methylene chloride was kept at 25 °C for 7 h and then for an additional 10 h after addition of a catalytic amount of dry hydrogen chloride. During the first stage of this reaction the amino group of **4** adds in a conjugate manner and specifically to the carbon β to the ketonic function of dimethyl 2-oxoglutaconate, and cyclization occurs to give the cyclized piperidinol **5**.[10] Addition of acid catalyst in the second stage of the annulation effects dehydration and aromatization to form the desired tricyclic product **6** which is isolated from the reaction mixture by washing with aqueous sodium bicarbonate followed by saturated brine solution, drying, and concentration in vacuo. The yield of **6**, obtained as yellow crystals, mp 224-225 °C, homogeneous by TLC (R_f 0.37 on silica gel with 4:1 methylene chloride-ethyl acetate), was >90%.[11]

Addition of ceric ammonium nitrate (5.5 equiv) to a solution of **6** in 4:1 acetonitrile-water at 0 °C, further reaction for 10 min at 0 °C, dilution with water, extraction with ethyl acetate-methylene chloride (4:1), and recrystallization of the solid product so obtained from hot acetonitrile afforded 60% of the quinone **7** as orange crystals, mp 260-263 °C dec, homogeneous by TLC (R_f 0.14 on silica gel with 4:1 methylene chloride-ethyl acetate); UV_{max} (H_2O) 252, 344 nm;[12] UV_{max} (CH_3OH) 251, 321, 373 nm.[13] Thus it was possible to introduce the *o*-quinone unit directly from the methyl ether **6** without deprotection and establish the complete functionality of methoxatin.

Successful conversion of the trimethyl ester **7** to methoxatin required considerable experimentation. Trifluoroacetic acid-water (2:1) treatment of **7** at 25 °C rapidly hydrolyzed one of the carbomethoxy groups (presumably that on the α carbon of the pyridine ring), and at 90 °C in this medium a second ester function could be hydrolyzed. The remaining carbomethoxy group (on the pyrrole ring) was resistant to hydrolysis under conditions which did not cause major decomposition. The sensitivity of the methoxatin system to base precluded the use of alkaline conditions. The triacid corresponding to **6** could be obtained readily by saponification of **6** with 0.5 M potassium carbonate in water at 85 °C for 4 h. Direct Ce(IV) oxidation of this triacid failed to give methoxatin. A variety of other approaches also proved fruitless.[14] A simple and effective solution was found as follows.

Reaction of **7** with 10 equiv of methyl orthoformate and a trace of *p*-toluenesulfonic acid in methanol at reflux for 4 h produced the monoketal **8** in 92% yield. Exposure of **8** to excess 0.5 M aqueous potassium carbonate at 85 °C for 4 h followed by acidification to pH 2.5 with hydrochloric acid produced a precipitate of methoxatin (**1**) which was obtained as a deep red solid after collection and drying in vacuo (98% yield). The UV absorption spectra,[3] fluorescence spectra,[4] and reversed-phase high-performance chromatographic (RP-HPLC) behavior[3] of synthetic and naturally derived methoxatin were identical.[15]

Treatment of synthetic **1** with dimethyl sulfate-potassium carbonate in dry dimethylformamide results in formation of a trimethyl ester, as previously described for native **1**,[3] which is identical with the synthetic intermediate trimethyl ester **7**.[16]

Exposure of synthetic **1** to 10% aqueous acetone brought to pH 9 with ammonium hydroxide at 23 °C for 30 min resulted in formation of the previously described "aldol" adduct of **1** with acetone (**9**),[1] the structure of which was ascertained by X-ray diffraction studies. The acetone adduct **9** derived from synthetic **1** was identical with that formed from native methoxatin as determined by measurement of UV spectra (UV_{max} 250, 317, 360 nm in water at pH 5.5), fluorescence (excitation at 365, fluorescence maximum at 465 nm), and proton and ^{13}C NMR spectra.[17] Synthetic and naturally derived **9** showed identical behavior by RP-HPLC analysis (retention volume for each 2.52 under the conditions described above for **1**; lit.[5b]), and a mixture of the two showed a single sharp elution peak.

