In assessing the ability of the phosphate group to replace waters of hydration of the cations to form direct-binding complexes, one may conclude that both Li^+ and Be^{2+} could from such direct complexes if one assumes additivity and that a single phosphate replaces two H_2O molecules.

Further comparison of the enthalpies of monohydration of Li^+ and of Be^{2+} (Table IVB) with the enthalpies of metal–phosphate complex formation (Table IVA) indicates that the phosphate Li^+ interaction is 4.4–4.9 times as great as the H_2O–Li^+ interaction, while the same ratio is 2.9–3.4 for Be^{2+}. Thus it appears that Li^+ can lose more waters of hydration than Be^{2+} during direct-site binding with the phosphate. It might thus be conjectured that Li^+ would more readily form direct complexes with the phosphate, while Be^{2+} might interact in a way which allows it to retain its primary hydration shell.

Although the question of ion mobility is not addressed directly in these calculations, estimates of the ease of cation dissociation in two perpendicular directions, given in Table V, indicate that monovalent cations would move more readily perpendicular to the C_2 axis, while divalent cations would have a tendency for separation along the C_2 axis.

Conclusions

Cations with significant charge transfer appear to have three important effects on the phosphate group: significant change in O_1PO_2 bond angle; significant atomic charge redistribution, i.e., decrease in positive charge of the phosphate group and negative charge on the backbone and anionic oxygen atoms; and significant change in bond density, i.e., strengthening of the phosphate–ester oxygen bond and weakening of the phosphate–anionic oxygen bonds. In spite of the ionic nature of its interaction, Na^+ also seems to have these same three direct effects on the phosphate group but to a lesser extent. Even without electron transfer, there is polarization of the charge distribution, particularly resulting in less negative charge at backbone oxygen atoms.

These calculated changes in phosphate anion charge distribution indicate the mechanism by which the presence of counterions can significantly alter interstrand backbone repulsion as well as specific base–backbone interactions leading to the observed structural changes. The tendency of the divalent cation to form partial covalent linkages with the phosphate oxygens and with water may play a major role in their association with nucleic acids. A tendency of Li^+ to form partial covalent linkages with these oxygens while Na^+ (and presumably large alkali metals) interacts totally electrostatically also suggests a cation specificity both in nature and in the extent of interaction with the phosphate group.

Acknowledgment. The authors gratefully acknowledge the support from a NASA Interchange agreement, N CA2-OR630-901, and helpful discussions with Dr. Stanley K. Burt.

Registry No. Li^+, 17341-24-1; Na^+, 17341-25-2; Be^{+2}, 22537-20-8; Mg^{+2}, 22537-22-0; $(OH)_2PO_2^-$, 14066-20-7; H_2O, 7732-18-5.

(π-Allyl)palladium Complex Ion Pairs Containing Two Different, Mobile π-Allyl Groups: NMR and X-ray Crystallographic Studies

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Abstract: The reaction of (π-allyl)palladium chloride dimer with TMEDA in THF produced an unusual complex ion pair **1**, in which two different π-allyl groups were present. This complex was characterized by high-field (360-MHz) NMR spectroscopy in solution and by solid-state ^{13}C NMR spectroscopy. In solution the two allyl groups in complex **1** underwent facile exchange with each other. The kinetic parameters E_a, $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta G^\ddagger$ for this exchange were determined. The proposed structure of complex **1** was confirmed by a single-crystal X-ray structure determination of the related complex **7**, which crystallized in the monoclinic space group $P2_1/c$ with $a = 11.55$ (1) Å, $b = 13.04$ (1) Å, $c = 13.98$ (1) Å, $\beta = 123.86$ (3)°, and $Z = 4$. Compound **7** was found to consist of discrete complex ion pairs, with allyl ligands bound to palladium in both the cation and the anion. Least-squares refinement of this structural model for 1833 unique, observed reflections resulted in $R = 0.063$ and $R_w = 0.077$.

Reactions of both (π-olefin)-[2-6] and (π-allyl)palladium[7-11] halide complexes with nucleophiles have found extensive application in organic synthesis. With both types of complexes, the addition of several equivalents of an external ligand is required to produce reasonable yields of products resulting from nucleophilic attack on the π-bound functional group. The course of these reactions is remarkably dependent upon the specific ligand used. For example, tertiary amines are required for the successful alkylation of (π-olefin)palladium complexes by carbanions,[5] whereas phosphines completely inhibit this reaction. In contrast, allylic alkylation of (π-allyl)palladium halide complexes requires tertiary phosphines as ligands, and the regiochemistry of alkylation is

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[2] For a recent review, see: B. M. Trost, *Tetrahedron*, **33**, 2615 (1977).

[3] L. S. Hegedus, G. F. Allen, J. J. Bozell, and E. L. Waterman, *J. Am. Chem. Soc.*, **100**, 5800 (1978).

[4] L. S. Hegedus, G. F. Allen, and D. J. Olsen, *J. Am. Chem. Soc.*, **102**, 3583 (1980).

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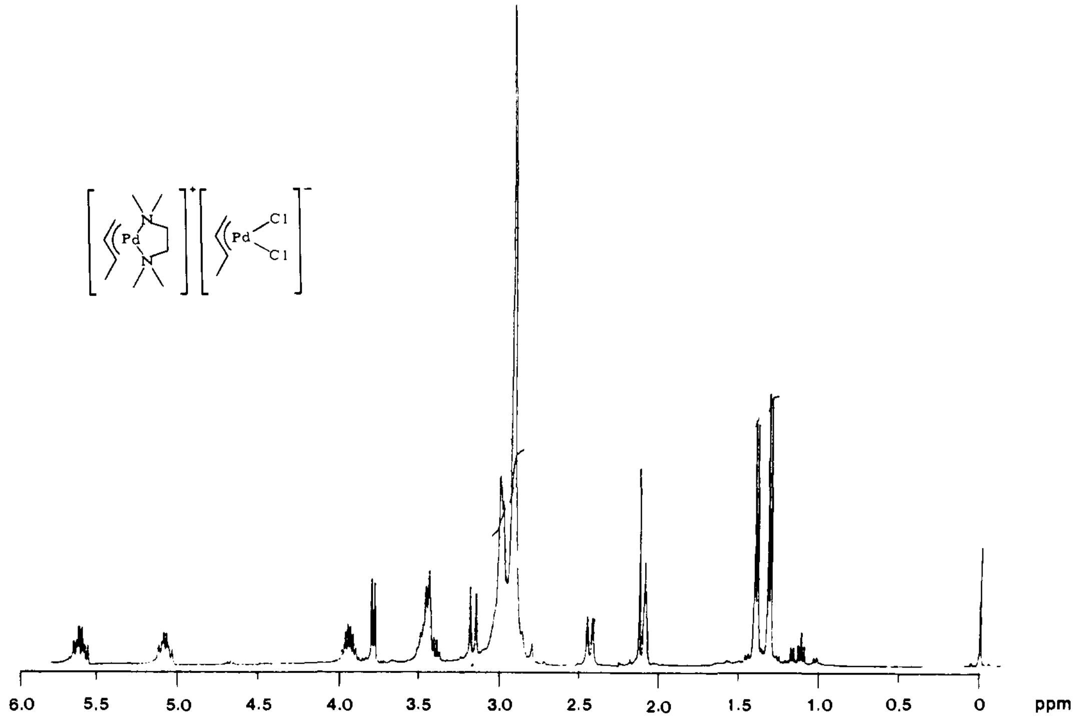
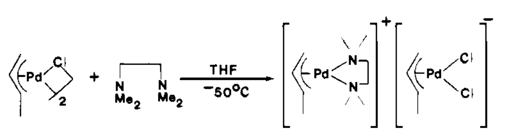


