of electron density rather than distinct peaks at these two positions, indicating the presence of rather loosely held atoms.

Over Ion Exchange. An aqueous cadmium halide solution contains Cd^{2+}, CdX^+, CdX_2, CdX_3^-, CdX_4^{2-}, and X^- in equilibrium.[27] Since a $CdCl_2$ solution is somewhat acidic, other species including $CdOH^+$, $Cd(OH)_2$, and CdClOH would also be expected to enter into this equilibrium. Consequently, the exchange solution used in this investigation contained both monopositive and dipositive ions. The resulting structure with 9.5 Cd^{2+} ions per unit cell may indicate a partial preference of the zeolite framework for monopositive ions, which can more evenly balance the local anionic charge of the zeolite framework. It is also apparent that Cd^{2+} prefers to complete its coordination sphere within the zeolite with anionic ligands (OH^- or Cl^- in this case) instead of H_2O.

Unpublished results[19] on the structures of zeolite A exchanged with 0.05 M cadmium acetate half-saturated with $Cd(OH)_2$ (pH ca. 7) indicate the exchange end point to be at $Cd_{7.5}(OH)_3$-A, a 25% overexchange. Like the results reported herein, 3 equiv of hydroxide has exchanged into the zeolite per unit cell from relatively neutral solution, and is located within the sodalite unit.[19]

Over ion exchange into zeolite A appears to be unusual. It has been noted before only with TlOH, and there to a lesser extent (only 8%) than with $CdCl_2$. Over ion exchange was not observed with KCl,[9] KOH,[9] RbOH,[2] CsOH,[8,28] $CsNO_3$,[17] $AgNO_3$,[29] $Co(NO_3)_2$,[30] $Mn(NO_3)_2$,[31] $Zn(NO_3)_2$,[32] $Ca(OH)_2$,[6] $Sr(OH)_2$,[6] $Ba(OH)_2$,[33] or $Eu(OH)_2$.[5]

Acknowledgments. This work was supported by the National Science Foundation (Grant CHE-76 81585). We are indebted to the University of Hawaii Computing Center.

Supplementary Material Available: Listings of the observed and calculated structure factors for both structures (Supplementary Tables 1 and 2) (4 pages). Ordering information is given on any current masthead page.

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Ring Opening of the *endo*-Alkoxytetraphenylcyclobutyl Ligand Coordinated to Palladium(II)

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Abstract: The reaction of η^3-*endo*-alkoxytetraphenylcyclobutenylpalladium chloride dimer with a variety of reagents leads to the formation of ring opened *cis*-1,*trans*-3-tetraphenyl-4-alkoxybutadien-1-yl complexes. Replacement of the chloride with either acac or hfac gave complexes which exist in solution as an equilibrium mixture of η^3-*endo*-alkoxytetraphenylcyclobutenyl $\rightleftharpoons$ η^3-butadienyl species (K_{eq} = 0.6–1.0 in $CDCl_3$). Reactions of these complexes with Me_2PhP gave η^1-butadienyl derivatives of the type $[(\eta^1\text{-dienyl-}C_4Ph_4OR)PdX(Me_2PhP)]_n$ [X = acac, hfac, n = 1; X = Cl, n = 2 (solid), n = 1 (solution)]. The η^3- and η^1-dienyl acac and hfac complexes exhibited temperature-dependent NMR spectra, which has been ascribed to a partial dissociation of a bidentate β-diketonate ligand to give a short-lived *three*-coordinate intermediate.

Introduction

The cyclooligomerization reactions of acetylenes, catalyzed by palladium(II) chloride, are well known and recent investigations have shown these reactions to proceed via structurally unusual complex intermediates.[1-3] One of the first organopalladium compounds, derived from a reaction with an acetylene, to be structurally characterized is the complex *endo*-ethoxytetraphenylcyclobutenylpalladium(II) chloride dimer (**1**).[4-9] The formation of **1** must occur via a stereospecific reaction pathway since treatment of **1** with HCl to give $[(\eta^4\text{-}C_4Ph_4)PdCl_2]_2$ followed by reaction with NaOEt gives the exo

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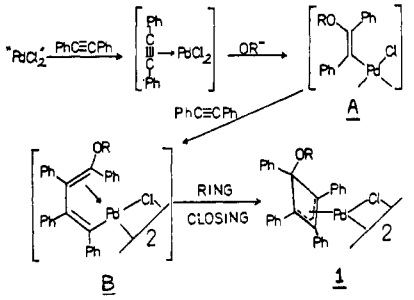
Table I. Analytical and Spectroscopic Data of the Series of Cyclobutenyl and Dienyl Complexes **3–6** and **9–12**

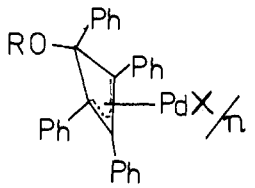
	Endo, exo, or dienyl	Ar	R	X	Physical appearance	Mp, °C	Anal., % Calcd C	Calcd H	Found C	Found H	Mol wt Calcd	Mol wt Found
												Complexes
3a	Exo	Ph	Me	acac	Yellow oil							
3b	Exo	Ph	Me	hfac	Yellow needles	89–95[d] 133–136	58.16	3.56	58.53	3.41	702	692
4a	Endo	Ph	Me	acac	Yellow prisms[a]	178–180	66.97[a]	5.00[a]	67.27	4.83	593	596
5a	Dienyl	Ph	Me	acac								
4b	Endo	Ph	Me	hfac	Yellow glass[b]	~74	59.73[b]	4.20[b]	59.80	3.95	701	697
5b	Dienyl	Ph	Me	hfac								
4c	Endo	Ph	Et	acac	Yellow prisms[c]	169–173	66.80[c]	5.18[c]	66.78	5.27	607	640
5c	Dienyl	Ph	Et	acac								
4d	Endo	Ph	Et	hfac	Yellow glass	~80	58.79	3.66	58.93	3.89	715	714
5d	Dienyl	Ph	Et	hfac								
4e	Endo	*p*-FC_6H_4	Me	hfac	Yellow prisms	141–143	52.81	2.58	53.35	2.81	772	725
5e	Dienyl	*p*-FC_6H_4	Me	hfac								
												Complexes
6a	Dienyl	Ph	Me	acac	Yellow needles	109–111	69.00	5.65	69.19	5.75	731	716
6b	Dienyl	Ph	Me	hfac	Yellow powder	76–80	60.12	4.20	60.34	4.25		
6c	Dienyl	Ph	Et	acac	Yellow prisms	143–145	69.31	5.82	69.52	6.03		
6d	Dienyl	Ph	Et	hfac	Yellow glass	70–75	60.54	4.37	60.63	4.31		
10	Dienyl	Ph	Me	Cl	Yellow needles	162–167	66.5	5.13	66.72	5.33	1334	820[m]
11 or 12					Solution						667	672
9	Exo	Ph	Me	Cl	Solution							

