order of the strength of these M–N bonds. Previously, Inskeep[4] discussed the origin of this order from the electronic configurations of the metals involved.

In addition to the M–N stretching bands, these complex ions are expected to show the N–M–N bending bands in the low-frequency region. They are difficult to identify, however, since they give only small isotopic shifts (1.5–0.2 cm^{-1}).[10] As stated previously, the bands at 220–210 cm^{-1} of the Fe(II) complexes have been tentatively assigned to the N–Fe–N bending modes. The complexes of Ni(II) and Zn(II) may exhibit similar bands at much lower frequencies.

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Metal Isotope Effect on Metal–Ligand Vibrations. III. π-Allyl Complexes of Palladium(II)[1]

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Abstract: The infrared and Raman spectra of four Pd(II) π-allyl complexes have been measured from 4000 to 100 cm^{-1}. The far-infrared spectra of $[^{104}Pd(\pi\text{-}C_3H_5)Cl]_2$ and its ^{110}Pd analog have been obtained. From the observed isotopic shifts, the Pd–allyl stretching bands have been assigned at *ca.* 400 and 370 cm^{-1}. The Pd–Cl (bridging) and Pd–Br (bridging) stretching bands are located at *ca.* 260–240 and 190–170 cm^{-1}, respectively.

Studies of metal–olefin stretching vibrations are important in understanding the nature of metal–olefin bonds. Previously, we[2] have studied the metal–olefin stretching vibrations of monoolefin complexes with Pt(II) and Pd(II), and have shown that these monoolefin complexes exhibit one metal–olefin stretching band per metal–olefin bond unless the vibration is forbidden by the selection rule. It is, therefore, of particular interest to extend similar studies to metal–allyl complexes to determine the number of the metal–allyl stretching vibrations in infrared spectra.

The infrared spectra (4000–300 cm^{-1}) of Pd(II)–allyl complexes have been studied by Fritz.[3] He assigned the band at 401 cm^{-1} of $[Pd(\pi\text{-}C_3H_5)Cl]_2$ to the Pd–allyl stretching band. However, his assignments in the low-frequency region have been questioned by several investigators.[4,5] The infrared spectra of $[Pd(\pi\text{-1-methylallyl})X]_2$ and $[Pd(\pi\text{-2-methylallyl})X]_2$ (X = Cl and Br) down to 200 cm^{-1} have been reported by Lupin, *et al.*[4] However, no band assignments on the Pd–allyl stretching bands have been made by these investigators.

In the previous papers of this series,[6–8] we have demonstrated that the metal isotope technique is extremely useful in assigning the metal–ligand vibrations of a variety of coordination compounds. In this paper we have applied this technique to assign the Pd–allyl stretching modes of four π-allyl complexes of Pd(II).

Experimental Section

Preparation of Compounds. (1) **Di-μ-chloro-bis(π-allyl)dipalladium(II), $[Pd(\pi\text{-}C_3H_5)Cl]_2$.** This compound was prepared by the method of Smidt and Hafner.[9] Further recrystallization was carried out from benzene.

Anal. Calcd for $PdCl(C_3H_5)$: C, 19.7; H, 2.95; Cl, 19.4. Found: C, 20.8; H, 2.86; Cl, 19.3.

(2) **Di-μ-bromo-bis(π-allyl)dipalladium(II), $[Pd(\pi\text{-}C_3H_5)Br]_2$.** This complex was prepared by the method described by Lupin, *et al.*[4]

Anal. Calcd for $Pd(C_3H_5)Br$: C, 15.9; H, 2.22; Br, 35.2. Found: C, 15.8; H, 2.34; Br, 34.3.

(3) **Di-μ-chloro-bis(π-2-methylallyl)dipalladium(II), $[Pd(\pi\text{-}C_4H_7)Cl]_2$.** This complex was prepared by the method used by Dent, *et al.*[5] Further recrystallization was carried out from benzene.

