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MOLECULAR ASYMMETRY OF π-ALLYLIC COMPOUNDS OF TRANSITION METALS

VI. β-KETOAMINE DERIVATIVES OF SYMMETRICALLY AND DISSYMMETRICALLY SUBSTITUTED π-ALLYLPALLADIUM COMPLEXES

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SUMMARY

It is shown that in solution, at equilibrium at room temperature, one of the two faces of an allyl group may be preferentially bound to the metal in π-allylic β-ketoamine palladium complexes if the ketoamine has a chiral centre. Analysis of the PMR spectra allows the assignment of the absolute stereochemistry of the coordinated allylic group provided that of the ketoamine is known.

INTRODUCTION

In previous papers in this series[1–5] we have shown that two types of molecular asymmetry exist for π-allylic complexes of palladium of the type (π-enyl)BPdX (X = halogen, B = base), depending on the substituent pattern in the allyl ligand coordinated to the metal. If a symmetrically substituted allyl ligand is π-coordinated, molecular asymmetry arises owing to the non coplanarity of the allyl ligand with the coordination plane of the metal. On the other hand, chiral, formally-tetragonal carbon atoms are formed if a dissymmetrically substituted (prochiral) allyl ligand is coordinated to the metal. PMR-distinguishable diastereoisomeric pairs have been obtained if the base B is asymmetrical. It has been found[3,4] for 1,2-substituted allyl complexes that when the asymmetrical ligand coordinated to the metal is α-phenylethylamine, the two expected diastereoisomers are present in equilibrium in practically equal amounts at room temperature.

The main aim of this work has been to bring about coordination to the metal of an asymmetric ligand such that in the room temperature equilibrium one of the two faces of the allyl ligand would be preferentially coordinated to the metal. It was found that the chelating ligand 4-(α-phenylethylamino)-3-penten-2-one gave the desired result in some cases. A preliminary account has appeared previously[5].

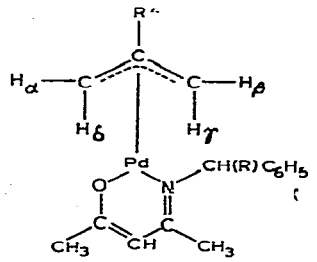
RESULTS AND DISCUSSION

The β-ketoamine π-allylic palladium complexes were prepared in good yield

by reaction of the corresponding π-allylic palladium chloride dimer with the potassium salt of the β-ketoamine, following the method of Everett and Holm[6] for the preparation of moisture-sensitive β-ketoamine complexes (see Experimental section). The coordinated β-ketoamines are represented in the text as ($PhCH_2N,O$) and (α-PhC_2H_4N,O) to indicate respectively 4-benzylamino-3-penten-2-onato and racemic 4-α-phenylethylamino-3-penten-2-onato.

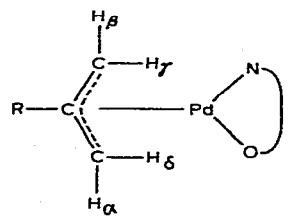
Symmetrically substituted allyl complexes

The PMR spectra of the *N*-benzyl- and *N*-α-phenylethylketoamine complexes (I a,b) were found to be complementary, thus allowing firm assignment of the *syn* and *anti* protons of the allyl ligand. The PMR spectral data of the *N*-benzyl derivatives are shown in Table 1.



(Ia), R = H
(Ib), R = CH_3

TABLE 1



100 MHz PMR SPECTRAL DATA FOR (1,2,3-h^3-2R-ALLYL)(4-BENZYLAMINO-3-PENTEN-2-ONATO)Pd COMPLEXES[a]

R	H_α	H_β	H_γ	H_δ	R
H[b]	3.73 $J_{\alpha\beta}$ 2; $J_{\alpha R}$ 7	2.78 $J_{\beta R}$ 7	2.32 $J_{\gamma R}$ 11	2.90 $J_{\delta R}$ 13	5.40
CH_3	3.48 $J_{\alpha\beta}$ 2.8	2.55	2.30	2.74	1.83 or 1.86[c]
tert-Butyl	3.64 $J_{\alpha\beta}$ 3.3; $J_{\alpha\delta}$ 0.9	2.76 $J_{\beta\gamma}$ 1.2	2.13	2.64	1.00
Phenyl	3.97 $J_{\alpha\beta}$ 3.1	3.07 $J_{\beta\gamma}$ 1.2	2.61	3.00	[d]

[a] All chemical shifts in ppm downfield from TMS, and coupling constants in Hz. Solvent $CDCl_3$, temperature 29°. [b] $-CH_2N$ shows as apparent doublet (centre part of AB quartet) centred on δ 5.14 ppm. [c] Indistinguishable from one of the chelate CH_3 groups. [d] Obscured by chelate phenyl resonances.

The resonances of the *syn* and *anti* protons of these compounds were readily assigned on the basis of the magnitude of the four-bond coupling (≈3 Hz) between the non-equivalent *syn* protons H_α and H_β since it has generally been found that in π-allylic complexes the *syn–syn* coupling is much larger than the *anti–anti* and geminal *syn–anti* couplings[3,7,8]. A further check was provided by comparison of the chemical shifts with those of the parent allyl complex, in which the assignment of the *syn* and *anti* protons were easily made on the basis of the differences in the couplings with the central proton. The assignment of the geminal *syn–anti* pairs was obtained by Nuclear Overhauser studies. Thus in the case of (1,2,3-h^3-2-methallyl)($PhCH_2N,O$)Pd, relatively low r.f. power irradiation of the *syn* resonance at δ 3.48 ppm produced an increase in the integrated intensity of the *anti* resonance at δ 2.74 ppm of the order of 20% (and *vice versa*) but no real change in the intensities of the other two allylic proton resonances. Since the Nuclear Overhauser effect, under optimum conditions of the relaxation time, is observed between protons of the same molecule which are close together in space[9], these enhancements in intensity confirm the relatively close proximity of the protons resonating at δ 3.48 and 2.74 ppm, *i.e.* that they form a geminal pair. Similarly, irradiation of the resonance at δ 2.55 ppm produced a similar enhancement in the intensity of that at δ 2.30 ppm (and *vice versa*), without significantly affecting the others, so confirming the other geminal pair assignment. It should be noted that the assignment of the protons as *cis* to the oxygen and nitrogen respectively, as shown in Table 1, is only based on comparison with the results obtained with compounds (Ib), in which an asymmetrical β-ketoamine is coordinated to the palladium (*vide infra*).

