Homogeneous Catalysis. Metal-Catalyzed Claisen Rearrangements of Allylic Thionobenzoates

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Received November 1, 1985

A variety of complexes of the metals Pd(II), Pt(II), Pd(0), Pt(0), Rh(I), and Ir(I) catalyzed the rearrangement of allylic thionobenzoates to allylic thiolobenzoates at 25 °C. Rate accelerations of the order of 10^5 are observed over the corresponding thermal rearrangements. All reactions proceed with retention of configuration when cyclic substrates are used, but only the Pd(II) and Pt(II) catalysts are regiospecific for all substrates. Three mechanisms are proposed: an intramolecular cyclization mechanism for the Pd(II) and Pt(II) catalysts, a catalytic allylation mechanism for the Pd(0) and Pt(0) catalysts, and a controlled metal-assisted ion-pair mechanism for the Rh(I) and Ir(I) catalysts.

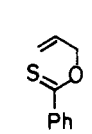
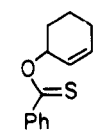
The thermal Cope and Claisen rearrangements (Figure 1) exchange the functionalities X and Y with high stereochemical control and, as such, are important chemical transformations. Except in special circumstances[1,2] and for particular substrates, these thermal [3,3] sigmatropic rearrangements require elevated temperatures and extended times for completion which limits their applicability in the late stages of synthetic strategies. It is for this reason that various attempts, some isolated others coherent, have been made to find catalysts which will accelerate these reactions[3,4] and, at the same time, to preserve the stereochemical control.

Most notable of these attempts is the work of Overman,[4] who showed that Hg(II) and Pd(II) complexes were the most versatile catalysts for both Cope and Claisen rearrangements. Rate accelerations of the order of 10^{10} were observed over the comparable thermal reactions, and in the case of Pd(II)-catalyzed Cope rearrangements,[5] the stereochemical control was similar to that observed for the thermal reaction.

We recently reported a detailed study of the mechanisms of the metal-catalyzed rearrangements of allylic imidates using Pd(0), Pd(II), Rh(I), and Ir(I) complexes.[6] Three distinct mechanisms were postulated, one for Pd(0), another for Pd(II), and a third for the Rh(I) and Ir(I) complexes. This paper reports a similar study of the catalyzed rearrangements of allylic thionobenzoates which, to our knowledge, have not been investigated before.

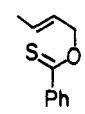
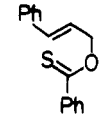
The thermal Claisen rearrangements of sulfur-containing substrates are frequently complicated by side products, and a method for catalyzing these transformations would have obvious advantages. There have been several isolated reports of metal-induced Claisen rearrangements of sulfur-containing substrates. A pronounced catalytic effect was observed with $[PdCl_2(PhCN)_2]$ in the rearrangement of *S*-allyl thioimidates to *N*-allyl thioamides.[7,8] Palladium(II)-catalyzed sulfur–nitrogen migration was also observed in the conversion of *S*-allyl iminothiocarbonates to *N*-allyl thiocarbamates.[3] Finally, Hg(II), but not Pd(II), catalysis of allylic thionocarbamate rearrangements has been reported.[9] None of these reports of sulfur-containing substrates involved mechanistic studies.

Table I. Transition-Metal-Catalyzed Rearrangement of Allylic Thionobenzoates in Chloroform Solution at 25 °C Using 5 Molar % Catalyst Except Where Indicated Otherwise[a]

	substr	
cat.		
$[PdCl_2(PhCN)_2]$	10 min	12 h[b]
$[PtCl_2(PhCN)_2]$	4 days	36 h[b]
$[Pt(C_2H_4)(PPh_3)_2]$	12 h	no rxn[c]
$[Pd(PPh_3)_4]$	30 min	36 h
$[Rh(COD)Cl]_2$	5 h	36 h[d]
$[Ir(COD)Cl]_2$	10 min	24 h[d,e]

[a] Times listed refer to the time required for >95% conversion of the substrate. [b] 15 molar % catalyst. [c] 10 molar % catalyst at 25 °C after 5 days. [d] At 50 °C. [e] 10 molar % catalyst.

