complex. The present cyclization reaction, which may involve the oxo-π-allylpalladium(II) complex as a key intermediate, is interestingly compared with π-allylpalladium(II) catalyzed synthetic reactions leading to the formation of carbon–carbon bonds.

Synthetic applications of oxo-π-allylpalladium(II) intermediates are now in progress.

## References and Notes

(1) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978,** *43,* 1011–1013.

(2) Recently we found a catalytic dehydrosilylation of silyl enol ethers with $Pd^{II}(OAc)_2$ catalyst, in which an active Pd(II) species is regenerated by $Cu^{II}(OAc)_2$ with $O_2$. For example, to a solution of 23 mg (0.1 mmol) of $Pd^{II}(OAc)_2$ and 36 mg (0.2 mmol) of $Cu^{II}(OAc)_2$ in 8 mL of acetonitrile, 184 mg (1 mmol) of 6-methyl-1-trimethylsilyloxy-1-cyclohexene was added with stirring at room temperature, and then the resultant solution was stirred by bubbling oxygen through the solution for 24 h. Gas chromatography of the reaction mixture indicated that 6-methyl-2-cyclohexenone was produced in a quantitative yield.

(3) Ito, Y.; Hirao, T.; Saegusa, T. unpublished work.

(4) Use of $Cu^{II}(OAc)_2$ in combination with $O_2$ as a reoxidant in the present cyclization did not give any successful results.

(5) NMR ($CCl_4$ with $Me_4Si$): **3b,** $\delta$ 1.10 (d, 3 H), 2.10 (s, 3 H), 1.73~3.00 (m, 3 H), 5.58 (m, 1 H); **3c,** $\delta$ 1.20 (s, 6 H), 2.03 (s, 3 H), 2.26 (s, 2 H), 5.73 (m, 1 H); **3d,** $\delta$ 1.83 (s, 3 H), 2.20 (dd, 1 H, $J_{H-H}$ = 19.3, 2.7 Hz), 2.79 (dd, 1 H, $J_{H-H}$ = 19.3, 6.9 Hz), 3.78 (br d, 1 H), 5.90 (m, 1 H), 6.80~7.93 (m, 5 H).

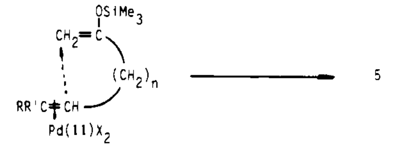
(6) The desired 3,3-dimethylcyclohexenone was not detected.

(7) The reaction of 2-trimethylsilyloxy-1,9-decadiene with $Pd^{II}Cl_2(PhCN)_2$ did not give any cycloalkenone derivatives but a stable oxo-π-allylpalladium complex corresponding to **2** in a high yield: IR (KBr disk) 1655, 1520, 990, 910 $cm^{-1}$

(8) NMR ($CDCl_3$ with $Me_4Si$): **3h,** $\delta$ 1.95 (s, 3 H), 4.45 (s, 2 H), 6.08 (m, 1 H), 6.58~7.98 (m, 4 H).

(9) NMR ($CDCl_3$ with $Me_4Si$): **3l,** $\delta$ 1.05~2.24 (m, 8 H), 2.05 (s, 3 H), 2.48 (m, 1 H), 2.77 (m, 1 H), 5.84 (m, 1 H).

(10) An alternative mechanism for the cyclization involves intramolecular attack of the palladium coordinated olefin on the electron-rich silyl enolate as shown. We disfavor this mechanism because silyl enol ether rapidly reacts with $Pd^{II}X_2$ to give the oxo-π-allylpalladium(II) complex prior to the cyclization.[7]



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## Fourier Transform Infrared Vibrational Circular Dichroism

*Sir:*

We report here the observation of vibrational circular dichroism (VCD) with a Fourier transform infrared (FT IR) spectrometer. The method used to obtain the VCD spectra represents the first demonstration of high-frequency modulated, differential FT IR spectroscopy, the general theory of which has been recently developed.[1] Since the initial discovery[2] and verification[3] of VCD, measurements have been achieved only with dispersive, grating instruments where spectra are generated by scanning a monochromator.[4] Since reported VCD signals are approximately four to five orders of magnitude smaller than the absorbance of the sample, signal-to-noise ratio enhancement using extensive electronic filtering and long scanning times is required. The present observation demonstrates the feasibility of measuring VCD using an FT IR spectrometer system having fundamental advantages over its dispersive counterpart in both signal quality due to increased throughput, Jacquinot's advantage,[5] and reduced measurement time due to spectral multiplexing, Fellgett's advantage.[5] The observation of FT IR-VCD points to a new dimension in VCD spectroscopy which should lead to significant improvements as this method is further developed and optimized.