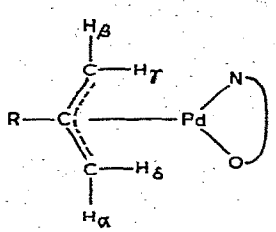
High temperature PMR spectra were also run with (1,2,3-h^3-2-methallyl)-($PhCH_2N,O$)Pd, but at temperatures as high as 100° (in toluene-d_8) only slight broadening of the allylic proton resonances was observed. This suggests that the σ,π equilibrium[10] of the coordinated allyl group, which would exchange *syn* and *anti* protons, is still slow on the NMR time scale. However "spin saturation labelling"[11] experiments have shown that *syn,syn* and *anti,anti* proton exchange is occurring*. Thus high r.f. power irradiation of one *syn* resonance caused a decrease in the integrated intensity of the other and similarly for the *anti* protons. The saturation stabilised at a 60% value at 65°. These results are consistent with an exchange of the chelate coordination sites probably through an exchange mechanism analogous to that proposed by Powell *et al.*[14] to explain the *syn,syn* and *anti,anti* proton averaging at 30° in π-allylpalladium picolinato complexes, although in our case it occurs more slowly.

The PMR spectra of complexes (Ib), in which an asymmetric carbon atom is attached to the nitrogen, are more complex than those of the *N*-benzyl derivatives, because of the formation of diastereoisomeric pairs. However a straightforward assignment of the resonances of each isomer was effected by following with PMR the epimerization of the pure diastereoisomers obtained by crystallization of the crude reaction mixtures; the PMR results are summarised in Table 2.

Thus, for example, dissolving crystalline (1,2,3-h^3-2-methallyl)(α-PhC_2H_4-N,O)Pd in chloroform-*d* at −50° and recording the spectrum soon afterwards at the

* Spin-saturation transfer experiments have been described by other authors for π-allylpalladium complexes[8,12,13].

TABLE 2



100 MHz PMR SPECTRAL DATA FOR (1,2,3-h^3-2R-ALLYL)(4-α-PHENYLETHYLAMINO-3-PENTEN-2-ONATO)Pd COMPLEXES

R	*Major diastereoisomer*[a]					*Minor diastereoisomer*[a]					*Diastereoisomer ratio*
	H_α	H_β	H_γ	H_δ	R	$H_{\alpha'}$	$H_{\beta'}$	$H_{\gamma'}$	$H_{\delta'}$	R'	
H	3.71	[b]	2.13	[b]	≈5.0[c]	3.71	[b]	1.25	[b]	≈5.0[c]	1[e]
	$J_{\alpha R}$ 7		$J_{\gamma R}$ 12			$J_{\alpha' R'}$ 12		$J_{\gamma' R'}$ 12			
	$J_{\alpha\beta}$ 2					$J_{\alpha'\beta'}$ 2					
CH_3	3.47	2.17	2.12	2.74	1.45	3.53	2.52	1.26	2.65	≈1.9	2.0±0.1
	$J_{\alpha\beta}$ 3.3		$J_{\gamma\delta}$ 0.8			$J_{\alpha'\beta'}$ 3.3	$J_{\beta'\gamma'}$ 1.3	$J_{\gamma'\delta'}$ 0.8			
tert-Butyl	3.75	2.31	1.92	2.83	0.91	3.69	2.73	≈1.0	2.60	1.18	1[e]
	$J_{\alpha\beta}$ 3.5	$J_{\beta\gamma}$ 1.0				$J_{\alpha'\beta'}$ 3.5	$J_{\beta'\gamma'}$ 2.0				
Phenyl	4.02	2.65	2.31	3.05	[d]	3.98	≈3.0	≈1.4	≈2.9	[d]	1.9±0.1
	$J_{\alpha\beta}$ 3.0	$J_{\beta\gamma}$ ≈1									

[a] All chemical shifts in ppm downfield from TMS, and coupling constants in Hz. Solvent $CDCl_3$, temperature 29°. The assignment as "major" and "minor" is referred respectively to stereochemistry (A) and (B) of Fig. 2 also in the cases where the ratio of the diastereoisomers is unity. [b] Resonances overlapping in the region δ 2.7 to 3.0 ppm. [c] Overlapping with –CHN resonances. [d] Obscured by chelate phenyl resonances. [e] Peak heights indicate a slight induction of asymmetry, but within experimental error integrals give a 1/1 ratio.

same temperature gave the simple spectrum shown in Fig. 1 in which the allylic proton resonances are readily recognizable. The lower field *syn* and *anti* resonances have almost the same chemical shifts as those in the corresponding *N*-benzyl derivative, but the remaining *syn* and *anti* peaks show a high-field shift relative to the *N*-benzyl values. The simplicity of the spectrum shows that on crystallization only one of the two isomers was obtained, and since this isomer crystallizes in almost quantitative yield it may be concluded that crystallization proceeds through a second order asymmetric transformation[15].

On raising the temperature, other signals gradually appeared, and are assignable to the other diastereoisomer*. At the probe temperature (Fig. 1) the relative proportion of the two isomers obtained by integration of the spectrum was found to be 2/1 in favour of the low temperature form, and this did not change on standing for several hours. The same probe temperature ratio was obtained in different solvents (carbon tetrachloride, methylene chloride, benzene and acetone), and so it may be safely concluded that there is an induction of asymmetry which is solvent independent. We have assigned the resonances α and δ, α′ and δ′ respectively, to the *syn* and *anti*

* On raising the temperature the signals sharpened and some variations in chemical shifts were noted. This temperature dependence was observed for all the diastereoisomeric complexes herein reported.