Table II. Regioselectivity of Metal-Catalyzed Claisen Rearrangements of Allylic Thionobenzoates in Chloroform Solution at 25 °C Using 5 Molar % Catalyst Except Where Indicated Otherwise[a]

	substr	
cat.	 [3,3]:[1,3] (time)	 [3,3]:[1,3] (time)
$[PdCl_2(PhCN)_2]$	100:0 (<10 min)	100:0 (2 days)
$[PtCl_2(PhCN)_2]$	100:0 (4 days)	100:0 (7 days)[b]
$[Pt(C_2H_4)(PPh_3)_2]$	35:65 (7 days)	no rxn (5 days)
$[Pd(PPh_3)_4]$	38:62 (12 h)	0:100 (20 min)
$[Rh(COD)Cl]_2$	67:33 (5 days)	no rxn (5 days)
$[Ir(COD)Cl]_2$	77:23 (3 h)	50:50 (3 h)

[a] Times listed refer to the time required for >95% conversion of the substrate. [b] 10 molar % catalyst.

Results

The possible metal-catalyzed rearrangement products are shown in Figure 2; both the Claisen [3,3] and anti-Claisen [1,3] rearrangements are possible. Table I collects

(1) Ireland, R. E.; Mueller, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 5897. Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868.
(2) Evans, D. A.; Baillargeon, D. J.; Nelson, J. V. *J. Am. Chem. Soc.* **1978**, *100*, 2242.
(3) Lutz, R. P. *Chem. Rev.* **1984**, *84*, 205.
(4) Overman, L. E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 579.
(5) Overman, L. E.; Knoll, F. M. *J. Am. Chem. Soc.* **1980**, *102*, 865. Overman, L. E.; Jacobsen, E. J. *J. Am. Chem. Soc.* **1982**, *104*, 7225.
(6) Schenk, T. G.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2058.
(7) Tamaru, Y.; Kagotani, M.; Yoshida, Z. *J. Org. Chem.* **1980**, *45*, 5221. Mizutani, M.; Sanemitsu, Y.; Tamaru, Y.; Yoshida, Z. *J. Org. Chem.* **1983**, *48*, 4585.
(8) Tamaru, Y.; Kagotani, M.; Yoshida, Z. *Tetrahedron Lett.* **1981**, *22*, 4245.
(9) Overman, L. E.; Campbell, C. B.; Knoll, F. M. *J. Am. Chem. Soc.* **1978**, *100*, 4822.

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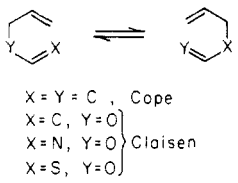


Figure 1.

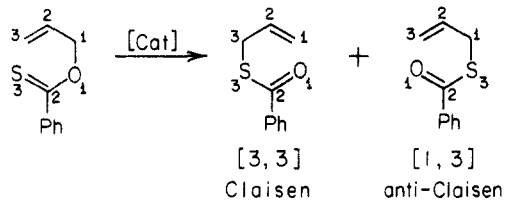
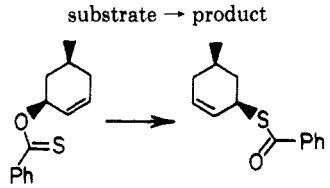


Figure 2. Possible metal-catalyzed rearrangement products of allylic thionobenzoates.

Table III. Degree of Retention of Configuration of Metal-Catalyzed Claisen Rearrangements in Chloroform Solution[a]



cat.	% retentn of configuratn (time)
$[PdCl_2(PhCN)_2]$[b]	70 (1 day)
$[PtCl_2(PhCN)_2]$[b]	76 (1 day)
$[Pt(C_2H_4)(PPh_3)_2]$	no rxn
$[Pd(PPh_3)_4]$[c]	82 (1 day)
$[Rh(COD)Cl]_2$[b]	84 (2 days)
$[Ir(COD)Cl]_2$[b]	75 (2 days)

[a] Times listed refer to the time required for >95% conversion of the substrate. [b] 20 molar % catalyst at 40 °C. [c] 10 molar % catalyst at 25 °C.

the results observed with a variety of catalysts using the two substrates shown. In all cases the rearrangements were clean, but considerable variation in catalytic activity is observed depending on the catalyst and the substrate. Table II contains the results obtained by using substrates which can reveal the regioselectivity of catalysis. Depending on the substrate and the catalyst, both [3,3] and [1,3] rearrangements are obtained, and for some catalysts, mixtures of products are observed. Finally, Table III shows the results of studies to determine the extent of configurational retention for the rearrangements. In all cases retention of configuration prevails, but in no case was configurational integrity fully maintained. We are uncertain, however, whether the loss of configuration occurs during the catalytic process or via a secondary reaction induced by impurities. The substrate in Table III is sensitive to heat and to chromatographic supports, and we were unable to fully purify it by either distillation or chromatography without accompanying decomposition. Circumstantial evidence suggests that the configurational loss occurs because of impurities.

