(97 mg, 60.7%). Mp: 71–73 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.04 (t, 3 H, J = 7.6 Hz, CH_3), 1.59 (dq, 1 H, J = 15.2 Hz, 7.6 Hz, CH_2CH_3), 1.97 (dq, 1 H, J = 15.2 Hz, 7.6 Hz, CH_2CH_3), 3.00 (d, 1 H, J = 18.0 Hz, H–C(4)), 3.45 (d, 1 H, J = 2.6 Hz, H–C(3)), 3.58 (dd, 1 H, J = 18.0 Hz, 2.6 Hz, H–C(4)), 3.65 (s, 3 H, CO_2CH_3), 3.81 (s, 3 H, $ArOCH_3$), 4.24 (s, 1 H, H–C(1)), 6.75 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 6.79 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 7.13 (t, 1 H, J = 8.0 Hz, H–C(7)). IR ($CHCl_3$): 3020 (w), 1735 (s), 1600 (m), 1475 (m), 1260 (m) cm^{-1}. MS: m/z 262 (8), 174 (17), 115 (27), 57 (100). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.43; H, 6.87.

1-(Carbomethoxy)-2-ethyl-2-hydroxy-5-methoxy-1,2,3,4-tetrahydronaphthalene (2).[6] To a suspension of **26** (10 mg, 0.0381 mmol) and NaBr (47 mg, 0.457 mml) in CH_3CN (3 mL) was added a solution of $TsOH{\cdot}H_2O$ (7.25 mg, 0.0381 mmol) in CH_3CN (1 mL) at room temperature over a period of 2 h, and then the solution was stirred for 3 h. The resulting suspension was diluted with ether, washed with H_2O (3×) and brine (1×), and dried ($MgSO_4$). $MgSO_4$ was filtered off, and ether was evaporated in vacuo to give a colorless oil, which was dissolved in MeOH (2 mL). To this solution was added AcOH (0.02 mL). NH_4OAc (8.0 mg), and Pd–C (10%, 20 mg), and the mixture was stirred for 4 h under a hydrogen atmosphere. Pd–C was filtered off, and MeOH was evaporated in vacuo to afford a pale yellow oil, which was dissolved in ether, washed with H_2O (2×) and saturated $NaHCO_3$ aqueous solution (1×), and dried ($MgSO_4$). $MgSO_4$ was filtered off, and ether was evaporated in vacuo to give a colorless oil, which was purified by column chromatography (SiO_2, 5 g; hexane/ether 4:1). Compound **2** was obtained as a colorless oil (7.2 mg, 71.5%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.05 (t, 3 H, J = 7.4 Hz, CH_3), 1.58 (dq, 1 H, J = 14.8 Hz, 7.4 Hz, CH_2CH_3), 1.65 (s, 1 H, OH), 1.66 (dq, 1 H, J = 14.8 Hz, 7.4 Hz, CH_2CH_3), 1.81–1.87 (m, 1 H, H–C(3)), 2.29 (ddd, 1 H, J = 13.8 Hz, 10.6 Hz, 7.2 Hz, H–C(3)), 2.68 (ddd, 1 H, J = 18.4 Hz, 10.6 Hz, 7.2 Hz, H–C(4)), 2.91 (ddd, 1 H, J = 18.4 Hz, 7.2 Hz, 2.6 Hz, H–C(4)), 3.68 (s, 3 H, CO_2CH_3), 3.83 (s, 3 H, $ArOCH_3$), 3.85 (s, 1 H, H–C(1)), 6.74 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 6.78 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 7.13 (t, 1 H, J = 8.0 Hz, H–C(7)). IR ($CHCl_3$): 3600 (w), 3020 (m), 2950 (m), 1730 (s), 1590 (m), 1470 (s), 1260 (s), 910 (s) cm^{-1}. MS: m/z 264 (8), 246 (5), 232 (31), 187 (60), 175 (87), 57 (100). High-resolution MS for $C_{15}H_{20}O_4$: calcd 264.1362, obsd 264.1360.

Acknowledgment. Financial support of this work by the Swiss National Science Foundation is gratefully acknowledged. We thank Mr. J. P. Saulnier, Mr. A. Pinto, and Mrs. D. Clément for NMR and MS measurements and Mr. P. Romanens for technical assistance.

Registry No. 1, 16234-96-1; **2**, 110174-16-8; **5**, 89557-95-9; **7a**, 134594-18-6; **7b**, 134594-19-7; **7c**, 134594-20-0; **7d**, 134594-21-1; **8a**, 134594-22-2; **8b**, 56894-94-1; **8c**, 134594-23-3; **8d**, 35689-27-1; **9**, 27969-97-7; **10a**, 134594-24-4; **10b**, 134594-25-5; **10c**, 134594-26-6; **10d**, 134594-27-7; **11a**, 89568-53-6; **11b**, 134594-28-8; **11c**, 134594-29-9; **12**, 13307-75-0; **13**, 134594-30-2; **17a**, 134594-31-3; **17b**, 134594-32-4; **17c**, 134594-33-5; **17d**, 134594-34-6; **19a**, 134594-35-7; **19b**, 134594-37-9; **19c**, 134594-38-0; **19d**, 134594-36-8; **20**, 134625-82-4; **21**, 56894-99-6; **22**, 134627-06-8; **23**, 134627-05-7; **24** (isomer 1), 134594-39-1; **24** (isomer 2), 134627-07-9; **25**, 134594-40-4; **26**, 134594-41-5; $Cr(CO)_6$, 13007-92-6; $(MeS)_3CH$, 5418-86-0; 1-methoxynaphthalene, 2216-69-5; 1,3-dithiane, 505-23-7; 2-(trimethylsilyl)-1,3-dithiane, 13411-42-2.

Supplementary Material Available: Tables of crystal data, all atomic coordinates, displacement parameters, and bond distances and angles and an X-ray structure of **19a** with atom numbering (7 pages); a table of structure factors for **19a** (13 pages). Ordering information is given on any current masthead page.

Isomerization of a Vinylcyclobutene to a Cyclohexadiene: A Nickel(I)-Promoted Rearrangement

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The nickel-promoted isomerization of a 3-vinylcyclobutene to the corresponding 1,4-cyclohexadiene was studied by using $(PPh_3)_2Ni(C_2H_4)$ as the nickel source. Through the use of chemical and electrochemical experiments, it was determined that nickel(I) and not nickel(0) promotes this isomerization reaction at room temperature. The corresponding platinum–vinylcyclobutene complex 4 has been characterized by a single-crystal X-ray diffraction study: $C_{46}H_{42}O_4P_2Pt$, monoclinic, $P2_1/n$, with a = 10.774 (1) Å, b = 20.281 (4) Å, c = 18.297 (2) Å, β = 97.37 (1)°, Z = 4, $R(F)$ = 0.0378, and $R_w(F)$ = 0.0371.

The ability of transition metals to promote the rearrangement (isomerization) of organic molecules is well-known.[2] However, in spite of all these reactions, there are very few examples of a net 1,3-migration of an sp^2-hybridized carbon.[3] Recently, we have been studying such a reaction in the $Ni(CO)_4$-promoted ring expansion of a vinylcyclobutene (**1**) to a cyclohexadiene (**2**), which occurs in refluxing benzene or THF over a few hours.[4,5]

1 **2**

In an attempt to find a solid (nonvolatile) nickel(0) source that would promote the isomerization of **1** to **2**, we began investigating the use of $(PPh_3)_2Ni(C_2H_4)$.[6] In this

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(1) (a) University of Cincinnati. (b) Miami University. (c) Correspondences concerning the X-ray structure should be addressed to this author.

