# A Novel $PtCl_4$-Catalyzed Cyclorearrangement of Allyl Propynyl Ethers to 3-Oxabicyclo[4.1.0]heptenes†

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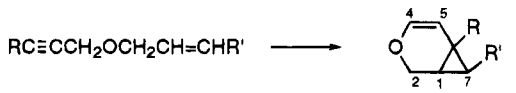
*Received March 15, 1995*®

Allyl propynyl ethers of general formula $RC{\equiv}CCH_2OCH_2CH{=}CHR'$ (**1**) undergo cyclorearrangement to 3-oxabicyclo[4.1.0]hept-4-enes (**2**) in oxygen-free benzene upon brief treatment at room temperature with catalytic amount of $PtCl_4$. The transformation of **1** to **2** is assumed to involve platinum–allene intermediates. The structure of 7-(1-naphthyl)-6-phenyl-3-oxabicyclo[4.1.0]hept-4-ene (**2c**) has been determined by X-ray diffraction analysis. The naphthyl and phenyl groups were shown to be oriented cis to each other. In the presence of $[(CO_2)Rh(\mu\text{-}Cl)]_2$ the oxabicycloheptenes **2** undergo cyclopropane-ring cleavage. 6,7-Diphenyl-3-oxabicyclo[4.1.0]hept-4-ene (**2b**) forms the rhodocyclic complex **3b**. In the absence of air, the oxygen-free analog of **1a**, $PhC{\equiv}C(CH_2)_3CH{=}CH_2$ (**4**), rearranges to the unstable 7-phenylbicyclo[3.2.0]hept-1(7)-ene (**5**), which can be trapped by oxygen as stable 2-(2-oxo-2-phenylethyl)cyclopentanone (**6**).

Derivatives of 3-oxabicyclo[4.1.0]hept-4-en-2-one have been the subject of numerous papers and patents[1] owing to their utility as key intermediates in the commercial production of dethamethrin and similar highly potent pyrethroid insecticides.[2] The carbonyl-free analogs of these compounds deserved, however, only very little attention in connection with the photolysis of dienones.[3] In this paper we report a one-pot synthesis of 3-oxabicyclo-[4.1.0]hept-4-enes by $PtCl_4$-catalyzed cyclorearrangement of the corresponding allyl propynyl ethers under exceedingly mild conditions.

## Results and Discussion

The allyl propynyl ethers **1a–1e** were prepared by the Williamson synthesis from the corresponding alkynols and allyl halides in the presence of NaH. Under exclusion of air these unsaturated ethers undergo readily cyclorearrangement by $PtCl_4$ to give 3-oxabicyclo[4.1.0]-hept-4-ene derivatives **2a–2e** (eq 1). Each of the enynes **1a–1d** which were isomerically pure *E*-compounds yielded,




(1)

**1**

(a): R = Ph R' = H
(b): R = R' = Ph
(c): R = Ph R' = 1-$C_{10}H_7$

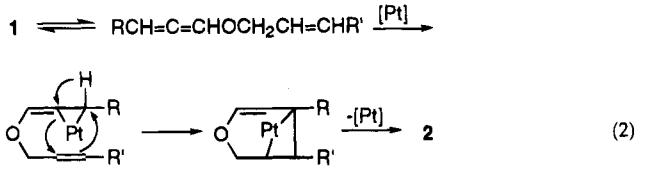
**2**

(d): R = Me R' = Ph
(e),(e'): R = Ph R' = Me

apart from some polymeric material, a single cyclic ether. The condensation product of phenylpropargyl alcohol and crotyl chloride, which consisted of a mixture of (*E*)- and (*Z*)-[3-(2-butenyloxy)-1-propynyl]benzene (**1e and 1e'**, respectively) gave upon cyclorearrangement two oxabicycloheptene derivatives.