Taken as a whole, the results contained in Table I–III suggest that three mechanisms operate for the rearrangements, one for the Pd(II) and Pt(II) catalysts, one for the Pd(0)- and Pt(0)-mediated reactions, and another for the Rh(I) and Ir(I) catalysis.

Mechanism of Pd(II) and Pt(II) Catalysis

The distinguishing feature of the Pd(II) and Pt(II) catalysts which separates them from the others is that for all substrates, exclusive [3,3] regioselectivity is observed. Additionally, like for the others, there is also prevailing retention of configuration (Table III). These features are the same as those observed for thermally induced Claisen rearrangements and suggest that the stereochemistry of one of the crucial catalytic intermediates resembles that involved in the cyclic concerted thermal process.

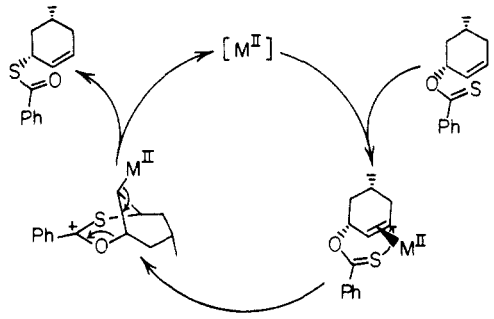


Figure 3. Intramolecular cyclization mechanism for the Pd(II)- and Pt(II)-catalyzed rearrangements of allylic thionobenzoates.

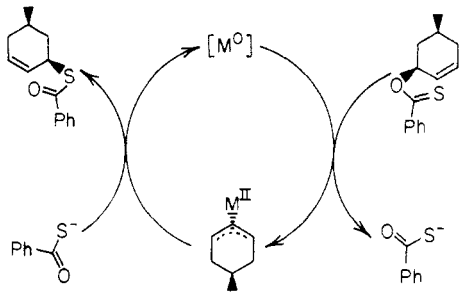


Figure 4. The allylation mechanism for the Pd(0)- and Pt(0)-catalyzed rearrangement of allylic thionobenzoates.

The proposed catalytic cycle is shown in Figure 3 for the cyclohexenyl substrate. This cyclization-induced mechanism involves coordination of the olefin to the metal which activates the olefin to internal nucleophilic attack, in this case by the thiono sulfur atom. Intramolecular attack gives the cyclic carbonium ion intermediate shown which then rearranges to the Claisen product. This mechanism was first proposed by Henry[10] for allylic acetate migration induced by Pd(II) and has been invoked for various Claisen and Cope rearrangements mediated by Hg(II), Pd(II) and Ag(I) species by Schmid,[11] by Overman,[4] and by us.[6] This mechanism explains satisfactorily the regioselectivity and predicts that for the cyclohexenyl substrate (Figure 3) the stereochemistry should be preserved after rearrangement. Although this mechanism has been widely invoked, the cyclic carbonium ion intermediate has yet to be detected or intercepted. The preceding steps, olefin coordination followed by intramolecular attack, however, are conventional.

Mechanism of Pd(0) and Pt(0) Catalysis

Unlike the Pd(II) and Pt(II) catalysis, the Pd(0) and Pt(0) catalysts display a different regioselectivity although for Pd(0), rearrangement proceeds with the same net retention of configuration. Thus Pd(0) and Pt(0) both give mixtures of [3,3] and [1,3] rearrangement products for the crotyl substrate, and with Pd(0), the cinnamyl substrate gives exclusively the anti-Claisen, [1,3], product. In each case the configuration of the double bond is *E* (trans). Such a regio product spread is typical of allylation reactions of these substrates[12] and suggests that the mechanism

(10) Henry, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 5200.
(11) Schlossarczyk, H.; Sieber, W.; Hesse, M.; Hansen, H. J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 875.