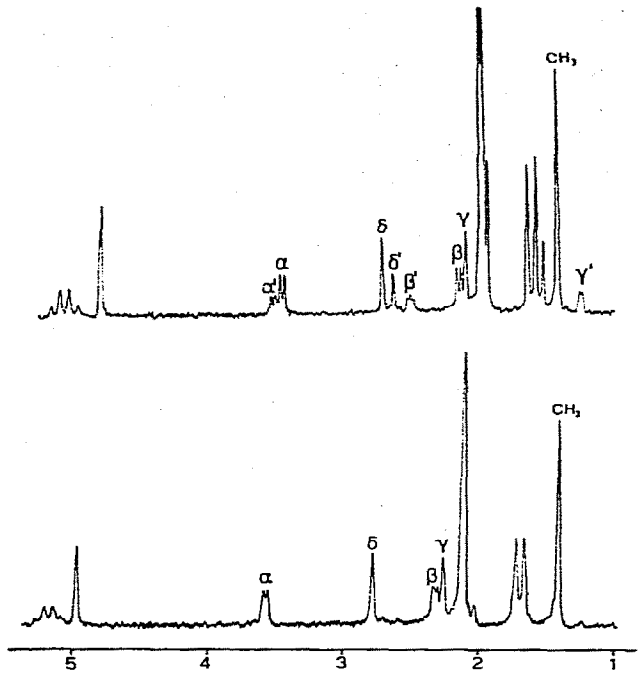


Fig. 1. 100 MHz PMR spectra of (1,2,3-h^3-2-methallyl)(α-PhC_2H_4N,O)Pd in $CDCl_3$. Lower trace, −50°; upper trace, 29°. Unlabelled peaks belong to the β-ketoamine ligand. The peak labelling refers to the formula of Table 2.

protons of the major and minor diastereoisomers which are *cis* to the oxygen of the chelate. This is based on the assumption that those protons which in both diastereoisomers are far from the asymmetric centre, would have similar chemical shifts. Contrariwise, a reasonably substantial difference in chemical shift would be expected between the corresponding protons in both isomers which are *cis* to the nitrogen, but nevertheless, the resonance of the highest field (*anti*) proton of the minor isomer appears at first sight to be at unexpectedly high field (δ 1.26 ppm). However examination of molecular models of the two possible diastereoisomers leads to a perfectly reasonable explanation, based on the well known anisotropic shielding of the benzene ring, *i.e.* on the "ring current effect"[16]. From such an examination it can be seen that the two diastereoisomers differ greatly in the relative positions, with respect to the allyl moiety, of the phenyl group of the asymmetric centre. In one diastereoisomer (Fig. 2A), the *syn* proton *cis* to the nitrogen is relatively close to and below the plane of the phenyl ring, in a position more nearly perpendicular to than parallel to the plane of the ring (*i.e.* shielded), whereas in isomer (B) of Fig. 2 this situation holds for the *anti* proton. Accordingly, the *syn* and *anti* resonances of the protons *cis* to the nitrogen in diastereoisomer (A) would be expected to resonate at higher and lower field with respect to the corresponding protons in the diastereoisomer (B). Analogously, the resonance of the C-2 methyl group of diastereoisomer (A) would be expected to occur at higher field than that of diastereoisomer (B). The assignments indicated in Fig. 1 are based on such an interpretation of the experimental results ($\Delta\delta_{syn}$ 0.35, $\Delta\delta_{anti}$ 0.86, $\Delta\delta_{CH_3} \approx 0.5$ ppm), which implies that the major and minor isomers have conforma-

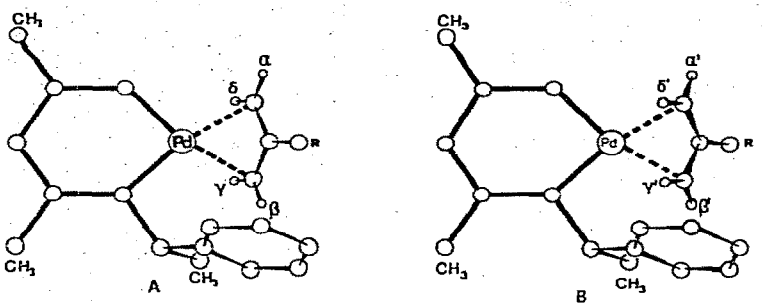


Fig. 2. Schematic structural models of the two diastereoisomers of (1,2,3-h^3-2R-allyl)(α-PhC_2H_4N,O)Pd.

tions (A) and (B) respectively. Further, this implies that the orientation of the allyl group with respect to the asymmetrical centre of the chelate is also known. Thus if we assume, for instance, that the asymmetrical carbon atom of the β-ketoamine has *S* configuration, then the major diastereoisomer (Fig. 2A) has *R* chirality, while the minor diastereoisomer (Fig. 2B) has *S* chirality. The chirality of the complexes were established by following the rules of Cahn, Ingold and Prelog[17] for planar chirality. The chiral plane is that orthogonal to the coordination plane of the metal containing the Pd–C-2 allyl bond, the "pilot atom" being the chelate oxygen atom.

An interesting feature of the PMR spectrum of the equilibrium mixture is that the geminal *syn–anti* coupling between the protons *cis* to the nitrogen in isomer (B) (1.3 Hz) is substantially larger than that in isomer (A) (unresolved), whereas in both isomers, within the limits of resolution ($\approx$0.3 Hz), no geminal coupling could be observed between the protons *cis* to the oxygen. This is a general phenomenon, observed for all complexes of type (B) stereochemistry in which the C-2 substituent of the allyl moiety and the phenyl group on the asymmetric carbon atom attached to the nitrogen are on opposite sides of the coordination plane of the palladium. Another interesting feature of the spectrum is the presence of an *anti–anti* coupling (0.8 Hz) in both diastereoisomers (see Table 2). These couplings, clearly shown by expansion of the spectrum, were confirmed as being *anti–anti* couplings by double irradiation experiments. Such an *anti–anti* coupling has also been found in some π-allylic palladium salicylaldiminato complexes[7,18].

The assignment of structure (A) to the crystalline (1,2,3-h^3-2-methallyl)-(α-PhC_2H_4N,O)Pd (low temperature PMR spectrum) on the basis of the chemical shifts observed has been confirmed by an X-ray structural determination[5], thus indicating that the most stable isomer has the same structure in solution as in the solid state.

Spin saturation and Nuclear Overhauser studies were also carried out on this compound, both at the probe temperature and at 65°. In this case, if a σ,π equilibrium exists then, for example, the *syn* proton on a given carbon atom will be transferred to the *anti* proton on the corresponding carbon atom of the other diastereoisomer. Thus any possible interference due to an Overhauser effect enhancement being superimposed on a saturation transmitted through the exchange mechanism is eliminated, unlike the situation with the benzylamine derivatives. These studies again confirmed the geminal pair assignments (Overhauser effect), and showed that ligand exchange was occurring (spin saturation), but no evidence for a σ,π mechanism was obtained.

Thus the σ,π mechanism must be slow on the NMR time-scale and slower than the ligand exchange.

