The closer agreement of γ_{theor} with γ_{exptl} suggests that the nonempirical approach might be more successful using a valence-state AO. Moreover, the AO obtained by minimizing a valence-state energy should[3] on theoretical grounds be more appropriate for calculations of molecular properties (not only energy) than are the orbitals obtained by minimizing the ^3P ground-state energy of the carbon atom.

In a future paper[34] we shall present a detailed theoretical and computational discussion of the valence state appearing in eq 1, its extension to π-electron excited states (including the associated changes in the σ- and π-AO's), and the effect of inclusion of molecular-orbital character in the σ-electron wave function.

(32) Computed using hydrogen-like orbital with $Z = 3.18$.
(33) Computed using ^3P carbon Hartree–Fock AO of E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.*, **127**, 1618 (1961).
(34) H. J. Silverstone and H. W. Joy, in preparation.

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Intermediates in the Conversion π- to σ-Allylic Complexes of Palladium

Sir:

The temperature dependence of the nmr spectra of π-allylic complexes of palladium provides evidence and clarification of intermediates[1] in the conversion of π- to σ-allylic complexes.

The temperature dependence of the 60-Mc/sec nmr spectrum of crotylpalladium(II) chloride in solution in $CDCl_3$, to which has been added 3 moles of DMSO-d_6/mole of Pd (20% DMSO-d_6 in $CDCl_3$), is shown in Figure 1, and the parameters for the low-temperature species ($-20°$) and the high-temperature species ($80°$) are listed in Table I. The spectrum of the low-temperature species indicates that the complex is in the π-allylic form with the resonances at τ 5.90 and 6.90 corresponding to the *cis* and *trans* protons b and c. Although all of the resonances are slightly affected by an increase in temperature, the *cis* and *trans* protons converge. The spectra clearly rule out the allylic rearrangement possible for symmetrical species[2] since this would necessitate the averaging of proton d also, and this does not occur over the temperature range

(1) J. Powell, S. D. Robinson, and B. L. Shaw, *Chem. Commun.* (London), 78 (1965).
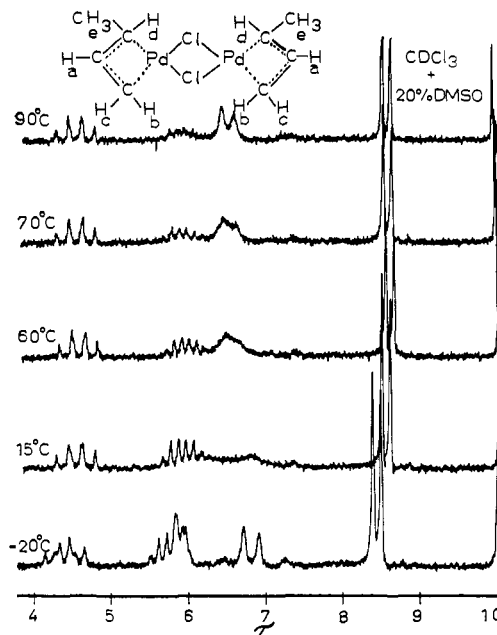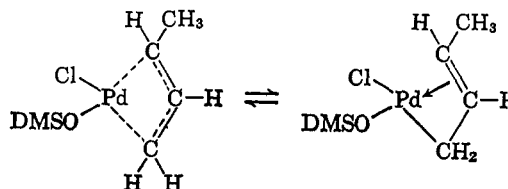(2) J. C. W. Chien and H. C. Dehm, *Chem. Ind.* (London), 745 (1961).

Figure 1. Temperature dependence of the nmr spectrum of crotyl-palladium(II)chloride in a 20% DMSO-d_6–$CDCl_3$ solution.

covered. The most likely process appears to be a π to σ equilibration

which is similar to the conversion postulated by Shaw and co-workers[1] for methallylpalladium(II) chloride upon addition of triphenylphosphine.