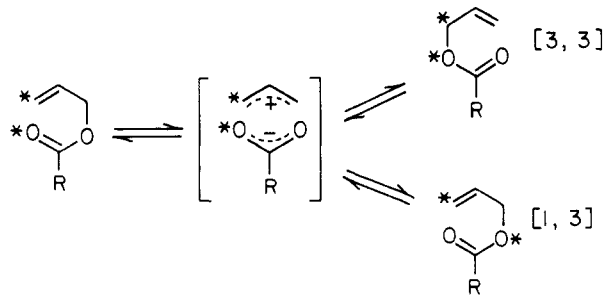


Figure 5. The proposed mechansm[17] for the solvolytic rearrangement of allylic benzoates.

of rearrangement for the Pd(0) and Pt(0) catalysts involves a metal–π-allylic intermediate which is the key entity in catalyzed allylation.

The proposed mechanism is outlined in Figure 4 by using the stereochemically labeled cyclohexenyl substrate. Oxidative addition by the metal(0) complex to the allylic thionobenzoate gives the metal(II)–π-allylic intermediate with the release of the thiobenzoate ion. This ion then attacks the intermediate to give the rearranged product and completes and catalytic cycle. It is known that oxidative addition to allylic acetates proceeds with inversion of configuration and that nucleophilic attack on the π-allylic intermediate leads to inversion.[13-15] If we assume that the same stereochemical sequence obtains for the present substrates, then the net retention observed for the present rearrangement is consistent with the π-allylic mechanism proposed because the π-allylic intermediate derived from our stereochemically labeled cyclohexenyl substrate is incapable of inversion via the π–σ–π mechanism.[16]

We should point out that thioacetates or thiobenzoates generally cannot be employed as nucleophiles in catalytic allylation because of their strong tendency to coordinate to or precipitate the catalyst and thus inactivate it. The fact that the allylation proceeds under the present conditions is probably because the nucleophile is in low concentrations, never being greater than that of the π-allylic intermediate. These substrates therefore potentially provide one method of obviating the catalyst inactivation that is associated with the use of sulfur nucleophiles in catalytic allylation.

Mechanism of Rh(I) and Ir(I) Catalysis

The regioselectivity of rearrangement by the Rh(I) and Ir(I) is different from that observed for either Pd(II) and Pt(II) or the Pd(0) and Pt(0) categories of catalysts. It is clear that the regioselectivity is inconsistent with the cyclization mechanism proposed for the Pd(II) and Pt(II) catalysts although the oxidative addition followed by nucleophilic attack mechanism invoked for the Pd(0) and Pt(0) catalysts cannot be completely excluded by the results collected in the tables. We have given a variety of reasons elsewhere[6] for excluding the latter mechanism for the Rh(I) and Ir(I) catalysts, the most obvious being that these catalysts are unlikely to undergo facile oxidative addition to these substrates.

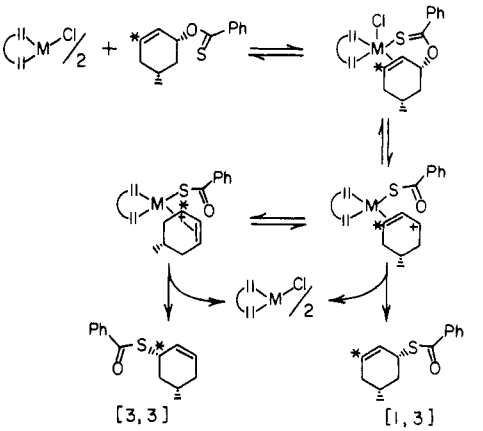


Figure 6. The metal-assisted ion-pair mechanism for the rearrangement of allylic thionobenzoates by the Rh(I) and Ir(I) catalysts.

In a number of ways the results for the Rh(I) and Ir(I) catalysts bear a strong resemblance to those observed by Goering[17] for the rearrangements that accompany solvolysis of allylic *p*-nitrobenzoates. In order to explain his results, Goering proposed that a tight ion pair is formed between the incipiently formed cationic allylic ion and the anionic benzoate ion which, upon collapse, can give [3,3] or [1,3] rearrangement products (Figure 5). We propose a similar mechanism for the Rh(I) and Ir(I) catalysis except that the ion pair is held and stabilized by the metal. The outlines of this mechanism are shown in Figure 6, using the stereochemically labeled cyclohexenyl substrate as an example.