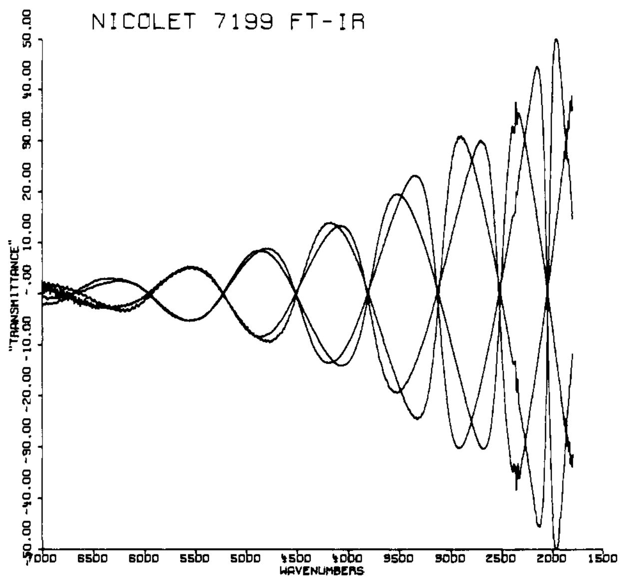

**Figure 1.** Four calibration curves where mirror image pairs are generated from the parallel and perpendicular position of the second polarizer with respect to the first. Pairs with shifted maxima are generated by exchanging the fast and slow axes of the retardation plate. Each curve represents 32 scans, with 0.145-cm/s mirror velocity, lock-in time constant of 0.7 ms, total measurement time of 90.3 s, small source aperture, and small area InSb detector.

The experimental method involves modulating the infrared beam between left and right circular polarization states at a frequency of 50 kHz, significantly higher than the Fourier interferogram frequencies. By first electronically demodulating the detector signal with a lock-in amplifier tuned to 50 kHz, a *new* interferogram is obtained representing the CD of the sample.[1] The components used in this experiment were a Nicolet 7199 FT IR spectrometer with a water-cooled glower source and a Ge-coated KBr beam splitter. Circular polarization was achieved with a $BaF_2$ wire grid polarizer (Molectron Corp.) and ZnSe photoelastic modulator.[4d,f] Intensities were measured with either a small area (1 $mm^2$, Nicolet) or a large area (144 $mm^2$, Spectronics, Inc.) InSb detector. Demodulation was achieved by a narrow band-pass 50-kHz filter and a lock-in amplifier (Princeton Applied Research Corp. Model 124A).

Figure 1 shows four CD calibration curves obtained by placing a sapphire retardation plate followed by a second $BaF_2$ polarizer in the sample position of the spectrometer. The theory of this measurement[1a,3b,6] and a dispersive spectrum[3b] have been published previously and the curve crossings above and below zero represent approximately unit CD magnitude. The calibration curves were optimized for magnitude by varying the interferometer mirror velocity, high and low pass electronic filters, retardation strength of the modulator, and time constant of the demodulating lock-in. The attenuation toward higher frequencies is due primarily to electronic filtering. The unusual nature of the CD interferogram, which results in positive and