[a–c] Complexes contain solvent of crystallization (identified by ^1H NMR): *a*, $\frac{1}{4}CH_2Cl_2$; *b*, $\frac{1}{2}$ hexane; *c*, $\frac{1}{3}CH_2Cl_2$. [d] Forms cubic crystals that melt at 133–136 °C. [e] Masses of Pd containing fragments based on ^{106}Pd. [f] Chemical shift data relative to Me_4Si and $CFCl_3$. Aromatic proton resonances, not included, observed in region 6.6–8.2: (q) = quartet; (t) = triplet; (d) = doublet; (b) = broad. [g] Fast exchange limit. [h] The ^{19}F resonance pattern for each of the *p*-FC_6H_4's is a triplet of triplets due to coupling with the aromatic protons; J_{H-F} = 5.5 and 8.8

Scheme I. Mechanism Proposed for the Stereospecific Formation of η^3-*endo*-Alkoxytetraphenylcyclobutenylpalladium Chloride Dimer[1-3]



isomer **2**.[4-9] To account for the formation of **1** the mechanism given in Scheme I has been proposed.[1-3] A trans attack by ROH on a coordinated acetylene has been postulated as the initial step of this reaction since "insertion" of a second diphenylacetylene into the vinyl palladium bond of A leads to the tetraphenylbutadienyl intermediate B. The stereochemistry of B will lead to the observed endo product **1** if the ring-closing step proceeds in a Woodward–Hoffmann allowed conrotatory manner. We here present evidence that under suitable conditions the ring-closing step (Scheme I) is reversible. An x-ray structural study of one of the butadienyl derivatives prepared in this study confirmed the previous postulate that the initial attack by alcohol on the coordinated acetylene (Scheme I) occurs stereospecifically in the trans position. A preliminary account of this work has appeared[10] and recently Maitlis and co-workers have described a similar ring-opening reaction of *endo*-[(C_4tolyl$_4$Ph)PdX] (X = acac, S_2CNR_2).[11]



2, X = Cl, n = 2

3a, X = acac, R = Me, n = 1

3b, X = hfac, R = Me, n = 1

Results and Discussion

(1) Preparation and Characterization of (*endo*- or *exo*-C_4Ph_4ORPdX) where X = acac or hfac. These complexes were prepared by the reaction of the appropriate endo or exo bridging chloride dimer with thallous acetylacetonate or hexafluoroacetylacetonate according to the equation

$$[(exo\text{- or } endo\text{-}C_4Ph_4OR)PdCl]_2 + 2TlX \rightarrow 2TlCl\downarrow + [(exo\text{- or } endo\text{-}C_4Ph_4OR)PdX] \quad (X = acac, hfac) \quad (1)$$

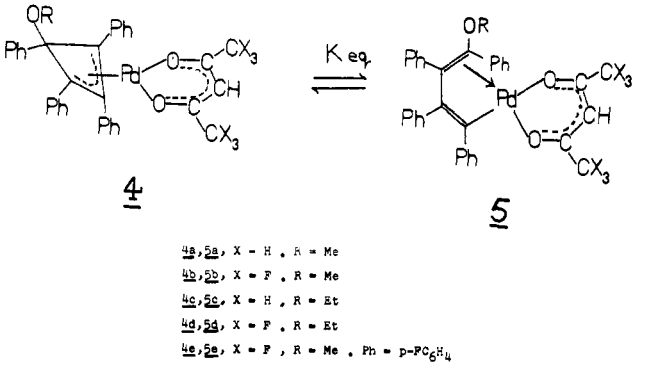
The products were characterized by analysis, osmometry, and mass spectroscopy. The solid state infrared spectra are consistent with the chelation of the acac or hfac to palladium via its oxygens (see Table I).

(2) NMR Variable Temperature Studies. The NMR data for all the complexes are collected in Table I. The temperature-invariant ^1H NMR spectra of the exo complexes [(*exo*-C_4Ph_4OMe)PdX] where X = acac (**3a**) or hfac (**3b**) in $CDCl_3$ consist of single sharp resonances for the methoxy and acac protons as expected. (The ^{19}F NMR spectrum consists of a singlet for the hfac CF_3 groups.) In contrast the NMR spectra of the endo isomers [(*endo*-C_4Ph_4OR)PdX] (X = acac or