With the successful completion of the synthesis of methoxatin and its ready accessibility, it is now feasible to study critically the chemistry of this interesting substance and such an investigation is under way.[18]

(10) The intermediate **5** was isolated and characterized spectroscopically. The NMR spectrum ($CDCl_3$) revealed the presence of indole NH (br s, δ 8.68) and CH (δ 7.06, d, J = 1.6 Hz, 1 H), and a single benzenoid proton (δ 6.93, s, 1 H), in addition to the other peaks expected for **5**; UV_{max} in C_2H_5OH 209 and 247 nm; M^+ (molecular ion) at 392. In a separate experiment **5** was transformed into the simple dehydration product which could also be isolated and characterized.

(11) Spectral data for **6** are as follows: NMR ($CDCl_3$, δ): 11.0 (br, 1 H, NH), 8.97 (s, 1 H), 7.35 (s, 1 H), 7.26 (d, 1 H), 4.17 (s, 3 H), 4.12 (s, 3 H), 4.09 (s, 3 H), 4.0 (s, 3 H); IR_{max} ($CHCl_3$, cm^{-1}) 3340, 3150, 2955, 1720, 1265, 1255; UV_{max} in C_2H_5OH 205.5, 275, 320.5 nm; M^+ at 372.

(12) The same UV_{max} have been reported[3] for methoxatin trimethyl ester (of natural origin) in aqueous solution.

(13) Other spectral data for **7** are as follows: NMR ($CDCl_3$, δ) 12.98 (br s, 1 H, indole NH), 8.87 (s, 1 H, quinoline β-H), 7.47 (d, J = 2 Hz, 1 H, indole β-H), 4.18, 4.07, 3.98 (each s, 3 H, OCH_3), essentially identical with that reported; IR_{max} ($CHCl_3$) 1722, 1687 cm^{-1}; fluorescence in H_2O 462 nm (excitation at 365 nm); fluorescence in CH_3OH 455 nm (excitation at 394 nm).

(14) For example, studies using the triisopropylsilyl, methoxymethyl and benzhydryl esters corresponding to **6**, prepared from the corresponding triacid, did not lead to success in the oxidation step.

(15) In aqueous solution at pH 5.5 synthetic methoxatin (**1**) showed UV_{max} at 247, 330 nm with a shoulder at 270 nm; at pH 2.5 UV_{max} at 250 and 340 nm were observed. Excitation of synthetic **1** in water at 365 nm results in $fluorescence_{max}$ at 483 nm. Synthetic methoxatin was homogeneous by RP-HPLC on a Waters Associates C_{18}-μ-Bondapak column using 95:5 water-methanol containing 0.1% acetic acid (pH ca. 4.5) and was eluted at 3.55 retention volumes. The ^{13}C NMR spectrum of synthetic **1** (in CD_3SOCD_3) showed peaks at (tetramethylsilane) δ 113.86, 122.76, 125.97, 127.71, 130.68, 137.60, 144.63, 146.41, 147.62, 161.25, 165.48, 166.45, 173.30, and 180.00.

(16) Attempted conversion of **1** to the trimethyl ester **7** using diazomethane in methanol-water was unsuccessful due to the high reactivity of the *o*-quinone unit with this reagent. Even the monomethylketal of **7** underwent rapid reaction with diazomethane to form an epoxide by methylene transfer to the dienone carbonyl.

(17) We are indebted to Professor Hugh S. Forrest for an authentic sample of **9** (200 μg) and spectral data. The ^{13}C NMR spectrum of synthetic **9** in CD_3SOCD_3 solution showed peaks at (tetramethylsilane) δ 29.77, 51.06, 74.82, 111.96, 120.75, 121.13, 125.59, 126.88, 135.21, 139.19, 144.92, 161.01, 161.47, 165.17, 168.61, 190.16, and 207.03.

