case of tri-*m*-tolylphosphine. Comparison of tri-*p*-tolylphosphine with triphenylphosphine probably involves only an electronic effect; the larger value of K_1 with the more electron-donating phosphine[50] is consistent with a stronger metal–olefin bond because of greater π donation to the olefin from the metal.

Equation 1 involves both formation of a metal–olefin bond and breaking of a metal–phosphorus bond, so that the free energy change is a sum of terms. However, we suggest that changes in K_1 with changes in the metal reflect primarily changes in metal–olefin bond strength. If the strength of the metal–olefin bond depends primarily on π donation from the metal to the antibonding π^* ethylene orbitals, then the metal with the greatest electron availability should give the most stable ethylene complex. On the basis of ionization potentials of the gaseous d^{10} metal atoms, nickel (5.8 eV) should be a better π donor than Pd or Pt (each *ca.* 8.3 eV). The same conclusion can be reached on the basis of the promotion energies $(n - 1)d^{10} \rightarrow (n - 1)d^9np$ with Ni] (1.72 eV) being a much better donor than Pt (3.23 eV), which is better than Pd (4.23 eV).[18] Ease of electron promotion in the sequence Ni(0) $\gg$ Pt(0) > Pd(0) is consistent with our electronic spectral data, where the longest wavelength maxima of the three $M(PPh_3)_3$ complexes are found at 393, 332, and 322 mμ, respectively. π-Donor ability of the zerovalent metals in this sequence may explain why Ni(0) forms a stable tetracarbonyl, whereas Pt(0) and Pd(0) do not, and is consistent with the results of X-ray crystal structure studies, which show a longer olefinic C–C bond length in (C_2H_4)-$Ni[PPh_3]_2$ (1.46 Å) than in $(C_2H_4)Pt[PPh_3]_2$ (1.43 Å).[14]

Finally, a word should be said about why these triarylphosphine complexes dissociate to tris complexes, while tetrakis complexes of other ligands are very stable to dissociation. Meier, Basolo, and Pearson[51] have argued that $Ni[P(OEt)_3]_4$ does not dissociate appreciably in solution, while $Ni[PPh_3]_4$ does because triphenylphosphine is a better electron donor and builds up too much negative charge on the metal. Ligand-exchange studies on zerovalent nickel have since shown that the phosphorus bond strength is primarily a consequence of steric effects.[52] The large ligand cone angle[52] of 145° for PPh_3 makes coordination of four phosphines in a tetrahedral array extremely difficult. That dissociation is due to steric rather than electronic effects is nicely illustrated by the behavior of $Ni[PMe_3]_4$. Trimethylphosphine is a better donor than PPh_3, but is considerably smaller, with a ligand cone angle of 118°. Not only does $Ni[PMe_3]_4$ show no evidence of ligand dissociation in solution,[52] but the compound can be purified by sublimation *in vacuo* at 80°.[53] Further studies on equilibria involving the dissociation of other NiL_4 complexes will be described subsequently.[54]

Acknowledgments. We are indebted to Professor C. D. Cook for a copy of his paper[14] in advance of publication, and to Mrs. F. C. Youngken for molecular weight determinations.

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Organometallic Conformational Equilibria. XV. Preparation and Resolution of 1,2,3-h^3-(1-Acetyl-2,3-dimethylallyl)-[(*S*)-α-phenethylamine]chloropalladium[1]

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Abstract: (+)-Bis[1,2,3-h^3-1-acetyl-2,3-dimethylallyl)chloropalladium(II)] and some of its amine derivatives are reported. These complexes will not epimerize, but they do isomerize.

The 1,2,3-h^3-(1-acetyl-2-methallyl)[(*S*)-α-phenethylamine]chloropalladium complex, which can be isolated in optically active form,[2-4] epimerizes rapidly in solution at ambient temperatures. It has been firmly established that the predominant mechanism whereby substituted π-allyl–palladium chloride complexes epimerize or racemize is *via* formation of a σ-bonded intermediate.[2-4] Our study of model allyl compounds showed that thermodynamic constraints are placed upon such rearrangements, suggesting the possibility of isolation of an allylic moiety which would not epimerize.[3] It was generalized that a chiral 1,2,3-trisubstituted allyl moiety with two different groups occupying the positions at the terminal