The structure of 7-(1-naphthyl)-6-phenyl-3-oxabicyclo-[4.1.0]hept-4-ene (**2c**) was determined by X-ray diffraction analysis of a single crystal.[4] The stereoscopic drawing shows clearly that the phenyl and naphthyl groups are oriented cis to each other and that all three cyclopropane carbon atoms, 1, 6, and 7, have the *RS* configuration. The identity of the NMR spectra of the analyzed crystal and the bulk product indicates that no other isomer of **2c** has been formed in the catalytic cyclorearrangement of **1c**. The close resemblance of the proton and $^{13}C$ NMR spectra of compounds **2a**, **2b**, **2d**, and **2e** to those of **2c** (see Experimental Section) suggests similar structures for the five compounds. The stereochemistry of **2b**, **2c**, **2d**, and **2e** in which the substituents at C6 and C7 are cis, and H1 and H7 are oriented trans to each other, was established by virtue of the similar coupling constants of H1 and H7 ($J_{1,7}$ = 5.8–6.3 Hz). Compound **2e'** which is the minor cyclization product of the mixture of **1e** and **1e'** has the methyl and phenyl groups located trans to each other and H1 and H7 have, therefore, the cis configuration ($J_{1,7}$ = 3 Hz).

The cyclization of compounds **1** differs entirely from the $PtCl_4$- and $H_2PtCl_6$-catalyzed rearrangement of the analogous dialkyne ether $(PhC{\equiv}CCH_2)_2O$, under phase transfer conditions.[5] The mechanism of the present process is assumed to involve platinum derivatives of the allene tautomers of enynes **1** as illustrated in eq 2.[6]




(2)

Intramolecular cyclization and metal elimination affords then the bicycloheptenes.

† Dedicated to Professor Herbert Schumann on the occasion of his 60th birthday.

® Abstract published in *Advance ACS Abstracts,* August 1, 1995.

(1) (a) See e.g., Mandal, A. K.; Borude, D. P.; Armugasamy, R.; Soni, N. R.; Jawalkar, D. G.; Mahajan, S. W.; Ratnam, K. R.; Goghare, A. D. *Tetrahedron* **1986**, *42*, 5714 and references cited therein. (b) Mitra, R. B.; Kulkarni, G. H.; Khanna, P. N. *Synth. Commun.* **1987**, *17*, 1089. (c) Fokin, A. A.; Baula, O. P.; Yurchenko, A. G.; Krasutskii, P. A.; Promonenkov, V. K. *Zh. Org. Khim.* **1990**, *26*, 1363.

(2) See e.g., J. R. Tessier In *Recent Advances in the Chemistry of Insect Control*; Janes, N. F., Ed.; Royal Soc. Chem.: London, 1985; p 26.

(3) (a) Schneider, R. A.; Meinwald, J. *J. Am. Chem. Soc.* **1967**, *89*, 2023. (b) Meinwald, J.; Kobzina, J. W. *J. Am. Chem. Soc.* **1969**, *91*, 5177.

(4) Detailed crystallographic data, including tables of positional and thermal parameters, tables of bond lengths and bond angles, table of least squares planes, and ORTEP are deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

(5) Badrieh, Y.; Blum, J.; Amer, I.; Vollhardt, K. P. C. *J. Mol. Catal.* **1991**, *66*, 295.

(6) Transition metal allene complexes have been shown to have also different structures (see e.g. references 7 and 8) which fit equally well in the mechanism outlines in eq 2.

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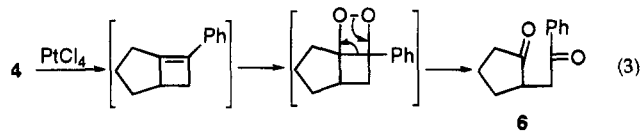
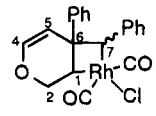
The highly strained cyclopropane moieties in **2** are easily cleaved by interaction with $[(CO)_2Rh(\mu\text{-}Cl)]_2$ to give four-membered rhodacyclic compounds. 6,7-Diphenyl-3-oxabicyclo[4.1.0]hept-4-ene (**2b**), for example, formed a yellow solid that analyzed for $C_{20}H_{16}ClO_3Rh$, and behaved under Rast analysis (mol wt 442 ± 2) as a mononuclear complex. This fact is of interest, since many of the reaction products of $[(CO)_2Rh(\mu\text{-}Cl)]_2$ with cyclopropane and cyclobutane derivatives studied previously formed dinuclearic compounds. It is also notable that unlike in many other cases where strained rings were cleaved by the rhodium dicarbonyl chloride dimer,[9] no carbonyl insertion into the organic moiety has occurred. The IR spectrum of **3b** has two strong metal carbonyl absorption at 2033 and 2089 $cm^{-1}$ but shows no absorption band in