(2) For some leading references see: (a) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461. (b) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley-Interscience Publication: New York, 1986. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(3) Hughes, R. P.; Robinson, D. J. *Organometallics* **1989**, *8*, 1015 and references cited therein.

(4) DiFrancesco, D.; Pinhas, A. R. *J. Org. Chem.* **1986**, *51*, 2098.

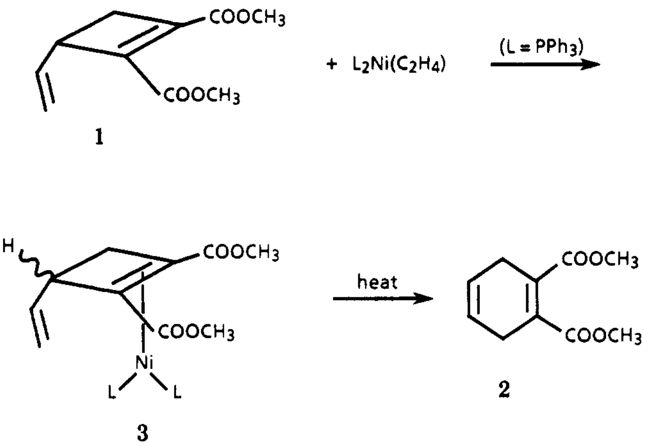
(5) Also see: DiFrancesco, D. M.S. Thesis, University of Cincinnati, 1988.

0276-7333/91/2310-2930$02.50/0

paper, we will show, as expected, that $(PPh_3)_2Ni(C_2H_4)$ does promote this rearrangement at elevated temperatures. More importantly, we will show that upon oxidation of the metal to the rare oxidation state nickel(I), the rearrangement proceeds smoothly at room temperature.

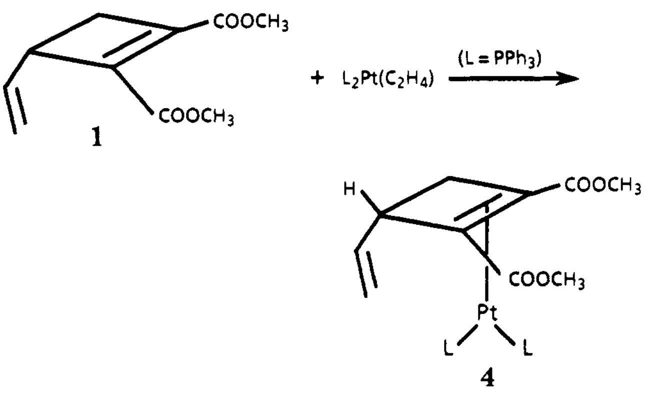
Results

Formation and Rearrangement of Olefin-Nickel Complex 3. When vinylcyclobutene 1 was mixed with $(PPh_3)_2Ni(C_2H_4)$ at room temperature in the glovebox, a new compound forms within minutes. On the basis of spectroscopic data, it was tentatively proposed that an approximately 50/50 mixture of two vinylcyclobutene-nickel bis(phosphine) complexes (3) was formed. In both, the nickel is coordinated to the electron-poor double bond of the ring, but one has the vinyl group syn to the metal and the other has the vinyl group anti. Unfortunately, the two isomers could not be separated from this mixture nor could a crystal suitable for an X-ray structure determination be obtained.



If kept under an inert atmosphere, this mixture is stable for extended periods of time at room temperature. However, upon heating in refluxing benzene or THF, vinylcyclobutene complexes 3 rearrange to cyclohexadiene 2, similar to the $Ni(CO)_4$ promoted rearrangement discussed above.

Formation of Olefin-Platinum Complex 4. Before proceeding any further in studying the chemistry of vinylcyclobutene-nickel complexes 3, it was hoped that the structure could be confirmed by X-ray analysis. Therefore, the reaction of 1 and $(PPh_3)_2Pt(C_2H_4)$ was run to obtain the platinum analogue (4). As expected, this compound is very stable (even in the presence of air) and forms very nice crystals. On the basis of spectroscopic data, the same type of metal olefin complex is formed with platinum as had been formed with nickel; however, whereas the nickel reaction generates two isomers, the platinum reaction generates only one.



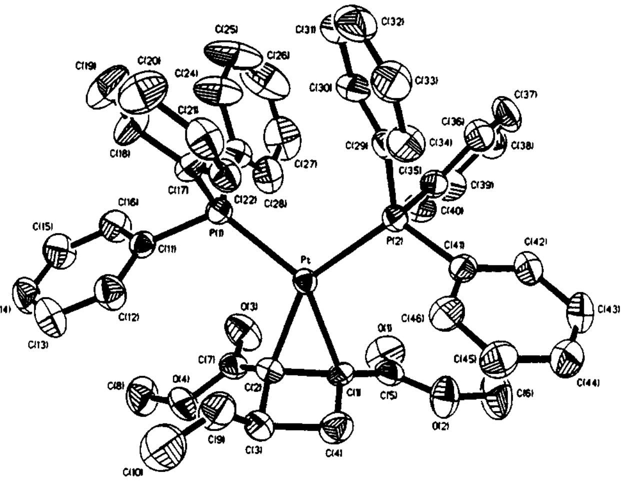


Figure 1. Thermal ellipsoid plot for platinum complex 4. Distances and angles are given in Table I.

Table I. Selected Distances (Å) and Angles (deg) for 4

Pt-P(1)	2.290 (2)	Pt-P(2)	2.294 (2)
Pt-C(1)	2.120 (6)	Pt-C(2)	2.097 (6)
P(1)-C(11)	1.833 (6)	P(1)-C(17)	1.824 (7)
P(1)-C(23)	1.832 (6)	P(2)-C(29)	1.824 (7)
P(2)-C(35)	1.832 (6)	P(2)-C(41)	1.833 (6)
O(1)-C(5)	1.203 (8)	O(2)-C(5)	1.353 (8)
O(2)-C(6)	1.439 (10)	O(3)-C(7)	1.210 (8)
O(4)-C(7)	1.346 (8)	O(4)-C(8)	1.446 (9)
C(1)-C(2)	1.486 (9)	C(1)-C(4)	1.535 (9)
C(1)-C(5)	1.451 (9)	C(2)-C(3)	1.561 (9)
C(2)-C(7)	1.466 (9)	C(3)-C(4)	1.557 (9)
C(3)-C(9)	1.489 (11)	C(9)-C(10)	1.296 (13)
Pt···C(9)	3.487 (8)	Pt···H(9)	3.088 (8)
Pt···O(1)	3.542 (5)	Pt···O(3)	3.341 (5)
Pt···H(4b)	3.157 (7)		
P(1)-Pt-P(2)	105.5 (1)	P(1)-Pt-C(1)	147.6 (2)
P(2)-Pt-C(1)	106.3 (2)	P(1)-Pt-C(2)	106.7 (2)
P(2)-Pt-C(2)	147.5 (2)	C(1)-Pt-C(2)	41.2 (2)
C(5)-O(2)-C(6)	116.0 (6)	C(7)-O(4)-C(8)	116.0 (5)
Pt-C(1)-C(2)	68.6 (3)	Pt-C(1)-C(4)	113.6 (4)
C(2)-C(1)-C(4)	92.2 (5)	Pt-C(1)-C(5)	114.9 (4)
C(2)-C(1)-C(5)	130.9 (5)	C(4)-C(1)-C(5)	123.9 (5)
Pt-C(2)-C(1)	70.2 (3)	Pt-C(2)-C(3)	114.6 (4)
C(1)-C(2)-C(3)	90.5 (4)	Pt-C(2)-C(7)	115.2 (4)
C(1)-C(2)-C(7)	130.0 (6)	C(3)-C(2)-C(7)	123.9 (5)
C(2)-C(3)-C(4)	88.5 (5)	C(2)-C(3)-C(9)	118.8 (6)
C(4)-C(3)-C(9)	115.3 (6)	C(1)-C(4)-C(3)	88.8 (5)
O(1)-C(5)-O(2)	122.4 (6)	O(1)-C(5)-C(1)	128.8 (6)
O(2)-C(5)-C(1)	108.8 (5)	O(3)-C(7)-O(4)	122.2 (6)
O(3)-C(7)-C(2)	127.3 (6)	O(4)-C(7)-C(2)	110.3 (5)
C(3)-C(9)-C(10)	127.2 (8)		
C(5),C(1),C(4); C(7),C(2),C(3)	74.3		
Pt,P(1),P(2); Pt,C(1),C(2)	6.4		