(1,2,3-h^3-2-phenylallyl)(α-PhC_2H_4N,O)Pd also shows the same behaviour as that of the π-methallyl analogue (Fig. 3). The assignment of the resonances of the major and minor isomers, which have structures of type (A) and (B) respectively, in Fig. 2, were obtained by the method and arguments given above for the methallyl complex. The ratio between the major and minor isomers at probe temperature was found to be 1.9/1, and, as with the π-methallyl analogue, was solvent independent. Further, the major isomer has the same structure in solution as in the solid state.

Unlike the (1,2,3-h^3-2-methallyl)(α-PhC_2H_4N,O)Pd and (1,2,3-h^3-2-phenylallyl)(α-PhC_2H_4N,O)Pd complexes, the corresponding allyl and 2-tert-butylallyl complexes exhibit very little induction of asymmetry. In fact the two diastereoisomers of type (A) and (B) occur in an almost 1/1 ratio at the probe temperature. In the case of the tert-butyl complex the low temperature spectrum showed the presence of only one isomer [type (A)], whereas that of the allyl complex showed the presence of both isomers in approximately equal amounts even at $-70°$ (CD_2Cl_2). Since rapid epimerization on dissolving at low temperatures is unlikely, we conclude that in the latter case crystallization occurs without preferential crystallization of one diastereoisomer. Finally protons β and β' of the diastereoisomers of the 1,2,3-h^3-allyl complex are slightly atypical of the examples reported in this section in that they have similar chemical shifts, the shielding effect of the phenyl ring being reflected mainly on the γ' proton ($\delta_{\gamma'}-\delta_{\gamma} \approx 0.9$ ppm).

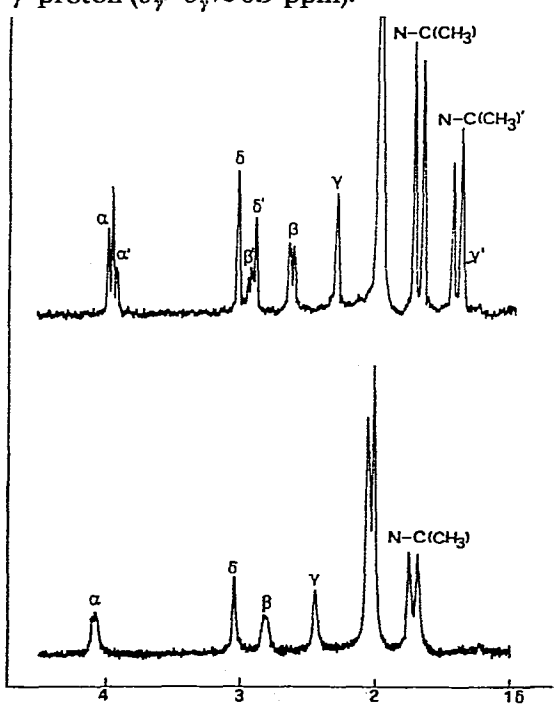
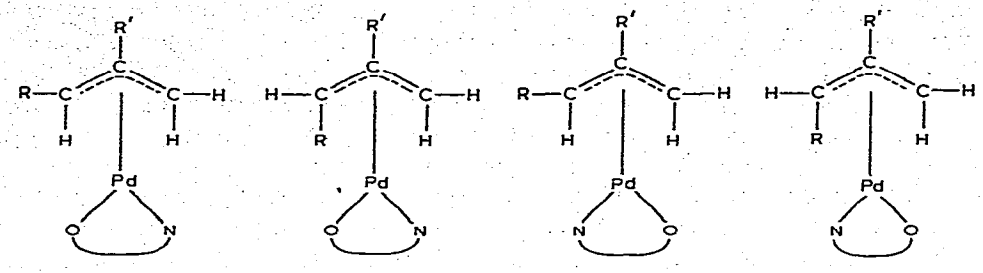


Fig. 3. 100 MHz PMR spectra of (1,2,3-h^3-2-phenylallyl)(α-PhC_2H_4N,O)Pd in $CDCl_3$. For peak labelling see formula of Table 2. Lower trace, $-50°$; upper trace, 29°. The *anti*-γ' resonance was located by double resonance experiments, varying the frequency and monitoring β'.

Dissymmetrically substituted π-allyl complexes

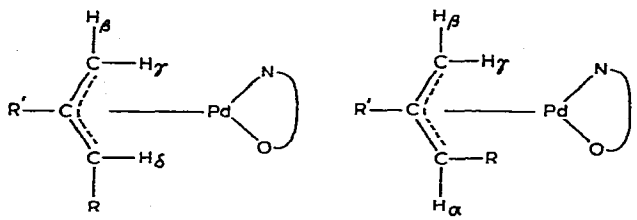
It is well known that 1,2-disubstituted π-allyl complexes of palladium[4,19] may exist as *syn–anti* isomers. If a β-ketoamine ligand is coordinated to the metal, another source of geometrical isomerism is introduced. In principle the four geometrical isomers indicated below are possible:



(IIa) (IIb) (IIc) (IId)

If an asymmetric carbon atom is attached to the nitrogen of the β-ketoamine ligand, then each of the complexes (II) exists as a diastereoisomeric pair. For simplicity we first discuss the *N*-benzyl (maximum 4 isomers) and then the *N*-α-phenyl-

TABLE 3



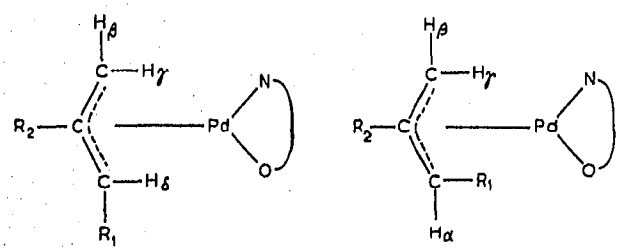
(I) (II)

100 MHz DATA FOR (1,2,3-h^3-1R-2R'-ALLYL)(4-α-BENZYLAMINO-3-PENTEN-2-ONATO)Pd COMPLEXES[a]

Compound	H_α	H_δ	H_β	H_γ	*R*	*R'*
(I) R=CH_3, R'=H		3.60 $J_{\delta R}$ 6 $J_{\delta R'}$ 11	2.61 $J_{\beta R'}$ 7	2.10 $J_{\gamma R'}$ 11	1.32	≈5.1
(I), R=R'=CH_3[d]		3.39 $J_{\delta R}$ 6	2.47	2.09	1.23	1.77
(I), R=CH_3, R'=phenyl		3.57 $J_{\delta R}$ 6.5 $J_{\delta\gamma} > 0.0$	2.58 $J_{\beta\gamma}$ 1.3	2.33	1.28	[b]
(I), R=$COCH_3$, R'=CH_3		3.63	2.67	2.57	1.99	2.15
(II), R=$COCH_3$, R'=CH_3	4.55		2.93	3.82	2.03	1.73
(II), R=Phenyl, R'=CH_3	4.28		2.35	2.61	[c]	[c]

[a] All chemical shifts in ppm downfield from TMS and coupling constants in Hz, temperature 29°. Solvent $CDCl_3$. [b] Signal obscured by the phenyl resonance of the chelate ligand. [c] Unassignable as signals overlap. Signals due to the *syn* isomer were present but assignment dubious due to the presence of other signals (see text). [d] Solvent C_6D_6.