**6**

the metal–acyl stretching region (cf, reference 10). Furthermore, under electron impact at 70 eV and 110 °C the mass spectrum consisted only of the molecular and fragment ions of **2b** free of any higher ions that could indicate addition of a CO to the organic part.[11]

The $PtCl_4$-catalyzed cyclorearrangement seems to be applicable not only to allyl propynyl ethers, but to other enynes as well. For example, when the oxygen atom in **1a** is substituted by $CH_2$, the (6-hepten-1-ynyl)benzene, $PhC{\equiv}C(CH_2)_3CH{=}CH_2$ (**4**) is rearranged at room temperature under exclusion of air to a labile hydrocarbon that readily polymerizes during the workup. The cyclorearrangement product could, however, be trapped by oxygen and yielded the known 2-(2-oxo-2-phenylethyl)-cyclopentanone (**6**).[12] Thus, when the reaction was conducted under ambient atmosphere, 90% of **6** was obtained. The formation of **6** suggests that the primary cyclization product is 7-phenylbicyclo[3.2.0]hept-1(7)-ene (**5**) rather than the analogous compound of **2a**, 1-phenylbicyclo[4.1.0]hept-2-ene (**7**). The conversion of **5** into **6** can be rationalized by dioxygen addition to **5** followed by cleavage of the O–O bond as illustrated in eq 3.




**3b**

## Experimental Section

(*E*)-[3-(2-Propenyloxy)-1-propynyl]benzene (**1a**),[13] (*E*)-[3-[(3-phenyl-2-propenyl)oxy]-1-propynyl]benzene (**1b**),[13] and 7-phenyl-(1-hepten-6-ynyl)benzene (**4**)[14] were prepared as described in the literature.

**(*E*)-[3-[(3-Naphthalen-1-yl-2-propenyl)oxy]-1-propynyl]-benzene (1c).** A mixture of 1.643 g (12 mmol) of 3-phenyl-2-propyn-1-ol and 500 mg (18 mmol) of NaH (50% in parafin oil) in 40 mL of dry benzene was stirred under Ar at room temperature for 3 h. A solution of 3.075 g (12 mmol) of 1-(3-bromo-1-propenyl)naphthalene[15] in 30 mL of the same solvent was added dropwise during 30 min and the mixture stirred first for 30 min at room temperature and then for 2 h at reflux. The cooled mixture was treated with a cold solution (5 °C) of 5 g of $NH_4Cl$ in 15 mL of water, and the resulting organic material was extracted into ether and purified by chromatography on silica gel (a mixture of 98% hexane and 2% ether served as eluent): $R_f$ = 0.21; yield of **1c** 3.0 g (87%); yellow oil; 200-MHz $^1H$ NMR ($CDCl_3$) δ 4.25 (dd, 2, $J_1$ = 4.0 Hz, $J_2$ = 1.3 Hz), 4.49 (s, 2) 6.35 (m, 1) 7.22 (m, 13);[16] 50-MHz $^{13}C$ NMR ($CDCl_3$) δ 57.92, 70.37, 85.16, 86.43, 122.61, 123.71, 123.92, 125.50, 125.67, 125.97, 128.01, 128.21, 128.37, 128.42, 128.47, 130.25, 131.08, 131.71, 133.52, 134.30; MS (70 eV, 70 °C), *m/z* 165 [$(M - C_9H_9O)^+$, 100).[16] Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.50; H, 6.20.

**(*E*)-4-[(3-Phenyl-2-propenyl)oxy]-2-butyne (1d).** A mixture of 500 mg (7 mmol) of 2-butyn-1-ol, 230 mg (10 mmol) of NaH, and 10 mL of dry PhH was stirred under $N_2$ at room temperature. After 3 h 1.372 g (7 mmol) of cinnamyl bromide in 10 mL of the same solvent was added dropwise during 30 min. The mixture was refluxed for 2 h, cooled and treated slowly at 5 °C with a solution of 5 g of $NH_4Cl$ in 15 mL of water. Extraction of the organic material into ether followed by chromatogrphy on silica gel (98% hexane and 2% ether as eluent) afforded 1.15 g (89%) of **1a** ($R_f$ = 0.23) as a pale yellow oil: 400-MHz $^1H$ NMR ($CDCl_3$) δ 1.89 (t, 3, $J$ = 2.2 Hz) , 4.18 (q, 2, $J$ = 2.2 Hz), 4.23 (dd, 2, $J_1$ = 0.3 Hz, $J_2$ = 4.9 Hz), 6.31 (m, 1), 6.66 (d, 1, $J$ = 16 Hz) 7.24–7.44 (m, 5);[16] 100-MHz $^{13}C$ NMR ($CDCl_3$) δ 55.72, 57.46, 69.81, 74.92, 82.37, 125.19, 125.49, 126.25, 127.49, 128.35, 132.72, 136.39; MS (70 eV, 50 °C), *m/z* 186 ($M^{\bullet+}$, 1).[16] Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.55; H, 7.53.