The molecular structure of 4 is shown in Figure 1 (selected distances and angles may be found in Table I). The observed coordination geometry of the metal is distorted trigonal planar with the platinum attached to two PPh_3 ligands and the double bond of the cyclobutene ring. Although the vinyl group is syn to the metal, based upon closest contacts for both the carbons and the hydrogens, it is too far to be involved in bonding interactions with the metal.

Oxidation of Nickel Complexes 3. As stated above, when left in the glovebox, the mixture of vinylcyclobutene-nickel complexes 3 is stable for extended periods

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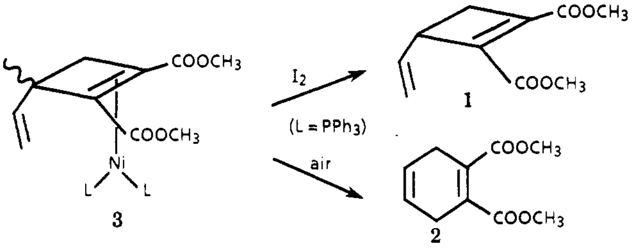
(6) $(PPh_3)_2Ni(C_2H_4)$ was synthesized by using a variation on the method of: Ashley-Smith, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 3019.

Table II. Cyclic Voltammetry Data[a]

substrate	$E_p$ox, V	$E_p$red, V	$E°'$, V
3	0.247		
Cp^*_2Fe	−0.078	−0.152	−0.12
Cp_2Fe	0.352	0.267	0.310
I_2[b]	0.49	0.34	0.42
$CpFe(C_5H_4COCH_3)$	0.584	0.483	0.533
$(C_5H_4COPh)_2Fe$	0.807	0.707	0.757
4	0.889		

[a] Cyclic voltammetry was performed at 22 °C under a nitrogen purge in freshly distilled THF/0.15 M tetrabutylammonium perchlorate. The substrate concentration was ca. 10^{-3} M. The reference electrode was saturated NaCl–SCE. Unless otherwise indicated, the working electrode was a Pt disk. The scan rate was 100 mV/s in each case. [b] A pseudoreversible process is observed. The reduction process is $^3/_2I_2 + e^- \rightarrow I_3^-$, the oxidation process is $I_3^- \rightarrow {}^3/_2I_2 + e^-$.

of time. The metal easily can be removed and vinylcyclobutene **1** reisolated upon exposure of **3** to I_2. However upon exposure of **3** to air, cyclohexadiene **2**, and not vinylcyclobutene **1**, is obtained. These results led to the possibility that the isomerization reaction could be facilitated not only by heating **3** but also by oxidizing it under mild conditions.



Oxidation Potential of 3 and Reduction Potentials of Various Oxidants. In an effort to predict which oxidizing agents would simply remove the metal from **3** to regenerate **1**, which would convert **3** into **2**, and which would have no effect on **3**, it was important to determine the oxidation potential of **3** and the reduction potentials of the various oxidants. As we had done previously for other nickel complexes,[7] this was accomplished by using cyclic voltammetry. The data may be found in Table II.

The ferrocene derivatives undergo reversible redox processes and, thus, generate classical cyclic voltammograms characteristic of reversible one-electron processes. Iodine undergoes a pseudoreversible redox process, as shown in Table II. On the other hand, the oxidation of nickel complex **3** at either a Pt or glassy-carbon electrode is irreversible. Although the oxidation wave at the Pt-disk electrode is well defined and the peak potential is only weakly dependent upon scan rate, verification that the peak potential is an accurate indication of the thermodynamic redox potential was desired. Accordingly, the effect of complex **3** on the electrochemistry of Cp^*_2Fe and Cp_2Fe was evaluated. Whereas **3** has no effect on the cyclic voltammetry of 10^{-3} M Cp^*_2Fe even when **3** is present in a 10-fold excess, the cyclic voltammogram of Cp_2Fe showed catalytic wave behavior with equimolar **3**. This catalytic wave behavior is characterized by an increase in the current associated with the oxidation of Cp_2Fe to Cp_2Fe^+ and a decrease in the current associated with the reduction of Cp_2Fe^+ to Cp_2Fe. This result indicates that complex **3** rapidly reduces Cp_2Fe^+, but not $Cp^*_2Fe^+$. The thermodynamic potential for the **3**/**3**$^+$ redox couple thus is in the range -0.12 V $< E°' <$ 0.31 V.

Table III. Product from the Reactions of 3 with Various Oxidants

oxidant	reaction prod	oxidant	reaction prod
$Cp^*_2Fe^+$	3	I_2 (1.5 equiv)	1
Cp_2Fe^+ (1 equiv)	2	$CpFe(C_5H_4COCH_3)^+$	1
Cp_2Fe^+ (4 equiv)	1	$(C_5H_4COPh)_2Fe^+$	1
I_2 (0.5 equiv)	1		

The cyclic voltammogram for $(PPh_3)_2NiBr_2$ in THF/0.15 M tetrabutylammonium perchlorate showed no reduction wave between 1.00 and −1.50 V vs NaCl–SCE. However, a broad oxidation wave (irreversible) is observed at E_p^{ox} = ca. 0.55 V with either a Pt-disk or glassy-carbon disk electrode. The reduction potential of the Ni(II) complex was indirectly determined to be between −0.12 and 0.31 V vs NaCl–SCE by observing its reaction with ferrocene derivatives—ferrocene itself is not oxidized in THF/0.15 M tetrabutylammonium perchlorate by excess $(PPh_3)_2NiBr_2$, whereas decamethylferrocene is rapidly oxidized by an excess of the Ni(II) complex to give pale blue $Cp^*_2Fe^+$ (detected both visually and by cyclic voltammetry).