Anal. Calcd for $Pd(C_4H_7)Cl$: C, 24.4; H, 3.58; Cl, 18.0. Found: C, 24.7; H, 3.76; Cl, 18.3.

(4) **Di-μ-bromo-bis(π-2-methylallyl)dipalladium(II), $[Pd(\pi\text{-}C_4H_7)Br]_2$.** This compound was prepared by the bromination of the chloro analog using the method of Lupin, *et al.*[4]

Anal. Calcd for $Pd(C_4H_7)Br$: C, 19.9; H, 2.92; Br, 33.1. Found: C, 20.0; H, 2.69; Br, 32.5.

Metal allyl complexes containing pure Pd isotopes were prepared on a milligram scale. In each case, metallic palladium (50 mg each) was converted into $Na_2[PdCl_4]\cdot 4H_2O$ and treated with the ligand using the method of Smidt and Hafner.[9] The purity of the isotopes was ^{104}Pd, 89.75%, and ^{110}Pd, 96.98%. The isotopes were purchased from Oak Ridge National Laboratory. The purity of each allyl complex was checked by comparing the spectrum with that reported in literature.[3,4]

Spectral Measurements. Infrared spectra were obtained on a Beckman IR 12 (4000–250 cm^{-1}) and a Hitachi Perkin-Elmer FIS-3 (400–33 cm^{-1}) spectrophotometer. The spectra between 4000 and 550 cm^{-1} were obtained in KBr pellets and those below 500 cm^{-1} were obtained as Nujol mulls sandwiched between polyethylene plates. The solution spectra were obtained by using polyethylene liquid cells (cell thickness, 1 and 2 mm).

The spectra of isotopic species were run with a scanning speed of 1–2 cm^{-1}/min. Reproducibility of the spectra was checked by running the spectra three to five times. The average error in fre-

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Table I. Infrared and Raman Spectra of Palladium Allyl Complexes in the High-Frequency Region (cm^{-1})[a]

$[Pd(C_3H_5)Cl]_2$ Ir	$[Pd(C_3H_5)Cl]_2$ Raman	$[Pd(C_3H_5)Br]_2$ Ir	$[Pd(C_3H_5)Br]_2$ Raman	$[Pd(C_4H_7)Cl]_2$[b] Ir	$[Pd(C_4H_7)Cl]_2$[b] Raman	$[Pd(C_4H_7)Br]_2$[b] Ir	$[Pd(C_4H_7)Br]_2$[b] Raman	Band assignment[c]
1491 (w)	1492 (m–w)	1490 (w)	1489 (m–w)	1469 (m)	1477 (w)	1469 (m)	1479 (w)	ν_a (CCC)
1461 (s)	1463 (w)	1459 (s)	1461 (w)	1452 (m)	1451 (w)	1450 (s)	1450 (w)	δ_a (CH_2)
1383 (s)	1389 (w)	1382 (vs)	1386 (w)	1381 (s)	1386 (w)	1381 (s)	1387 (w)	δ_s (CH_2)
1230 (w)	1231 (w)	1229 (w)	1227 (w)	1337 (m)	1338 (w)	1337 (m)	1340 (sh)	ρ_r (CH_2)
1193 (w)	1199 (w)	1197 (w)	1197 (w)					δ (CH)
1024 (s)	1023 (m)	1020 (s)	1021 (w)	1031 (s)	1029 (w)	1029 (w)	1029 (s)	ν_s (CCC)
998 (m)	1006 (w)	999 (m)	1004 (w)	953 (s)[d]	963 (w)	950 (s)[d]	957 (m)[d]	ρ_t (CH_2)
968 (s)	974 (w)	961 (s)	968 (w)	953 (s)[d]	954 (sh)	950 (s)[d]	957 (m)[d]	ρ_w (CH_2)
943 (vs)	956 (w)	941 (vs)	950 (w)	933 (s)	940 (w)	932 (s)	936 (m)	ρ_w (CH_2)
913 (w)	920 (w)	913 (w)	918 (w)					π (C–H)
767 (m)[d]	775 (w, sh)	763 (m)[d]	771 (w)	786 (s)	789 (w)	785 (m)	788 (w)	ρ_r (CH_2)
767 (m)[d]	759 (w)	763 (m)[d]	769 (w, sh)	766 (w)	766 (w)	764 (w)	762 (w)	ρ_t (CH_2)
512 (s)	510 (s)	505 (vs)	505 (s)	570 (w)	570(m)	566 (m)	568 (s)	δ (CCC)