Figure 1. 360-MHz ^{1}H NMR spectrum of complex **1** at −25 °C in acetone-d_6.

strongly dependent on the specific ligand and on the nature of the carbanion.[9,10] Finally, the reaction of stabilized carbanions with either (π-4-chloro)- or [π-4-(diethylmalonato)]butenylpalladium chloride complexes proceeds best in the presence of tetramethylethylenediamine (TMEDA) as ligand, whereas the use of tertiary phosphine ligands leads to destruction of these complexes.[12] In all of these reactions, it has previously been assumed that the added ligands are necessary to displace a halide ligand and generate cationic organopalladium intermediates, facilitating the nucleophilic addition process. With (π-allyl)palladium complexes this ionic species was assumed to be a simple ion pair of the type $[(\pi\text{-allyl})PdL_2]^+Cl^-$.[10] However, a number of recent studies have indicated that the situation is considerably more complex, and the nature of the reactive intermediate formed is strongly dependent on the specific ligand, nucleophile, and solvent used. Conductivity measurements in our laboratories showed that the reaction of (π-allyl)palladium chloride complexes with phosphines in THF did *not* produce ionic (π-allyl)palladium species in detectable amounts, but rather promoted nucleophilic attack (amination) reactions through S_N2' attack on (σ-allyl)-palladium species.[13] Similar arguments based on polarimetric data from asymmetric palladium-catalyzed allylic alkylations have been advanced.[14] In contrast, reaction of tetramethylethylenediamine (TMEDA) with (π-allyl)palladium halides *did* produce ionic species in THF. However, these were not simple ion pairs, but rather complex ion pairs with π-allyl ligands on both cationic and anionic palladium centers (eq 1). Because of the current intense interest in, and the mechanistic uncertainty about, reactions of (π-allyl)palladium chloride complexes, and because of the potential role of complex ion pairs such as **1** in at least some[12] of these reactions, a detailed examination of this unusual complex was undertaken.



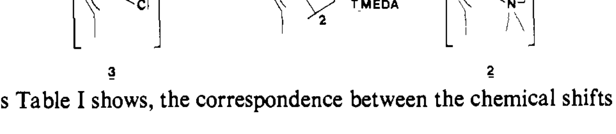
(1)

1

Results and Discussion

Reaction of (π-2-butenyl)palladium chloride with TMEDA in THF resulted in the uptake of only 0.5 equiv of TMEDA for each available equivalent of palladium, even in the presence of excess TMEDA. This was unexpected, since it was thought that the chelating diamine would displace chloride to form the nitrogen analogue of the proposed reactive intermediate in the reactions of (π-allyl)palladium chloride complexes with nucleophiles, that is, the simple ion pair $[(\pi\text{-2-butenyl})Pd\text{-}(TMEDA)]^+Cl^-$. Instead, a stable yellow crystalline solid having the constitution $[(\pi\text{-2-butenyl})PdCl]_2(TMEDA)$ was isolated in quantitative yield.

At room temperature the NMR spectrum of the (π-2-butenyl)palladium chloride TMEDA complex consisted of a series of broad peaks of indeterminate shape. This spectrum indicated that some dynamic process which scrambled the protons of this complex was occurring. Upon cooling to −25 °C, two distinct sets of peaks, corresponding to *two different π-allyl groups*, were observed (Figure 1). This spectrum is consistent with the complex ion pair structure **1**. Table I lists the chemical shifts for these two different π-allyl groups. The assignments of chemical shifts were made by analogy to known π-allyl complexes[15-17] and by complete decoupling experiments and are based on the assumption that the chemical shift of the central proton of the π-allyl ligand will occur at higher field in the anionic portion of the complex (due to increased shielding) than it will in the cationic portion of the complex. This assumption was verified by synthesis of the corresponding cationic and anionic portions of **1** separately (eq 2).



(2)

3

2

As Table I shows, the correspondence between the chemical shifts

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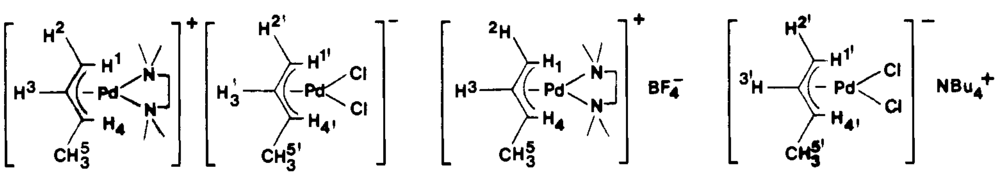
[17] G. L. Statton and K. C. Ramey, *J. Am. Chem. Soc.*, **88**, 1327 (1966).

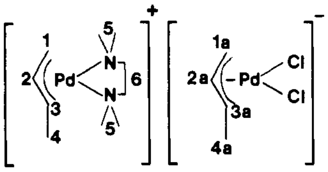
Table I. ^{1}H Spectra of 1, 2, and 3 in Acetone-d_6, at −25 °C



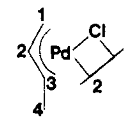
1		2	3
H_1 3.21 $J_{1,3}$ 12.3*	$H_{1'}$ 2.43 $J_{1',3'}$ 11.6	H_1 3.03 $J_{1,3}$ 12.5	$H_{1'}$ 2.48 $J_{1',3'}$ 12
H_2 3.80 $J_{2,3}$ 7.0	$H_{2'}$ 3.46	H_2 3.80**	$H_{2'}$ 3.50
H_3 5.61	$H_{3'}$ 5.09	H_3 5.57	$H_{3'}$ 5.11
H_4 3.98 $J_{3,4}$ 13.31	$H_{4'}$ 3.46	H_4 3.80**	$H_{4'}$ 3.50
H_5 1.40 $J_{4,5}$ 6.2	$H_{5'}$ 1.33 $J_{4',5'}$ 6.2	H_5 1.41 $J_{4,5}$ 6.2	$H_{5'}$ 1.29 $J_{4',5'}$ 5.0

*J values in Hz.
**Protons H_2 and H_4 overlap in the NMR spectrum.