TABLE 4



100 MHz PMR SPECTRAL DATA FOR (1,2,3-h^3-1R_1-2R_2-ALLYL)(4-α-PHENYLETHYLAMINO-3-PENTEN-2-ONATO)Pd COMPLEXES[a]

Compound	*Major diastereoisomer*[b]						*Minor diastereoisomer*[b]						*Diastereoisomer ratio*
	H_α	H_δ	H_β	H_γ	R_1	R_2	$H_{\alpha'}$	$H_{\delta'}$	$H_{\beta'}$	$H_{\gamma'}$	R'_1	R'_2	
(I), R_1=CH_3, R_2=H		3.5 $J_{\delta R_1}$ 6	1.93	1.91	1.2	4.4–4.6		≈3.5 $J_{\delta'\gamma'}$ > 0 $J_{\delta' R'_1}$ 6	2.67 $J_{\beta'\gamma'}$ 2 $J_{\beta' R'_2}$ 6.5	0.95 $J_{\gamma' R'_1}$ 12	1.2	4.4–4.6	1
(I), R_1=R_2=CH_3[f]		3.23 $J_{\delta R_1}$ 6.5	1.97	1.81	1.21	1.29		3.17 $J_{\delta' R'_1}$ 6.5 $J_{\delta'\gamma'}$ > 0.0	2.44 $J_{\beta'\gamma'}$ 1.5	1.08	1.17	1.58	2.0 ± 0.1
(I), R_1=CH_3, R_2=phenyl		3.74 $J_{\delta R_1}$ 6.5	2.22 $J_{\beta\gamma}$ 0.9	2.26	1.17	[c]		3.58 $J_{\delta' R'_1}$ 6.5	2.59 $J_{\beta'\gamma'}$ 2.0	≈1.2	1.07	[c]	[e]
(II), R_1=$COCH_3$, R_2=CH_3	4.50		2.71	3.56	1.9–2.1[d]	1.27	4.59		2.77	2.85	1.9–2.1[d]	1.9–2.1[d]	2.0 ± 0.1
(II), R_1=Phenyl, R_2=CH_3	4.19		2.13 or 2.12	2.12 or 2.13	[c]	1.54	4.07		2.61	1.23	[c]	~1.8[d]	1.9 ± 0.1

[a] All chemical shifts in ppm downfield from TMS and coupling constants in Hz, temperature 29°. Solvent $CDCl_3$. [b] The assignment as "major" and "minor" is referred respectively to stereochemistry of type (A) and (B) of Fig. 2 also in the cases where the ratio of the diastereoisomers is unity. [c] Obscured by the phenyl resonance of the ligand. [d] Overlapping with chelate CH_3 resonances. [e] Some induction of asymmetry present but within experimental errors of integrals the ratio is 1/1. [f] Solvent C_6D_6.

ethyl (maximum 8 isomers) derivatives. The PMR data are summarised in Tables 3 and 4.

The spectra of (1,2,3-h^3-1-methylallyl)-, (1,2,3-h^3-1,2,-dimethylallyl)- and (1,2,3-h^3-1-methyl-2-phenylallyl)($PhCH_2N,O$)Pd are simple, and readily interpretable as being of type (IIa) or (IIc), because of the absence of any long range *syn–syn* coupling which would be expected if the structure was that of type (IIb) or (IId). Structure (IIa), which is sterically less crowded than structure (IIc), seems more probable for these complexes. This assumption was also found to be consistent with the PMR spectra of the corresponding *N*-α-phenylethyl derivatives.

In order to ascertain whether the σ,π equilibrium was occurring at a rate comparable with the NMR time-scale, the 1,2-dimethylallyl complex was chosen as a typical example of this type of complex, and high temperature PMR experiments were performed on it. Up to 90° (in toluene-d_8) no broadening of the signals was observed, showing that, as for the 2-substituted allyl complexes, the σ,π equilibrium is slow on the NMR time-scale.

While the above mentioned complexes exist in solution as the *syn* isomers, (1,2,3-h^3-1-acetyl-2-methylallyl)- and (1,2,3-h^3-1-phenyl-2-methylallyl)($PhCH_2N,O$)-Pd at room temperature exist in solution as a mixture of *syn,anti* isomers. In the solid state the 1-acetyl-2-methylallyl complex exists as the *syn* isomer (IIa), according to the PMR spectrum run at −50° of a solution of the complex made in chloroform-*d* at the same temperature. In the room temperature equilibrium, which is reached after several hours, the *anti* isomer (IIb) is predominant (*anti/syn* equilibrium ratio ca. 2/1). This suggests that crystal packing forces are responsible for the stability of the *syn* isomer in the solid state. By contrast, (1,2,3-h^3-1-phenyl-2-methylallyl)($PhCH_2$-N,O)Pd was found to be in the *anti* form in the solid state. The room temperature spectrum of this complex, after standing for several hours in solution, was too complex to allow a firm assignment of the signals of the *syn* isomer. The number of signals present indicated that either other geometrical isomers [(IIc), (IId)] were present in solution or that partial decomposition had occurred.

The *N*-α-phenylethylketoamine derivatives of 1,2-dimethyl-, 1-phenyl-2-methyl-, 1-methyl-2-phenyl- and 1-acetyl-2-methyl-π-allylpalladium exist as only one diastereoisomer in the solid state. Figure 4 shows the PMR spectrum of (1,2,3-h^3-1,2-dimethylallyl)(α-PhC_2H_4N,O)Pd. The spectrum at −20° was run on a sample dissolved in dichloromethane-d_2 at a lower temperature. The assignment of the resonances of the two expected diastereoisomers were made by arguments analogous to those used previously for the methallyl complex. At room temperature the two diastereoisomers, which are *syn* isomers, are present in a 2/1 ratio in favour of that form present in the crystal.