**(*E*)- And (*Z*)-[3-(2-butenyloxy)-1-propynyl]benzene (1e, 1e').** In a similar manner to the preparation of **1d**, 10 g (75 mmol) of 3-phenyl-2-propyn-1-ol in 100 mL of PhH was treated with 2.7 g (117 mmol) of NaH, and the resulting alcoholate was reacted at 78 °C with 6.8 g (75 mmol) of crotyl chloride in 50 mL of the same solvent. After decomposition with aqueous $NH_4Cl$, followed by column chromatography on silica gel, there was obtained 11.7 g (84%) of a 4:1 mixture of the *E* and *Z* isomers **1e** and **1e'**, respectively, as a pale yellow oil: 400-MHz $^1H$ NMR of **1e** and **1e'** ($CDCl_3$) δ 1.73 (m, 3), 4.06 (d, 0.4, $J$ = 1 Hz), 4.07 (dd, 1.6, $J_1$ = 5.6 Hz, $J_2$ = 1 Hz), 4.08 (s, 0.8), 4.21 (s, 0.2), 5.60–5.82 (m, 2), 7.26–7.47 (m, 5);[16] 100-MHz $^{13}C$ NMR of **1e** and **1e'** ($CDCl_3$) δ 13.13, 17.72, 57.45, 57.61, 64.70, 70.32, 85.16, 85.20, 86.02, 86.05, 122.62, 122.64, 125.96, 126.75, 128.17, 128.19, 128.21, 128.28, 128.31, 128.65, 128.95, 130.57, 131.64, 133.19; MS (70 eV, 70 °C) *m/z* 186 ($M^{\bullet+}$, 0.4).[16] Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.61; H, 7.23.

**6-Phenyl-3-oxabicyclo[4.1.0]hept-4-ene (2a).** A solution of 1.72 g (10 mmol) of **1a** and 170 mg (0.5 mmol) of anhydrous $PtCl_4$ in 50 mL of dry PhH was stirred at room temperature under Ar for 90 min. Concentration of the solution followed by chromatography on silica gel (heptane as eluent) afforded 400 mg (20%) of **2a** as a pale yellow oil: $R_f$ = 0.4. 400-MHz $^1H$ NMR ($CDCl_3$) δ 1.28 (dd, 1, $J_{1,7}$ = 5.8 Hz, $J_{7,7'}$ = 5.0 Hz), 1.48 (dd, 1, $J_{1,7'}$ = 8.5 Hz, $J_{7,7'}$ = 5.0 Hz), 1.638 (dddd, 1, $J_{1,2}$ = 1.2 Hz, $J_{1,2'}$ = 2.0 Hz, $J_{1,7}$ = 5.8 Hz, $J_{1,7'}$ = 8.5 Hz), 3.89 (dd, 1, $J_{1,2}$ = 2.0 Hz, $J_{2,2'}$ = 10.6 Hz), 4.17 (dd, 1, $J_{1,2}$ = 1.2 Hz, $J_{2,2'}$ = 10.6 Hz), 5.35 (d, 1, $J_{4,5}$ = 6.1 Hz), 6.23 (d, 1, $J_{4,5}$ = 6.1 Hz), 7.15–7.30 (m, 5);[16] 100-MHz $^{13}C$ NMR ($CDCl_3$) δ 20.21, 20.58, 28.11, 61.85, 108.98, 125.90, 126.62, 128.37, 141.18, 144.22; MS (70 eV, 50 °C) *m/z* 172 ($M^{\bullet+}$, 92).[16] Anal. Calcd for $C_{12}H_{12}O$: C, 83.60; H, 7.02. Found: C, 83.60; H, 6.98.