The basic steps in the cycle involve first the coordination of the substrate as a bidentate chelate which is then followed by cleavage of the carbon–oxygen bond to form the coordinated thiobenzoate ion and a bound allylic carbonium ion. Whereas this carbonium ion is assumed to be stabilized by the metal, we have presented evidence elsewhere[6] which suggests that the metal is not oxidized to the +3 oxidation state to form a conventional π-allylic complex but rather that the intermediate resembles the shown charged allylic system. The final step in the cycle is the carbon–sulfur bond formation. Either this can occur at the allylic terminus originally bound to the oxygen atom ([1,3] product) or, after rotation, carbon–sulfur bond formation can occur at the other terminus ([3,3] product).

This mechanism is consistent with the observed retention of configuration of the stereochemically labeled cyclohexenyl substrate provided the allylic carbonium ion does not dissociate, and the mechanism can accommodate the regio product spread that is observed. We should point out that the use of cyclic substrates "loads" the result in favor of configurational retention.

Discussion

The rearrangement catalysis of allylic thionobenzoates appears to occur by three distinct mechanisms, only one of which (Pd(II) and Pt(II)) is an intramolecular cyclization resembling the thermal path. The Pd(0) and Pt(0) mechanisms appear to be a form of catalytic allylation where fragmentation occurs releasing the thiobenzoate ion which attacks the produced π-allylic intermediate inter-

(12) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385.
(13) Trost, B. M.; Weber, L. *J. Am. Chem. Soc.* **1975**, *97*, 1611. Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 630.
(14) Hyashi, T.; Hagihara, T.; Konishsi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767.
(15) Mackenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2046.
(16) Faller, J. W.; Thomsen, M. E.; Mattina, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 2642. Faller, J. W.; Tully, M. T. *J. Am. Chem. Soc.* **1972**, *94*, 2676.
(17) Goering, H. L.; Doi, J. T. *J. Am. Chem. Soc.* **1960**, *82*, 5850. Goering, H. L.; Pombo, M. M.; McMichael, K. D. *J. Am. Chem. Soc.* **1963**, *85*, 905. Goering, H. L.; Josephson, R. R. *J. Am. Chem. Soc.* **1962**, *84*, 2779. Goering, H. L.; Doi, J. T.; McMichael, K. D. *J. Am. Chem. Soc.* **1964**, *86*, 1951. Goering, H. L.; Koermer, G. S.; Linsay, E. C. *J. Am. Chem. Soc.* **1971**, *93*, 1230.

molecularly. The Rh(I) and Ir(I) mechanisms resemble those of Pd(0) and Pt(0) except that all of the steps occur intramolecularly. For practical purposes the Pd(II) catalyst may be the most useful synthetically because of the high turnover rate and the greater steric control implicit in the cyclization mechanism.

The thermal rearrangement reactions of allylic thionobenzoates are slow,[18] having half-lives of about 10 h at 100 °C. This suggests that the present catalysts accelerate the rearrangements by about 10^4–10^6 over the thermal uncatalyzed reactions. Although these accelerations are considerable, they are significantly less than have been observed for non-sulfur-containing substrates[4,6] which typically give accelerations of 10^{10}. The probable impediment to the catalytic turnover rate with the present substrates is the strong tendency of the thiono sulfur group to bind, and hence deactivate, the catalysts. The rather erratic performance of the Pt(0) catalyst may be because of sulfur coordination. Nonetheless these catalysts provide an attractive alternative to the thermal rearrangements of sulfur-containing substrates which are generally accompanied by extensive side products because of the elevated temperatures required.

Experimental Section

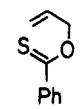
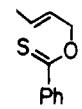
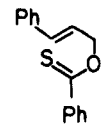
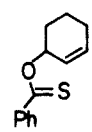
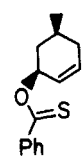
^{1}H NMR spectra were recorded on Varian T-60, Varian XL-200, Varian XL-400, or Brucker WH-400 spectrometers. The parameters given refer to $CDCl_3$ solutions at 60 MHz relative to Me_4Si unless otherwise specified.