Mass spectral data[e] Major organic fragment (*m/e*)	IR data, β-diketonate ligand[24] $\nu_{C=O}$, cm^{-1}	$\nu_{C=C}$, cm^{-1}	^1H and ^{19}F NMR chemical shift data, ppm[f] OMe or OEt	CH	acac or hfac CH_3	CF_3	*p*-F of FC_6H_4, or Me of Me_2PhP
$[(\eta^3\text{-}C_4Ar_4OR)PdX]$							
			3.52	5.13	1.81		
	1632	1550	3.55	5.88		70.22	
	1582	1510	3.90 3.56	5.26 5.29	1.87 1.82[g]		
$C_4Ph_4OCH_2^+$ (386)	1630	1550	3.77 3.53	5.95 5.95		70.04 69.84[g]	
	1588	1512	3.9,[k] 1.42 (t) 3.9,[k] 1.31 (t)	5.24 5.33	1.91 1.84[g]		
P^+ (714), $C_4Ph_4OC_2H_4^+$ (400)	1635	1548	4.07 (q), 1.37 (t) 3.83,[k] 1.27 (t)	5.98 5.98		69.88 69.64[g]	
P^+ (772)			3.81 3.58	5.98 5.98		69.87 69.69[g]	99.6, 102.6, 105.1[h,i] 101.9, 102.7, 104.8, 104.9[h,j]
$[(\eta^1\text{-}C_4Ph_4OR)PdX(Me_2PhP)]_n$							
	1585	1520	3.28	5.39	1.98 1.89		1.00 (d) J_{PH} = 11.0 0.96 (d) J = 11.3
P^+ (838), $C_4Ph_4OCH_2^+$ (386)	1632	1550	3.16	6.07		69.19[g]	1.11 (d)[g] J_{PH} = 11.0
			3.47,[l] 1.07 (t)	5.34	1.99 1.90		0.99 (d) J_{PH} = 10.8 0.97 (d) J_{PH} = 11.3
			3.29 (q), 0.98 (t)	6.08		69.32[g]	8.87 (d)[g] J_{PH} = 11.0
			3.34				1.12 (d,b) J_{PH} = 11
			3.80				1.35 (d)[g] J_{PH} = 9
			3.44				1.22 (d) J_{PH} = 9 0.97 (d)

Hz. [i] The three resonances are in a 1:2:1 ratio. [j] The four resonances are in a 1:1:1:1 ratio. [k] Resonance obscured by overlap. [l] This is the center of the AB portion of an ABX_3 pattern in which both J_{AX} and J_{BX} = 7.1 Hz as shown in Figure 2. [m] Observed molecular weight ca. 10 min after dissolution of **10**. Molecular weight is essentially that of monomer after 30 min. Extrapolation of kinetic plots suggests that **10** is a dimer.

hfac) show the presence of two species in solution. Since osmometry is consistent with only monomer being present, the observed equilibrium is apparently between two structural isomers of $[(C_4Ph_4OR)PdX]$. The ^1H NMR spectrum of [(*endo*-C_4Ph_4OMe)Pdacac] is illustrated in Figure 1. One of the isomers present is symmetric with respect to its acetylacetonate methyl groups as expected for the η^3-allylic structure **4a**. The other isomer has a molecular asymmetry which differentiates the acac Me groups as is evident at −30 °C (Figure 1). On warming, a concentration-independent exchange process is initiated which collapses the methyl resonances of the asymmetric isomer to a single broad peak at 37 °C (Figure 1) with further sharpening above 37 °C. This asymmetric isomer has the spectrum expected of the ring-opened η^3-dienyl **5a** which has been illustrated with the trans terminal vinyl stereochemistry based on subsequent x-ray studies, although this is uncertain on the basis of the NMR data. Recently Maitlis et al.[11b] have structurally characterized an η^3-dienyl palladium complex by x-ray crystallography.



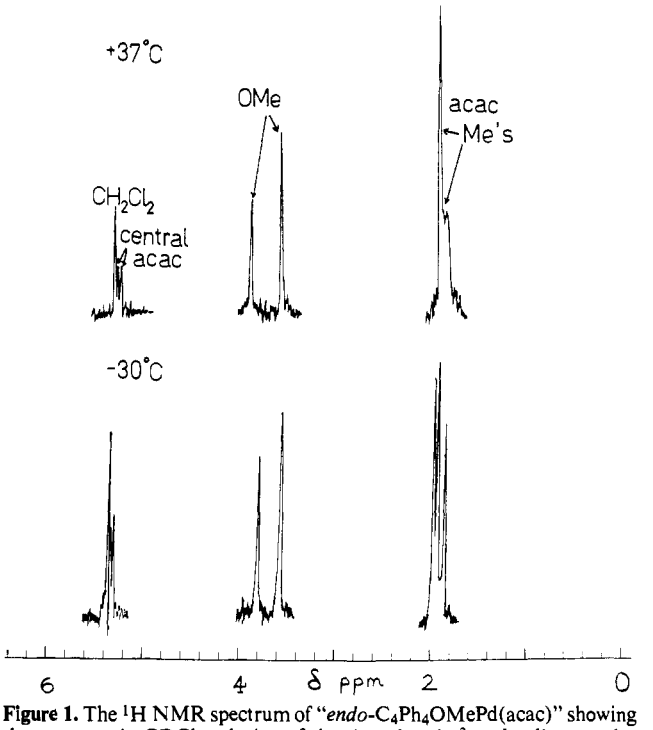


Figure 1. The ^1H NMR spectrum of "*endo*-$C_4Ph_4OMePd(acac)$" showing the presence in $CDCl_3$ solution of the ring-closed η^3-*endo*-alkoxycyclobutenyl complex **4a** and the ring opened η^3-butadienyl complex **5a**.

