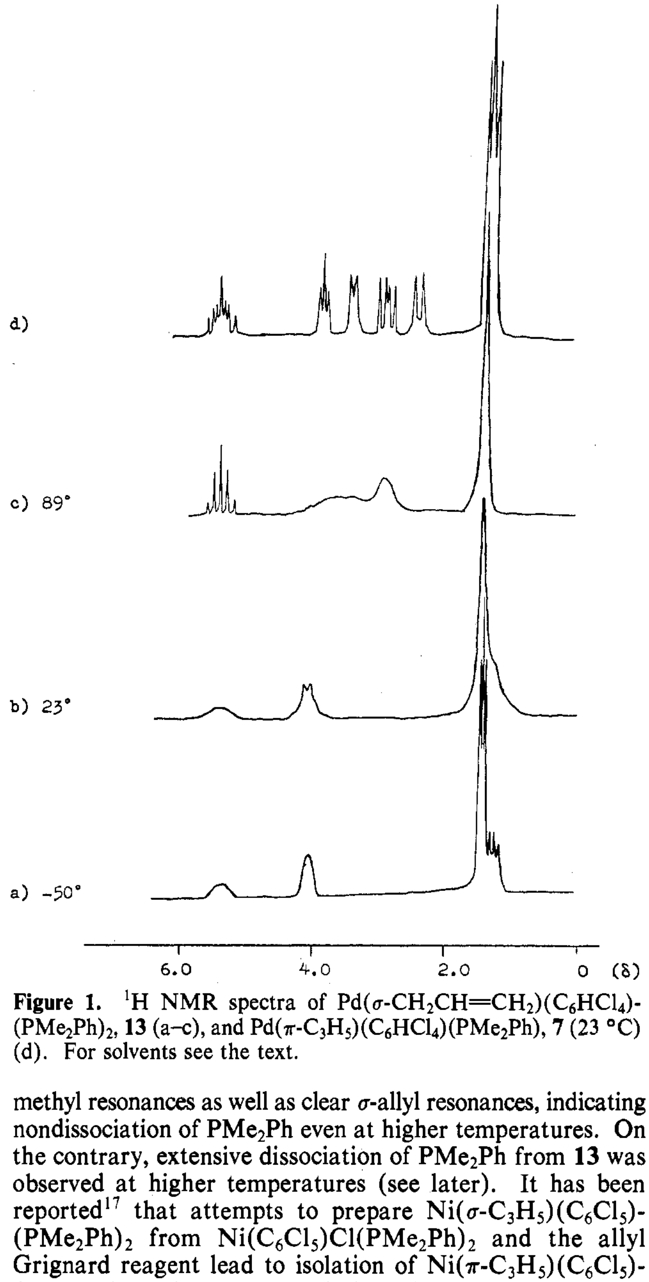
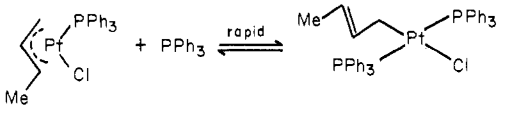


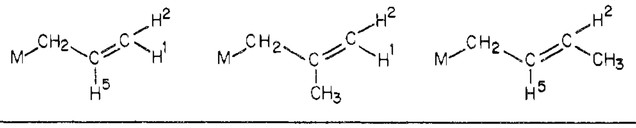
Figure 1. ^1H NMR spectra of $Pd(\sigma\text{-}CH_2CH{=}CH_2)(C_6HCl_4)(PMe_2Ph)_2$, **13** (a–c), and $Pd(\pi\text{-}C_3H_5)(C_6HCl_4)(PMe_2Ph)$, **7** (23 °C) (d). For solvents see the text.

We have suggested previously,[10] on the basis of vibration spectral evidence, the presence of the *trans*-σ-allylic structure in $Pt(CH_2CH{=}CHR)Cl(PPh_3)_2$, in the solid state for R = H and in benzene for R = Me (eq 2). Some chemical evidence also suggested the *trans*-crotyl skeleton for R = Me, but unambiguous ^1H NMR data were lacking owing to a rapid π–σ interconversion. Thus, establishment of the σ-allyl as well as σ-*trans*-crotyl structures with the trans-phosphine ar-



(2)

Table III. ^{1}H NMR Data[a] for σ-Allyl Complexes of Pt(II) and Pd(II) in $CDCl_3$ at 23 °C