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(9) See e.g. (a) Bishop, K. C., III. *Chem. Rev.* **1976**, *76*, 461. (b) Halpern, J. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. II, pp 705–730.
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(11) Cf., e.g., Zlotogorski, C.; Blum, J.; Osawa, E.; Schwarz, H.; Höhne, G. *J. Org. Chem.* **1984**, *49*, 971.
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(16) Detailed $^1H$ NMR with complete peak assignment as well as detailed mass spectral data are available from the authors upon request.

**6,7-Diphenyl-3-oxabicyclo[4.1.0]hept-4-ene (2b).** In the manner described for **2a**, 360 mg of **1b** gave after 5 min reaction and chromatography (99% heptane and 1% ether as eluent) 350 mg (97%) of **2b** as colorless crystals: $R_f$ = 0.47; mp 62–64 °C; 400-MHz $^1$H NMR ($CDCl_3$) $\delta$ 2.46 (ddd, 1, $J_{1,2}$ = 1 Hz, $J_{1,2'}$ = 2.1 Hz, $J_{1,7}$ = 5.8 Hz), 2.78 (d, 1, $J_{1,7}$ = 5.8 Hz, H7), 4.08 (dd, 1, $J_{1,2'}$ = 2.1 Hz, $J_{2,2'}$ = 10.4 Hz), 4.41 (dd, 1, $J_{1,2}$ = 1 Hz, $J_{2,2'}$ = 10.4 Hz), 5.35 (d, 1, $J_{4,5}$ = 6.0 Hz), 6.27 (d, 1, $J_{4,5}$ = 6.0 Hz), 7.03–7.66 (m, 10);[16] 100-MHz $^{13}$C NMR $\delta$ 20.22, 22.76, 37.36, 61.46, 110.89, 125.69, 125.91, 126.48, 126.62, 127.69, 128.25, 128.37, 129.77, 140.61; MS (70 eV, 50 °C) $m/z$ 248 ($M^{\bullet+}$, 71).[16] Anal. Calcd for $C_{18}H_{16}O$: C, 87.07; H, 6.49. Found: C, 87.19; H, 6.72.

**(1*RS*,6*RS*,7*RS*)-7-Naphthalene-1-yl-6-phenyl-3-oxabicyclo[4.1.0]hept-4-ene (2c).** Reaction of 400 mg (1.34 mmol) of **1c** and 50 mg (0.15 mmol) of $PtCl_4$ for 5 min as above gave after chromatography on silica gel (98% hexane and 2% ether as eluent) 11 mg (28%) of **2c**: $R_f$ = 0.32; colorless crystals, mp 128–130 °C; 400-MHz $^1$H NMR ($CDCl_3$) $\delta$ 2.84 (ddd, 1, $J_{1,2}$ = 0.8 Hz, $J_{1,2'}$ = 1.9 Hz, $J_{1,7}$ = 6.3 Hz), 3.31 (d, $J_{1,7}$ = 6.3 Hz), 4.18 (dd, 1, $J_{1,2'}$ = 1.9 Hz, $J_{2,2'}$ = 10.4 Hz), 4.53 (dd, 1, $J_{1,2}$ = 0.8 Hz, $J_{2,2'}$ = 10.4 Hz), 5.65 (d, 1, $J_{4,5}$ = 6.0 Hz), 6.42 (d, 1, $J_{4,5}$ = 6.0 Hz), 6.90–6.99 (m, 6) 7.21 (t, 1, $J_{3,4,5}$ = 7.5 Hz), 7.47–7.57 (m, 3) 7.76 (d, 1, $J$ = 8 Hz), 8,29 (d, 1, $J$ = 8 Hz);[16] 100-MHz $^{13}$C NMR ($CDCl_3$) $\delta$ 27.66, 29.92, 35.56, 61.76, 110.89, 123.77, 124.42, 124.87, 125.54, 125.88, 126.05, 126.78, 127.69, 128.27, 128.42, 133.34, 133.38, 133.42, 139.45, 141.24; MS (70 eV, 50 °C) $m/z$ 298 ($M^{\bullet+}$, 40).[16] Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.60; H, 5.89.