Table II. ^{13}C NMR Spectra of 1 and 4 (in ppm)



1



4

d_6-acetone −25°C					CDCl$_3$	DMSO
C_1	59.46	C_{1A}	54.32	C_1	58.30	62.43
C_2	118.25	C_{2A}	108.74	C_2	111.39	117.82
C_3	76.0	C_{3A}	74.93	C_3	81.42	86.27
C_4	18.18	C_{4A}	16.84	C_4	18.01	17.29
C_5	50.99					
C_6	60.86					

found in **2** and **3** and the assigned chemical shifts for the complex ion pair **1** is very good. By decoupling the methyl groups, protons H_4 and $H_{4'}$ could be unequivocally identified. The protons syn and anti to the central proton were assigned on the basis of both the chemical shift (the anti protons appear at higher field than the syn protons) and the magnitude of the coupling constants between these protons and this central proton, which are similar to cis and trans olefin coupling constants.[17]

The ^{13}C spectrum of **1** also demonstrates the existence of two different allyl ligands at low temperature. The chemical shifts are listed in Table II, and the assignments were made by analogy to the chemical shifts of the (π-allyl)chloro-bridged dimer **4**[18] with the same assumption previously discussed.

As the temperature is raised, the NMR spectrum of **1** changes dramatically. The resonances due to the two different π-allyl ligands broaden and finally coalesce at 47 °C (Figures 2 and 3). At the coalescence temperature, the chemical shift of each peak is the average of the two corresponding signals at low temperature.

Table III. Kinetic Parameters for π-Allyl Ligand Exchange in 1

temp, °C	cationic (C_2) $\delta\nu_a$, Hz	anionic (C_2a) $\delta\nu_b$, Hz
+7.05	21.11	18.91
+3.41	12.22	11.61
−1.35	8.57	7.59
−5.47	4.76	4.62
E_a, kcal	16.9 ± 1.6	16.3 ± 0.8
$\Delta H^{\ddagger}$, kcal	16.3 ± 1.6	15.8 ± 0.8
$\Delta S^{\ddagger}$, eu	8 ± 6	6.0 ± 3
correlation	0.991529	0.997352

Table IV. Concentration Effect on Rate of Exchange for 1[a]

concn, mol/L	$\delta\nu$ (cationic), Hz	$\delta\nu$ (anionic), Hz
0.46	10.94 ± 1.2	10.45 ± 0.8
0.21	10.81 ± 1.2	9.35 ± 0.9

[a] Rate $K = \pi\delta\nu$.

This indicates that, at 47 °C, the two π-allyl ligands in the complex ion pair **1** exchange in some manner and become equivalent. Both the existence of the complex ion pair **1** and its corresponding dynamic behavior are also observed in THF-d_8. This is important because much of the chemistry of (π-allyl)palladium halide complexes has been carried out in THF solvent.

The kinetic parameters of this exchange process were measured by using standard line-broadening techniques[19,20] and are listed in Table III. These parameters were determined by measuring the line broadening of the ^{13}C signal of the central carbon of the π-allyl ligand in both the cationic and anionic protions of the complex ion pair separately. These are two independent determinations, since it is only necessary to observe one site involved in an exchange process to determine the rate of exchange from which the kinetic parameters were calculated. As shown in Table III, there is good agreement between the two measurements. The $\Delta S^{\ddagger}$ in both cases is near zero, indicating that there is virtually no entropy change in the transition state during the exchange of the π-allyl ligands between the two palladium atoms. This in-

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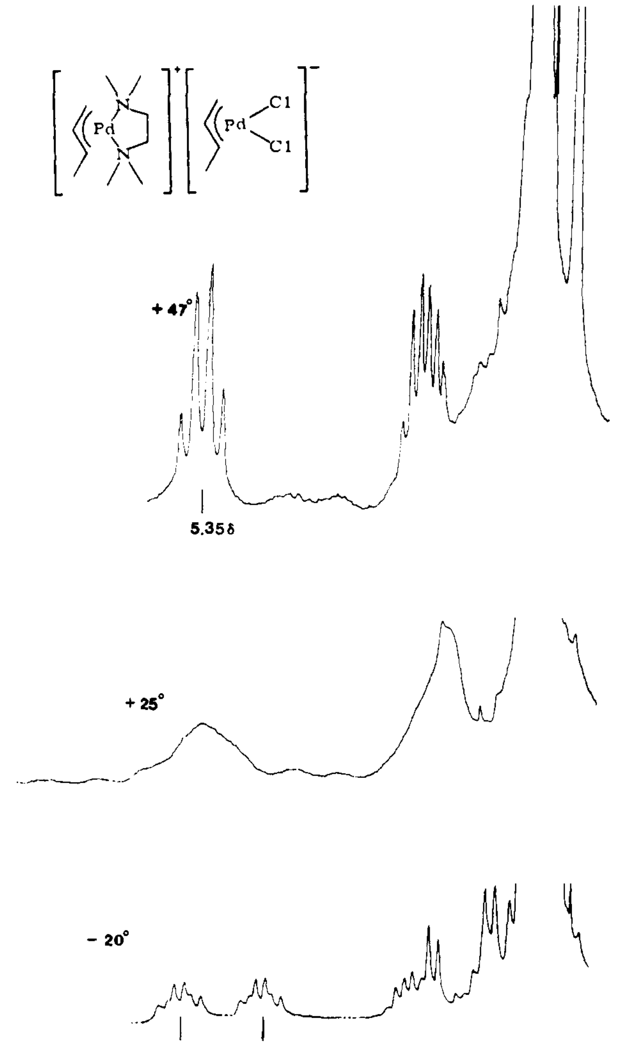
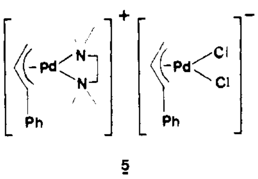


Figure 2. Coalescence of H^3 and $H^{3'}$ in complex **1**.

dicates that exchange occurs in a tight ion pair. If this hypothesis is true, then no dependence of the rate upon concentration should be observed. As shown in Table IV, the rate of exchange of π-allyl ligands between palladium atoms was found to be independent of the concentration. From the coalescence temperature, $\Delta G^{\ddagger}$ was calculated[21] to be 15.7 kcal, a figure in fair agreement with the value of $\Delta G^{\ddagger}$ derived from the previously determined $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, 13.8 kcal.

The rate of allyl exchange is dependent upon the specific π-allyl ligand involved. Complex **5**, synthesized as in eq 1, underwent this exchange process at a much slower rate than **1**. At room temperature, the signals for the central protons of the two allyl groups of **5** are only slightly broadened, in contrast to those of complex **1**.