Reaction of Nickel Complexes 3 with Various Oxidants. The reaction between nickel complexes **3** and each oxidant was run to determine the effect oxidant strength has on the rearrangement reaction. Unfortunately, in each of the reactions with ferrocenium, the large amount of ammonium salts present from the synthesis of the ferrocenium and the ferrocene obtained as a byproduct from the oxidation reaction obscured the peaks due to **1** and **2** in the gas chromatogram and made the analysis of the reaction mixture impossible. It was found that the entire solution could be quenched with I_2 and the organic compound (either **1** or **2**) could be quantitatively extracted into pentane, away from everything else. This made the product analysis straightforward but prevented a determination of whether the oxidant did not react with complex **3** or just removed the metal from **3**; in either of these cases, after I_2, only compound **1** would be observed. However, this latter information was obtained as described in the previous section of this manuscript—by cyclic voltammetry it can be determined whether or not a reaction has occurred between **3** and the oxidant but the product of that reaction cannot be determined. Taking these data together readily reveals the effect of each oxidant upon being allowed to react with complex **3** (Table III).

When the reaction between nickel complex **3** and $(PPh_3)_2NiBr_2$ was monitored by ^1H NMR spectroscopy, both **1** and **2**, and none of **3**, were initially observed, but within 4 h only **2** was observed. When the same reaction was monitored by IR spectroscopy, another compound, as well as **1** and **2**, was observed within 30 min, and only **2** was observed after 24 h. On the basis of its ester carbonyl stretch (1702 cm^{-1}), this third compound in the reaction mixture is most likely an olefin–nickel complex, which if it were paramagnetic, would not be observed by NMR spectroscopy.

Platinum complex **4**, as shown by the data in Table II, is much harder to oxidize than nickel complex **3**. Consistent with this result, **4** was found to be stable to all attempted oxidations by air, $(PPh_3)_2NiBr_2$, and Cp_2Fe^+. Upon reaction with I_2 or with the very powerful oxidant tris(4-bromophenyl)aminium hexachloroantimonate, cyclobutene **1** is generated.

Reaction of Nickel(I) with Compound 1. It was next decided to react a nickel(I) complex directly with vinylcyclobutene **1** rather than to first form a metal complex

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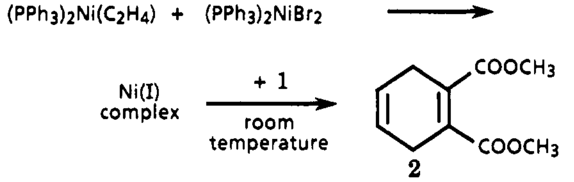
[7] Pinhas, A. R.; Hershberger, J. W. *Organometallics* **1990**, *9*, 2840.

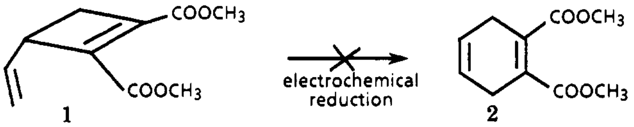
and then oxidize it. When $(PPh_3)_2Ni(C_2H_4)$ (E_p^{ox} = 0.18 V) and $(PPh_3)_2NiBr_2$(E_p^{red} = −0.57 V) were mixed together,



a new metal complex forms, as indicated by the appearance of a new peak in the cyclic voltammogram at E_p^{red} = −1.07 V.[8] On the basis of literature precedent, this is most likely a nickel(I) complex derived from the ready syn proportionation of nickel(0) and nickel(II).[9] When compound 1 was added to this nickel(I) complex at room temperature, the sole product obtained was cyclohexadiene 2.

When this reaction was monitored by ^1H NMR spectroscopy, cyclobutene 1 mainly is observed and then it slowly isomerizes to cyclohexadiene 2. When this reaction was monitored by IR spectroscopy, initially compound 1 is present and with time this isomerizes to compound 2. Unlike the reaction which starts with complex 3, here a peak at 1702 cm^{-1}, which is indicative of a complex with the ring double bond of 1 coordinated to the nickel, was not observed.

Electrochemical Reduction of Vinylcyclobutene 1. In an attempt to determine if the nickel(I) complex was simply reducing vinylcyclobutene 1 to its radical anion and if the radical anion is undergoing the rearrangement reaction, the electrochemistry of 1 was studied. By cyclic voltammetry, it was found that for 1 E_p^{red} = −1.87 V, which indicates that it is a very difficult compound to reduce.[10] Upon preparative scale reduction, 1 gives only unknown oligomeric products; no cyclohexadiene 2 was detected by gas chromatography.



Discussion

The reaction between vinylcyclobutene 1 and $(PPh_3)_2Ni(C_2H_4)$ was found to generate complex 3, which, in turn, could be converted to cyclohexadiene 2 thermally or oxidatively. Due to the thermodynamic redox potential of 3 (−0.12 V < $E^{\circ\prime}$ < 0.31 V), weak oxidants, for example $Cp^*_2Fe^+$($E^{\circ\prime}$ = −0.12 V), has no effect on the nickel complex. On the other hand, more potent oxidants, for example Cp_2Fe^+ ($E^{\circ\prime}$, = 0.31 V) and $(PPh_3)_2NiBr_2$ (−0.12 V < $E^{\circ\prime}$ < 0.31 V), oxidize the metal to Ni(I), causing the isomerization reaction to occur. Very strong oxidants, for example $CpFe(C_5H_4COCH_3)^+$ ($E^{\circ\prime}$ = 0.53 V) and $(C_5H_4COPh)_2Fe^+$ ($E^{\circ\prime}$ = 0.76 V), most likely oxidize the metal all the way to Ni(II), and the nickel then simply is removed from the complex. Note that if an excess of Cp_2Fe^+ is used, the metal is simply removed from complexes 3. In the case of I_2, it is likely that a two-electron oxidation occurs on the basis of the observation that the oxidation of 3 with 0.5 equiv of I_2 or 1.5 equiv of I_2 generates vinylcyclobutene 1.

There are other indications that for the isomerization reaction to occur at room temperature requires the nickel(0) to be oxidized to nickel(I) and not to the much more common oxidation state nickel(II). For example, compound 1 is stable in the presence of the nickel(II) complex $(PPh_3)_2NiBr_2$. In addition, when $(PPh_3)_2Ni(C_2H_4)$ and $(PPh_3)_2NiBr_2$ were first allowed to react, they generated a new complex, which has been previously shown to contain nickel(I),[9] and this complex very nicely isomerizes 1 to 2. Although this latter reaction is slow, it is catalytic in metal complex—addition of about 0.1 equiv of $(PPh_3)_2Ni(C_2H_4)$ and $(PPh_3)_2NiBr_2$ promotes about 90% conversion of 1 to 2 after 10 days. The exact role the nickel(I) plays in this isomerization reaction is not known because no metal complex intermediate between complex 3 and the final organic product 2 has been well characterized. One speculation is that the electron-rich Ni(0) will coordinate only to the electron-poor double bond of the ring, at room temperature. However, upon oxidation, the metal now will coordinate with the more electron-rich vinyl group, and it is this vinyl–metal complex[3] that is an essential intermediate in the isomerization reaction.

Conclusion

The isomerization of vinylcyclobutene 1 to cyclohexadiene 2 is promoted by nickel(0) in refluxing THF or benzene, or by nickel(I) at room temperature. Under the former set of conditions, the reaction is stoichiometric in nickel; however, under the latter set of conditions, it is catalytic but very slow.