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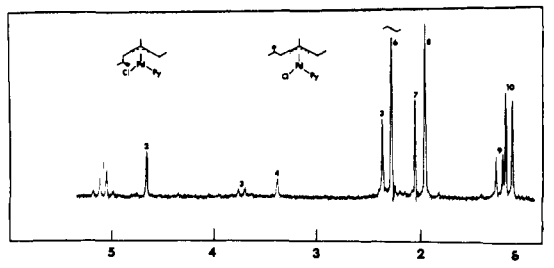


Figure 1. Nmr spectrum (100 MHz) of 1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)(pyridine)chloropalladium in a 3:1 deuteriochloroform–benzene solution at 27° (py = pyridine).

carbon atoms may isomerize but not epimerize. We present here the results obtained for the bis[1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)chloropalladium] complex and its amine derivatives, a previously unreported complex which will not epimerize but does isomerize.

Experimental Section

Nmr spectra were measured on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe. Optical rotatory dispersion and circular dichroism measurements were obtained with a Cary 60 spectropolarimeter with a CD attachment.

Palladium chloride was allowed to react with 4-methyl-3-hexen-2-one[5] according to the procedure of Moiseev, *et al.*,[6] to give a π-allyl dimer. The light green solid which formed was dried and then recrystallized from tetrahydrofuran to give a yellow powder which decomposed above 175°. This material was shown to be bis[1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)chloropalladium(II)].

The dimer was treated with a 5% excess of (*S*)-α-phenethylamine in ethyl acetate. Upon standing, an amine complex crystallized which was then filtered, dried, and recrystallized from 1:1 methylene chloride–cyclohexane solution. On cooling, pale yellow needles melting with decomposition at 139–140° were obtained. After reaching equilibrium in solution, the complex still showed a large rotation, $[\alpha]_{546}$ +544° (*c* 0.564, chloroform). Attempts to crystallize the more soluble diastereoisomer, (−)-1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)[(*S*)-α-phenethylamine]chloropalladium, have proven unsuccessful.

Addition of a methylene chloride solution of (+)-1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)[(*S*)-α-phenethylamine]chloropalladium to a neutral alumina chromatography column produced a yellow band, which was eluted with a 1:1 mixture of chloroform and methanol. The solvent was removed *immediately* and the residue dissolved in chloroform. The chloroform solution was washed with distilled water, dried over magnesium sulfate, and evaporated. The solid was recrystallized from tetrahydrofuran to give the optically active dimer. Bis[(+)-1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)chloropalladium] had a rotation of $[\alpha]_{546}$ +1380° (*c* 0.158, chloroform) at equilibrium. Addition of the appropriate quantity of (*S*)-α-phenethylamine to this optically active dimer and the observation of the equilibrium specific rotation demonstrated that the amine derivative had been converted to the optically active dimer and back to the amine complex with an overall retention of optical activity of 93%.

The optically active dimer could also be prepared by shaking a chloroform solution of the amine derivative with 1 *N* HCl. Stronger acid caused racemization.

Results and Discussion

Reaction of 4-methyl-3-hexen-2-one with palladium chloride gave a π-allyl derivative, which was presumably either a 1-acetyl-2,3-dimethylallylpalladium complex and/or a 1-acetyl-2-ethylallyl complex. The nmr spectrum of the pyridine derivative is shown in Figure 1. The absence of a methyl triplet, an AB methylene pattern, and three singlet allylic resonances eliminated the possibility of significant formation of the 1-acetyl-2-ethylallyl complex. For a 1-acetyl-2,3-dimethylallyl moiety, syn–anti isomerism of both terminal substituents with respect to the central methyl group is possible. A total of 20 resonances would be expected; however, only 10 resonances are observed. The chemical shifts and intensities of resonances 5, 6, 7, and 8 (Figure 1) correspond closely to those observed for the acetyl and methyl resonances of the 1-acetyl-2-methallyl complex,[3] indicating that syn–anti isomerism exists for the acetyl group, with the anti isomer predominating in solution. This implies that the 3-methyl group must exist totally in either a *syn*-methyl configuration or an *anti*-methyl configuration. Comparison of the chemical shifts for the dimethyl portion with similar complexes reported in the literature, *e.g.*, bis[1,2,3-h^3-(1,2-dimethylallyl)chloropalladium],[7] indicates that the 3-methyl groups are most likely in a syn configuration. The geometric isomers of the 1-acetyl-2,3-dimethylallyl complex found in solution are illustrated in Figure 2. Nmr parameters for the dimer and its various amine derivatives are given in Table I.