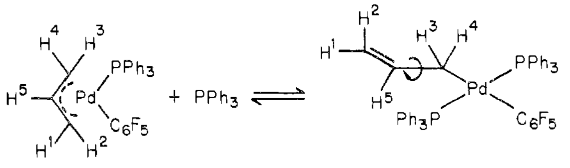
Complex	-CH_2-	H^5	H^2	H^1	CH_3	P-CH_3	C_6HCl_4
8	1.52 q $J_5 = 7$ $J_P = 7$ $J_{Pt} = 72$	5.40 m	3.55 dd $J_5 = 16$ $J_1 = 1.5$	3.76 dd $J_5 = 10$ $J_2 = 1.5$			6.50 s
9	1.38 q $J_5 = 7$ $J_P = 7$ $J_{Pt} = 74$	4.92 dt $J_2 = 16$ $J_{CH_2} = 7$	3.76 dq $J_5 = 16$ $J_{CH_3} = 7$		1.04 d $J_2 = 7$ $J_{Pt} = 8$		6.48 s
10	2.12 q $J_5 = 8$ $J_P = 8$ $J_{Pt} = 87$	5.32 m	3.60 d $J_5 = 18$ $J_{Pt} = 24$	4.04 d $J_5 = 10$ $J_{Pt} = 22$			
11	1.47 q[b] $J_5 = 8$ $J_P = 8$ $J_{Pt} = 72$	5.50 ddt $J_2 = 16$ $J_1 = 9$ $J_{CH_2} = 8$	4.17 m			1.52 t $J_P = 7$ $J_{Pt} = 33$	7.05 s
12	1.46 t[b] $J_P = 8$ $J_{Pt} = 72$		3.86 d $J_1 = 1.5$	4.00 d $J_2 = 1.5$	1.42 s	1.55 t $J_P = 7$ $J_{Pt} = 33$	7.06 s
13[c]	1.24 q $J_5 = 7$ $J_P = 7$	5.40 b	4.04 b			1.42 t $J_P = 7$	7.08 s
14	2.36 q $J_5 = 8$ $J_{P^1} = 8$ $J_{P^2} = 8$ $J_{Pt} = 96$	5.72 m	4.02 d $J_5 = 15$ $J_{Pt} = 40$	4.04 d $J_5 = 9$ $J_{Pt} = 30$			7.06 s
15	2.44 q $J_5 = 8$ $J_{P^1} = 8$ $J_{P^2} = 8$	5.82 m	4.08 d $J_5 = 16$	4.09 d $J_5 = 8$			7.04 s
16	2.60 bs	5.70 m	3.80–4.20 bm				

[a] Chemical shift in ppm downfield from TMS, J in Hz; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddt = doublet of doublet of triplets; J_x = coupling constants with proton numbered x, J_P = coupling constants with ^{31}P, J_{Pt} = coupling constants with ^{195}Pt. [b] Calculated from their ^{195}Pt satellites. [c] At −50 °C.

rangement in **8**–**10** has special relevance to clarifying the ambiguities in the previous work.

Kinetic Aspects of π–σ Allyl Interconversion. Although the rate of π–σ allyl interconversion in the present system in general is slow due to bulky polyhalophenyl groups, the following two dynamic cases seem of special interest in gaining insight into the kinetic aspects of ligand-induced π–σ allyl interconversion.

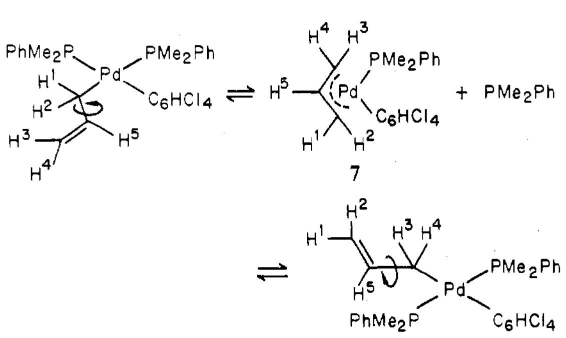
In contrast to nondynamic character of **5** in the presence of added PPh_3,[12] addition of PPh_3 (10 mol/1 g-atom of Pd) to a $CDCl_3$ solution of **6** at room temperature caused the resonances due to H^3 and H^4 to coalesce into a sharp doublet ($J_{H^5} = 10$ Hz) at δ 3.26, while the resonances due to H^1 and H^2 became only broader without any appreciable change in their chemical shifts. This result thus can be explained by the formation of *trans*-Pd(σ-$CH_2CH{=}CH_2$)(C_6F_5)$(PPh_3)_2$ from **6** and PPh_3 as an intermediate species in which the exchange of H^3 and H^4 occurs readily[2] (see eq 3).