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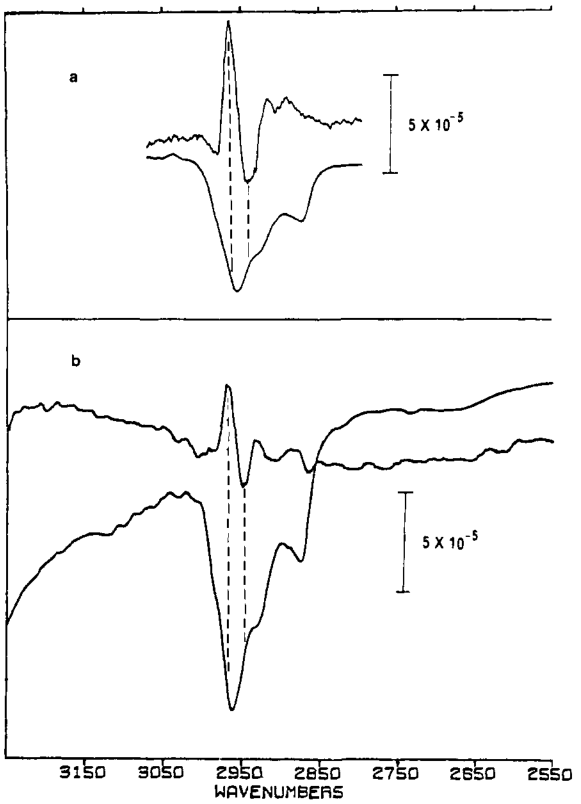

**Figure 2.** (a) Dispersive VCD and transmission spectrum (below) of 0.5 M (+)-camphor solution in $CCl_4$. The scale of VCD intensity in terms of $\Delta A$ is shown. The VCD was recorded with a 10-s, 18-db time constant over a period of 66 min. (b) Fourier transform VCD obtained from 4098 scans requiring 160 min. The $\Delta A$ scale was determined from the magnitude of the calibration spectrum including an external gain factor of 400. The VCD measurement used a mirror velocity of 0.145 cm/s, lock-in time constant of 0.7 ms, large source aperture, large area InSb detector, and an optical filter passing radiation between 3400 and 2600 $cm^{-1}$. Zero transmission is given by the horizontal line below each transmission spectrum.

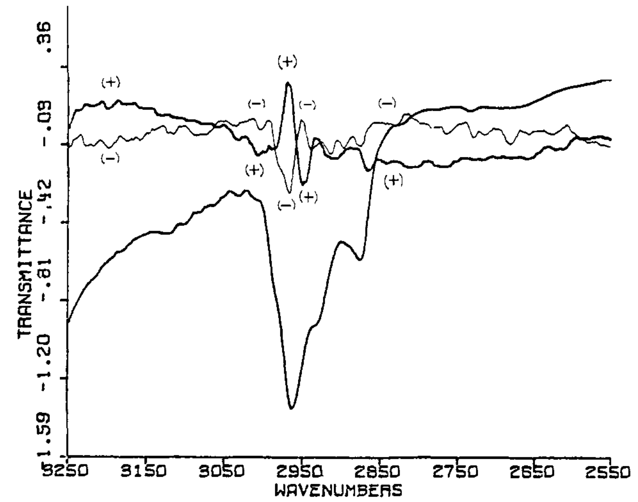

**Figure 3.** FT IR-VCD and single-beam transmission spectra of (+)-camphor and (−)-camphor. The (+)-camphor spectrum is the same as that given in Figure 2b and (−)-camphor was recorded under identical spectroscopic conditions with a total of 1024 scans requiring 40 min.

negative transmittance values, necessitates the transfer of both the linear and nonlinear phase corrections from the interferogram of the calibration's transmission spectrum. The same phase procedure was employed for the VCD measurements by using the sample's transmission interferogram as a phase reference.

In Figure 2 we show a comparison of a dispersive and the FT IR-VCD of 0.5 M (+)-camphor in $CCl_4$ solution in the C-H stretching region. The dispersive VCD was measured with the instrument at Syracuse University.[4d,f] The VCD intensity between the major positive and negative peak located near 2950 $cm^{-1}$, divided by the measured absorbance at the 2960-$cm^{-1}$ peak, is given by $\Delta A/A = 8.2 \times 10^{-5}/0.77 = 10.6 \times 10^{-5}$ for the dispersive spectrum and $\Delta A/A = 5.2 \times 10^{-5}/0.76 = 6.8 \times 10^{-5}$ for the FT IR result. By comparison, the previously published result of 0.56 M (+)- and (−)-camphor solutions[3b] yields $\Delta A/A = 6.2 \times 10^{-5}/0.74 = 8.4 \times 10^{-5}$. The FT IR-VCD was obtained from four reproducible blocks of 1024 interferometric scans. The resolution was 2 $cm^{-1}$ with smoothing applied to the final result to yield ~8-$cm^{-1}$ resolution, while the dispersive VCD has a resolution of ~14 $cm^{-1}$. Comparison of the FT IR-VCD of the (+)- to the (−)-camphor under identical spectroscopic conditions and 1024 scans is given in Figure 3. Before the FT IR-VCD was plotted, results were graphically compensated for to straighten the background base line and to remove a transmission dependence which was approximately three times larger than the VCD magnitude. The same compensation was applied to the VCD of both enantiomers. This compensation, which would also be applied to a racemic sample to obtain a straight base line, is a potentially serious problem. However, in our experiments, the compensation was always a fixed fraction of the total transmission for different samples and could be routinely removed as an instrumental correction.