5

There are two possible mechanisms for the equilibration of the allyl groups observed in the NMR spectrum. Either the allyl groups exchange between the metal centers or the tetramethylethylenediamine and chloride ligands exchange with each other. In view of the well-established stereochemical nonrigidity of (π-allyl) transition-metal complexes,[22] it is believed that the allyl groups of **1** are the species which exchange between the cationic palladium center and the anionic palladium center. A feature supporting this is seen in the coalesced spectrum of **1** at 47 °C (Figure 2) in which the central proton of **1** is a quartet, indicating that syn–anti interchange is occurring in addition to the other dynamic processes. If the allyl groups are exchanging, syn–anti interchange *should be observed*, since a σ–π allyl metal complex, the known intermediate for syn–anti interchange, is a probable intermediate in the mechanism of exchange of the allyl groups (vide infra). If the π-allyl groups are not exchanging, but rather, the tetramethylethylenediamine and chloride ligands are exchanging, syn–anti interchange would only occur as a fortuitous and independent process. In the NMR spectrum of the (π-butenylallyl)palladium-TMEDA·BF_4 complex **2**, no syn–anti interchange was observed at 47 °C. If the syn–anti interchange observed for **1** were indeed an independent process, then it should also be observed for complex **2**. This experiment favors a mechanism in which the allyl groups exchange between palladium atoms.

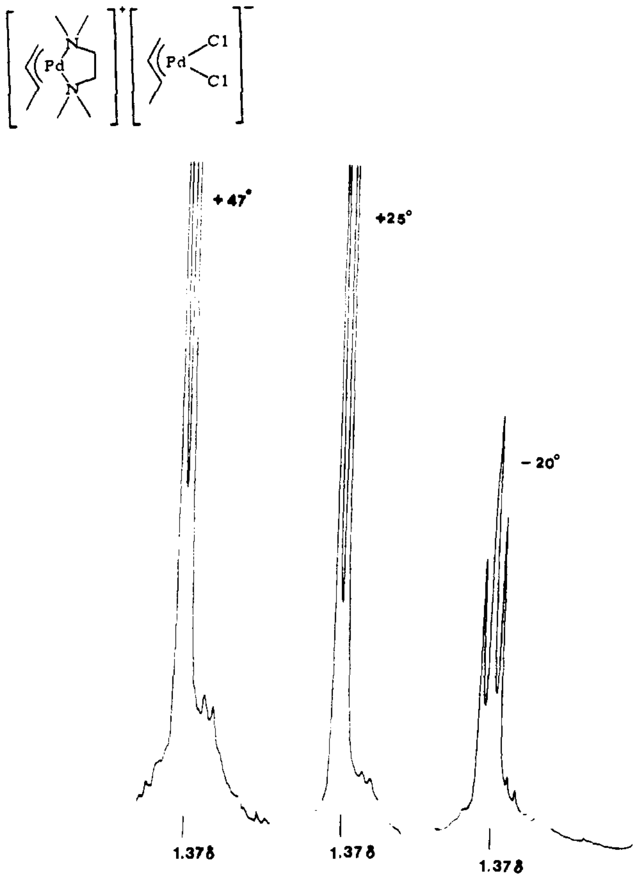


Figure 3. Coalescence of 5-CH_3 and 5′-CH_3 in complex **1**. (100 MHz)

A mechanism for the exchange of π-allyl ligands between palladium atoms which is consistent with the data presented is shown in Scheme I. In this mechanism, the π-allyl ligands undergo the π–σ–π motion, which is the accepted mechanism for syn–anti interchange. During this motion, the olefins migrate and the π-allyl ligands bridge the palladium atoms to form intermediate **6**. This compound then rearranges via a σ–π intermediate to re-form complex **1** in which the π-allyl ligands have been exchanged between the palladium atoms. Structure **6**, having two metals bridged by allyl groups which are σ-bonded to one metal

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(21) F. R. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, NY, 1969, p 190.

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Scheme I. Mechanism for Allyl Ligand Exchange Process in Complex 1

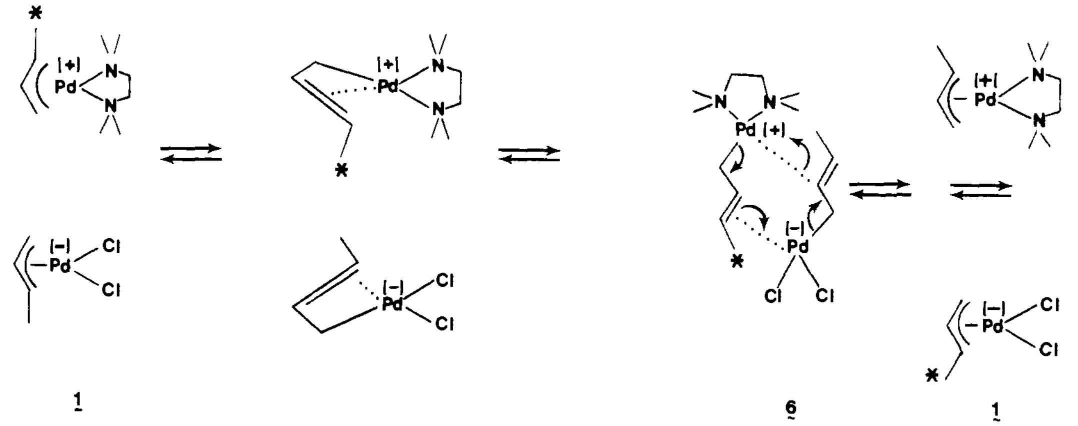


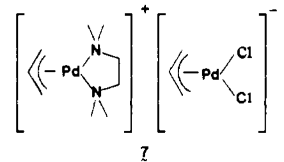
Table V. Selected Bond Lengths (Å) and Angles (deg) for Crystal Structure of 7

Bond Lengths	
Pd1–N1 2.15 (1)	Pd2–Cl1 2.390 (5)
Pd1–N2 2.16 (2)	Pd2–Cl2 2.400 (5)
Pd1–C1 2.15 (3)	Pd2–C1A 2.14 (2)
Pd1–C2 2.06 (3)	Pd2–C2A 2.09 (3)
Pd1–C3 2.15 (3)	Pd2–C3A 2.16 (2)
C1–C2 1.36 (3)	C1A–C2A 1.43 (3)
C2–C3 1.44 (3)	C2A–C3A 1.45 (2)
N1–C4 1.48 (2)	N2–C6 1.48 (2)
N1–C5 1.47 (3)	N2–C7 1.52 (2)
N1–C9 1.45 (4)	N2–C8 1.48 (3)
C8–C9 1.25 (3)	
Angles	
C1–Pd1–C3 70.5 (8)	C1A–Pd2–C3A 71.2 (8)
N1–Pd1–N2 84.6 (5)	Cl1–Pd–Cl2 97.9 (2)
C1–C2–C3 125 (2)	C1A–C2A–C3A 121 (2)

and π-bonded to the other, has excellent analogy in the platinum analogue of the starting $[(\pi\text{-allyl})PdCl]_2$ complex **4**. The corresponding platinum complex is a tetramer, $[(\pi\text{-allyl})PtCl]_4$, in which *all* allyl groups bridge two metals in exactly this σ–π manner.[23] Alternatively, this equilibration of allyl groups could take place by the complex ion pair **1** being in equilibrium with TMEDA and the starting chloro-bridged dimer. The detailed mechanism of this exchange awaits experimental proof.