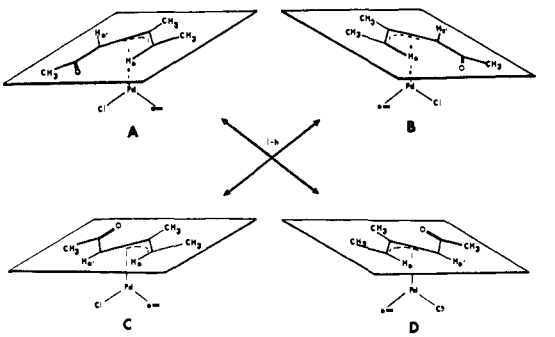
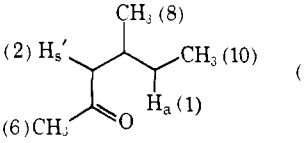
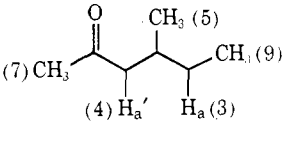


Figure 2. The epimers of the 1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)-(amine)chloropalladium complex.

Table I. Nmr Parameters for Bis[1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)chloropalladium] and Its Amine Derivatives[c]





	Dimer	Complex (*S*)-α-Phenethylamine	Complex Pyridine
δ_1[a]	4.89	4.55,[b] 4.69	5.05
δ_2	4.54	4.27, 4.30[b]	4.62
δ_3	3.55	3.28, 3.32[b]	3.69
δ_4	3.22	3.01,[b] 3.10	3.35
δ_5	2.27	2.06	2.38
δ_6	2.17	2.20	2.25
δ_7	2.15	2.15	2.02
δ_8	1.85	1.55, 1.67[b]	1.93
δ_9	1.12	1.05, 1.15[b]	1.23
δ_{10}	1.16	1.12,[b] 1.18	1.14

[a] δ in parts per million with respect to TMS. Spectra were taken at 33°. [b] Resonances due to the less soluble epimers. [c] Solvent, 3:1 $CDCl_3$–C_6H_6.

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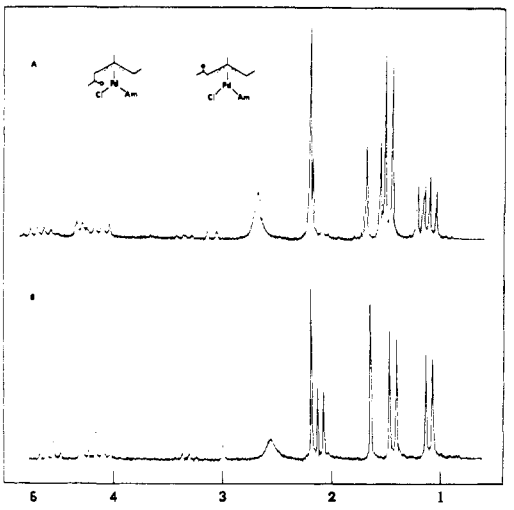

Figure 3. (A) Nmr spectrum (100 MHz) of a 3:1 deuteriochloroform–benzene solution of bis[1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)-chloropalladium] and (*S*)-α-phenethylamine at 33°. Resonances at δ 1.44, 2.57, and 4.12 are due to the (*S*)-α-phenethylamine (Am = (*S*)-α-phenethylamine). (B) Nmr spectrum (100 MHz) of a 3:1 deuteriochloroform–benzene solution of the crystallized 1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)[(*S*)-α-phenethylamine]chloropalladium complex at 33°.