Catalysts were prepared by methods described elsewhere: $[PdCl_2(PhCN)_2]$,[19] $[PtCl_2(PhCN_2)_2]$,[20] $[Pt(PPh_3)_2(C_2H_4)]$,[21] $[Pd(PPh_3)_4]$,[22] $[Rh(COD)Cl]_2$,[23] and $[Ir(COD)Cl]_2$.[24] The following compounds were prepared by modifications of literature methods: cyclohexen-3-ol,[25] 5-methyl-1,3-cyclohexanedione,[26] 3-ethoxy-5-methyl-2-cyclohexenone,[27] 5-methyl-2-cyclohexenone,[27,28] *cis*-5-methyl-2-cyclohexen-1-ol,[29] and (thiobenzoylthio)acetic acid.[30]

Preparation of Substrates. Allyl, Crotyl, Cinnamyl, 2-Cyclohexenyl, and 5-Methyl-2-cyclohexenyl Thionobenzoates.[31] To a stirred slurry of NaH (1.0 g, 24 mmol) was added in portions (thiobenzoylthio)acetic acid (2.57 g, 12 mmol). After the initial efferverscence had ceased, imidazole (0.82 g, 12 mmol) was added. The mixture was heated at reflux for 5 min, and then the allylic alcohol (12 mmol) was added. The resulting mixture was refluxed an additional 5 min, was allowed to cool, and then was stirred at 25 °C for 1.5 h. The reaction was quenched by decantation into ice water (500 mL), and the product was extracted into ether. The combined ether extracts were washed with water, dried over Na_2SO_4, filtered, and concentrated in vacuo to give the crude product (20–40%).

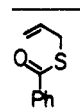
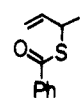
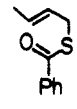
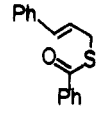
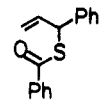
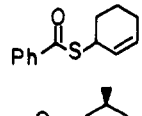
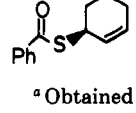
Only two of the substrates were purified by short-path distillation, the allyl thionobenzoate, bp 80–85 °C (0.5 mm) (lit.[18] 84–86 °C (0.5 mm)), and the crotyl thionobenzoate, bp 95–98 °C (0.5 mm) (lit.[18] 93–95 °C (0.3 mm)). These materials were pure by ^{1}H NMR. The cinnamyl, 2-cyclohexenyl, and 5-methyl-2-cyclohexenyl substrates could not be a distilled without effecting rearrangement and/or decomposition. These compounds are sensitive to both acid and base, and attempts to chromatograph them over available grades of silica gel or alumina (neutral and basic) resulted in decomposition. After the residual allylic alcohol was removed from these compounds by short-path distillation (0.5 mm), the remaining portion was predominantly (>95%) substituted allyl thionobenzoate containing some residual alcohol and a few percent of an unidentified aromatic compound. These

Table IV. ^{1}H NMR Data of Allyl Thionobenzoates

allyl thionobenzoate	^{1}H NMR[a] data, δ
	5.2–5.8 (m, 4 H), 5.8–6.7 (m, 1 H), 7.1–7.9 (m, 3 H), 8.1–8.9 (m, 2 H)
	1.75–1.95 (m, 3 H), 5.3 (d, J = 5 Hz, 2 H), 5.9–6.3 (m, 2 H), 7.4–7.9 (m, 3 H), 8.3–8.6 (m, 2 H)
	5.5 (d, J = 5 Hz, 2 H), 6.3–7.0 (m, 2 H), 7.6–8.0 (m, 3 H), 8.3–8.6 (m, 2 H)
	1.5–2.2 (m, 6 H), 5.8–6.2 (m, 3 H), 6.8–7.5 (m, 3 H), 8.0–8.2 (m, 2 H)
	0.9–2.6 (m, 8 H), 5.5–6.5 (m, 3 H), 6.9–7.5 (m, 3 H), 8.0–8.2 (m, 2 H)

[a] Obtained at 60 MHz in $CDCl_3$ solution.