In the complex [{*endo*-$C_4(p\text{-}C_6H_4F)_4OMe$}Pdhfac], the ^{19}F resonances of the *p*-fluorophenyl substituents should give rise to three resonances in a 1:2:1 ratio for the η^3-allylic structure **4e** and four resonances in a 1:1:1:1 ratio for the ring-opened

Table II. The Exchange Parameters for Acetylacetonate Substituent Site Exchange (CH_3 or CF_3) in the Complexes [(dienyl-C_4Ph_4OR)PdX] where X = acac or hfac as Shown in Scheme II[a]

Complex	Solvent	T_c, K	$\Delta\nu$, Hz	$\Delta G^{\ddagger}_{T_c}$, kJ mol^{-1}
5b	*n*-Pentane	290	49	60
	n-Heptane	291	51	60
	$CDCl_3$	271	35	56
	Acetone	209	37	43
	Methanol	186	>35	<38
5d	$CDCl_3$	284	42	59
5a	$CDCl_3$	306	7.0	68
5c	$CDCl_3$	317	5.9	71

[a] Spectra recorded at 60 MHz. The free energies of activation at the coalescence temperature, $\Delta G_{T_c}^{\ddagger}$, have been calculated by the usual methods.

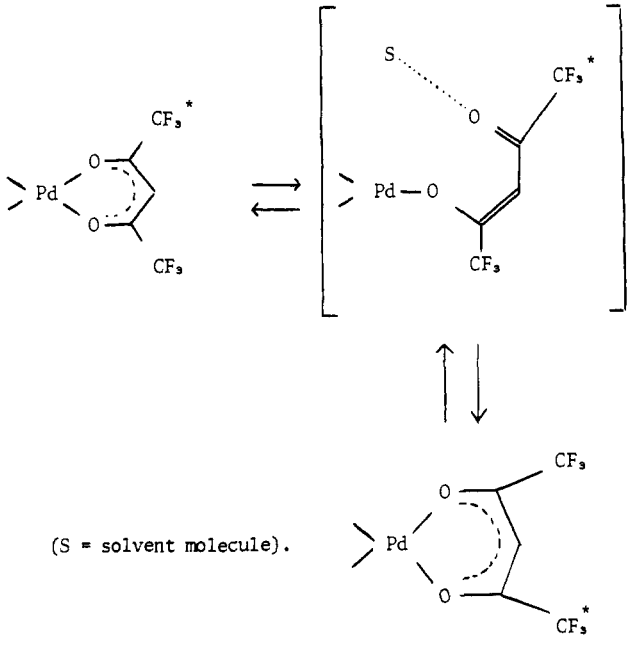
Table III. The Ratio of Ring Opened (Dienyl) to Ring Closed (Cyclobutenyl) for the Equilibrium **4b** ⇌ **5b** as Determined by ^1H and ^{19}F NMR[a]

Solvent	% ring opened isomer	Solvent	% ring opened isomer
n-Pentane	29	THF	49
Cyclohexane	37	Dichloromethane	51
Benzene	39	Acetone	59
Chloroform	40	Methanol[b]	100
		Ethanol[b]	
Diethyl ether	43	Acetonitrile	
		Pyridine	
$C_6H_5NO_2$	49	Dimethyl sulfoxide	

[a] All solutions 0.27 M (except as indicated). Data recorded at 37 °C. [b] Saturated solution.

η^3-dienyl isomer **5e**. This has been observed, as required, in the ^{19}F NMR spectrum (see Table I). In addition, the ratio of **4e** to **5e** on the basis of integration of these ^{19}F resonances and on the basis of the methoxy protons is identical (0.62 and 0.64, respectively).[12] At 34 °C, the hfac CF_3 groups in [{dienyl-$C_4(p\text{-}FC_6H_4)_4OMe$}Pdhfac] (**5e**) are already in fast exchange such that only one sharp ^{19}F resonance is observed for this isomer. Variable temperature ^{19}F NMR studies have shown the CF_3 site exchange process to be independent of concentration, unaffected by added hexafluoroacetylacetone, and solvent sensitive, the rate of exchange increasing in the order dry *n*-pentane ~ dry *n*-heptane < $CDCl_3$ < acetone < methanol (see Table II). These observations indicate that the exchange mechanism is an intramolecular process and the fact that site exchange is observed to occur in dry *n*-pentane indicates that a mechanism *not* involving ligand solvolysis is involved. We have observed similar CF_3 (or CH_3) site exchange reactions in other dienyl and allyl hfac (or acac) complexes of palladium(II) and platinum(II) and mechanistic possibilities for the exchange process have been reduced to a square planar ⇌ tetrahedral rearrangement or a partial dissociation of the hfac (or acac) to give a short-lived three-coordinate intermediate.[13] A dissociative mechanism is currently thought to be the more probable, viz., Scheme II. The effect of solvent may be associated with solvation of a unidentate hfac intermediate. However, the rate of CF_3 site exchange in acetone or MeOH may be enhanced by an additional associative solvolysis pathway. The observation of similar acac methyl group site exchange in the ^1H NMR of asymmetric square planar complexes is rare. In three reported instances, [(Ph_3P)EtNiacac],[14] [$(\eta^3$-1-phenylallyl)Pdacac],[15] and [{$Ph(C_2Me_2)_3$}Pdacac],[16] no mechanisms were suggested.

Scheme II



(S = solvent molecule).

(3) The Ring Opened ⇌ Ring Closed Equilibrium. Coalescence of the resonances of **4** and **5** due to rapid interconversion of these isomers on the NMR time scale was *not observed* for any of the systems studied up to temperatures of 90 °C. Likewise NMR spin saturation (Forsen-Hoffman) experiments failed to give any indication of **4** ⇄ **5** exchange. This would place a *minimum* of ca. 80 kJ mol^{-1} for the free energy of activation for the ring opening of the *endo*-alkoxycyclobutenyl ligand in **4**. The ratio of the symmetric η^3-allylic isomer **4b** to the ring-opened isomer **5b** is tabulated in Table III, for various solvents. Increasing solvent polarity favors the ring-opened η^3-dienyl structure. In polar solvents with good coordinating properties such as MeOH, Me_2SO, or pyridine only one isomer is observed and it is probable that a η^1-dienyl species [(η^1-C_4Ph_4OR)Pd(hfac)(solvent)], containing a coordinated solvent molecule, is the major solution species. The ratio of ring opened to ring closed in $CDCl_3$ solutions is only slightly affected by changes in concentration and temperature with the amount of ring-opened dienyl product being slightly greater for the hfac relative to the acac complexes. This latter observation is in sharp contrast to Maitlis et al.'s[11a] observation that while *endo*-[(C_4tolyl$_4$Ph)Pd(acac)] reacts with a variety of donor ligands to give ring-opened η^1-dienyl derivatives, no analogous ring opening reactions were observed for the complex *endo*-[(C_4tolyl$_4$Ph)Pd(hfac)].