Although all of the physical and spectroscopic properties of complex **1** were consistent with the proposed complex ion pair structure, unequivocal proof of this required an X-ray diffraction study.

X-ray Diffraction Study. Recrystallization of complex **1** from a variety of solvents failed to produce crystals of sufficient size and quality for X-ray diffraction study. Hence, the more symmetrical (π-allyl)palladium complex ion pair **7** was synthesized.



7

This compound exhibited the same dynamic NMR behavior as complex **1**. While all crystals of **7** of sufficient size for structural study were found to be twinned, cleavage of a large twinned crystal yielded an untwinned crystal fragment suitable for crystallographic study. Using this fragment, we determined the structure of **7**. Figure 4 shows the structures of the cation and the anion for one formula unit of **7**. This X-ray diffraction study confirmed that **7** is the novel ionic π-allylic compound suggested above, consisting of a (π-allyl)tetramethylethylenediaminepalladium(II) complex cation and a dichloro(π-allyl)palladium(II) complex anion. Table V lists the bond lengths and angles characteristic of the complex ion pair **7**.

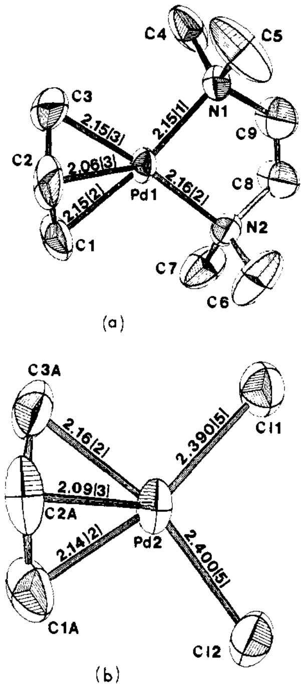


Figure 4. Structures of the cation (a) and anion (b) of the compound 7, with selected bond lengths (Å).

The Pd–C bond lengths in the cationic complex ion of **7** are equal (within experimental error) to the corresponding Pd–C bond lengths in the anionic complex. For both complex ions, the central carbon atom of the π-allyl ligand is slightly closer to the palladium atom than are the terminal carbon atoms (2.06 (3) Å vs. 2.15 (3) Å for Pd1, 2.09 (3) Å vs. 2.15 (2) Å for Pd2). The Pd–C and C–C(allyl) bond distances found in **7** are within the range of bond lengths found in other structural studies of palladium complexes involving π-allyl ligands.[24-30] The C–C bond length difference

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Table VI. Chemical Shifts of 1, Solid-State NMR (in ppm)

$C_1 + C_{1A}$, 52 (overlap with $C_5 + C_6$)	$C_3 + C_{3A}$, 74
C_2, 114	$C_4 + C_{4A}$, 18
C_{2A}, 110	$C_5 + C_6$, 52 (overlap with $C_1 + C_{1A}$)

found for the π-allyl ligand of the cationic complex is not significant, given the rather large experimental uncertainties characteristic of these bond lengths in the present study.

The trans influence of the π-allyl ligands is responsible both for the long palladium–chlorine bond lengths (2.390 (5) Å, 2.400 (5) Å) seen in the anionic portion of **7** and for the long palladium–nitrogen bond lengths (2.15 (1) Å, 2.16 (2) Å) observed for the cationic portion. Other structural studies[24,27,29-33] have demonstrated similar degrees of π-allyl ligand trans influence on Pd–Cl and Pd–N bond lengths. Disorder in the dimethylene bridge of the TMEDA ligand (vide infra) is reflected in the high thermal parameters observed for C_8 and C_9 (see Figure 4) and the very short internuclear distance (C_8–C_9 = 1.25 (3) Å) derived from the final coordinates for these two atoms.

The importance of this structure does not lie in the details of the palladium coordination geometries, since these details are similar to those observed in previous studies. It lies instead in the proof of the ionic nature of compound **7**, and the present work is the first structural report for such a complex ion pair containing both a cationic (π-allyl)palladium complex and an anionic (π-allyl)palladium complex. In retrospect, it now seems clear that earlier workers[34] synthesized complexes analogous to **1** and **7** but did not fully characterize them.

Solid-State NMR Spectrum of 1. The data presented above characterizes complex ion pairs **1** and **7** in solution (NMR) and (for **7**) as a solid (X-ray crystal structure). The new technique of solid-state NMR spectroscopy presents an opportunity to compare the solid-state and solution properties of **1** directly. The ^{13}C solid-state NMR spectrum of **1** was obtained, and the chemical shifts found are listed in Table VI. Despite the poor resolution, the chemical shifts of these carbons in the solid state agree with the chemical shifts found in the solution NMR. The overlap of resonances makes detailed analysis of the spectrum difficult, but the observation of the central carbons of the cationic π-allyl portion and the anionic π-allyl portion indicates that in the solid state there are two different π-allyl ligands. This is similar to the ^{13}C spectrum of **1** at −20 °C in which no exchange of π-allyl groups between metal centers occurs and is in agreement with the X-ray crystal structure. An exchange of ligands is unlikely in the solid state, and the normal thermal parameters found for the two different π-allyl ligands in the crystal structure indicate that exchange does not occur.

Conclusions

The research reported above, combined with our previous work in the area,[13] demonstrates that the nature of the reactive intermediate formed in the reaction of (π-allyl)palladium halide complexes with various ligands is very much dependent upon the nature of the ligand and the solvent. In relatively nonpolar solvents such as THF, simple ion pairs are rarely formed in detectable amounts. Monophosphines produce primarily σ-allyl intermediates; only in conjunction with $AgBF_4$ are significant amounts of ionic species produced.[13] With TMEDA, complex ion pairs such as **1** are produced. All three types of allyl complexes react with nucleophiles, and all are potential contributors to reactions of (π-allyl)palladium halides with nucleophiles.

This paper clearly establishes the existence and structural properties of complex ion pairs of (π-allyl)palladium complexes. The role of these and related complex ion pairs in the chemistry of both (π-allyl)palladium halide and (π-olefin)palladium(II) complexes is currently being investigated.