Experimental Section

General Considerations. All reactions were carried out in oven-dried glassware, under an argon atmosphere or in a drybox, using freshly distilled solvents. Gas chromatography conditions, mass spectral conditions, and the complete characterization of compounds 1 and 2 were reported previously.[4,5] All IR spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer using KBr cells. All NMR spectra were recorded on a Nicolet NT-300 or a Bruker 250 MHz spectrometer and referenced to TMS at 0.00 ppm.

Preparation of $(PPh_3)_2Ni(C_2H_4)$.[6] To diethylaluminum ethoxide (3.88 mL, 6.2 mmol) was added dropwise, at ice bath temperature, degassed absolute ethanol (0.74 mL, 12.4 mmol), and the reaction mixture was allowed to stir at 0 °C for 20–25 min in order to form ethylaluminum diethoxide. To a mixture of anhydrous nickel acetylacetonate (0.5 g, 1.82 mmol) and triphenylphosphine (1.02 g, 3.9 mmol) in ether (10 mL), saturated with ethylene gas, was added dropwise at 0 °C the freshly prepared ethylaluminum diethoxide. Ethylene gas was bubbled into the ether solution throughout the addition. The reaction mixture was allowed to stir at 0 °C for 12–13 h and then at room temperature for 10–12 h. At the end of this period, the yellow precipitate that formed was taken into the drybox. Inside the drybox it was suction-filtered and washed with ether to give $(PPh_3)_2Ni(C_2H_4)$ as a yellow solid. $(PPh_3)_2Ni(C_2H_4)$ must be used in the drybox because it is very air sensitive. ^1H NMR (C_6D_6), δ: 2.63 (s, 4 H), 6.99 (br s, 18 H), 7.53 (br s, 12 H).

Preparation of Vinylcyclobutene 1. Dimethyl 1,2-dichloro-3-vinylcyclobutane-1,2-dicarboxylate was synthesized as described in ref 4. To this dichlorovinylcyclobutane (0.25 g, 0.94 mmol) dissolved in degassed THF (60 mL) was added, in the drybox, $(PPh_3)_2Ni(C_2H_4)$ (0.74 g, 1.2 mmol). The reaction was allowed to stir at room temperature for 1 h. The mixture was then removed from the drybox, and the solvent was removed by vacuum distillation. Then, 2–3 mL of hexane were added to the residue. The solid that formed was filtered, and the hexane solution was concentrated. Following this, THF (2 mL) and methyl iodide (0.60 g, 4.0 mmol) were added. The mixture was allowed to stir at room temperature for 30 min. The white precipitate ($Ph_3PCH_3^+I^-$) was filtered. After the solvent was removed from the filtrate, the residue was purified by using a short Florisil column, eluting with 33% THF in petroleum ether. A

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[8] The redox processes are all irreversible, and the peaks are broad and poorly defined. Thus, the potentials given in the text cannot be taken as a good measure of the thermodynamic redox potentials. The potentials were obtained at a glassy-carbon electrode with a scan rate of 200 mV/s.

[9] (a) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319. (b) Nilges, M. J.; Barefield, E. K.; Belford, R. L.; Davis, P. H. *ibid.* **1977**, *99*, 755. (c) Heimbach, P. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 648.

[10] Yeh, L.-S. R.; Bard, A.J. *J. Electrochem. Soc.* **1977**, *124*, 189, 355.

pale yellow oil for compound 1 was obtained (0.08 g, 0.4 mmol, 40% yield).

Formation and Thermal Rearrangement of Nickel Complex 3. To 1 (0.08 g, 0.4 mmol) dissolved in degassed THF (5 mL) was added, in the drybox, $(PPh_3)_2Ni(C_2H_4)$ (0.32 g, 0.52 mmol). The reaction was monitored by IR spectroscopy. The ester carbonyl stretches (all strong in intensity) for 1 at 1740 and 1724 cm^{-1} immediately shifted to 1701 cm^{-1}. The new carbonyl stretch for the nickel complex remained unchanged as long as the reaction mixture was left in the drybox.

Compound 1 (0.031 g, 0.16 mmol) and $(PPh_3)_2Ni(C_2H_4)$ (0.11 g, 0.18 mmol) were dissolved in benzene-d_6 for ^1H and ^{13}C NMR spectroscopic analyses. In the ^1H NMR spectrum, the two singlets (3.38 and 3.39 ppm) for the methyl esters of 1 are replaced by two sets of singlets. One set is at 2.96 and 2.98 ppm, and the other set is at 3.11 and 3.15 ppm. (These peaks have the same chemical shifts at both 80 and 300 MHz.) In addition, the olefin methine peak moves downfield by 0.5–0.8 ppm (6.15–6.25 and 6.45–6.55 ppm). The ^{13}C NMR spectrum of nickel complex 3 has peaks at δ 32.6, 33.9, 42.0, 44.4, 49.6, 50.0, 50.2, 59.0 (d, J = 20.6 Hz), 59.7 (d, J = 21.4 Hz), 66.2 (d, J = 25.6 Hz), 66.8 (d, J = 22.7 Hz), 112.7, 112.8, 142.1, 144.8, 171.3, 172.7, and 173.1. (A large number of aromatic resonances due to phenyl groups of 3 are between 129.1 and 135.6 ppm).

Nickel complex 3 prepared in a well-capped NMR tube was allowed to stand in an oil bath (76 °C) for 6 h, and the reaction occasionally was monitored by ^1H NMR spectroscopy during this period. A substantial amount of cyclohexadiene 2 was observed along with nickel complex 3 within 2 h, and the amount of 2 slowly increased. At the end of 6 h, 50% of 3 had converted to 2, as determined by the ratio of methyl peaks of 3 and 2 in the ^1H NMR spectrum.

Formation of Platinum Complex 4. Into a test tube were added 1 (0.06 g, 0.3 mmol), THF (1.5 mL), and $(PPh_3)_2Pt(C_2H_4)$ (0.23 g, 0.31 mmol) in the drybox. The mixture was allowed to stand at room temperature for 1 h, and then petroleum ether (6 mL) was slowly added. The test tube was capped, and the mixture was allowed to stand at room temperature for 48 h. At the end of this period, the crystals formed were isolated by decanting the solvent. ^1H NMR (C_6D_6), δ: 2.21–2.28 (m, 1 H), 3.07 (s, 3 H), 3.11 (s, 3 H), 3.16–3.23 (m, 1 H), 4.03–4.13 (m, 1 H), 4.83 (dd, J = 2.1, 10.2 Hz, 1 H), 5.23 (dd, J = 2.1, 17.1 Hz, 1 H), 6.25 (ddd, J = 8.7, 9.9, 17.1 Hz, 1 H), 6.94–6.96 (m, 18 H), 7.42–7.47 (m, 6 H), 7.51–7.57 (m, 6 H). ^{13}C NMR (C_6D_6), δ: 34.2, 42.2, 50.2, 50.4, 60.0 (d, J = 43.7 Hz), 66.6 (d, J = 38.8 Hz), 112.5, 146.2, 146.2 (d, J = 41.3 Hz), 172.3, 172.5 (plus a large number of aromatic resonances). IR (THF): 3053 (w), 2916 (vs), 1698 (vs), 1480 (s), 1435 (vs), 1339 (m), 1267 (s) cm^{-1}.

X-ray Crystal Structure of 4. A pale tan crystal of 4 ($C_{46}H_{42}O_4P_2Pt$) approximately 0.10 × 0.22 × 0.28 mm in size was isolated, mounted on a glass fiber with epoxy cement, and transferred to a Siemens R3m/V four-circle diffractometer for characterization and data collection.