Table V. ^{1}H NMR Data of Thioloesters

allyl thioloesters	^{1}H NMR[a] data, δ
	3.7 (d, J = 5 Hz, 2 H), 5.15–5.67 (m, 2 H), 5.8–6.5 (m, 1 H), 7.4–7.9 (m, 3 H), 8.1–8.4 (m, 2 H)
	1.4 (d, J = 6 Hz, 3 H), 4.6 (qt, J = 6 Hz, 1 H), 5.1–5.7 (m, 2 H), 5.8–6.5 (m, 1 H), 7.4–7.9 (m, 3 H), 8.0–8.3 (m, 2 H)
	1.6–1.9 (m, 3 H), 3.8 (d, J = 6 Hz, 2 H), 5.1–6.5 (m, 2 H), 6.9–7.8 (m, 3 H), 8.0–8.3 (m, 2 H)
	3.85 (d, J = 6 Hz, 2 H), 5.8–6.8 (m, 2 H), 7.0–7.5 (m, 3 H), 7.9–8.0 (m, 3 H)
	4.9–5.7 (m, 3 H), 5.8–6.6 (m, 1 H), 7.1–7.6 (m, 3 H), 7.8–8.0 (m, 2 H)
	1.4–2.5 (m, 6 H), 4.2–4.5 (m, 1 H), 5.3–6.3 (m, 2 H), 7.0–7.6 (m, 3 H), 7.8–8.0 (m, 2 H)
	0.73–2.5 (m, 8 H), 4.2–4.6 (m, 1 H), 5.2–6.0 (m, 2 H), 7.0–7.7 (m, 3 H), 7.8–8.1 (m, 2 H)

[a] Obtained at 60 MHz in $CDCl_3$ solution.

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samples were used in the catalytic reactions.

The substrates showed only infrared bands at 1270 and 1230 cm^{-1}, characteristic for allyl thionobenzoates,[18] and none of the bands observed for the thiolobenzoates, 1660, 1210, and 910 cm^{-1}. The substrates and products exhibited the expected ^1H NMR spectra (Tables IV and V).

The thioloesters were stable to chromatography (silica gel), but isolation and purification were only carried out on *cis*-5-methyl-2-cyclohexen-1-yl thiolobenzoate.

The ratio of geometric 5-methyl-2-cyclohexen-1-yl thionobenzoate isomers was determined by the relative integrated intensities of the 2-vinylic hydrogen at 200 MHz. ^1H NMR (200 MHz): δ 1.04 (d, J = 5 Hz, 3 H), 1.22–1.61 (m, 1 H), 1.66–2.4 (m, 4 H), 5.72–6.04 (m, 2 H), 6.06–6.21 (m, 0.13 H), 6.22–6.37 (m, 0.87 H), 7.21–7.59 (m, 3 H), 8.1–8.21 (m, 2 H). The major cis geometry was correlated with that of the allylic alcohol used in the preparation.

Catalytic Rearrangements Monitored by ^1H NMR. The catalyzed transformations of the allyl, crotyl, cinnamyl and cyclohexenyl thionobenzoates were performed in 5-mm ^1H NMR tubes and were monitored periodically. A typical reaction is described.

The catalyst (1.54×10^{-2} mmol) was weighed into a 5-mm NMR tube, was flushed with either nitrogen or argon for 15 min, and then was dissolved in $CDCl_3$ (0.5 mL). The thionobenzoate (0.31 mmol) was then added to the solution, and the reaction was monitored periodically. Table IV contains the ^1H NMR parameters of the thionobenzoates, and Table V contains the corresponding parameters for the rearranged thioloesters.

Rearrangement of 5-Methyl-2-cyclohexen-1-yl Thionobenzoate with $Pd(PPh_3)_4$. To a stirred solution of $Pd(PPh_3)_4$ (0.25 g, 0.2 mmol) in dry dichloromethane (5 mL) was added *cis*-5-methyl-2-cyclohexen-1-yl thionobenzoate (0.5 g, 2 mmol). The resulting solution was stirred for 24 h at 25 °C and then was filtered to remove a pale yellow solid. After removal of the solvent in vacuo, the residue was adsorbed on Celite and chromatographed over silica gel with hexane/ethyl acetate. The rearranged thioloester (0.35 g, 70%) was isolated as a pale yellow liquid.

Rearrangements of *cis*-5-methyl-2-cyclohexen-1-yl thionobenzoate with the $[PdCl_2(PhCN)_2]$, the $[PtCl_2(PhCN)_2]$, and the $[Rh(COD)Cl]_2$ catalysts were performed in an analogous manner to that given for the $[Pd(PPh_3)_4]$ catalyst, except that these reactions were carried out at 40 °C and 0.4 mmol (20 mol %) of the catalyst was used.