Table VII. Crystal Data and Data Collection Parameters for 7

formula: $Pd_2C_{12}H_{26}N_2Cl_2$
space group: $P2_1/c$
a = 11.55 (1) Å
b = 13.04 (1) Å
c = 13.98 (1) Å
β = 123.86 (3)°
V = 1748 Å^3
ρ_{calcd} = 1.83 g cm^{-3} (Z = 4); ρ_{obsd} = 1.85 g cm^{-3}
μ = 23 cm^{-1}
θ–2θ scans, width 1.2°, Mo Kα radiation
no. of reflections collected = 2476
no. of "observed" reflections = 1833
no. of variables (least squares) = 163
data/parameter ratio = 11.25

Table VIII. Positional Parameters (Fractional Coordinates)

atom	*x*	*y*	*z*
Pd1	0.82321 (12)	0.07048 (8)	0.66953 (8)
Pd2	0.34113 (12)	0.10412 (8)	0.90603 (8)
Cl1	0.3526 (4)	0.2115 (3)	0.0497 (3)
Cl2	−0.1551 (4)	0.0055 (3)	0.1273 (3)
N1	−0.1691 (12)	0.1756 (8)	0.7913 (9)
N2	−0.2567 (13)	−0.0366 (9)	0.7371 (9)
C1	0.160 (2)	0.021 (1)	0.450 (2)
C2	−0.175 (3)	0.420 (2)	0.023 (2)
C3	−0.085 (2)	0.160 (1)	0.599 (1)
C1A	0.376 (2)	0.024 (1)	0.791 (1)
C2A	0.423 (2)	0.127 (1)	0.807 (1)
C3A	0.523 (2)	0.167 (1)	0.921 (2)
C4	−0.028 (2)	0.281 (2)	0.370 (2)
C5	−0.268 (3)	0.239 (2)	0.236 (2)
C6	0.406 (2)	0.060 (2)	0.346 (2)
C7	0.172 (2)	0.135 (1)	0.220 (2)
C8	−0.241 (3)	0.480 (1)	0.336 (2)
C9	−0.217 (4)	0.386 (2)	0.350 (2)

Experimental Section

General Procedures. Infrared spectra were recorded on either a Beckman Acculab 3 or Beckman 4240 spectrophotometer and are reported in cm^{-1}. Routine ^1H NMR were measured with either a Varian Model T-60 or EM-360 spectrometer using Me_4Si as an internal standard and are reported in δ.

All reactions, except where noted, were run in a 100-mL one-necked round-bottomed flask equipped with a magnetic stirring bar and a septum. A dry ice/2-propanol bath was utilized to keep the temperature at −50 °C.

Materials. All solvents were freshly distilled before use and stored under an argon atmosphere. THF (Mallinckrodt, reagent grade) was heated at reflux over sodium/benzophenone and distilled at atmospheric pressure. Acetone (reagent grade) was dried over and then distilled from K_2CO_3. *N,N,N′,N′*-Tetramethylethylenediamine (Aldrich, Gold label) was distilled at reduced pressure. The (π-allyl)palladium chloride dimers were prepared by the method of Dent et al.[35] $AgBF_4$ was purchased from commercial sources and used without further purification.

NMR Procedures. The 360-mHz spectrum were run on a Nicolet NT 360 spectrometer. The E_a, coalescence, concentration, and temperature studies were run on a Jeol JNM-FX 100 spectrometer. The solid-state ^{13}C NMR was run on a highly modified Nicolet NT 200 spectrometer. This spectrometer was modified by the CSU Regional NMR center and operated at 25 mHz for ^{13}C NMR studies. KINPAR, obtained from Dr. Jack Norton, was used as the linear least-squares line-fitting program for the E_a study.

The kinetic parameters were determined by established procedures using the following equations: rate of exchange $k = 1/\Upsilon_a = \pi\delta\nu_a$ where $\delta\nu_a$ is the corrected line width at half peak height and $1/\Upsilon_a$ is the rate of exchange as observed at site a in the process a $\rightleftarrows$ b.[17,18] Provided saturation has not occurred, then $\delta\nu_a = (1/\pi)\ [(1/T_{2a})\ (\text{static}) + (1/T_{2a})\cdot(\text{exchange})]$. $(1/T_{2a})$ (static) can be solved for by subtracting the peak width at half height in the absence of exchange $[(1/T_{2a})\ (\text{exchange})]$.[18] Here the assumption was made that the Me_4Si line width

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Table IX. Anisotropic Thermal Parameters[a] ($\times 10^3$)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd1	42.6 (7)	51.0 (6)	31.3 (4)	−3.0 (5)	25.1 (5)	2.0 (5)
Pd2	35.8 (7)	60.9 (7)	39.5 (5)	11.5 (5)	25.7 (5)	10.6 (5)
Cl1	53 (3)	76 (3)	54 (2)	−0.03 (9)	34 (2)	−7 (2)
Cl2	39 (2)	81 (3)	58 (2)	−2.0 (2)	29 (2)	−2 (2)
N1	41 (8)	47 (6)	46 (6)	5 (6)	29 (5)	2 (5)
N2	47 (8)	55 (7)	43 (6)	−14 (6)	29 (6)	−6 (5)
C1	143 (20)	61 (10)	78 (11)	3 (11)	93 (14)	0.9 (9)
C2	140 (23)	152 (22)	72 (12)	48 (17)	92 (15)	28 (13)
C3	114 (18)	81 (12)	62 (10)	−31 (12)	66 (12)	−2 (9)
C1A	92 (15)	74 (11)	68 (10)	3 (10)	65 (11)	−1 (8)
C2A	60 (12)	91 (13)	64 (10)	37 (10)	48 (10)	27 (9)
C3A	56 (12)	60 (10)	90 (12)	0 (11)	57 (10)	9 (8)
C4	43 (11)	129 (17)	80 (11)	16 (11)	31 (9)	65 (11)
C5	115 (20)	131 (19)	77 (13)	−83 (17)	30 (12)	5 (12)
C6	40 (12)	142 (19)	77 (13)	−28 (12)	14 (9)	23 (12)
C7	63 (14)	50 (10)	121 (15)	9 (9)	50 (11)	29 (9)
C8	233 (31)	71 (12)	110 (15)	59 (16)	148 (20)	31 (11)
C9	292 (39)	91 (15)	155 (21)	78 (19)	202 (27)	31 (10)

[a] The form of the anisotropic thermal ellipsoid is given by $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$.

at half height was equal to the line width at half height in the absence of exchange. With the rate of exchange determined, the activation energy was determined by the Arrhenius equation: $k = A(\exp(-E_a/RT))$.[17] A plot of log k vs. $1/T$ was linear and yielded E_a. From the Eyring equation, $k = k(T/h) \exp(-\Delta H^{\ddagger}/RT) \exp(\Delta S^{\ddagger}/R)$. Values were obtained utilizing, as in the Arrhenius plot, a linear least-squares line-fitting program, KINPAR, obtained from Dr. Norton. The $\Delta G_{47}^{\ddagger}$ was calculated from the equation: $\Delta G_{T_c}^{\ddagger} = 4.58\ T_c\ [10.32 + \log(T_c/K_r)]$ where T_c = temperature of coalescence and $k_r = (\pi\Delta\delta/\sqrt{2})$; $\Delta\delta$ = chemical shift difference in Hz between peaks in the absence of exchange.[19]