The calibration results in Figure 1 correspond to theoretical expectation and demonstrate unequivocally that the high-frequency modulated differential FT IR method works as predicted.[1a] Figure 2 demonstrates that the measured VCD signal for (+)-camphor corresponds closely to the dispersive result in both the location of the major peaks and their overall magnitude. Finally, Figure 3 shows that the VCD spectrum of (−)-camphor has major peaks of the opposite sign compared with that of (+)-camphor.

The signal quality of the FT IR spectra is lower than the corresponding dispersive spectra, since only those variables available to us during these initial experiments were optimized. Work is currently in progress to improve the FT IR-VCD spectral quality to levels where Jacquinot's advantage and Fellgett's advantage may be directly realized. These preliminary results are regarded as encouraging since many promising directions remain to be explored in the development of this new approach to VCD spectra.

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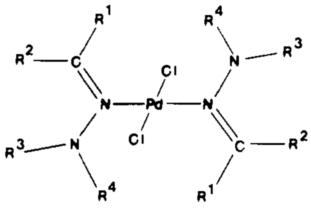
## On the Dynamic Behavior of Trans-Dihalide-Bishydrazone-Palladium(II) Complexes

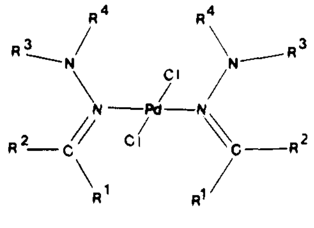
*Sir:*

A recent article[1] in this journal dealt with the dynamic behavior of *trans*-PdCl$_2$(Me$_2$C=NNMePh)$_2$ (I) and *trans*-PdCl$_2$(Pr$^i$MeC=NNMePh)$_2$ (II) and pointed out that (i) in compound I, at low temperature, the two hydrazones are unequivalent as a consequence of the alternating character of the palladium-alkyl interaction with the two ligands; (ii) compound II exists in two isomeric forms, II$_1$ and II$_2$, one of which (II$_2$) reveals unequivalence of the two ligands within the same molecule as I; (iii) a concerted intramolecular exchange mechanism occurring through oscillation of small amplitude about the Pd-N bond, rather than complete rotation of the two ligands about the metal-ligand bonds, is responsible for the fluxionality of I and II$_2$.

The same arguments[2] were used by those authors to challenge an independent note[3] of ours in which the two sets of NMR signals observed in I, as well as in a whole series of bishydrazone palladium derivatives, were assigned to two rotational isomers (each one having equivalent ligands) differing by mutual orientation of the two hydrazone molecules (isomers A and B).[3,4]



**A**



**B**

The two sets of signals of equal intensity observed in I could arise from the same molecular species (either A or B)[5] as well as from two isomers present in equal concentration. However, the presence in I of only one isomer should have been quite suspect since the authors themselves[1] admit that space-filling molecular models indicate that there is no obvious difference between A and B in compound I while isomer B appears more crowded than A in compound II, where both isomers are found in different concentration.

These sterical considerations are by themselves an argument in favor of the existence of the two rotational isomers in equal concentration in compound I; this is strongly supported by the subsequent observation that, by increasing the size of R$^1$ (R$^1$ = Me, Et, or Pr$^i$),[6] one set of signals becomes increasingly more intense ([A]/[B] = 1, 1.6, and 2.7, respectively).