6

(3)

The kinetic aspect exhibited by the system **7** + $PMe_2Ph \rightleftharpoons$ **13** appears to be more interesting. As shown in Table III and Figure 1a, the ^{1}H NMR spectrum of **13** at −50 °C can be best explained as due to a rigid *trans*-σ-allyl structure. At room temperature, the phosphine methyl resonances appear as a broad singlet, probably owing to intermolecular exchange of PMe_2Ph. Since the chemical shifts of the vinylic protons[18] are almost the same as those at −50 °C, the σ-allyl species may still predominate at room temperature. At 89 °C in *o*-dichlorobenzene, the spectrum of **13** gave a broad singlet (δ 2.86, 2 protons), a very broad signal (δ 3.40, 2 protons), and a sharp quintet (δ 5.32, 1 proton, $J_H = 9$ Hz) (see Figure 1c). The chemical shifts of the former two bands are very close to the average of the H^3 and H^4 resonances and that of the H^1 and H^2 resonances of **7** (Table II, Figure 1d), respectively. Further, the spin-coupling pattern of the resonances at δ 5.32 is consistent with that of H^5 in **7** where the rates of both exchange between H^1 and H^2 and that between H^3 and H^4 are rapid on the NMR time scale. However, the rate of the exchange between H^1/H^2 and H^3/H^4 groups appears to be much slower. Thus, it is probable that the dissociation of PMe_2Ph from **13** to form **7** is extensive at 89 °C with not only the trans but also *cis*-σ-allyl species being formed as intermediates (eq 4). Although a more quantitative access to this process is difficult at present, such syn–anti proton exchange at both ends of the allyl ligand may in part be related to the



7

(4)

13

strong NMR trans influence of the C_6HCl_4 group.

Registry No. **1**, 58260-07-4; **2**, 62415-30-9; **3**, 62415-31-0; **4**, 62415-32-1; **5**, 58260-06-3; **6**, 62415-33-2; **7**, 62415-34-3; **8**, 62415-35-4; **9**, 62415-36-5; **10**, 62415-37-6; **11**, 62415-38-7; **12**, 62415-39-8; **13**, 62415-40-1; **14**, 62415-24-1; **15**, 62415-25-2; **16**, 62415-26-3; $Pt(\pi\text{-}C_3H_5)Cl(PPh_3)$, 35770-09-3.

References and Notes

(1) Part 5: S. Numata and H. Kurosawa, *J. Organomet. Chem.*, in press.
(2) P. M. Maitlis, "The Organic Chemistry of Palladium", Vol. 1, Academic Press, New York, N.Y., 1971, p 210; P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel", Vol. 1, Academic Press, New York, N.Y., 1974, p 329.
(3) For example, the infrared spectral study[4a] of the solution containing $[Pd(\pi\text{-}C_3H_5)Cl]_2$ and 2 mol of PPh_3/g-atom of Pd led Cotton et al. to suggest that substantial amounts of σ-allyl complexes are formed in such solutions, though the main species were thought yet to be π-allyls. Similarly, Powell and Shaw suggested[4b] that $[Pd(\pi\text{-}2\text{-}MeC_3H_4)Cl]_2$ is converted largely into $Pd(\sigma\text{-}2\text{-}MeC_3H_4)Cl(PMe_2Ph)_2$ in the presence of 2 mol of PMe_2Ph, whereas Vrieze et al.[5] ascribed the resonances in this system as due to mainly $[Pd(\pi\text{-}2\text{-}MeC_3H_4)(PMe_2Ph)_2]^+Cl^-$.
(4) (a) F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, **6**, 179 (1967); (b) J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 1839 (1967).
(5) K. Vrieze, A. P. Praat, and P. Cossee, *J. Organomet. Chem.*, **9**, 527 (1967).
(6) W. Keim, Ph.D. Dissertation, Technische Hochschule Aachen, 1963.
(7) P. Fitton, M. P. Johnson, and J. E. McKeon, *Chem. Commun.*, 6 (1968).
(8) B. E. Mann, B. L. Shaw, and G. Shaw, *J. Chem. Soc. A*, 3536 (1971).
(9) H. C. Clark and C. R. Jablonski, *Inorg. Chem.*, **14**, 1518 (1975).
(10) G. Yoshida, S. Numata, and H. Kurosawa, *Chem. Lett.*, 705 (1976); H. Kurosawa and G. Yoshida, *J. Organomet. Chem.*, **120**, 297 (1976).
(11) J. Powell and A. W. L. Chan, *J. Organomet. Chem.*, **35**, 203 (1972).
(12) S. Numata, H. Kurosawa, and R. Okawara, *J. Organomet. Chem.*, **102**, 259 (1975).
(13) As for the complex **1** in Table II, we have erroneously reported in ref 12 the ^1H NMR data due to a different complex.
(14) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
(15) The resonances due to the vinylic CH_2 and CH protons were shifted to high field by 1–1.5 ppm from those in free alkenes, probably owing to the large anisotropy effect of the phosphine-substituted phenyl groups.
(16) S. H. Mastin, *Inorg. Chem.*, **13**, 1003 (1974).
(17) M. Wada and T. Wakabayashi, *J. Organomet. Chem.*, **96**, 301 (1975).
(18) It was impossible to see the shape of the allylic CH_2 proton resonances at room temperature owing to overlapping with the broad phosphine methyl resonance.