(4) Dimethylphenylphosphine Derivatives [(η^1-dienyl-C_4Ph_4OR)PdX(Me_2PhP)]. (a) X = acac or hfac. The complexes **6a–d** were isolated as yellow, crystalline solids from the stoichiometric addition of Me_2PhP to the complexes [(*endo*-C_4Ph_4OR)PdX] (where X is acac or hfac) in chloroform. The solid state infrared data for the acac or hfac are consistent with chelation via oxygen coordination for these ligands. Osmometry has established that the chloroform solution species are monomers of the molecular weight expected for the formulation [(C_4Ph_4OR)PdX(Me_2PhP)]. The NMR spectroscopic and analytical data for these complexes are compiled in Table I. The ^1H NMR spectrum of a specific example, [(C_4Ph_4OEt)Pdacac(Me_2PhP)] (**6c**), in $CDCl_3$ is shown in Figure 2. The nonequivalence of the Me_2PhP methyl groups in **6c** means that the complex does not have a plane of molecular symmetry which relates the Me_2PhP methyl groups. Further, the acac methyl substituents are also nonequivalent.

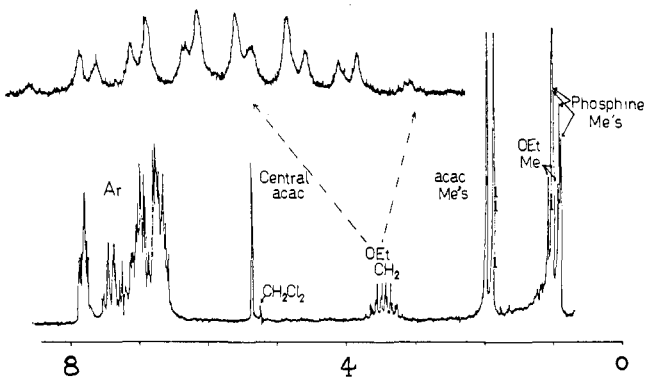


Figure 2. The ^1H NMR spectrum of [(η^1-dienyl-C_4Ph_4OEt)-Pdacac-(Me_2PhP)] (**6c**) in $CDCl_3$ at 34 °C, 100 MHz. The inset is the expanded coupling pattern of the nonequivalent methylene protons of the OEt group.

The unusual coupling pattern observed for the ethoxy methylene protons, as seen in the expanded scale inset in Figure 2, is an ABX_3 coupling pattern which arises from the nonequivalence of the ethoxy methylene protons. The symmetric nature of the methylene proton coupling pattern and the sharp triplet observed for the ethoxy methyl protons require that $J_{AX} = J_{BX}$ for this complex. All of the above features may be accommodated by a η^1-dienyl structure such as **6c**. This structure and the trans orientation of the ethoxy substituent relative to the single C-C bond of the butadienyl moiety are confirmed by an x-ray structural study of **6c** (see Figure 3).[10,17] Owing to large steric interactions between the neighboring phenyl groups and between the dienyl and cis ligands, rotations about the C-Pd and the central C-C bond of the C_4Ph_4OEt ligand are severely restricted. As a consequence of this the methylene protons of the ethoxy group and the methyl groups of the Me_2PhP ligand in **6c** are diastereotopic.

The dimethylphenylphosphine hfac derivatives **6b** and **6d** have low-temperature NMR spectra which correspond to the analogous acac complexes. However, on warming, a *concentration-independent* exchange process is initiated which simultaneously exchanges the hfac CF_3 sites and the Me_2PhP methyl sites, and in the case of the ethoxy complex **6d** collapses the low-temperature broad ABX_3 coupling pattern for the ethoxy methylene protons to a sharp quartet at room temperature (i.e., the nonequivalent methylene protons are also site exchanged by the same process). The parameters for the process based on the observation of the exchange in both the hfac and Me_2PhP resonances are compiled in Table IV. The exchange process does not involve intermolecular exchange of the Me_2PhP ligand since the addition of excess Me_2PhP has no effect on the exchange rate. Indeed coordinated $\rightleftharpoons$ free Me_2PhP exchange is slow on the NMR time scale at room temperature and this can be ascribed to the steric bulk of the C_4Ph_4OR ligand which inhibits associative ligand exchange. On the basis of these observations and the data in Table IV it seems probable that the same process is responsible for both CF_3 and phosphine-methyl site exchange. A possible mechanism for such an exchange process is schematically drawn in Scheme III. However a dissociative mechanism involving a three-coordinate intermediate for which rotation about the Pd-dienyl bond is not restricted cannot be excluded. The free energy of activation for the hfac CF_3 site exchange processes in **6b** and **6d** are slightly lower than found for the corresponding [(dienyl-C_4Ph_4OR)Pdhfac] complexes **5b** and **5d** (see Table II). This lower free energy of activation is anticipated in Scheme III since the intermediates **7** and **8** are stabilized by the chelation of the dienyl-C_4Ph_4OR ligand. The physical and spectral properties of the dimethylphenylphosphine derivatives