When correct molar portions of bis[1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)chloropalladium] and (*S*)-α-phenethylamine were combined in deuteriochloroform and an nmr spectrum was taken of the resulting solution, the expected epimeric resonances for both the *syn*- and *anti*-acetyl isomers were obtained (see Figure 3A). However, when crystalline 1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)[(*S*) - α - phenethylamine]chloropalladium[8] was dissolved at −20° and an nmr spectrum taken, resonances attributable to only one of the epimers of the *anti*-acetyl isomer were observed. When the temperature was raised, resonances attributable to only one of the epimers of the *syn*-acetyl isomer appeared. Thus at 33° only the resonances of the one epimer of the *anti*-acetyl isomer and the one epimer of the *syn*-acetyl isomer were present (see Figure 3B). No other resonances appeared even after standing several days; thus, we have observed isomerization[9] but no epimerization.

This occurrence can readily be explained. Assuming that it were the (*S*)-*anti*-acetyl isomer, 2A, which crystallized, then formation of a 1-*h* σ-bonded intermediate would give the (*S*)-*syn*-acetyl isomer, 2D, *i.e.*, isomerization would occur. This is indeed what was observed. If a 3-*h* σ-bonded intermediate were formed, it would invert the configuration about carbon 1, but it would also result in the 3-methyl group being placed in an anti position. This is thermodynamically unfavorable; thus, only a small amount of that isomer would be found in solution. At no time would the epimers of the individual isomers interconvert; *i.e.*, if A fractionally crystallizes out, it may isomerize to D but will not epimerize to B. One would thus expect the solution to exhibit a substantial optical rotation and this is what is observed.

A sample of the 1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)[(*S*)-α-phenethylamine]chloropalladium complex at equilibrium had a specific rotation of +544° at 546 nm (*c* 0.564, chloroform). At equilibrium, the ratio of *anti*-/*syn*-acetyl isomers as determined by nmr spectroscopy was 70/30. While the (+)-1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)[(*S*)-α-phenethylamine]chloropalladium complex is easily crystallized, all attempts to crystallize the more soluble (−)-1,2,3-h^3-(1-acetyl-2,-3-dimethylallyl)[(*S*)-α-phenethylamine]chloropalladium complex were unsuccessful.

The optically active allylic moiety could be isolated by converting the amine derivative back to the dimer. This was accomplished by two methods. Chromatography of a solution of (+)-1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)[(*S*) - α - phenethylamine]chloropalladium on neutral alumina gave (+)-bis[1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)chloropalladium]. The (+) dimer could also be obtained by extracting a solution of the amine derivative with dilute HCl. (+)-Bis-1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)chloropalladium crystallizes as the *syn*-acetyl isomer. With a free energy of activation for isomerization of about 25 kcal/mol, a time on the order of hours would be required for a solution to attain equilibrium at ambient temperatures. Thus the value which would be obtained for the specific rotation immediately upon solution would reflect to a great extent the true specific rotation of the *syn*-acetyl isomer. An initial specific rotation of +955° at 546 nm (*c* 0.158, chloroform) was recorded. At equilibrium a value of +1380° was obtained. Thus both the *syn*- and *anti*-acetyl allyl moieties exhibit similar signs for the Cotton effect at long wavelengths. For the dimer at equilibrium, the ratio of *anti*-/*syn*-acetyl isomers as determined by nmr spectroscopy was 67/33; thus the specific rotation of the *anti*-acetyl allylic moiety would be ~+1590° at 546 nm.

Table II. Optical Activity Data for (+)-Bis[1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)chloropalladium] and (+)-1,2,3-h^3-(1-Acetyl-2,3-dimethylallyl)[(*S*)-α-phenethylamine]chloropalladium

Complex	$[\alpha]_{546}$[a]	λ_{max}, nm	$[\theta]$[b] at λ_{max}
(+)-Bis[1,2,3-h^3-(*syn*-1-acetyl-2,3-dimethylallyl)chloropalladium]	+955°	375	18,880
(+)-Bis[1,2,3-h^3-(*syn*,*anti*-1-acetyl-2,3-dimethylallyl)chloropalladium]	+1380°	372	20,300
(+)-1,2,3-h^3-(*syn*,*anti*-1-Acetyl-2,3-dimethylallyl)[(*S*)-α-phenethylamine]chloropalladium	+544°	353	17,700

[a] In chloroform at 25°. [b] Molecular ellipticity in methylene chloride. Value was calculated per optically active allyl moiety.

CD studies of olefin–platinum complexes have shown that the absolute configuration of the optically active coordinated olefin is reflected in the lowest energy d → d transition of the platinum atom (~400 nm).[10-12]

(8) The yellow solid was readily crystallized from either a methylene chloride–cyclohexane solution or carbon tetrachloride. It melted at 139–140° with decomposition.