[a] Both ir and Raman spectra were obtained in the crystalline state. [b] In addition to those listed in Table I, these compounds exhibit the bands characteristic of the C–CH_3 group (see text). [c] ν, stretching; δ, bending; ρ_r, rocking; ρ_w, wagging; ρ_t, twisting; π, out-of-plane bending; a, antisymmetric; s, symmetric. [d] Overlapped bands.

quency reading was 0.5 cm^{-1}. Raman spectra were obtained on a Cary Model 81 Raman spectrophotometer with a He–Ne gas laser.

Results and Discussion

According to X-ray analysis,[10–12] the two Pd atoms in [Pd(π-allyl)Cl]$_2$ are joined by two chloride bridges to form a square-planar $(PdCl)_2$ group, and the allyl groups are bonded to the Pd atoms with their planes tilted by 111.5° with respect to the $(PdCl)_2$ plane so as to give the overall symmetry of C_{2h}. Since this molecule consists of 20 atoms, it has 54 ($3 \times 20 - 6$) normal vibrations. They are classified into $15A_g$, $12A_u$, $12B_g$, and $15B_u$ under C_{2h} symmetry. The $12A_u$ and $15B_u$ vibrations are infrared active, and the $15A_g$ and $12B_g$ vibrations are Raman active.

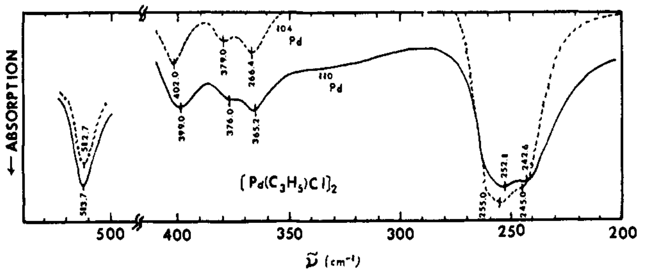

Figure 1. Far-infrared spectra of $[^{104}Pd(\pi\text{-}C_3H_5)Cl]_2$ and its ^{110}Pd analog in the solid state.

The Allyl Vibrations. As is shown above, 27 normal vibrations are active both in the infrared and Raman spectra of $[Pd(\pi\text{-}C_3H_5)X]_2$ type compounds (X = Cl and Br). Among these 27 vibrations, 18 ($3 \times 8 - 6$) vibrations originate in the allyl group. Table I lists 13 vibrations of the allyl group. The remaining 5 vibrations are the CH stretching modes which appear between 3100 and 2900 cm^{-1}. Table I also lists the observed frequencies of [Pd(π-2-methylallyl)X]$_2$ (X = Cl and Br). The last column of Table I gives the empirical band assignments.