It is important to notice that the C-1 and C-2 carbon atoms of the allyl moiety are not independent chiral centres. Moreover, it may be easily recognized from molecular models and application of the sequence rule of Cahn, Ingold and Prelog[17] that the two asymmetric carbon atoms have the same configuration. By considering the shielding effect of the phenyl ring attached to the nitrogen on the geminal *syn,anti* pair of the allyl moiety *cis* to nitrogen, the relative steric position of the C-2 substituent of the allyl group and of the phenyl ring can be established as being either that shown in structure (A) or that in structure (B) of Fig. 2. This means that the absolute configuration of C-2 and consequently of C-1 can be decided on if that of the asymmetric β-

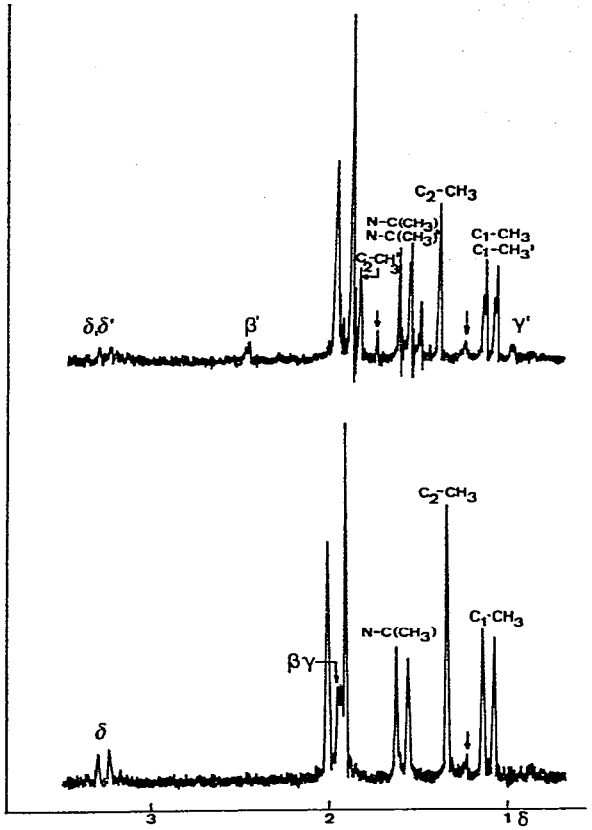


Fig. 4. 100 MHz PMR spectra of (1,2,3-h^3-1-*syn*, 2-dimethylallyl)(α-PhC_2H_4N,O)Pd in CD_2Cl_2. Lower trace, −20°; upper trace, 29°C (β,γ obscured by ligand methyls at $\delta \approx 1.95$ ppm). The peaks are labelled as in the formula of Table 4, the arrows indicating impurity resonances.

ketoamine is known. Thus for an *R* or *S* configuration of the amine, carbon atoms C-1 and C-2 of the allyl group of the major diastereoisomer [type (A) structure] have the configurations *R,R* and *S,S* respectively. Similarly, for the minor isomer [type (B) structure] configurations *S,S* and *R,R* for C-1 and C-2, respectively, correspond to the *R* or *S* configuration of the amine.

(1,2,3-h^3-1-methyl-2-phenylallyl)(α-PhC_2H_4N,O)Pd also exists as only one diastereoisomer in the solid state, having *syn* geometry at C-1 as shown by its low temperature spectrum. In the room temperature equilibrium, which is reached after a few hours, the two expected diastereoisomers are in 1/1 ratio, showing that there is no appreciable induction of asymmetry. The absolute configuration of the C-1 and C-2 carbon atoms can be established by reasoning similar to that used above for the 1,2-dimethylallyl complex, the crystalline form having type (A) geometry with carbon configurations either *R,R* or *S,S*, depending on the *R* or *S* stereochemistry of the ketoamine. The opposite of course holds true for the other (high temperature) form. The epimerization rate at 26° of the 1-methyl-2-phenylallyl complex was measured by integrating the signal areas of the two diastereoisomers over a period of several hours, the value being 3.86×10^{-5} sec^{-1}. This corresponds to a $\Delta G^{\neq}$ of 21.5 kcal/mole.

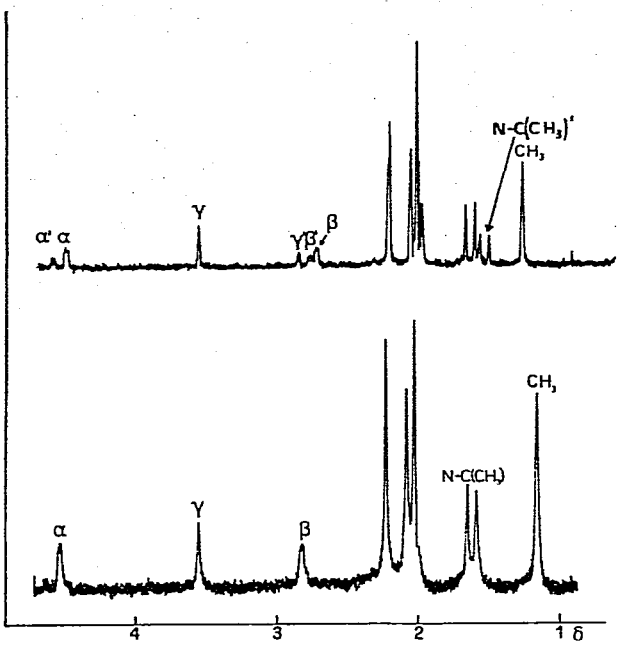


Fig. 5. 100 MHz PMR spectra of (1,2,3-h^3-1-*anti*-acetyl-2-methallyl)(α-PhC_2H_4N,O)Pd in $CDCl_3$. Lower trace, −50°; upper trace registered at 29° before onset of the *syn* isomerization. For peak labelling and assignment see Table 4.