(9) Kinetic data for isomerization were obtained by monitoring the rate at which the isomer grew in. For the 1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)[(*S*)-α-phenethylamine]chloropalladium complex, which crystallized as the *anti*-acetyl isomer, a value of 21.1 kcal/mol was obtained for the free energy of activation ($k = 1.89 \times 10^{-4}$ at 7°). Bis-[1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)chloropalladium] crystallized as the *syn*-acetyl isomer. The free energy of activation for isomerization to the *anti*-acetyl isomer was 24.8 kcal/mol ($k = 4.4 \times 10^{-4}$ at 62°).

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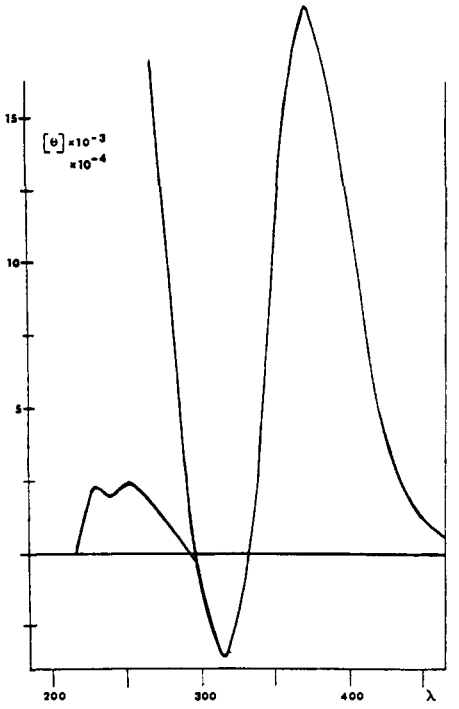

Figure 4. CD spectrum of (+)-bis[1,2,3-h^3-(*syn,anti*-1-acetyl-2,3-dimethylallyl)chloropalladium] in methylene chloride.

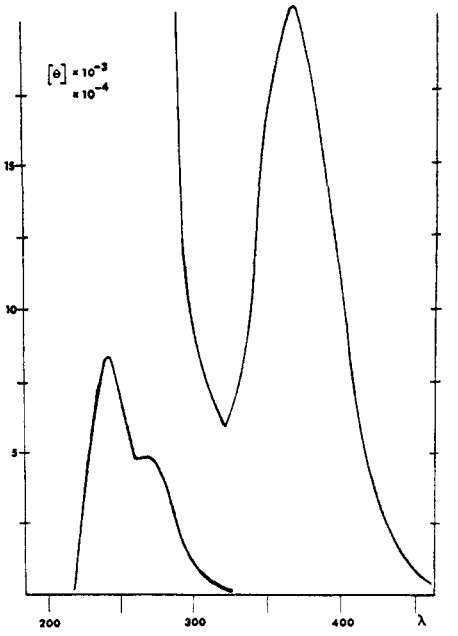

Figure 5. CD spectrum of (+)-1,2,3-h^3-(*syn,anti*-1-acetyl-2,3-dimethylallyl)[(*S*)-α-phenethylamine]chloropalladium in methylene chloride.

It appears that it is equally true for allyl palladium complexes. The CD curves for (+)-bis[1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)chloropalladium] and (+)-1,2,3-h^3-(1-acetyl-2,3-dimethylallyl)[(*S*)-α-phenethylamine]chloropalladium are shown in Figures 4 and 5. Both curves are for equilibrium solutions; *i.e.*, both *syn*- and *anti*-acetyl isomers are present. A bathochromic shift of the lowest energy d → d transition was noted in going from the (*S*)-α-phenethylamine derivative to the dimer. These results (Table II) and the changes observed on dissolving the samples are consistent with expectations derived from quadrant or hexadecant rule considerations, but it is premature to comment further at this point.

From the above one can conclude that the stability of the various isomers in solution plays a very important role in determining whether an optically active allyl moiety once isolated will epimerize. Knowledge of the stability of isomers should allow one in principle to design systems under which reactions on the coordinated ligand would lead stereospecifically to asymmetric products. Studies in this general direction are now being pursued.

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