Unit cell parameters were determined from the angular settings of 25 well-centered reflections ($21 < 2\theta < 30°$); a = 10.774 (1) Å, b = 20.281 (4) Å, c = 18.297 (2) Å, β = 97.37 (1)°, and V = 3965 (1) $Å^3$. Axial photographs and a limited search through an octant of reciprocal space revealed systematic absences and symmetry consistent with the monoclinic space group $P2_1/n$.

One quadrant of data ($\pm h,+k,+l$) was collected in the 2θ–θ scan mode with 2θ ranging from 3.0 to 55.0°. Scan speeds varied from 4.0 up to 8.0°/min. A total of 9688 reflections were measured and corrected for Lorentz–polarization and absorption effects (empirical correction based on five azimuthal reflections).

The minimum and maximum drift corrections (based on a set of three standards measured for every 37 reflections) were 0.9959 and 1.0282, and the minimum and maximum transmission factors were 0.4662 and 0.9614, respectively. Data processing yielded 9145 unique reflections of which 5653 had $F > 6\sigma(F)$ with R(int) = 0.0283 for the averaging of equivalent reflections.

The structure was successfully solved by heavy-atom methods (XS:PATT) in the monoclinic space group $P2_1/n$ (No. 14) and refined by full-matrix least squares. The non-hydrogen atoms were refined with anisotropic temperature parameters, hydrogen atoms were allowed to ride on their respective carbons [C–H = 0.96 Å, U(H) = 0.08 $Å^2$], no extinction correction was made, and a weighting scheme based on $\sigma(F)$ was employed. The final residuals were $R(F)$ = 0.0378 and $R_w(F)$ = 0.0371 with a value of 1.15 for the goodness-of-fit. The largest and mean |shift/esd| in the final cycle were 0.001 and 0.000, and the minimum and maximum excursions in the final difference map were −1.52 and 1.03 $e^-/Å^3$, respectively. The three largest peaks on the final difference map corresponded to 1.03, 0.94, and 0.91 $e^-/Å^3$ and were situated 0.88, 0.94, and 0.97 Å from the platinum atom.

Cyclic Voltammetry. Cyclic voltammetry was performed with a BAS-100 electrochemical analyzer employing a Pt-disk working electrode and, in the same compartment, a Pt-wire counter electrode. The solvent was THF with 0.2 M tetrabutylammonium perchlorate. The reference electrode (saturated NaCl–SCE) was immersed in a reservoir of solvent and electrolyte, which was isolated from the working compartment by a cracked-glass junction designed to minimize solution transfer. The cell was oven dried and cooled under a stream of argon prior to each use. An argon atmosphere was maintained over the working solution at all times.

Cyclic voltammograms were obtained at low substrate concentrations, typically 5×10^{-4} M, to minimize the *ir* drop error inherent in a low-conductivity nonaqueous medium. Low substrate concentrations were required to minimize fouling of the working electrode. All peak potentials are reported relative to ferrocene (Cp_2Fe/Cp_2Fe^+ couple is taken to have $E°'$ equal to 0.31 V).[11]

Preparation of Ferrocenium Tetrafluoroborate Salts. The ferrocene, decamethylferrocene, acetylferrocene, or 1,1′-dibenzoylferrocene (100–500 mg) was dissolved in 80 mL of acetonitrile containing 0.1 M of either tetrabutylammonium tetrafluoroborate or tetraethylammonium tetrafluoroborate. The solution was placed in the working compartment of a three-compartment preparative cell equipped with a Pt-gauze working electrode. Counter and reference electrode compartments were separated from the working solution by a fine glass frit or a cracked-glass junction. The controlled-potential oxidation was performed at approximately 200 mV positive of the $E°'$ for the ferrocene derivative. Current was discontinued after the desired number of coulombs had passed through the cell. The working solution was transferred to a Schlenk flask, and the acetonitrile was removed under vacuum. The dry salt mixture was completely stable in the cases of ferrocenium tetrafluoroborate and decamethylferrocenium tetrafluoroborate. This was demonstrated by reconstituting the working solution with acetonitrile and performing an exhaustive reduction 200 mV negative of $E°'$. More than 90% of the expected cathodic current was passed in these cases, and a clear, homogeneous solution of the ferrocene derivative was obtained. Some small amount of decomposition occurs for the acetylferrocenium ion. This is evidenced by the passage of slightly more than 100% of the expected cathodic current through reconstituted solutions of this species. Furthermore, the solution resulting from exhaustive reduction contains traces of insoluble precipitate. The 1,1′-dibenzoylferrocenium species showed marked instability. Reconstituted solutions of this ion only permitted the passage of ca. 60% of the expected cathodic current. The resulting solution contained insoluble precipitate and a noticeable brown discoloration.

Reaction of 1 with $(PPh_3)_2NiBr_2$. To 1 (0.05 g, 0.3 mmol) dissolved in 2 mL of THF was added 0.20 g (0.30 mmol) of $(PPh_3)_2NiBr_2$. The reaction mixture was allowed to stir at room temperature overnight. At the end of this period, only vinylcyclobutene 1 was observed by gas chromatography and by IR spectroscopy.

Ring Expansion of 3 upon Exposure to Air. To 1 (0.051 g, 0.26 mmol) dissolved in THF (10 mL) was added $(PPh_3)_2Ni(C_2H_4)$ (0.19 g, 0.31 mmol) in the drybox. The mixture was allowed to stir at room temperature for 2–3 h. Then the reaction was worked-up in a manner similar to that used in the dechlorination of dichlorovinylcyclobutane with $(PPh_3)_2Ni(C_2H_4)$. A pale yellow oil for compound 2 was obtained (0.02 g, 0.1 mmol, 40% yield), as determined by ^1H and ^{13}C NMR spectroscopy and gas chromatography.

Reaction between 3 and Iodine. To 1 (0.05 g, 0.26 mmol)

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(11) Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* 1983, *2*, 1470.

dissolved in THF (4 mL) was added $(PPh_3)_2Ni(C_2H_4)$ (0.16 g, 0.26 mmol) in the drybox. The mixture was allowed to stir for 15 min, and then iodine (0.03 g, 0.12 mmol) was added. After 25 min, vinylcyclobutene 1 was the only compound observed by gas chromatography.

In a second experiment, to 1 (0.15 g, 0.76 mmol) dissolved in THF (4 mL) was added $(PPh_3)_2Ni(C_2H_4)$ (0.70 g, 1.0 mmol) in the drybox. The mixture was allowed to stir for 3 h and then iodine (0.29 g, 1.1 mmol) was added. After 20 min, the reaction was monitored by IR spectroscopy. The ester carbonyl stretches were observed at 1740 and 1724 cm^{-1}. (Both peaks were very intense.) After a workup in the usual manner, only vinylcyclobutene 1 was recovered.

Ring Expansion of 3 with $(PPh_3)_2NiBr_2$. To 1 (0.1 g, 0.5 mmol) dissolved in THF (2.5 mL) was added $(PPh_3)_2Ni(C_2H_4)$ (0.47 g, 0.77 mmol). The mixture was allowed to stir for 2–3 h in the drybox, and then $(PPh_3)_2NiBr_2$ (0.57 g, 0.77 mmol) was added. After 1 h, the reaction was monitored by IR spectroscopy. Carbonyl stretches were observed at 1737, 1724, and 1702 cm^{-1}. (All peaks were strong in intensity.) After 24 h, the reaction again was monitored, but this time the only carbonyl stretch observed was at 1724 cm^{-1}. When this reaction was injected into the gas chromatograph without allowing the solution to come into contact with air, only 2 was observed. After a workup in the usual manner, the product was exclusively cyclohexadiene 2.