We also looked for more compelling evidence and, assuming that the isomer ratio could be affected by a difference in the substituents at the hydrazone as well as by a difference in the halide ions, we have prepared the bromo analogue of I. The spectra, shown in Figure 1, indicate that the same sets of signals are present in both cases and, since they are not necessarily of equal intensity, they must belong to two isomeric species and not to a single molecule.

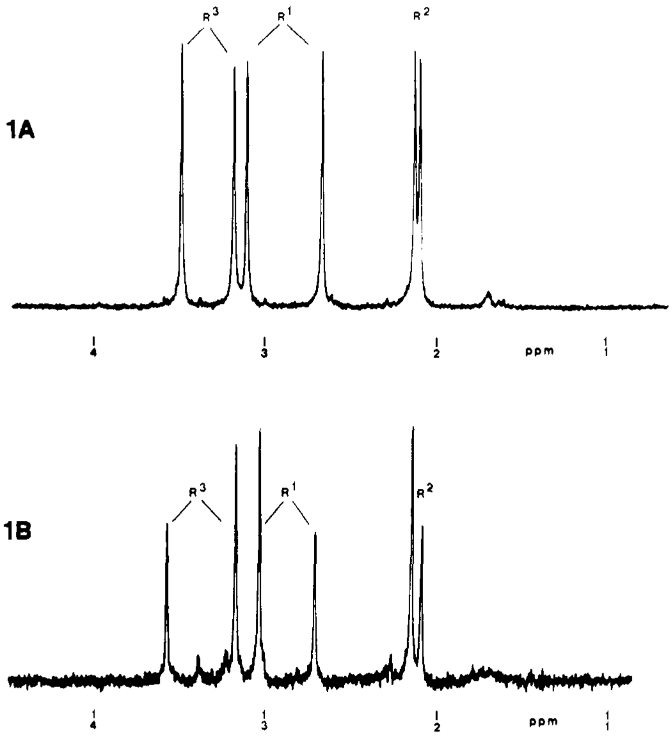


Figure 1. $^1$H NMR spectra of *trans*-PdCl$_2$(Me$_2$C=NNMePh)$_2$ (A) and its bromo analogue *trans*-PdBr$_2$(Me$_2$C=NNMePh)$_2$ (B) at 90 MHz and 0 °C, solvent CDCl$_3$.

The different intensity of the two sets of signals in the bromo derivative[7] also allows an unequivocal assignment of the signals belonging to each set in compound I; this agrees with our previous assignment[3,4] and is in contrast with that of Postel et al.[1,2]

The behavior of compound II as described by Postel et al.[1,2] did not appear convincing since the only evidence for the presence of a third set of resonances in CDCl$_3$ (instead of the two observed in I and in all other analogous complexes investigated by us) was a splitting by 0.01 ppm in one resonance. They said that the three signals arising from each methyl group were better resolved when the spectra were run in toluene rather than in chloroform, but they did not gave the relative values. We have reinvestigated this compound and, in order to better ascertain any possible splitting, we have run the NMR spectra of solutions of this complex, whose purity was controlled by HPLC,[8] in deuteriochloroform and in deuteriotoluene, at 270 MHz on a Bruker HX 270 instrument.[9] The spectra, shown in Figure 2, indicate that only two sets of signals of intensity ratio 2.7:1 are present either in CDCl$_3$ or in C$_7$D$_8$.[10] Therefore, two isomers, none of which shows the dynamic process suggested by Postel, are present.

To show that the separation between the two sets of signals reflects the different situation of the ligands in the two isomers (as determined by the reciprocal influence of the trans ligands) rather than a difference between the two hydrazones in the same molecule, we have prepared the mixed complex *trans*-PdCl$_2$(Me$_2$C=NNMePh)(Me$_2$C=NNMe$_2$).[8] The isomer split of the -NMePh hydrazone, which was large in compound I, is small in the mixed complex, since its protons face in both isomers a Me group from the trans ligand. On the contrary, the isomer split of the -NMe$_2$ hydrazone, which was small in *trans*-PdCl$_2$(Me$_2$C=NNMe$_2$)$_2$, is large in the present case, since the protons face alternately a Me and a Ph group from

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