Contribution from the Department of Chemistry,
Emory University, Atlanta, Georgia 30322

Oxidation of the Tetraammineplatinum(II) Cation with the Peroxodisulfate Ion and with Hydrogen Peroxide. Synthesis of Sulfatoplatinum(IV) Complexes

THOMAS D. HARRIGAN and RONALD C. JOHNSON*

Received January 13, 1977 AIC70021R

Peroxodisulfate ion reacts with $Pt(NH_3)_4^{2+}$ to form primarily $Pt(NH_3)_4OHSO_4^+$ and $Pt(NH_3)_4(SO_4)_2$. The rate of reaction at 30 °C and ionic strength 1.0 is $5.1[Pt(NH_3)_4^{2+}][S_2O_8^{2-}]$. A radical mechanism involving SO_4^- and $Pt(NH_3)_4SO_4^+$ is proposed. Hydrogen peroxide reacts with $Pt(NH_3)_4^{2+}$ to produce *trans*-$Pt(NH_3)_4(OH)_2^{2+}$ with a rate at 35 °C of $0.0010[Pt(NH_3)_4^{2+}][H_2O_2]$. A one-step two-electron oxidation mechanism is proposed. Significant amounts of *trans*-$Pt(NH_3)_4Br_2^{2+}$ are formed in both neutral and acidic $S_2O_8^{2-}$ reaction mixtures containing bromide ion but only in acidic H_2O_2 solutions.

Introduction

The oxidation of square-planar complexes of platinum(II) produces octahedral platinum(IV) complexes. The mechanisms for a variety of such reactions have been investigated in which the oxidizing agent has been another platinum(IV) complex,[2] a halogen,[3] the ions Ce^{4+}, VO_2^+, $Cr_2O_7^{2-}$, ClO_3^-, and MnO_4^-,[4] organic halides,[5] $IrCl_6^{2-}$,[6] Fe^{3+},[7] and $AuCl_4^-$.[8] Hydrogen peroxide is known to react with a variety of platinum(II) complexes to yield *trans*-dihydroxoplatinum(IV) complexes.[9] We had observed that these reactions were slow enough for convenient kinetic studies. Although studies on the rate or mechanism of peroxide oxidations of square-planar d^8 systems do not seem to have been reported, peroxide oxidations of a variety of other metal complexes have been carried out.[10-13] In most of these reactions one-electron oxidation and the formation of radicals are observed. However, hydrogen peroxide is known to oxidize many substances in a one-step two-electron process.[14]

The reactions of $Pt(NH_3)_4^{2+}$ with H_2O_2 and $S_2O_8^{2-}$ were studied in order to determine the products and mechanisms of these reactions and to enhance the understanding of the oxidation of square-planar d^8 systems.

Results

The reaction of $Pt(NH_3)_4^{2+}$ with H_2O_2 has been reported to produce *trans*-$Pt(NH_3)_4(OH)_2^{2+}$.[9,15] Consistent with this is our analysis of reaction mixtures using high-pressure ion-exchange chromatography which indicates only one product which absorbs 205-nm radiation. The rate of the reaction at 35.0 °C is $d[Pt(NH_3)_4(OH)_2^{2+}]/dt = 0.0010\cdot[Pt(NH_3)_4^{2+}][H_2O_2]$. Rate data are presented in Table I. The reaction rate is insensitive to changes in ionic strength. The rate is 30% greater in 0.10 M perchloric acid than in its absence. The activation parameters are $\Delta H^* = 13.8 \pm 0.5$ kcal/mol and $\Delta S^* = -28 \pm 2$ cal/(mol deg). The disappearance of the yellow color of a colloidal solution of the

Table I. Rate Data[a] for $Pt(NH_3)_4^{2+} + H_2O_2 \rightarrow$ *trans*-$Pt(NH_3)_4(OH)_2^{2+}$

Temp, °C	$[H_2O_2]$, M	10^4k_2, $M^{-1}\ s^{-1}$	Temp, °C	$[H_2O_2]$, M	10^4k_2, $M^{-1}\ s^{-1}$
35.2	0.030	10.0[b]	40.3	0.049	14.6
	0.030	9.3[c]		0.101	14.4
	0.098	10.1			
	0.098	10.0[d]	45.1	0.027	19.3
	0.098	13.2[e]		0.050	19.5
	0.203	9.5			
			50.2	0.027	26.0
				0.051	28.7

[a] $[Pt(NH_3)_4(ClO_4)_2] = 1.08 \times 10^{-3}$ M; $k_2 = k_{obsd}/[H_2O_2]$. [b] [NaCl] = 0.010 M. [c] [NaBr] = 0.010 M. [d] $[NaClO_4] = 0.10$ M. [e] $[HClO_4] = 0.10$ M.