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Oxidative Addition of Allyl Acetate to Pd(0) Complexes

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It is generally accepted that the interaction of Pd compounds such as $Pd(PPh_3)_4$ with allyl acetates, $R^1CH{=}CHCHR^2OAc$, causes activation of the allyl-O bond of allyl acetate to afford η^3-allyl(acetato)palladium-type species. Actually a variety of organic synthetic reactions proceeding through the supposed η^3-allyl(acetato)palladium intermediate have been developed.[1-4] There is, however, no example in which the η^3-allyl(acetato)-palladium intermediate was isolated from the reaction mixture

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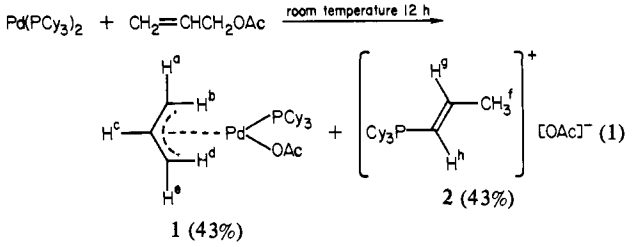
to support the proposed mechanism. In this paper we report isolation of the η^3-allyl(acetato)palladium complexes from mixtures of Pd compounds and allyl acetates as well as some chemical reactivities of the complexes isolated.

We first attempted isolation of the η^3-allyl(acetato)palladium-type complex from a mixture of allyl acetate and coordinatively saturated $Pd(PPh_3)_4$[5] which has been most widely employed as the catalyst for the organic synthesis mentioned above. However, no apparent change was observed with the mixture even at elevated temperatures (80 °C), though it was found to catalyze 1,3 shift of allyl-D_2 acetate as revealed later. In contrast to the reaction of $Pd(PPh_3)_4$, that of coordinatively unsaturated $Pd(PCy_3)_2$[6] (PCy_3 = tricyclohexylphosphine) with allyl acetate proceeds smoothly at room temperature to give yellow $Pd(\eta^3\text{-}C_3H_5)(OAc)(PCy_3)$ (**1**) and white $[(E)\text{-}Cy_3PCH{=}CHCH_3]^+[OCOCH_3]$ (**2**) in 43% yield, respectively (recrystallized from acetone). Formation of a bi-



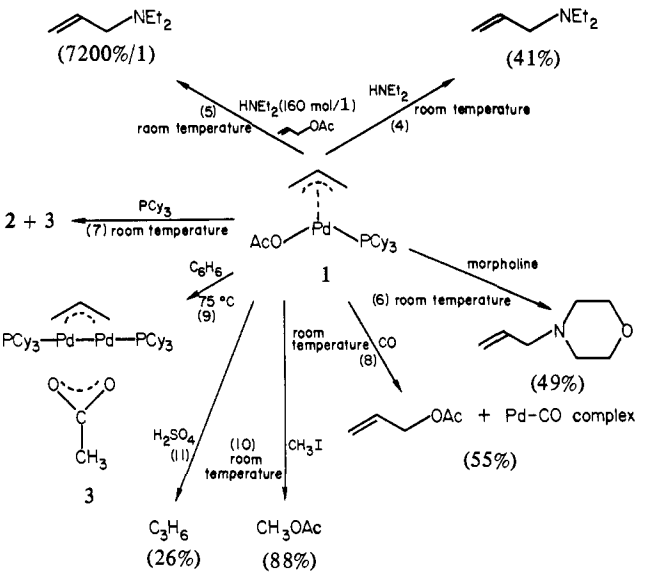
nuclear complex, $(PCy_3)_2Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}OAc)$ (**3**), which is considered to be formed through a coupling reaction between $Pd(PCy_3)_2$ and **1** (vide infra), sometimes accompanies reaction 1, depending on reaction conditions. **1**: mp 134–136 °C. Anal. Calcd: C, 56.7, H, 8.4. Found: C, 57.1; H, 8.9. IR (KBr) ν(COO) 1600, 1360 cm^{-1}; ^1H NMR δ (−71 °C, acetone-d_6) 1.1–2.1 (33 H, PCy_3)*, 1,80 (3 H, $OCOCH_3$)*, 2.40 (1 H, d, H^b)*, 3.24 (1 H, d, H^a), 3.70 (1 H, dd, H^d), 4.40 (1 H, t, H^e), 5.28 (1 H, m, H^c); $J(H^a - H^c)$ = 6 Hz, $J(H^b - H^c)$ = 12 Hz, $J(H^c - H^d)$ = 14 Hz, $J(H^c - H^e)$ = 8 Hz, $J(H^d - {}^{31}P)$ = 9 Hz, $J(H^e - {}^{31}P)$ = 8 Hz (asterisk indicates overlap). At room temperature the two doublets at 2.40 and 3.24 ppm are averaged to give rise to a doublet (J = 9 Hz) at 2.90 ppm due to rapid movement of the η^3-C_3H_5 ligand.[7] **2**: mp 107–109 °C. Anal. Calcd: C, 72.6; H, 10.8. Found: C, 71.8; H, 11.2. The disagreement between the found and calculated values seems to be due to partial incorporation of H_2O into **2**. IR (KBr) ν(COO) 1650, 1280 cm^{-1}; ^1H NMR (CD_2Cl_2) 1.2–2.0 (33 H, PCy_3)*, 1.8 (3 H, $OCOCH_3$)*, 2.10 (3 H, dt, H^f), 5.80 (1 H, ddq, H^h), 6.75 (1 H, tq, H^g). $^1H\{^{31}P\}$-, $^{13}C\{^1H\}$-, $^{31}P\{^1H\}$-, and homo-decoupled NMR spectra of **1** and **2** are consistent with the structures. The electric conductivity of acetone solution of **2** is comparable to that of Na[BPh_4] having the same molar concentration, whereas acetone solution of **1** shows minor electric conductivity, suggesting that **1** has an essentially nonionic structure. Compounds **1** and **2** can be synthesized through different reaction pathways, (2) and (3),