The ratio of geometric thioloester isomers produced in these catalytic reactions was determined by the relative integrated intensities of the two methyl doublets at 400 MHz. The ^1H NMR spectrum for the $Pd(PPh_3)_4$ catalyzed rearrangement product is reported. ^1H NMR (C_6D_6, 400 MHz): δ 0.75 (d, J = 5 Hz, 2.13 H), 0.81 (d, J = 5 Hz, 0.87 H), 1.17–2.15 (m, 5 H), 4.60–4.70 (m, 1 H), 5.58–5.82 (m, 2 H), 6.88–7.23 (m, 3 H), 8.00–8.07 (m, 2 H).

The ^1H NMR parameters of the major geometric isomer were established by experiments which follow.

***cis*-5-Methyl-2-cyclohexene-1-thiol.** To a stirred solution of KOH (1.09 g, 20 mmol) in water (25 mL) was added *cis*-5-methyl-2-cyclohexen-1-ol (2.0 g, 18 mmol). The mixtures was cooled to 0 °C, and CS_2 (1.0 mL, 17 mmol) was added dropwise. The resulting solution was stirred at 22 °C for 1 h and then at 100 °C for 15 h to induce the Claisen rearrangement. The product was then quenched in dilute HCl. The product was extracted into ether, and the combined ether layers were washed with water and brine and then dried (Na_2SO_4). After chromatography over alumina with hexanes the thiol (1.2 g, 52%) was isolated as an orange oil. ^1H NMR: δ 0.76–1.17 (m, 3 H), 1.17–2.48 (m, 5 H), 3.3–3.8 (m, 1 H), 5.63–5.90 (m, 2 H).

***cis*-5-Methyl-2-cyclohexen-1-yl Thiolobenzoate.** To a stirred solution of *cis*-5-methyl-2-cyclohexene-1-thiol (1.3 g, 10 mmol) in dichloromethane (50 mL) at −25 °C was added triethylamine (2.10 mL, 15 mmol) followed by benzoyl chloride (1.30 mL, 11 mmol). The resulting solution was allowed to slowly warm to 22 °C and was then stirred for 22 h. Removal of the solvents under reduced pressure left a residue which was suspended in hexanes and filtered. The precipitate was washed with hexanes, and then the combined filtrates were concentrated under reduced pressure to give a yellow oil. Chromatography over silica gel with hexane/benzene gave the thioloester (1.5 g, 53%) having an identical ^1H NMR with that observed for the catalytic rearrangement product.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

Registry No. $[PdCl_2(PhCN)_2]$, 14220-64-5; $rptCl_2(PhCN)_2]$, 14873-63-3; $[Pt(C_2H_4)(PPh_3)_2]$, 12120-15-9; $[Pd(PPh_3)_4]$, 14221-01-3; $[Rh(COD)Cl]_2$, 12092-47-6; $[Ir(COD)Cl]_2$, 12112-67-3; PhC(S)$OCH_2CH{=}CH_2$, 16315-94-9; PhC('S)$OCH_2CC{=}CHPh$, 102614-55-1; $HOCH_2CH{=}CHCH_3$, 6117-91-5; PhC(S)OR (R = 2-cyclohexenyl), 102614-56-2; PhC(S)OR (R = *cis*-5-methyl-2-cyclohexenyl, 102614-57-3; PhC(O)$SCH_2CH{=}CH_3$, 41820-25-1; PhC(O)$SCH(CH_3)CH{=}CH_2$, 102614-58-4; PhC(O)$SCH_2CH{=}CHCH_3$, 91142-35-7; PhC(O)$SCH_2CH{=}CHPh$, 102614-59-5; PhC(O)SCH(Ph)$CH{=}CH_2$, 102614-60-8; PhC(O)SR (R = 2-cyclohexenyl, 102614-61-9; PhC(O)SR (R = *cis*-5-methyl-2-cyclohexenyl), 102614-62-0; $HOCH_2CH{=}CH_2$, 107-18-6; $HOCH_2CH{=}CHPh$, 104-54-1; HOR (R = 2-cyclohexyl), 822-67-3; HOR (R = 5-methyl-2-cyclohexyl), 3718-55-6; HSR (R = *cis*-5-methyl-2-cyclohexyl), 102614-63-1; HOR (R = *cis*-5-methyl-2-cyclohexyl), 22049-46-3; PhC(O)Cl, 98-88-4; ((thiobenzoyl)thio)-acetic acid, 942-91-6.