The present assignments are different from those of Fritz[3] for several bands. Fritz assigned the strong band at 1461 cm^{-1} of $[Pd(\pi\text{-}C_3H_5)Cl]_2$ to the antisymmetric CCC stretching mode. However, we have assigned the weak band at 1491 cm^{-1} to it since the Raman spectrum definitely shows a band of medium-weak intensity at 1492 cm^{-1}. The bands at 1461 and 1383 cm^{-1} have been assigned to the antisymmetric and symmetric CH_2 scissoring modes, respectively. The remaining CH_2 group vibrations have been assigned based on the results previously obtained for the coordinated ethylene.[2] The bands at 1193 and 913 cm^{-1} are not present in the 2-methylallyl compounds, and can be assigned to the in-plane and out-of-plane CH bending modes, respectively. The 2-methylallyl compounds exhibit the bands characteristic of the C–CH_3 group; degenerate deformation (*ca.* 1430 cm^{-1}), symmetric deformation (*ca.* 1350 cm^{-1}), rocking (1050 and 960 cm^{-1}), and C–CH_3 stretching (*ca.* 835 cm^{-1}), which are not listed in Table I.

The lowest frequency fundamental of the allyl group is the CCC bending mode at *ca.* 505 cm^{-1}. However, the 2-methylallyl compounds show two in-plane CH_3–C(–C)–C bending bands (*ca.* 570 and 450 cm^{-1}) and one out-of-plane bending band (*ca.* 405 cm^{-1}). These three bands correspond to those at 530, 484, and 385 cm^{-1} reported for acetone.[13]

The $(PdX)_2$ Vibrations. Table II lists the frequencies observed between 500 and 200 cm^{-1}. According to Adams and Chandler,[14] *trans*-$[Pd_2L_2Cl_4]$ type complexes (L = neutral ligand) exhibit one terminal Pd–Cl stretching at 370–345 cm^{-1} and two bridging Pd–Cl stretching bands at 310–300 and 280–250 cm^{-1}. $[Pd(\pi\text{-}C_3H_5)Cl]_2$ exhibits bands at 403, 379–369, and 254–245 cm^{-1} in the solid state. Since this compound has no terminal Pd–Cl bonds, the bands observed above 340 cm^{-1} cannot be assigned to the Pd–Cl stretching modes. Then the strong bands at 254 and 245 cm^{-1} must be assigned to the bridging Pd–Cl stretching vibrations. As will be shown later, this assignment has been confirmed by the ^{104}Pd–^{110}Pd substitution (Table III). Lupin, *et al.*,[4] and Dent, *et al.*,[5] have also assigned the bands near 250 cm^{-1} to the same modes.

The Pd(II) analog of Zeise's dimer, $[Pd(C_2H_4)Cl_2]_2$, exhibits two bridging Pd–Cl stretching bands at 306 and 270 cm^{-1}.[2] The frequency separation of the two

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Table II. Low-Frequency (500–200 cm^{-1}) Vibrations of Pd–Allyl Complexes

	δ (CCC)	π (CCC)	ν (Pd–allyl)	ν (Pd–allyl)	ν(Pd–Cl$_b$)
		[Pd(C$_3$H$_5$)Cl]$_2$			
Ir (in Nujol)			403 (m)	379 (sh) 369 (w)	254 (s) 245 (s)
Ir (in benzene)			401 (m)	371 (m)	255 (s)
Raman (crystals)			406 (s)	372 (vs)	255 (s)
		[Pd(C$_3$H$_5$)Br]$_2$[a]			
Ir in (Nujol)			398 (m)	373 (m) 361 (sh)	
Ir (in benzene)			395 (m)	370 (m)	
Raman (crystal)			400 (s)	367 (vs)	
		[Pd(C$_4$H$_7$)Cl]$_2$			
Ir (in Nujol)	448 (m)	406 (vw)	380 (m)	368 (m)	252 (vs)
Ir (in benzene)	442 (m)	400 (vw)	383 (m)	372 (sh)	256 (vs) 250 (sh)
Raman (crystal)	450 (s)	407 (m)	389 (s)	368 (s)	261 (s)
		[Pd(C$_4$H$_7$)Br]$_2$[a]			
Ir (in Nujol)	447 (m)		380 (s)	360 (sh)	
Ir (in benzene)	440 (m)	400 (vw)	380 (br)[b]	380 (br)[b]	
Raman (crystal)	448 (s)	404 (w, sh)	387 (s)	360 (s)	

[a] ν (Pd–Br$_b$) is at 187 cm^{-1} in [Pd(C$_3$H$_5$)Br]$_2$ and at 186.4 and 176.4 cm^{-1} in [Pd(C$_4$H$_7$)Br]$_2$. [b] Overlapped bands.