$$[Pd(\eta^3\text{-}C_3H_5)(OAc)]_2 + PCy_3 \rightarrow \mathbf{1} \qquad (2)$$

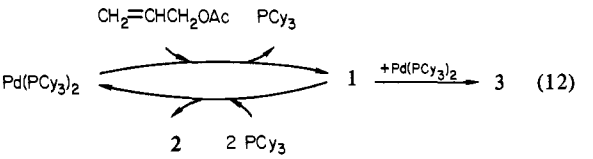
$$PCy_3 + CH_2{=}CHCH_2Br \rightarrow [Cy_3P{-}CH_2CH{=}CH_2]^+Br^- \xrightarrow{+AgOAc} \mathbf{2} \qquad (3)$$

the fact also supporting the formulation of the compounds. Concerning reaction 3, it is known that AcO^- ion catalyzes isomerization of $[R_3P{-}CH_2CH{=}CH_2]^+$ to $[R_3P{-}CH{=}CHCH_3]^+$.[8] The reaction of 2-methylallyl acetate with $Pd(PCy_3)_2$ also causes similar C–O bond cleavage as shown in eq 1, giving $Pd[\eta^3\text{-}CH_2C(CH_3)CH_2](OAc)(PCy_3)$ (60%) and $[Cy_3P{-}CH{=}C(CH_3)_2]^+[OAc]^-$.

Scheme I



Scheme I shows chemical reactivities of **1**. The nucleophilic attack of amines at the allyl ligand in **1** as well as the catalytic conversion of allyl acetate and diethylamine to allyldiethylamine promoted by **1** lend support to the usually supposed allylation mechanism with interaction of a Pd(0) complex (reactions 4–6). Recently Stakem and Heck reported allylation of nucleophiles by other isolated η^3-allylpalladium complexes.[9] The reaction of **1** with PCy_3 affords **2** and the binuclear complex **3** (eq 7). The binuclear complexes of the type $(R_3P)_2Pd_2(\mu\text{-allyl})(\mu\text{-OAc})$ have been prepared from $[(\eta^3\text{-allyl})Pd(\mu\text{-OAc})]_2$ and $Pd(PR_3)_2$ by Werner and his co-workers.[10] Complex **3** was actually prepared by the Werner's method and proved to be identical with the one prepared according to reaction 7. Reaction 7 seems to proceed through initial transfer of the allyl ligand in **1** to PCy_3 to give **2** and $Pd(PCy_3)_2$ followed by coupling reaction between $Pd(PCy_3)_2$ and remaining **1** to give **3**. These results suggest that **2** in eq 1 and **3**, the byproduct of reaction 1, are formed by a mechanism shown below. According to the mechanism, the amount of the