The reaction of 3 with $(PPh_3)_2NiBr_2$ also was monitored by ^1H NMR spectroscopy. Within 30 min of adding $(PPh_3)_2NiBr_2$ to nickel complex 3, both cyclohexadiene 2 and vinylcyclobutene 1 were observed, in a ratio of 1:2 based on the integration of the methyl groups. After 3 h, cyclohexadiene 2 mainly was observed.

Ring Expansion of 3 with $Cp_2Fe^+BF_4^-$. To ferrocenium tetrafluoroborate (0.1 mmol) dissolved in THF (5 mL) was added, in the drybox, 3 (0.1 mmol) prepared as described above [0.02 g of 1 and 0.06 g of $(PPh_3)_2Ni(C_2H_4)$]. The reaction mixture was allowed to stir for 1–2 h, and then iodine (0.03 g, 0.1 mmol) was added. After 30 min, the reaction mixture was removed from the drybox and hexane (10 mL) was added. The resulting precipitate was filtered. The filtrate was washed two times with a saturated sodium bisulfite solution, dried with potassium carbonate, and concentrated. Only cyclohexadiene 2 was observed by gas chromatography.

In a second experiment, to ferrocenium tetrafluoroborate (2.01 mmol) dissolved in THF (10 mL) was added, in the drybox, 3 (0.5 mmol), prepared as described above [0.10 g of 1 and 0.30 g of $(PPh_3)_2Ni(C_2H_4)$]. The reaction mixture was allowed to stir for 1.3 h, and then iodine (0.13 g, 0.5 mmol) was added. After 30 min, the reaction solution was worked-up as described above. Only vinylcyclobutene 1 was obtained, as determined by gas chromatography.

Reaction between 3 and $Cp^*{}_2Fe^+BF_4^-$. To decamethylferrocenium tetrafluoroborate (0.08 mmol) dissolved in THF (5 mL) was added 3 (0.08 mmol) prepared as described above [0.016 g of 1 and 0.05 g of $(PPh_3)_2Ni(C_2H_4)$]. The reaction mixture was allowed to stir overnight. At the end of this time, iodine (0.02 g, 0.08 mmol) was added to the mixture with stirring. After 30 min, the reaction was worked-up in a manner similar to that used in the reaction of 3 with the ferrocenium salt. Only 1 was recovered, as determined by gas chromatography.

Reaction between 3 and $CpFe(C_5H_4COCH_3)^+BF_4^-$. To acetylferrocenium tetrafluoroborate (0.37 mmol) dissolved in THF (10 mL) was added 3 (0.37 mmol) prepared as described above [0.072 g of 1 and 0.226 g of $(PPh_3)_2Ni(C_2H_4)$]. The reaction mixture was allowed to stir for 1 $^1/_3$ h. Then the reaction was worked-up by using iodine (0.094 g, 0.37 mmol) in the usual manner. Only cyclobutene 1 was reisolated, as determined by gas chromatography.

Reaction between 3 and $(C_5H_4COPh)_2Fe^+BF_4^-$. To 1,1'-dibenzoylferrocenium tetrafluoroborate (0.26 mmol) dissolved in THF (5 mL) was added 3 (0.26 mmol) prepared as described above [0.050 g of 1 and 0.16 g of $(PPh_3)_2Ni(C_2H_4)$]. The reaction mixture was allowed to stir at room temperature for 1.5 h. At the end of this time, iodine (0.14 g, 0.55 mmol) was added to the mixture with stirring. After 30 min, the reaction was worked-up in a manner similar to that used in the reaction of 3 with the ferrocenium salt. Only 1 was recovered as determined by gas chromatography and GC/MS. Similarly, a reaction between 3 and the 1,1'-dibenzoylferrocenium salt was worked-up without using iodine, and again only compound 1 was obtained.

Ring Expansion of Compound 1 with the Nickel(I) Complex. To $(PPh_3)_2Ni(C_2H_4)$ (0.11 g, 0.18 mmol) dissolved in benzene-d_6 was added $(PPh_3)_2NiBr_2$ (0.14 g, 0.19 mmol). The mixture was allowed to stir at room temperature for 30 min and then 1 (0.031 g, 0.16 mmol) was added. The reaction was monitored by ^1H NMR spectroscopy. Within 30 min of adding 1 to the nickel(I) complex, a small amount of cyclohexadiene 2 was observed along with 1. The amount of 2 increased over time and only 2 was observed after 48 h. The reaction of 1 with the nickel(I) complex in THF also was monitored by IR spectroscopy and gas chromatography. The ester carbonyl stretches initially were observed at 1740 and 1724 cm^{-1}, with the peak at 1724 cm^{-1} becoming more intense over time. After 48 h, the only carbonyl stretch observed was at 1724 cm^{-1}. Similarly, both 1 and 2 were observed by gas chromatography within a few hours of adding 1 to the nickel(I) complex, and only 2 was observed after 48 h.

This reaction was also attempted by using a catalytic amount of the nickel(I) complex—$(PPh_3)_2Ni(C_2H_4)$ (0.014 g, 0.023 mmol) and $(PPh_3)_2NiBr_2$ (0.016 g, 0.022 mmol) were dissolved in 1 mL of THF. The mixture was allowed to stir at room temperature for 20 min and then 1 (0.035 g, 0.18 mmol) was added. The reaction was monitored by gas chromatography. After 5 days, 1 and 2 were observed in a ratio of 2 to 3. After 10 days, 1 and 2 were observed in a ratio of 1 to 9.

Electrochemical Reduction of 1. A three-compartment preparative cell with a 5-mL working solution capacity was used. The working electrode was a glassy-carbon rod and the counter electrode was platinum foil. To 5 mL of a THF solution which was 0.2 M in tetrabutylammonium tetrafluoroborate was added 30 ng (2×10^{-7} mmol) of vinylcyclobutene 1. This solution was reduced at −1.70 V (vs NaCl–SCE) for 5.0 C with a current of approximately 1.2 mA. Gas chromatographic analysis of the resulting mixture showed only high molecular weight products, i.e., no cyclohexadiene 2 was obtained.

Reaction between 4 and $(PPh_3)_2NiBr_2$. To 4 (0.2 mmol) generated by combining 1 (0.04 g) and $(PPh_3)_2Pt(C_2H_4)$ (0.17 g) in benzene-d_6 (3 mL) was added $(PPh_3)_2NiBr_2$ (0.17 g, 0.20 mmol). The reaction mixture was allowed to stand at room temperature overnight. Then, the reaction was monitored by ^1H NMR spectroscopy. Only 4 was observed.

Reaction between 4 and $Cp_2Fe^+BF_4^-$. To ferrocenium tetrafluoroborate (0.09 mmol) dissolved in THF (5 mL) was added 4 (0.09 mmol) generated by combining 1 (0.014 g) and $(PPh_3)_2Pt(C_2H_4)$ (0.07 g) in THF (2 mL). This mixture was allowed to stir overnight. Then, iodine (0.024 g, 0.090 mmol) was added to the reaction mixture. After 30 min, solvent was removed and petroleum ether was added to the residue. The precipitate that formed was filtered, and the petroleum ether solution was washed with a saturated sodium bisulfite solution. The petroleum ether layer was dried with potassium carbonate and concentrated. Compound 1 was recovered, as determined by gas chromatography.