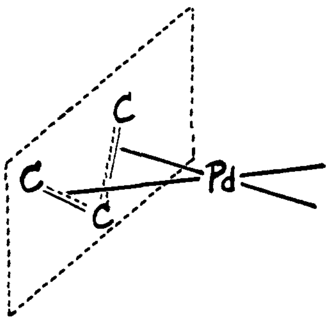
bridging modes in this compound is larger than that of the allyl compounds because the *trans* effects of C$_2$H$_4$ and Cl are markedly different.

The Pd–Allyl Vibrations. The allyl and 2-methylallyl groups exhibit the lowest frequency fundamentals at *ca.* 510 and 400 cm^{-1}, respectively. On the other hand, the (PdCl)$_2$ group exhibits the highest frequency fundamental at *ca.* 250 cm^{-1}. All the four compounds studied exhibit two or three bands of medium or strong intensity between 405 and 360 cm^{-1}. In this paper, these bands have been assigned to the Pd–allyl stretching modes.

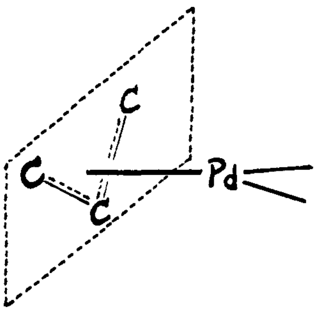
In order to confirm our assignments, we have prepared [^{104}(π-C$_3$H$_5$)Cl]$_2$ and its ^{110}Pd analog and compared their infrared spectra in the solid state. Figure 1 shows an actual tracing of the spectra and Table III lists the observed frequencies. The results indicate that the bands at 402.0, 379.0, and 366.4 cm^{-1} of the ^{104}Pd compound are shifted to lower frequencies by the ^{104}Pd–^{110}Pd substitution. Thus, these bands must be assigned to the Pd–allyl stretching modes. As is shown in Table II, the bands at 379 and 369 cm^{-1} observed for [Pd(π-C$_3$H$_5$)Cl]$_2$ (natural abundance) merge into one band (371 cm^{-1}) in benzene solution. A similar observation was also made for bromo analog. Thus, the splitting of the 371–370-cm^{-1} band in the solid state has been attributed to crystal field effect. Although the spectra of the complexes containing pure metal isotopes were not obtained in solution, it is safe to conclude that they would also show only one band near 370 cm^{-1} in benzene solution.

Table III. Isotope Effect on Infrared Spectra of [Pd(π-C$_3$H$_5$)Cl]$_2$ (cm^{-1})

^{104}Pd	^{110}Pd	Isotopic shift	Assignment
512.7	512.7	0.0	δ (CCC)
402.0	399.0	3.0	ν (Pd–allyl)
379.0	376.0	3.0	ν (Pd–allyl)
366.4	365.2	1.2	
255.0	252.8	2.2	ν (Pd–Cl$_b$)
245.0	243.6	1.4	



Bonding scheme A



Bonding scheme B

Figure 2. Bonding schemes for the Pd–allyl bond.

The foregoing discussion together with Table II shows that all the four Pd–π-allyl complexes exhibit two Pd–allyl stretching bands at *ca.* 400 and 370 cm^{-1}. This result can be accounted for if we assume bonding scheme A shown in Figure 2. In this scheme, two valence bonds (dsp^2 hybrid orbitals) of the Pd(II) atom are directed to the allyl group. Since the overall symmetry of the molecule is C_{2h}, only two Pd–allyl stretching bands are infrared active. These two bands can be designated as the antisymmetric and symmetric Pd–allyl stretching modes. Alternatively, they can be called the ring–tilt and metal–ring stretching modes,[15] respectively, if the allyl group is regarded as a semi-ring.