byproduct, **3**, is considered to increase with increase in the relative concentration of **1** to allyl acetate, the experimental results being in accordance with this view. The phosphonium salt (**2**) is not available by the direct reaction of PCy_3 with allyl acetate, but **2** can be catalytically formed from PCy_3 and allyl acetate in the presence of **1** or $Pd(PCy_3)_2$. Complex **1** is converted into **3** on heating a benzene solution of **1**.

The reaction of **1** with CO causes reductive elimination of allyl acetate from **1** (eq 8), demonstrating that the oxidative addition of allyl acetate to Pd is a reversible process. Reactions of **1** with CH_3I and H_2SO_4 afford CH_3OAc and C_3H_6, respectively.

As mentioned before, the reaction of $Pd(PPh_3)_4$ with allyl acetate at room temperature gives no apparent change. However, an experiment using allyl-*1,1*-d_2, acetate $CH_2{=}CHCD_2OAc$, clearly indicates that $Pd(PPh_3)_4$ catalyzes a clean pairwise 1,3 shift of allyl acetate at room temperature to afford a mixture of $CH_2{=}CHCD_2OAc$ and $CD_2{=}CHCH_2OAc$ without giving any

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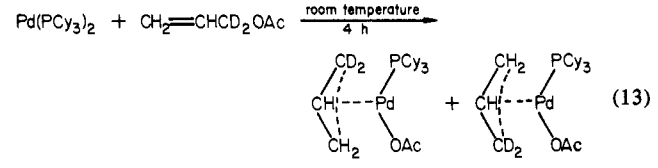
H-D scrambled species such as CHD=CHCHDOAc and CH_2=CDCHDOAc. A small amount of coordinatively unsaturated Pd(0) species such as $Pd(PPh_3)_2$ partly formed seems to be responsible for the catalytic 1,3-shift reaction on interaction with allyl acetate.

Employment of CH_2=$CHCD_2OAc$ in the reaction with $Pd(PCy_3)_2$ affords a mixture of cis and trans isomers of $Pd(\eta^3\text{-}CH_2CHCD_2)(OAc)(PCy_3)$ and a mixture of $[Cy_3P\text{—}CD{=}CHCH_2D]^+[OAc]^-$ and $[Cy_3P\text{—}CH{=}CHCHD_2]^+[OAc]^-$.



(13)

5:5

Allyl-d_2 acetate remaining after the reaction was a mixture of CH_2=$CHCD_2OAc$ and CD_2=$CHCH_2OAc$ in a 6:4 ratio. The reaction of *trans*-$PdEt_2(PEt_3)_2$[11] with allyl acetate at room temperature leads to the C-O bond cleavage to yield $[Pd(\eta^3\text{-}C_3H_5)(PEt_3)_2]^+[OAc]^-$.

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Ultra-High-Field NMR Spectroscopy: Observation of Proton-Proton Dipolar Coupling in Paramagnetic Bis[tolyltris(pyrazolyl)borato]cobalt(II)

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In high-resolution NMR spectra of liquids undergoing rapid molecular tumbling, the observed transition frequencies are averages derived from orientation-dependent local magnetic fields.[2a] Conversely, in solids the motion is quenched, and the spectra contain additional transitions because of orientation-dependent terms in the Hamiltonian,[2b] specifically, dipole-dipole interactions, quadrupole coupling, and chemical shift anisotropy. Spectra obtained in nematic liquid crystal solvents[3] bridge this gap by providing partial orientation in a mobile environment.

The extensive work by Lohman and MacLean[4] on diamagnetic compounds, and our recent study of paramagnetics,[5] show that small partial alignment can also be achieved by application of a strong magnetic field to solutions of magnetically anisotropic molecules containing deuterium. The ensuing order produces a residual deuterium quadrupolar splitting from which magnetic parameters can be deduced. Here we report the first observation of dipole-dipole couplings between *protons* in isotropic solution. This result is significant because of the direct structural information contained in the magnitude of dipolar couplings between $I = {}^1/_2$ spins.