Preparation of [(η^3-2-Butenyl)(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)palladium(II)] Dichloro(η^3-2-butenyl)palladate. (1) Di-μ-chloro-bis[η^3-2-butenyl]dipalladium (480 mg, 1.2 mmol) was dissolved in 40 mL of distilled acetone and the temperature lowered to −50 °C. *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine (141.7 mg, 1.2 mmol, 0.184 mL) was added dropwise, and the solution was stirred for 1 h at −50 °C. The solvent was removed under reduced pressure giving a yellow oil. Trituration with 3 × 10 mL of distilled ether and drying under reduced pressure gave a yellow solid (651.7 mg, 100%): NMR (acetone-d_6, Me_4Si) δ 1.36 (d, J = 6 Hz, 3, $-CH_3$), 2.95 (s, 12, NCH_3), 3.0 (s, 6, $N-CH_2$, exchanging *anti*-$CCCH_2$), 3.50 (brs, 4, exchanging *syn*-$CCCH_2$, exchanging *anti*-$CH_3\mathit{CH}CC$), 5.30 (brs, 2, exchanging central protons CCHC); IR (KBr) 3030 (w), 2980 (w), 2955 (m), 2665 (s), 2830 (s), 1505 (w), 1460 (s), 1425 (s), 1400 (m), 1377 (m), 1278 (m), 1230 (m), 1190 (m), 1168 (m), 1122 (m), 1040 (m), 1015 (s), 955 (s), 800 (s), 755 (m) cm^{-1}; mp 90–92 °C dec. Anal: ($C_{14}H_{30}Cl_2N_2Pd_2$) C, H, N.

Preparation of [η^3-2-Butenyl](*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)palladium(II) Tetrafluoroborate. (2) Di-μ-chloro-bis[η^3-2-butenyl]dipalladium (52.0 mg, 0.13 mmol) was dissolved in 10 mL of THF in a 50-mL test tube and $AgBF_4$ (51.4 mg, 0.26 mmol) was added. AgCl precipitated immediately, and the reaction mixture was stirred for 10 min. The AgCl was then removed by the centrifugation at low rpm and the supernatant decanted. The AgCl was washed with 2 × 2 mL of THF, and the combined THF extracts were placed in a round-bottomed flask. *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine (30.7 mg, 0.26 mmol, 0.04 mL) was added dropwise and the solution stirred for 10 min. Removal of the solvent under reduced pressure gave a white solid (96.4 mg, 100%): NMR (acetone-d_6, Me_4Si) δ 1.40 (d, J = 6 Hz, 3, CH_3), 2.95 (s, 12, $N-CH_3$), 3.0 (s, 5, $N-CH_2$, *anti*-$CCH\mathit{CH}_2$), 3.80 (m, 2, *syn*-$CCH\mathit{CH}_2$, *anti*-$CCH\mathit{CH}CH_3$), 5.60 (m, 1, $C\mathit{CH}C$); IR (KBr) 2960 (m), 2895 (m), 2840 (m), 2790 (m), 1460 (s), 1280 (m), 1050 (vs, vbr), 955 (m), 800 (s), 755 (m) cm^{-1}; mp 128–130 °C dec. Anal: ($C_{10}H_{23}BF_4N_2Pd$) C, H, N.

Preparation of [η^3-3-Phenyl-2-propenyl](*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)palladium(II) Dichloro(η^3-3-phenyl-2-propenyl)palladate(II). (5) Di-μ-chloro-bis[η^3-3-phenyl-2-propenyl]dipalladium (54.1 mg, 0.10 mmol) was dissolved in 15 mL of distilled acetone and the temperature was lowered to −50 °C. *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine (12.1 mg, 0.10 mmol, 0.016 mL) was added dropwise and the solution stirred for 1 h at −50 °C. The solvent was removed under reduced pressure giving a viscous yellow oil (72.2 mg, 100%): NMR (acetone-d_6, Me_4Si, −20 °C) δ 2.57 (s, 6, $N-CH_3$), 2.79 (s, 7, NCH_3, anionic *anti*-$CCCH_2$), 3.31 (s, 4, $N-CH_2-CH_2N$), 3.49 (d, J = 12 Hz, 1, cationic *anti*-$CCCH_2$), 3.67 (d, J = 6.2 Hz, 1, anionic *syn*-CCCH), 3.90 (d, J = 7.3 Hz, 1, cationic *syn*-CCCH), 4.40 (d, J = 11.4 Hz, 1, anionic *anti*-$Ph\mathit{CH}-CC$), 4.89 (d, J = 12 Hz, 1, cationic *anti*-$Ph\mathit{CH}-C-C$), 5.81 (m, 1, anionic CCHC), 6.35 (m, 1, cationic CCHC), 7.19–7.74 (m, 10, cationic and anionic ArH); IR (neat) 3055 (m), 2980 (m), 2950 (m), 2870 (m), 2825 (m), 2780 (m), 1473 (m), 1460 (s), 1425 (m), 1278 (m), 1120 (m), 1065 (w), 1053 (w), 1940 (m), 1013 (m), 950 (m), 799 (s), 752 (s), 690 (s) cm^{-1}. Anal: ($C_{24}H_{28}Cl_2N_2Pd_2$) C, H, N.

Preparation of [η^3-2-Propenyl](*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)palladium(II) Dichloro(η^3-2-propenyl)palladate(II). (7) Di-μ-chloro-bis(η^3-2-propenyl)dipalladium (54.0 mg, 0.15 mmol) was dissolved in 15 mL of distilled acetone and the temperature lowered to −50 °C. *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine (17.1 mg, 0.15 mmol, 0.022 mL) was added and the solution was stirred for 1 h at −50 °C. The solvent was removed under reduced pressure giving the product (74.0 mg, 100%), a yellow solid. Recrystallization from acetone/toluene (1:1) at −20 °C gave yellow crystals which were fragmented for use in the single-crystal X-ray diffraction study: NMR ($CDCl_3$, Me_4Si), δ 3.02 (s, 20, TMEDA and exchanging *syn*-CH–C–CH), 3.82 (brs, 4, exchanging *anti*-CH-C-CH), 5.52 (brs, 2, exchanging C–CH–C); IR (KBr) 3050 (m), 3000 (w), 2978 (w), 2960 (w), 2945 (w), 2880 (m), 2795 (w), 2780 (w), 1455 (s), 1425 (m), 1400 (m), 1382 (m), 1290 (m), 1275 (m), 1240 (m), 1198 (m), 1170 (m), 1122 (m), 1099 (m), 1012 (s), 988 (m), 955 (s), 940 (s), 930 (m), 805 (s), 770 (m) cm^{-1}. Anal: ($C_{12}H_{26}Cl_2N_2Pd_2$) C, H, N, Cl; mp 108–110 °C dec.