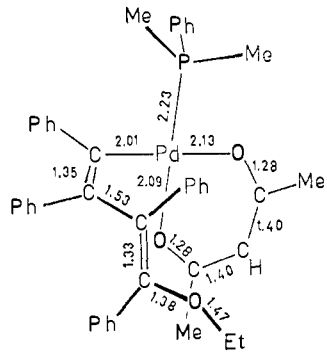
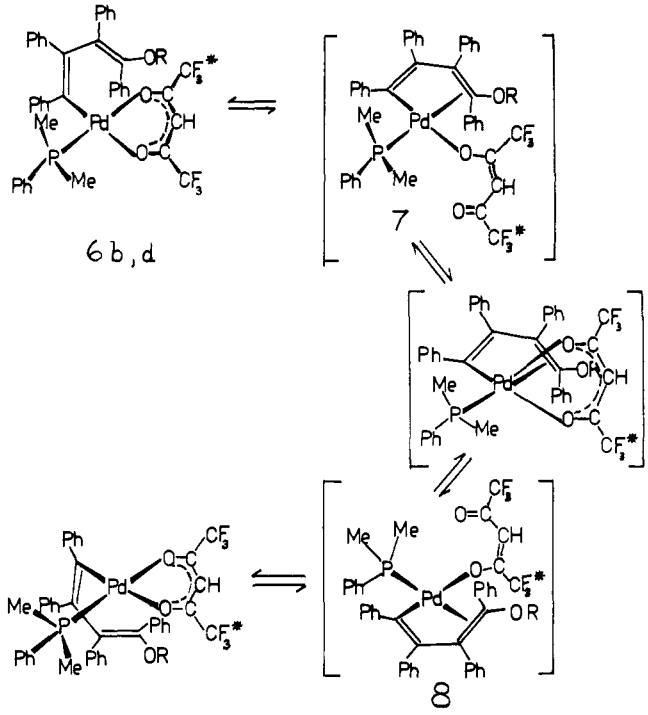


Figure 3. The molecular structure of **6c** as determined by x-ray crystallography.[10,19] Bond lengths in Å.

Table IV. The Site Exchange Parameters for hfac CF_3 and Me_2PhP Methyl Groups in [(Dienyl-C_4Ph_4OR)Pdhfac(Me_2PhP)] in $CDCl_3$, 60 MHz

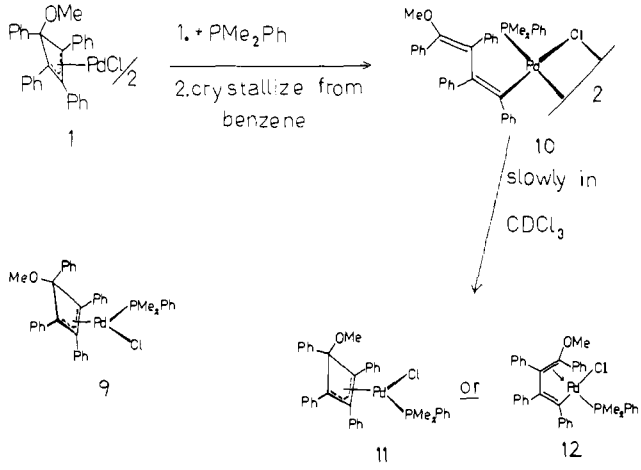
		^{19}F hfac			^1H Me_2PhP		
	R	$\Delta\nu$, Hz	T_c, K	$\Delta G^{\ddagger}_{T_c}$, kJ mol^{-1}	$\Delta\nu$, Hz	T_c, K	$\Delta G^{\ddagger}_{T_c}$, kJ mol^{-1}
6b	Me	114.2	267.0	53	12.0	241.6	52
6d	Et	111.0	260.5	51	12.0	237.2	51

Scheme III. Mechanism of CF_3 Site Exchange in the Complexes **6b** and 6d



[(C_4Ph_4OR)PdX(Me_2PhP)] are compatible with the ring-opened dienyl structures **6a–d** being the sole solution species.

(b) The Chloride Complexes, [(C_4Ph_4OMe)PdCl(Me_2PhP)]$_\eta$. The exo complex, [(*exo*-η^3-C_4Ph_4OMe)PdCl(Me_2PhP)], was prepared in an NMR tube by the stoichiometric addition of Me_2PhP to [(*exo*-η^3-C_4Ph_4OMe)PdCl]$_2$ in $CDCl_3$ under nitrogen. The ^1H NMR spectrum of this phosphine derivative was that expected for the η^3-allylic complex **9** (see Table I). The two Me_2PhP methyl doublet resonances ($J_{^{31}P-H}$ = 9.0 Hz) which arise from the nonequivalent Me_2PhP methyl groups in **9** are temperature invariant up to 62 °C in $CDCl_3$ and 80 °C in bromoform (at which temperature decomposition oc-



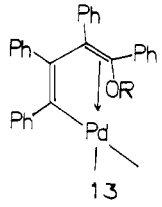
curs). Attempts to isolate the pure complex [(*exo*-η^3-C_4Ph_4OMe)PdCl(Me_2PhP)] (**9**) by recrystallization in benzene/hexanes in the open air failed owing to the oxidation of the Me_2PhP ligand to give Me_2PhPO and regenerate the chloride dimer **2**. Disproportionation of [(*exo*-η^3-C_4Ph_4OMe)PdCl(Me_2PhP)] in $CDCl_3$ solution to *cis,trans*-$(Me_2PhP)_2PdCl_2$ (50% total Pd, identified by ^1H NMR)[18] occurs on standing overnight in the absence of air.