It should be noted that bonding scheme B involving only one valence bond may also exhibit the ring–tilt and metal–ring stretching modes. In this case, however, the ring-tilt frequency is expected to be much lower than the metal–ring stretching frequency because the former mode is regarded as a pure bending vibration involving the change in the angle between the valence bond and the allyl plane. Our infrared study seems to favor bonding scheme A since the frequencies of two Pd–allyl vibrations are relatively close (*ca.* 400 and 370 cm^{-1}).

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Sulfur-Bridged Dimeric Complexes of Iron(III)

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Abstract: Iron(III) dimers of general formula $[Fe(S_2CSR)_2(SR)]_2$, R = C_2H_5, *n*-C_3H_7, *n*-C_4H_9, $C_6H_5CH_2$, have been synthesized. Under identical conditions, only the known monomeric compound $[Fe(S_2CSR)_3]$ has been isolated for R = *t*-C_4H_9. Molecular weight and proton nmr spectral studies of the diamagnetic dimers in solution have been carried out. The pmr spectrum of the ethyl dimer, assigned on the basis of spin-decoupling experiments, is consistent with a structure which contains bridging ethyl sulfide and both bridging and terminal ethyl thioxanthate ligands. Cyclic voltammetric and conventional polarographic studies of the metal–metal bonded dimers reveal a two-electron reduction wave and a one-electron oxidation wave, both irreversible. Tris(*t*-butylthioxanthato)iron(III) is monomeric in solution and exhibits reversible one-electron oxidation and one-electron reduction waves. The complex contains low-spin iron(III) with an effective moment of 2.46 BM at room temperature in the solid and over the limited temperature range, $210° < T < 293°K$, in dichloromethane solution. The solid-state reflectance and solution electronic spectra of all the dimers are nearly identical, implying similar structures, but differ significantly from the corresponding spectra of the *t*-butyl monomer. Infrared spectra are reported and discussed.

Sulfur-bridged dimers of iron in low formal oxidation states have been prepared[2–5] and structurally characterized.[6–8] In addition, several dimeric 1,2-dithiolene complexes of iron in formally higher oxidation states have been synthesized,[9] and the solid-state structure of at least one member of this series has been determined.[10] An objective in a continuing study[11–13] of the coordination chemistry of iron–sulfur complexes of possible relevance to certain non-heme iron protein systems has been to synthesize iron(III) dimers or oligomers with bridging sulfide or alkyl mercaptide ligands. As reported in a preliminary communication,[13] this has been accomplished for one system by means of the carbon disulfide elimination reaction of iron(III) alkylthioxanthate complexes.

Carbon disulfide elimination reactions appear to be characteristic of metal thioxanthate complexes.[14] For example, it has recently been shown[15] that $Ni(S_2CSR)_2$ complexes may be decomposed, with loss of carbon disulfide, to the dimeric species $[Ni(S_2CSR)(SR)]_2$ reported earlier.[16] A similar reaction occurs in the thermal conversion of monomeric $[(\pi\text{-}C_5H_5)Fe(CO)(S_2CSR)]$ compounds to $[(\pi\text{-}C_5H_5)Fe(CO)(SR)]_2$.[4] Tris(alkylthioxanthate) compounds of iron(III) have been previously described and their instability has been noted.[17] The decomposition products were not identified, however. As outlined in the present report, carbon disulfide elimination occurs to form the series of dimeric compounds, $[Fe(SR)(S_2CSR)_2]_2$, the properties of which have been investigated by a variety of physical techniques. A detailed discussion of the crystal structure determination, geometry, and structural evidence for metal–metal bonding in $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ will be taken up separately.[18]

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