Again, (1,2,3-h^3-1-acetyl-2-methylallyl)(α-PhC_2H_4N,O)Pd exists as only one diastereoisomer in the solid state, having an *anti* geometry on C-1. The signals of the other diastereoisomer appeared at higher temperatures, giving a probe temperature equilibrium ratio of 2/1 in favour of the form present in the crystal (Fig. 5). On standing at probe temperature, the signals of the diastereoisomers having *syn* geometry appeared. The *syn,anti* equilibrium at room temperature is reached within a few hours (*syn/anti* 1/2), without producing any change in the ratio of the *anti* diastereoisomers. The resonances of the *syn* diastereoisomers have been only partially assigned owing to the low intensities, and so the following discussion is limited to the *anti* diastereoisomers. All the resonances of the *anti* diastereoisomers have been assigned by considering, once again, the shielding effect of the phenyl ring on the geminal *syn,anti* proton pair *cis* to nitrogen, especially the relatively large difference (≈0.7 ppm) in chemical shifts between the *anti* protons γ and γ′ so produced. Following the sequence rules, C-1 and C-2 of the allyl group have opposite configurations; thus, depending on whether the configuration of the ketoamine is *R* or *S*, the configurations at C-1 and C-2 of the major isomer are *S,R* or *R,S*. For the minor diastereoisomer the opposite holds.

The behaviour of (1,2,3-h^3-1-phenyl-2-methylallyl)(α-PhC_2H_4N,O)Pd is slightly different from that of the 1-acetyl-2-methylallyl analogue. In the solid the complex exists as only one diastereoisomer, having *anti* geometry on C-1 as shown by the PMR spectrum run at −50°, which was also the temperature at which the solution was made. From the analysis of the low temperature spectrum it appears that the allyl group of the complex in the solid state has the same stereochemistry as the minor

diastereoisomer of the corresponding *anti*-1-acetyl-2-methylallyl derivative, *i.e.* the C-2 methyl group of the allyl and the phenyl ring of the ketoamine are on opposite sides with respect to the coordination plane of the metal. The other *anti* diastereoisomer (C-2 methyl group of the allyl and phenyl ring of the ketoamine on the same side with respect to the metal) appears at higher temperatures, and becomes the more abundant species at room temperature (1.9/1). On standing at room temperature the *syn* diastereoisomers appeared, and equilibrium was reached after a few hours without change in the *anti* diastereoisomer ratio. As with (1,2,3-h^3-1-acetyl-2-methylallyl)-(α-PhC_2H_4N,O)Pd, the assignment of the absolute configurations of the C-1 and C-2 carbon atoms of the *syn* diastereoisomers was not attempted because of their low abundance.

In the case of (1,2,3-h^3-1-methylallyl)(α-PhC_2H_4N,O)Pd the crystallization of the crude reaction mixture does not proceed through a second order asymmetric transformation, since at both low and probe temperature the two diastereoisomers are present. The diastereoisomers ratio was 1/1, with no induction of asymmetry.

CONCLUSIONS

(1,2,3-h^3-2-R-allyl)(β-ketoamine)Pd complexes are chiral. The plane containing the metal and the C-2 carbon atom of the allyl moiety and orthogonal to the coordination plane of the metal may be considered a chiral plane. If the β-ketoamine ligand is asymmetric, then diastereoisomeric complexes are obtained. We have found that if 4-(α-phenylethylamino)-3-penten-2-onato is coordinated to the metal, depending on the C-2 substituent of the allyl moiety, the crystallization of the two diastereoisomers may proceed through a second order asymmetric transformation. Moreover, for some complexes the equilibrium constant of the two diastereoisomers at room temperature was found to be different from unity.

The magnetic anisotropy of the phenyl ring attached to the nitrogen of the β-ketoamine causes significant differences in the chemical shifts of corresponding *syn,anti* protons of the allyl group, especially the *anti* ($\Delta\delta \approx 0.9$ ppm), and gives a criterion for establishing the orientation of the allyl group with respect to the asymmetrical centre of the chelate ligand.

The epimerization of (1,2,3-h^3-2-R-allyl)(α-PhC_2H_4N,O)Pd may occur through two different mechanisms: by dissociation of the β-ketoamine ligand, to give an exchange of the coordination sites of N and O of the ligand itself, or by a σ,π equilibrium of the allyl ligand, which allows coordination of the other face of the allyl group to the metal. Spin saturation experiments have shown that ligand exchange occurs at a faster rate than the σ,π equilibrium, and thus represents the most likely epimerization pathway for these complexes. It can be assumed that the exchange occurs through a mechanism substantially similar to that proposed by Powell *et al.*[14] for the analogous picolinato complexes.

Induction of asymmetry in solution has also been observed for some (1,2,3-h^3-1R-2R′-allyl)(α-PhC_2H_4N,O)Pd complexes. The absolute configuration of the asymmetrical carbon atoms C-1 and C-2 of the coordinated allyl group has been related to that of the ketoamine ligand.

The epimerization pathway for (1,2,3-h^3-1R-2R′-allyl)(α-PhC_2H_4N,O)Pd can be readily interpreted as occurring *via* a σ,π equilibrium on C-3, *i.e.* the least sub-

stituted carbon atom, which allows coordination of the other face of the allyl group to the metal. This equilibrium is slow as shown by the results of high temperature experiments carried out on (1,2,3-h^3-1,2-dimethylallyl)($PhCH_2N$,O)Pd and also by the epimerization rate at room temperature found for (1,2,3-h^3-1-methyl-2-phenyl-allyl)(α-PhC_2H_4N,O)Pd. A σ,π equilibrium on C-1 (*i.e.* the most substituted carbon atom) which brings about *syn,anti* isomerization has been observed for some of these complexes, but it appears to occur at an even slower rate than that on C-3. This phenomenon is quite general for π-allyl complexes of palladium and has been studied by several authors[4,19-21].

It appears, from the data reported in Tables 2 and 4, that for both (1,2,3-h^3-2R-allyl)(α-PhC_2H_4N,O)Pd and (1,2,3-h^3-1R-2R'-allyl)(α-PhC_2H_4N,O)Pd the presence of a substituent on C-2 is an important factor in determining whether there is preferential coordination of one face of the allyl group to the metal. It is noteworthy that a 2/1 induction of asymmetry has been observed for all the complexes in which a methyl group is on the C-2 carbon atom; this ratio corresponds to a difference in free energies between the two diastereoisomers of ≈ 0.4 kcal/mole. However, from an inspection of molecular models it does not appear clear why the more abundant diastereoisomer has the C-2 substituent and the phenyl ring of the β-ketoamine on the same side with respect to the coordination plane of the metal, since it is clear that the C-2 allyl substituent does not interfere sterically with the $-NCH(CH_3)Ph$ group of the ketoamine. Thus, although even further data are necessary in order to draw definitive conclusions, the possibility cannot be excluded that the effect produced by changing the C-2 substituent is mainly an electronic one, producing a subtle change in the hybridization of the allyl moiety. This change in hybridization may in turn affect the steric interaction between the substituents on the nitrogen and the neighbouring allyl *syn,anti* protons, thus affecting the ratio of the two diastereoisomers.