The corresponding complex [(C_4Ph_4OMe)PdCl(Me_2PhP)] (**10**), prepared from the endo isomer, [(*endo*-η^3-C_4Ph_4OMe)PdCl]$_2$, **1**, and Me_2PhP could be recrystallized from benzene/hexanes as yellow needles. Osmometry revealed, however, that the solid state molecular structure was probably dimeric but that the complex slowly dissociated in chloroform solution to give a monomeric species by a first-order process with the rate constant $k \sim 1.7 \pm 0.2 \times 10^{-3}$ mol s^{-1} (37 °C) based on ten molecular weight data points. The limiting molecular weight found was 672 as expected for the monomer [(C_4Ph_4OMe)PdCl(Me_2PhP)] (667). The dissociation process could also be followed by ^1H NMR spectroscopy (35 °C) and was again found to be a first-order reaction with the average rate constant for both osmometric and NMR studies being $k \sim 1.3 \pm 0.6 \times 10^{-3}$ mol s^{-1} (0.02 M solutions). The $CDCl_3$ ^1H NMR of the freshly dissolved dimer [(C_4Ph_4OMe)-PdCl(Me_2PhP)]$_2$ is of limited use in establishing the structural nature of the (C_4Ph_4OMe) ligand as it consists of a broad, temperature invariant doublet for the Me_2PhP methyl protons and a very broad, temperature invariant methoxy proton resonance as listed in Table I. A reasonable structure for the dimer would be **10**.

The ^1H NMR of the monomer [(C_4Ph_4OMe)-PdCl(Me_2PhP)] obtained from the above dissociation reaction of **10** was identical with that of the species prepared in situ by the stoichiometric addition of Me_2PhP to a $CDCl_3$ solution of [(*endo*-η^3-C_4Ph_4OMe)PdCl]$_2$. The ^1H NMR of the monomeric species [(C_4Ph_4OMe)PdCl(Me_2PhP)] is temperature dependent owing to a concentration-independent process which rapidly exchanges the Me_2PhP methyl sites of the monomer. (The methyl groups of the Me_2PhP ligand are stereochemically nonequivalent at low temperatures.) The parameters for this process are $\Delta\nu = 8.0$ Hz, $T_c = 295$ K, and $\Delta G_{Tc}^{\ddagger} = 65$ kJ mol^{-1} and are independent of the presence of the dimer, which therefore plays no role in the exchange mechanism. Further, the ^1H NMR at low temperature is consistent with the presence of only one monomeric isomer for which there are two possible structures, **11** and **12**.

It has not been possible to distinguish which one of these structures is the correct one. However, in view of the observations of Maitlis et al.[11a] and the fact that a simple bridge cleavage of **10** to give **12** would be expected to be reasonably facile[19] it is probable that the correct structure for the monomeric species is the ring-closed endo-η^3-allylic structure **11**. The ring-closing reaction required in the conversion of the η^1-dienyl dimer **10** to the η^3-cyclobutenyl monomer **11** would account for the relatively high free energy of activation ($\Delta G^{\ddagger} \sim 90$ kJ mol^{-1}) observed for this dissociation.

Ring Opening of the *exo*-Alkoxytetraphenylcyclobutenyl Ligand. In contrast to the endo complexes the reaction of *exo*-alkoxytetraphenylcyclobutenylpalladium(II) complexes with a variety of chemical reagents does *not* lead to ring-opened products. If a conrotatory ring opening were to occur the expected product would have the dienyl structure **13**. Such a



structure should be reasonably stable since a similar structure with OR replaced by Cl is a postulated intermediate in the "$PdCl_2$-catalyzed" trimerization of diphenylacetylene[1-3] (i.e., cis addition of Cl to coordinated acetylene). Thus it is difficult to conceive of an obvious rationalization of the differing reactivities of the exo and endo isomers. Initially it was thought that unfavorable steric interactions between neighboring phenyl groups in the transition state may inhibit the formation of **13** (all phenyl groups cis). However, the observation of "ring opening" reactions for *endo*-[(C_4tolyl$_4$Ph)-PdX] clearly negates this postulate.[11a] To date it is not clear as to why the exo alkoxy cyclobutenyl derivatives fail to ring open.

Prolonged irradiation (20 h) of a cyclohexane solution of the exo complexes **3a** or **3b** (ca. 10^{-3} M) using long wavelength UV (Pyrex glassware, 360-nm lamp) results in the formation of an equilibrium mixture of **4a** ⇌ **5a** or **4b** ⇌ **5b**, respectively (ca. 30–40% conversion). The products were identified by their characteristic ^1H NMR spectra and by addition of PMe_2Ph to give **6a** and **6b**, also identified by their ^1H NMR. Irradiation of the endo complexes under similar conditions did not give any exo product. Thus it may be that irradiation of the exo complexes results in a disrotatory ring opening of the *exo*-alkoxytetraphenylcyclobutenyl ligand to give the *cis*-1,*trans*-3-tetraphenyl-4-methoxybutadien-1-yl complex which will then equilibrate with the endo structure.

Experimental Section

NMR spectra were recorded on Varian Associates Model A56/60D, T60, and HA 100 spectrometers. Temperature calibrations were obtained using the method of van Geet.[20] IR spectra were recorded as KBr disks or Nujol mulls on Perkin-Elmer 337 and 180 spectrometers. Mass spectra were recorded on a Bell and Howell Model 21-490 spectrometer at an ionization of 70 eV. Molecular weights were measured using a Mechrolab Model 301A vapor pressure osmometer. Melting points were determined on a Kofler hot stage and are corrected.

The di-μ-chloro-bis(*endo*-η^3-4-alkoxy-1,2,3,4-tetraphenylcyclobutenyl)dipalladium(II) complexes and their exo analogues were prepared as described by Maitlis.[5]

Preparation of the β-Diketonate Complexes 3–5. These complexes were prepared by the reaction of the appropriate chloride dimer (**1** or **2**) with either Tlacac or Tlhfac. Two examples of their preparation are given.

(1) Acetylacetonato(*endo*-η^3-4-methoxy-1,2,3,4-tetraphenylcyclobutenyl)palladium(II). Thallous acetylacetonate (0.630 g) and [(*endo*-C_4Ph_4OMe)PdCl]$_2$ (1.091 g) were stirred in CH_2Cl_2 (30 mL) for 4 h, then filtered to remove thallous chloride. Hexane was added to the filtrate to promote crystallization. [(*endo*-C_4Ph_4OMe)Pd-acac]·¼CH_2Cl_2 was collected as yellow prisms (0.708 g, 58%). Evaporation of the mother liquor yielded more yellow solid (0.324 g, 84% total yield). Integration by ^1H NMR spectroscopy supports the incorporation of ¼CH_2Cl_2 per mol of complex.