A suitable crystal for X-ray diffraction analysis was obtained by slow recrystallization from hexane. Data were measured on an Enraf-Nonius CAD-4 automatic diffractomer. Cu $K_\alpha$ ($\lambda$ = 1.54178 Å) radiation with a graphite crystal monochromater in the incident beam was used. The standard CAD-4 centering, indexing, and data collection programs were used. The unit cell dimensions were obtained by a least-squares fit of 24 centered reflections in the range of $21 \le \theta \le 28°$. Intensity data were collected using the $\omega-2\theta$ technique to a maximum $2\theta$ of 120°. The scan width, $\Delta\omega$, for each reflection was 0.80 + 0.15 tan $\theta$. An aperture with a height of 4 mm and a variable width, calculated as (2.0 + $^1/_2$ tan $\theta$) mm, was located 173 mm from the crystal. Reflections were first measured with a scan of 8.24° min$^{-1}$. The rate of the final scan was calculated from the preliminary scan results so that the ratio $I/\sigma(I)$ would be at least 40 and the maximum scan time < 60 s. If in a preliminary scan $I/\sigma(I) < 2$, this measurement was used as datum. Scan rates varied from 1.26 to 8.24° min$^{-1}$. Of the 96 steps in the scan, the first and the last 16 steps were considered to be background. During data collection the intensities of three standard reflections were monitored after every 60 min of X-ray exposure. No decay was observed. In addition, three orientation standards were checked after 100 reflections to check the effects of crystal movement. If the standard deviation of the $h$, $k$, and $l$ values of any orientation reflection exceeded 0.06, a new orientation matrix was calculated on the basis of the recentering of the 24 reference reflections. Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by using the results of the SHELXS-86 direct method analysis.[17] After several cycles of refinement[18] the positions of the hydrogen atoms were found and added to the refinement process. Refinement proceeded to convergence by minimizing the function $\sum w(|F_o| - |F_c|)^2$. A final difference Fourier synthesis map showed several peaks less than 0.15 e/Å$^3$ scattered about the unit cell without a significant feature. The discrepancy indices, $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.042$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.066$. Other crystallographic data for **2c**: space groups *Iba*2; $a$ = 14.519(1) Å; $b$ = 29.356(2) Å; $c$ = 7.532-(3) Å; $V$ = 3210.3 (5) Å$^3$; $Z$ = 8; $\varrho_{calcd}$ = 1.24 g cm$^{-3}$; $\mu$(Cu $K_\alpha$ = 5.37 cm$^{-1}$; no. of unique reflections 1292, and no. of reflections with $I \ge 3\sigma(I)$ 1208.[4]

**6-Methyl-7-phenyl-3-oxabicyclo[4.1.0]hept-4-ene (2d)** was obtained as a yellow oil in 27% yield by reaction of 550 mg (2.97 mmol) and 50 mg (0.15 mml) of $PtCl_4$ for 5 min followed by chromatography on silica gel with 98% hexane and 2% of ether as eluent: $R_f$ = 0.56. 400-MHz $^1$H NMR ($CDCl_3$) $\delta$ 0.91 (s, 3), 1.77 (dd, 1, $J_{1,2}$ = 2.2 Hz, $J_{1,7}$ = 5.8 Hz), 2.45 (d, 1, $J_{1,7}$ = 5.8 Hz), 3.91 (dd, 1, $J_{1,2}$ = 2.2 Hz, $J_{2,2'}$ = 10.4 Hz), 4.25 (d, 1, $J_{2,2'}$ = 10.4 Hz),5.18 (d, 1, $J_{4,5}$ = 6.0 Hz), 6.23 (d, 1, $J_{4,5}$ = 6.0 Hz, H4), 7.16–7.26 (m, 3), 7.27–7.31 (m, 2);[16] 100-MHz $^{13}$C NMR ($CDCl_3$) $\delta$ 19.06, 26.55, 28.74, 35.42, 61.54, 111.62, 125.94, 128.01, 128.74, 138.05, 140.91; MS (70 eV, 120 °C) $m/z$ 186 ($M^{\bullet+}$, 95).[16] Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.83; H, 7.81.