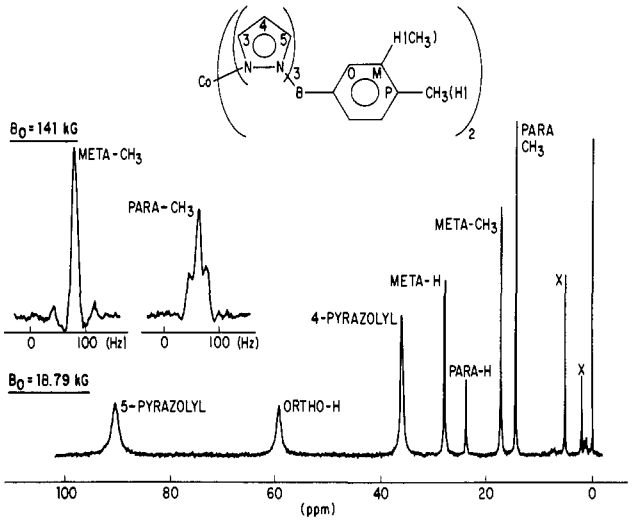

Figure 1. ^{1}H NMR spectrum of bis[tolyltris(pyrazolyl)borato]cobalt(II) at 80 MHz with the inset showing the methyl resonances at 600 MHz and 293 K. The spectrum is a mixture of *m*-CH_3 and *p*-CH_3 isomers; the para complex is of D_{3d} symmetry. Assignments are shown on the 80-MHz spectrum; the 3-pyrazolyl resonance is approximately 89 ppm upfield of Me_4Si. The 600-MHz spectrum has been resolution enhanced to more clearly reveal the dipolar coupling.

The key to the successful observation of dipolar splitting in our spectra is the 141-kG field currently available[6] for high-resolution NMR spectroscopy. Proton spectra of D_{3d} bis[tolyltris(pyrazolyl)borato]cobalt(II), $Co(TTPB)_2$,[7] are shown in Figure 1 at 80 MHz (B_0 = 18.79 kG) and 600 MHz (B_0 = 141 kG). The para methyl resonance is clearly split into a 1:2:1 triplet ($3D \sim 16$ Hz) at 600 MHz while the meta methyl is unsplit. The corresponding deuterium NMR spectrum of $Co(TTPB\text{-}d_7)_2$ shows all lines split into doublets in the high-field spectrum. The resolving power, or ratio of splitting to line width, is approximately 6 in the deuterium spectrum but near 1 in the proton spectrum. This difference reflects both the increasing difficulty of observing the smaller proton-proton dipolar coupling and a shorter proton T_2.

The deuterium quadrupolar splittings can be measured to give the order parameter S_0 for the alignment at 293 K as previously reported.[4,5]

$$S_0 = (\chi_\parallel - \chi_\perp)B_0^2/15kT = 5.09 \times 10^{-4} \qquad (1)$$

The proton spectrum of the methyl group is easily accounted for with the same alignment (order parameter) and the dipole-dipole interaction term[3,8] to give the dipolar splitting

$$3D_{ij} = \left[\left(\frac{-3\gamma_H{}^2h}{4\pi^2}\right)S_0\right]\left(\frac{1}{2}\left\langle\frac{3\cos^2\alpha_{ij} - 1}{R_{ij}{}^3}\right\rangle\right) \qquad (2)$$

where α_{ij} is the angle between the interproton vector and the principal axis of the susceptibility tensor, R_{ij} is the distance between protons, and the other symbols have their usual meanings. For a standard methyl geometry (R_{CH} = 1.08 Å) the predicted splitting of the para resonance (α = 90°) is 16.7 Hz, in good agreement with the measured value of 16 Hz. The calculated splitting of 4 Hz for the meta resonance (α = 60°) is obscured by the paramagnetic line width.

The observation of dipolar splittings provides an alternative approach to the deuterium quadrupole method[5] for determining the susceptibility anisotropy in paramagnetic complexes. The two

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