(2) **Hexafluoroacetylacetonato(*endo*-η^3-4-methoxy-1,2,3,4-tetraphenylcyclobutenyl)palladium(II).** The problems encountered in the purification of the hexafluoroacetylacetonate complexes are due to their very high solubility in organic solvents (even hexanes) which make recrystallization difficult, and their ability to incorporate solvent molecules into the solid state.

Thallous hexafluoroacetylacetonate (0.466 g) and [(*endo*-C_4Ph_4OMe)$PdCl]_2$ (0.644 g) were stirred in CH_2Cl_2 (20 mL) for 4 h, then filtered through a short column of Florisil. The evaporation of the filtrate left a yellow, bubbly glass which was pumped overnight under vacuum. The glass was redissolved in hexanes, recolumned (Florisil), evaporated down, and placed under vacuum. [(*endo*-C_4Ph_4OMe)Pdhfac] was isolated as a yellow glass, mp ~74 °C (0.58 g, 68% yield). Microanalysis (Table I) and the ^1H NMR integration supports the incorporation of $\frac{1}{2}$ (hexane).

Preparation of the Complexes [(η^1-Dienyl-C_4Ph_4OR)PdX(Me_2PhP)] Where X = acac or hfac (6a–d) or Cl (10). Acetylacetonato(η^1-4-methoxy-1,2,3,4-tetraphenylbutadienyl)dimethylphenylphosphinepalladium(II) (6a). Dimethylphenylphosphine (0.065 mL) in CH_2Cl_2 (5 mL) was added slowly to a stirred CH_2Cl_2 solution (10 mL) of [(*endo*-C_4Ph_4OMe)Pdacac] (0.290 g) under nitrogen. After 10 min the reaction mixture was columned in air through a short column of alumina. The pale yellow eluate isolated by evaporation of the solvent (CH_2Cl_2) was recrystallized from benzene/cyclohexane to give [(*endo*-C_4Ph_4OMe)Pdacac(Me_2PhP)] as yellow needles (0.240 g, 67% yield). Complexes **6b–d** were prepared in a similar manner from the appropriate acac or hfac complex.

Di-μ-chloro-bis(η^1-4-methoxy-1,2,3,4-tetraphenylbutadienyl)bis(dimethylphenylphosphine)dipalladium(II) (10). To [(*endo*-C_4Ph_4OMe)$PdCl]_2$ (0.43 g) in CH_2Cl_2 (15 mL) under nitrogen was added a solution of Me_2PhP (0.112 mL) in CH_2Cl_2 (5 mL). After 3 min, the solution was opened to the air and evaporated to an orange solid. Recrystallization from benzene/hexane gave [(*endo*-C_4Ph_4OMe)$PdCl(PMe_2Ph)]_2$ as yellow needles (0.45 g, 83% yield).

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(12) The ^{13}C NMR spectra of solutions of **4** ⇌ **5** gave similar results. Thus, for example, the ^{13}C NMR spectrum of **4b** ⇌ **5b** exhibited six of the expected seven singlet resonances assignable to the quaternary carbon atoms of the η^3-cyclobutenyl and η^3-butadienyl skeleton. By comparison with the data of Maitlis et al.[11a] the assignments follow: **4b**, δC_1–C_3 86.7, δC_2 119.4; δC_4 67.4 ppm. **5b**, three of four expected singlets observed at 91.8, 140.3, and 144.1 ppm. (Presumably the fourth singlet resonance assignable to the dienyl carbon skeleton is obscured by the aromatic resonances.)
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Formation of a Cobalt–Carbon Bond under Mild Conditions. Preparation and Crystal Structure of an Acetonyl Adduct of *N,N'*-Ethylenebis(3-fluorosalicylideniminato)cobalt(II)

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Abstract: The structure of Aquo, acetonyl-*N,N'*-ethylenebis(3-fluorosalicylideniminato)cobalt(III), crystallized with 0.32 mol of H_2O and 0.39 mol of acetone solvate, has been determined from three-dimensional x-ray data collected by counter methods. The compound contains a $CH_3COCH_2^-$ group carbon bonded to the cobalt atom; the cobalt–carbon bond was formed under very mild conditions. The material crystallizes in the monoclinic space group $C2/c$ with a = 18.108 (4), b = 13.674 (2), c = 18.466 (3) Å, and β = 118.15 (2)°. The observed density is 1.52 g/cm^3 and the calculated density is 1.531 g/cm^3 for 8 formula units of $CoC_{16}H_{12}O_2N_2F_2 \cdot CH_2COCH_3 \cdot H_2O(0.39CH_3COCH_3)(0.32H_2O)$ in the cell. The structure was refined on F^2 using 2627 unique reflection intensities measured greater than zero; the final conventional R index for all those reflections is 0.051. The geometry of the 3-fluorosalicylideniminato–Co portion of the complex is normal. A water molecule occupies one axial position with the acetonyl group trans to it; the Co–C bond length is 2.01 (1) Å and the Co–O (water) distance is 2.128 (2) Å.

Introduction

The oxygen-carrying cobalt complex *N,N'*-ethylenebis(salicylideniminato)cobalt(II) (CoSalen) was synthesized in 1938 by Tsumaki;[1] it has been studied extensively since then.[2,3] Our own efforts have focused on the preparation of crystalline dioxygen adducts of CoSalen and various substituted derivatives. We have succeeded in preparing the monomeric adducts of three substituted complexes and have reported their structures.[4-6] Thus far, the only crystalline complex we have prepared containing the parent compound has been a dimeric species with a dioxygen bridge between the two cobalt atoms.[7]

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