**7-Methyl-6-phenyl-3-oxabicyclo[4.1.0]hept-4-ene (2e, 2e′).** Reaction of 520 mg (2.8 mmol) of a 4:1 mixture of **1e** and **1e′** and 50 mg (0.15 mmol) of $PtCl_4$ yielded after 5 min, 400 mg (76%) of a 4:1 mixture of the two isomers **2e** and **2e′** as a pale yellow oil. 400-MHz $^1$H NMR ($CDCl_3$) $\delta$ 0.82 (d, 2.4, $J_{7,CH_3}$ = 6.4 Hz), 1.22 (d, 0.6, $J_{7,CH_3}$ = 6.4 Hz), 1.52 (dq, 0.8, $J_{1,7}$ = 5.8 Hz, $J_{7,CH_3}$ = 6.4 Hz), 1.54 (unresolved dq, 0.2 $J_{1,7}$ = 3 Hz), 1.73 (m, 1), 4.17 (dd, 0.2 $J_{1,2}$ = 1.7 Hz, $J_{2,2'}$ = 11.3 Hz), 4.18–4.30 (m, 2), 4.31 (dd, 0.8 $J_{1,2}$ = 1.2 Hz, $J_{2,2'}$ = 10.5 Hz), 5.19 (d, 0.2, $J_{4,5}$ = 6 Hz), 5.32 (d, 0.8, $J_{4,5}$ = 6 Hz), 6.17 (d, 0.8, $J_{4,5}$ = 6 Hz), 6.41 (d, 0.2, $J_{4,5}$ = 6 Hz), 7.20–7.38 (m, 5);[16] 100-MHz $^{13}$C NMR (**2e** + **2e′**) ($CDCl_3$) $\delta$ 8.48, 14.73, 23.10, 26.09, 26.59, 26.82, 26.93, 30.35, 60.60, 61.73, 102.25, 111.86, 125.83, 126.30, 126.88, 128.34, 129.22, 139.86, 140.98, 141.18, 145.66; MS (70 eV, 110 °C) $m/z$ 186 ($M^{\bullet+}$, 4).[16] Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.58; H, 7.44.

**2-(2-Oxo-2-phenylethyl)cyclopentanone (6).** A solution of 500 mg (2.97 mmol) of **4**, 50 mg (0.15 mmol) of $PtCl_4$, and 1 mL of PhH was stirred at room temperature for 75 min in the presence of air. Chromatography on silica gel with a 9:1 mixture of hexane and ether as eluent afforded 535 mg (90%) of **6** as pale yellow crystals with identical mp (53–54 °C), IR and NMR with those reported in the literature.[12]

**Reaction of 2b with $[(CO)_2Rh(\mu\text{-}Cl)]_2$.** A mixture of 100 mg (0.4 mmol) of **1b**, 156 mg (0.4 mmol) of $[(CO)_2Rh(\mu\text{-}Cl)]_2$, and 2 mL of PhH was stirred under Ar atmosphere for 3 h at 60 °C. The solvent was removed and the residue recrystallized from hexane: yield of **3b** 15.7 mg (18%); orange-yellow crystals; mp 114–115 °C; IR (Nujol) 2033, 2089 cm$^{-1}$ (RhC≡O); 400-MHz $^1$H NMR ($C_6D_6$) $\delta$ 2.74 (m, 2), 2.88 (d, 1, $J_{2,2'}$ = 9.5 Hz), 3.17 (dd, 1, $J_{1,2}$ = 2.5 Hz, $J_{2,2'}$ = 9.5 Hz), 4.75 (d, 1, $J_{4,5}$ = 4 Hz), 6.54 (d, 1, $J_{4,5}$ = 4 Hz), 6.63–7.67 (m, 10);[16] 100-MHz $^{13}$C NMR ($C_6D_6$) $\delta$ 19.15, 19.33, 46.31, 68.16, 91.30, 101.67, 126.78, 127.38, 127.84, 128.22, 128.46, 129.85, 130.17, 130.28, 130.62, 131.07, 136.60, 145.52. Anal. Calcd for $C_{20}H_{16}ClO_3Rh$: mol wt 442.7; C, 54.26; H, 3.64. Found: mol wt (Rast) 442 ± 2, C, 54.61; H, 3.51.

**Acknowledgment.** We thank Dr. Shmuel Cohen for his help in the X-ray analysis of **2c**, and the Israel Science Foundation (administered by the Israel Academy of Sciences and Humanities) for financial support of this study.

JO950504T

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(18) All crystallographic computing was performed on a VAX 9000 computer at the Hebrew University of Jerusalem, using the TEXSAN Structure Analysis Software.