Reaction between 4 and Iodine. To 4 (0.2 mmol) prepared by combining 1 (0.04 g) and $(PPh_3)_2Pt(C_2H_4)$ (0.17 g) in THF (2 mL) was added iodine (0.06 g, 0.2 mmol) with stirring. After 30 min, the reaction was monitored by gas chromatography. (As soon as iodine was added to 4, a precipitate formed.) Only 1 was observed by gas chromatography.

Reaction between 4 and $(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$. To 4 (0.1 mmol), prepared by combining 0.02 g of 1 and 0.09 g of $(PPh_3)_2Pt(C_2H_4)$ in CH_2Cl_2 (2 mL), was added 0.12 g (0.15 mmol) of $(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$. As soon as the $(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$ was added to 4, a precipitate formed. The reaction mixture was allowed to stir for 1 h. At the end of this period, only 1 was observed by gas chromatography.

Treatment of 4 with Heat. Into an NMR tube were added 1 (0.04 g, 0.2 mmol), benzene-d_6 (1 mL), and $(PPh_3)_2Pt(C_2H_4)$ (0.17 g, 0.23 mmol). The mixture was allowed to stand in an oil bath (70 °C) overnight. At the end of this time, only 4 was observed by ^1H NMR spectroscopy.

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Supplementary Material Available: Textual presentation of the X-ray analysis, tables of structure determination data, atomic coordinates, thermal parameters, bond distances and angles, dihedral, vector–plane, and torsion angles, least-squares planes, and nonbonded distances, and ORTEP diagrams for **4** (22 pages); a listing of structure factors for **4** (33 pages). Ordering information is given on any current masthead page.

Cycloaddition Reactions of Transition-Metal 2-Alkynyl Complexes with a Disulfur Monoxide Source. Transition-Metal-Mediated Syntheses of Five-Membered-Ring Thiosulfinate Esters

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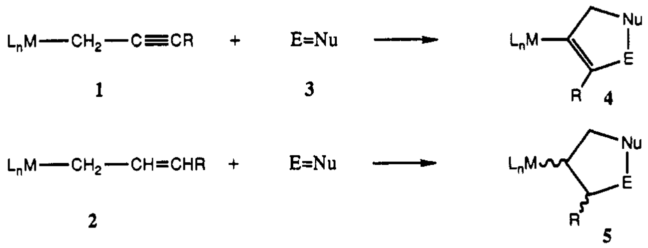
Reactions of cyclopentadienyl- and (pentamethylcyclopentadienyl)iron dicarbonyl 2-alkynyl complexes as well as cyclopentadienylmolybdenum tricarbonyl 2-alkynyl complexes with 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide (**37**) have been shown to yield transition-metal-substituted five-membered-ring thiosulfinate esters in moderate to excellent yield. The transition metal can subsequently be cleaved from these cyclic metallothiosulfinate esters with ceric ammonium nitrate to yield carboethoxy-substituted five-membered-ring thiosulfinate esters. Reactions of chiral, racemic 2-alkynyl complexes with **37** also yield five-membered-ring thiosulfinate esters as the kinetic products of cyclization. The diastereoselectivity of these cycloadditions can be altered by the addition of $MgBr_2$.

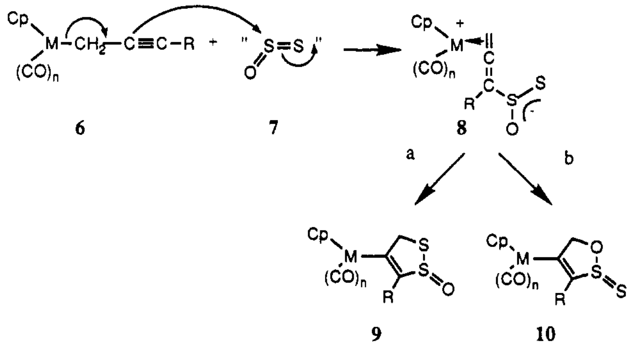
Introduction

Cycloaddition reactions between transition-metal 2-alkynyl (**1**) and η^1-allyl complexes (**2**) and unsaturated electrophilic reagents (**3**) have been studied in detail over the last 20 years by a number of research groups.[1] These 3+2 cycloaddition reactions have been shown to yield transition-metal-substituted five-membered-ring heterocycles and carbacycles (**4**, **5**) (Scheme I), and they offer organic chemists alternative approaches to these ring systems when the metal is subsequently cleaved from the ring.[1a,c–h,2]

Scheme I



Scheme II



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[1] (a) Rosenblum, M.; Watkins, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 6316. (b) Lee, G.-H.; Peng, S.-M.; Yang, G.-M.; Lush, S.-F.; Lin, R.-S. *Organometallics* **1989**, *8*, 1106. (c) Rosenblum, M. *J. Organomet. Chem.* **1986**, *300*, 191. (d) Hu, Y.-R.; Leung, T. W., Su, S.-C. H.; Wojcicki, A.; Calligaris, M.; Nardin, G. *Organometallics* **1985**, *4*, 1001. (e) Baker, R.; Keen, R. B.; Morris, M. D.; Turner, R. W. *J. Chem. Soc., Chem. Commun.* **1984**, 987. (f) Baker, R.; Rao, V. B.; Erdik, E. *J. Organomet. Chem.* **1983**, *243*, 451. (g) Abram, T. S.; Baker, R.; Exon, C. M.; Rao, V. B. *J. Chem. Soc., Perkin Trans. I* **1982**, 285, 295, 301. (h) Bucheister, A.; Klemarczyk, P.; Rosenblum, M. *Organometallics* **1982**, *1*, 1679. (i) Bell, P.; Wojcicki, A. *Inorg. Chem.* **1981**, *20*, 1585. (j) Rosenblum, M.; Waterman, P. S. *J. Organomet. Chem.* **1980**, *187*, 267. (k) Chen, L. S.; Su, S. R.; Wojcicki, A. *Inorg. Chim. Acta* **1978**, *27*, 79. (l) Downs, R. L.; Wojcicki, A. *Inorg. Chim. Acta* **1978**, *27*, 91. (m) Williams, J. P.; Wojcicki, A. *Inorg. Chem.* **1977**, *16*, 2506. (n) Chen, L. S.; Lichtenberg, D. W.; Robinson, P. W.; Yamamoto, Y.; Wojcicki, A. *Inorg. Chim. Acta* **1977**, *25*, 165. (o) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S., Rosau, A., Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495. (p) Cutler, A.; Ehntholt, D.; Lennon, P.; Nicholas, K.; Marten, D. F.; Madhavarao, M.; Raghu, S.; Rosan, A.; Rosenblum, M. *J. Am. Chem. Soc.* **1975**, *97*, 3149. (q) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122 and references therein. (r) Chen, L. S.; Su, S. R.; Wojcicki, A. *J. Am. Chem. Soc.* **1974**, *96*, 5655. (s) Wojcicki, A. *Adv. Organomet. Chem.* **1974**, *12*, 31 and references therein. (t) Wojcicki, A. *Ann. N.Y. Acad. Sci.* **1974**, *239*, 100 and references therein.

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