Crystallographic Procedures. Structure Determination for (η^3-2-Propenyl)(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)palladium(II) Dichloro(η^3-2-propenyl)palladate(II) (7). The crystal fragment used in photographic work and data collection was obtained by growing large twinned crystals of **7** and by cleaving them with a razor blade. By this method an untwinned crystal fragment was found. Preliminary Weissenberg and precession photographs of this crystal fragment revealed Laue symmetry $2/m$ and exhibited the following conditions for the observation of reflections: $h0l$, $l = 2n$; $0k0$, $k = 2n$. These conditions are consistent only with the space group $P2_1/c$.[36]

This crystal fragment was attached to a glass fiber and mounted on the Enraf-Nonius CAD-3 diffractometer with the c^* axis nearly coincident with the diffractometer ϕ axis. The unit-cell parameters (Table VII) and the orientation matrix for data collection were obtained from least-squares calculations on the automatically determined setting angles (at 20 ± 1 °C) of 27 reflections for which $18° < 2\theta < 32°$. The density of the crystals of **7** (Table VII) was determined by the neutral buoyancy technique in a mixture of carbon tetrachloride and 1,2-dibromoethane.

The intensities of three reference reflections (600, 170, and 008; one measured every 25 reflections) remained constant during data collection. This observation indicated that the blackening of the crystals on exposure to the X-ray beam was not associated with serious structural disruption. Data collection and reduction was carried out as previously described,[37] with the intensities of all reflections for which $4.5° < \theta < 25.0°$, $k \geq 0$, and $l \geq 0$ being measured. The g factor for calculation of the standard deviations in the intensities was taken as 0.05.[37,38] Programs used in the

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(36) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1969.

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calculations have been described previously.[39] Due to the low absorption coefficient ($\mu = 23\ cm^{-1}$), the small size (approximately 0.23 × 0.40 × 0.20 mm), and the very irregular shape of the data collection crystal, no absorption correction was performed.

The positions of the palladium atoms were assigned from Harker sections of the Patterson map and confirmed by direct methods (MULTAN 78). Initial positions for all nonhydrogen atoms were then obtained from Fourier syntheses phased by the metal atoms. Scattering factors for palladium, chlorine, nitrogen, and carbon were taken from ref 40, as were the correction terms $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to palladium. Disorder was detected in the dimethylene bridge of the TMEDA ligand (C8–C9), and attempts were made to model this disorder by including four fractional carbon atoms. This model proved to be unsatisfactory, and the dimethylene bridge of TMEDA was best modeled by two whole carbon atoms. Refinement was continued, with anisotropic thermal parameters for all atoms, until all shifts in parameters, both thermal and positional, were less than 15% of the estimated standard deviation for that parameter.

The final R value was 0.063 (unobserved reflections not included), while the final R_w was 0.077. The error in an observation of unit weight was 2.24. The calculated and observed intensities of the 25 most intense reflections were examined, and correction for secondary extinction was not deemed necessary. In the final difference Fourier map, peaks with intensities of 1.2, 1.1, and 1.0 e Å^{-3} were associated with Pd1. A peak of intensity of 0.8 e Å^{-3} was associated with C2, while two peaks of 0.8 e Å^{-3} were associated with Pd2 and Pd1, respectively. All other peaks were less than 0.7 e Å^{-3}. Final atomic positional and anisotropic thermal parameters are listed in Tables VIII and IX.

Acknowledgment. This work was supported under Grant No. CHE 80-19573 from the National Science Foundation (L.S.H.) and by the Swedish National Science Research Council and the Swedish Board for Industrial Development (B.Å.). High-field and ^{13}C NMR spectra were run by the Colorado State University Regional NMR Center, funded by National Science Foundation Grant No. CHE 78-18581. Computer funds for the X-ray structure determination were supplied by Colorado State University.

Supplementary Material Available: A list of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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[39] The following programs were used in structure determination: Zalkin's FORDAP Fourier program; Ibers' NUCLS, a group–nongroup least-squares version of the Busing–Levy ORFLS program; Ibers' CELREF for least-squares refinement of cell parameters; ORFFE, Busing and Levy's function and error program; ORTEP, C. K. Johnson's thermal ellipsoid plotting program. The program for data reduction and Lp correction was locally written. MULTAN 78 (P. Main and M. Woolfson) was obtained from G. J. B. Williams (Brookhaven National Laboratory).

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Reaction of Isopropyl(pentaaquo)chromium(III) Ion with Molecular Oxygen in Aqueous Solution: Kinetics of the Chain Reaction and Effects of Chain-Breaking Reagents and of Variable Ionic Strength[1]

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Abstract: The reaction referred to in the title occurs according to the idealized stoichiometry $(H_2O)_5CrCH(CH_3)_2^{2+} + O_2 + H^+ = Cr(H_2O)_6^{3+} + (CH_3)_2CO$, although smaller amounts of $HCrO_4^-$, $Cr_2(OH)_2^{4+}$, and $(CH_3)_2CHOH$ are also formed. The rate of reaction is given by $-d[CrCH(CH_3)_2^{2+}]/dt = k[CrCH(CH_3)_2^{2+}]^{3/2}$, with $k = 0.49 \pm 0.06\ M^{-1/2}\ s^{-1}$ at 25.0 °C and 1.0 M ionic strength, independent of $[O_2]$ and $[H^+]$ (0.003–0.1 M). The kinetics are consistent with a chain mechanism initiated by unimolecular homolysis of $CrCH(CH_3)_2^{2+}$ ($k_H = (1.78 \pm 0.11) \times 10^{-4}\ s^{-1}$). The preferred mechanism is the one consistent with the striking inhibition by Fe^{2+} or high concentrations of Cu^{2+}, 0.02–0.40 M; in the latter case the rate law for the chain reaction becomes $-d[CrCH(CH_3)_2^{2+}]/dt = k_{Cu}[CrCH(CH_3)_2^{2+}][O_2][Cu^{2+}]^{-1}$. In this chain mechanism, $(CH_3)_2\dot{C}H$(R·) and $(CH_3)_2CHO\dot{O}$(ROO·) are the chain-carrying intermediates. One propagation step is the bimolecular (S_H2) displacement of $\dot{R}$ by $RO\dot{O}$ through attack at the metal center of the organochromium complex. The rate of reaction is unchanged by addition of the inert electrolytes lithium perchlorate or perchloric acid in the range of ionic strength 0.0033–0.043 M. This effect, which is diagnostic of mechanism in a chain reaction, unlike the situation with nonchain reactions, supports the mechanism above and rules out a kinetically equivalent mechanism in which the chain-carrying intermediates are Cr^{2+} and CrO_2^{2+}. The latter mechanism can also be ruled out on other grounds, including the failure of the independently prepared CrO_2^{2+} to react with Cu^{2+}.

Metal salts often function as catalysts for the oxidation of organic compounds in processes of considerable commercial importance,[2a] accounting for the continuing interest given to the ability of soluble metal complexes to activate molecular oxygen.[2b] Although complexes between the metal and molecular oxygen do not appear to be involved in the major reaction pathways for hydrocarbon autoxidation,[2a] reactions of organometals with molecular oxygen may play an important role. The reactions of main group organometallic complexes[3a] have been studied much more thoroughly than have reactions of transition-metal complexes. Detailed studies of the kinetics and mechanisms of reactions of metal alkyls with O_2 are limited indeed, but it is well established

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