The temperature dependence of the 100-Mc/sec spectrum of this latter complex $[CH_2C(CH_3)CH_2Pd(Ph_3P)Cl]$ in $CDCl_3$ is shown in Figure 2, and the nmr
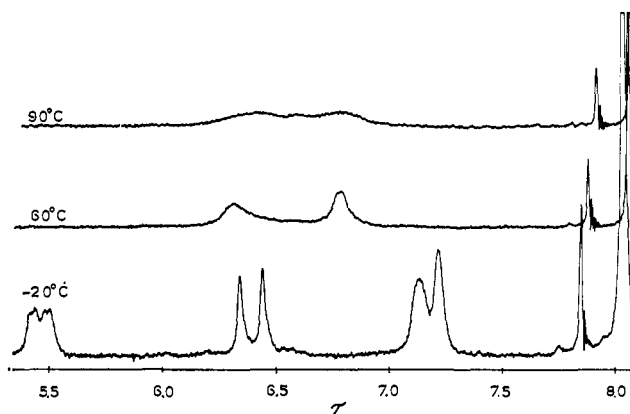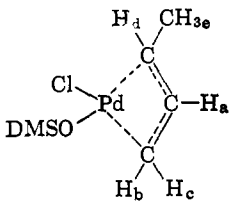
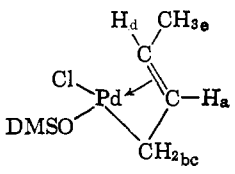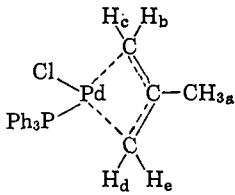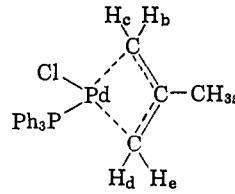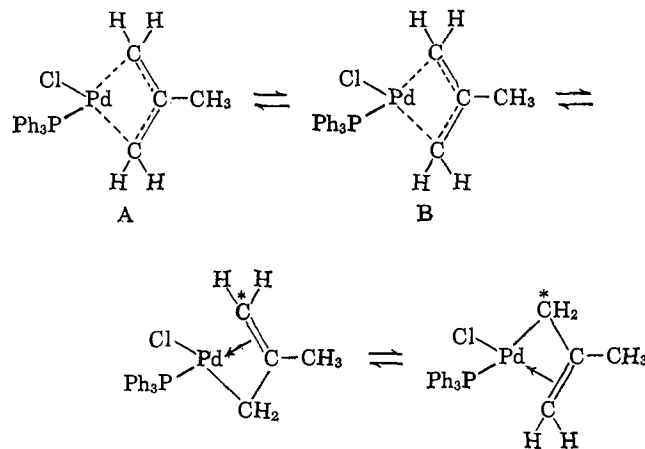Figure 2. Temperature dependence of the nmr spectrum of the triphenylphosphine adduct of methallylpalladium(II) chloride in solution in $CDCl_3$.

parameters for the equilibrating species are listed in Table I. The resonances centered at τ 7.19 were previously interpreted as corresponding to methylene pro-

Table I. Nmr Parameters of the Allylic Complexes of Palladium

Predicted structure	Temp, °C	Chemical shifts, τ values					Coupling constants, cps
(structure: Cl, Pd, DMSO, H_d CH_{3e}, $C-H_a$, H_b H_c)	−20°	a 4.42	b 6.90	c 5.90	d 5.90	e 8.45	$J_{ab} = 12.5$ $J_{ac} = 7.0$ $J_{ad} = 12.5$ $J_{dc} = 7.0$
(structure: Cl, Pd, DMSO, H_d CH_{3e}, $C-H_a$, CH_{2bc})	80°	a 4.60	bc 7.24		d 6.01	e 8.63	$J_{abe} = 10.0$ $J_{ad} = 11.0$ $J_{dc} = 7.0$
(structure: Cl, Pd, Ph_3P, H_c H_b, $C-CH_{3a}$, H_d H_e)	−20°	a 8.05	b 5.48	c 6.41	d 7.21	e 7.15	$J_{be} = 3.0$ $J_{bP} = 6.0$ $J_{cP} = 10.0$
(structure: Cl, Pd, Ph_3P, H_c H_b, $C-CH_{3a}$, H_d H_e)	60°	a 8.07	be 6.28	cd 6.81			

tons split either by coupling to the phosphorus or by restricted rotation.[1] Comparison of the 60- and 100-Mc/sec spectra shows that the separation between the two components is dependent on field strength which rules out phosphorus coupling. Detailed analysis of the spectrum indicates that the components do not correspond to an AB quartet which rules out the latter postulate. Furthermore, the downfield component centered at τ 7.15 shows an interaction of approximately 3 cps with the proton at τ 5.48. A tentative assignment of the four resonances can be made on the basis of the preferential coupling of phosphorus with protons in the *trans* position[3] and the preferential coupling of protons in a planar zig-zag arrangement.[4,5] The complex is thus in the π-allylic form at room temperature. As the temperature is increased to 60°, the four resonances converge into two. The positions of these new resonances (half-way between b and e, and half-way between c and d) seem to indicate that the π-allylic species A, which has four nonequivalent protons, converts into a second π-allylic species B for which the *cis* protons (b and e) are equivalent and the *trans* protons (c and d) are equivalent. As the temperature is further increased, these resonances first broaden, as illustrated in Figure 2, and then converge into a broad singlet at 140°. The latter spectrum was obtained using *o*-dichlorobenzene as a solvent. The equilibration may be depicted as

(structures A ⇌ B ⇌ ...)

A   B

The temperature dependence of the nmr spectrum of the triphenylarsine adduct yielded similar results, and a complete study on a number of allylic complexes of palladium will be reported in the near future.

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(3) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1625 (1964).
(4) S. Sternhill, *Rev. Pure Appl. Chem.*, 14, 15 (1964).
(5) M. Barfield, *J. Chem. Phys.*, 41, 3825 (1964).

A Convenient Synthesis of the Cubane System

Sir:

Although cyclobutadiene *per se* is unavailable for purposes of organic synthesis because of its extreme chemical instability, nonetheless initial experiments