The results allow us to conclude that in π-allylic Pd complexes of 4-(α-phenylethylamino)-3-penten-2-one the β-ketoamine in some cases causes preferential coordination of one face of the allyl group to the metal. Moreover, the stereochemistry of the coordinated allyl group may be inferred from the PMR spectra by attributing the differences in chemical shifts of corresponding protons of diastereoisomers to anisotropic shielding by the phenyl ring. Further studies are in progress to establish the stereo-electronic factors which control the induction of asymmetry.

EXPERIMENTAL

The PMR spectra were mainly recorded with a Varian HA-100 spectrometer. The Nuclear Overhauser and spin saturation experiments were carried out with a Brucker HFX-90 spectrometer on carefully deoxygenated samples. In these studies the CH- and NCH- or NCH_2-resonances of the β-ketoamine chelate were used as internal standards for the integrated intensity measurements.

Melting points are uncorrected. Elemental analyses were performed by A. Bernhardt Mikroanalytisches Laboratorium, Elbach, W. Germany.

(π-allylPdCl)$_2$, (π-methallylPdCl)$_2$, (π-crotylPdCl)$_2$ were prepared according to Dent, Long and Wilkinson[22]. (1-acetyl-2-methyl-π-allylPdCl)$_2$ was prepared according to Parshall and Wilkinson[23]. All the other π-allylic palladium chloride complexes were prepared by the method of Volger[21].

All the β-ketoamine complexes which are listed in Table 5 were prepared following essentially the method described by Everett and Holm[6]. Thus, the appropriate ketoamine was added in a stoichiometric amount to an anhydrous solution of potassium tert-butoxide in tert-butanol. The mixture was warmed, and then added dropwise, at room temperature, to the π-allyl palladium chloride complex (molar ratio 1/1) dissolved in toluene. After stirring for 30–60 min the solvent was evaporated off *in vacuo*. The residue was extracted with warm heptane. The β-ketoamine complex

TABLE 5

ANALYTICAL DATA[a]

Compound	*Found (calcd.) (%)*				
	C	*H*	*N*	*Pd*	*M.p.* (°C)
(1,2,3-h^3-allyl)($PhCH_2N,O$)Pd	52.25 (53.66)	5.59 (5.70)	4.00 (4.17)	31.34 (31.69)	83
(1,2,3-h^3-2-methallyl)($PhCH_2N,O$)Pd	55.01 (54.94)	6.24 (6.05)	4.14 (4.00)	30.19 (30.42)	85
(1,2,3-h^3-2-tert-butyllyl)($PhCH_2N,O$)Pd	58.41 (58.24)	7.08 (6.94)	3.74 (3.57)	27.07 (27.15)	103
(1,2,3-h^3-2-phenylallyl)($PhCH_2N,O$)Pd	61.13 (61.24)	5.50 (5.63)	3.53 (3.40)	25.64 (25.84)	126 (dec)
(1,2,3-h^3-1-methallyl)($PhCH_2N,O$)Pd	55.09 (54.94)	6.16 (6.05)	4.13 (4.00)	30.12 (30.42)	113 (dec)
(1,2,3-h^3-1,2-dimethylallyl)($PhCH_2N,O$)Pd	55.94 (56.13)	6.28 (6.37)	3.70 (3.85)	29.05 (29.25)	58
(1,2,3-h^3-1-acetyl-2-methallyl)($PhCH_2N,O$)Pd	55.33 (55.18)	5.75 (5.92)	3.67 (3.57)	27.03 (27.16)	92
(1,2,3-h^3-1-methyl-2-phenylallyl)($PhCH_2N,O$)Pd	62.25 (62.05)	6.03 (5.92)	3.33 (3.29)	24.94 (24.98)	128
(1,2,3-h^3-1-phenyl-2-methylallyl)($PhCH_2N,O$)	62.12 (62.05)	5.87 (5.92)	3.44 (3.29)	24.75 (24.98)	99
(1,2,3-h^3-allyl)(α-PhC_2H_4N,O)Pd	54.76 (54.94)	6.04 (6.05)	4.09 (4.00)	30.19 (30.42)	77 (dec)
(1,2,3-h^3-2-methallyl)(α-PhC_2H_4N,O)Pd	56.29 (56.13)	6.50 (6.37)	3.90 (3.85)	28.98 (29.25)	89 (dec)
(1,2,3-h^3-2-tert-butylallyl)(α-PhC_2H_4N,O)Pd	59.36 (59.19)	7.32 (7.20)	3.61 (3.45)	25.93 (26.22)	68
(1,2,3-h^3-2-phenylallyl)(α-PhC_2H_4N,O)Pd	61.88 (62.05)	6.10 (5.92)	3.30 (3.29)	24.88 (24.98)	107
(1,2,3-h^3-1-methallyl)(α-PhC_2H_4N,O)Pd	56.03 (56.13)	6.48 (6.37)	3.98 (3.85)	28.86 (29.25)	100 (dec)
(1,2,3-h^3-1,2-dimethylallyl)(α-PhC_2H_4N,O)Pd	57.08 (57.22)	6.71 (6.67)	3.87 (3.70)	28.03 (28.16)	82
(1,2,3-h^3-1-acetyl-2-methallyl)(α-PhC_2H_4N,O)Pd	56.36 (56.23)	6.28 (6.21)	3.55 (3.45)	25.95 (26.22)	110 (dec)
(1,2,3-h^3-1-methyl-2-phenylallyl)(α-PhC_2H_4N,O)Pd	62.98 (62.80)	6.23 (6.19)	3.07 (3.18)	23.94 (24.19)	95
(1,2,3-h^3-1-phenyl-2-methylallyl)(α-PhC_2H_4N,O)Pd	62.65 (62.80)	6.02 (6.19)	3.27 (3.18)	24.05 (24.19)	102 (dec)

[a] All the complexes are yellow or pale yellow.

crystallized upon cooling. The β-ketoamine complexes were shown to be monomeric by osmometric molecular weight measurements. The complexes are rather stable in hydrocarbon solvents, and less so in chlorinated solvents. They are stable indefinitely in the solid state if kept below 0° under nitrogen.

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