Reaction of 3,5-Dehydronoriceane[1] with Tetracarbonylbis(μ-chloro)dirhodium [$Rh_2(CO)_4Cl_2$]: Evidence for the Oxidative Addition of Rh(I) Complex to a Bicyclo[2.1.0]pentane System

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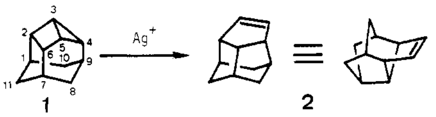
Received April 18, 1984

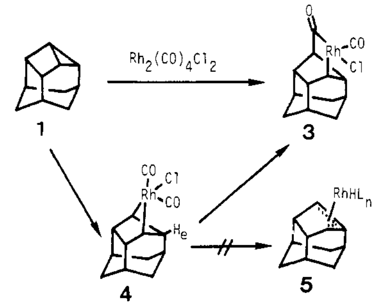
A stoichiometric reaction of the title compound (1) with $Rh_2(CO)_4Cl_2$ gives a stable acylrhodium complex (3). This is the first experimental evidence for the oxidative addition of Rh(I) complex to a bicyclo[2.1.0]pentane system. Treatment of 3 with 2 equiv of triphenylphosphine gives rise to the starting bicyclo[2.1.0]pentane (1), instead of a keto compound. This contrasts markedly with reactions of acylrhodium complexes derived from other strained systems with triphenylphosphine to yield ketones. The structure of 3 is further confirmed by hydride reduction of 3 affording *exo*-3-(hydroxymethyl)noriceane (8), along with a small amount of two hydrocarbons, noriceane (9) and *exo*-3-methylnoriceane (10).

Reactions of strained organic molecules with transition metals, especially Rh(I) and Ag(I), have attracted a considerable attention from both synthetic as well as mechanistic points of view.[2] Gassman et al. first reported that bicyclo[2.1.0]pentane rearranged to cyclopentene upon treatment with a catalytic amount of $Rh_2(CO)_4Cl_2$.[3] Wiberg and Bishop also studied Rh(I)-catalyzed isomerization of substituted bicyclo[2.1.0]pentanes and postulated an oxidative addition mechanism of Rh(I) complex into the central bond of the bicyclo[2.1.0]pentane system.[4,5] Meanwhile, several acylrhodium complexes have been isolated in the reactions of $Rh_2(CO)_4Cl_2$ with quadricyclane,[6] cubane,[7] 1,3-bisomocubane,[8] bicyclo[2.2.0]hexane,[9] and *syn*-tricyclo[4.2.0.0^{2,5}]octane.[9] However, no acylrhodium complex has been reported for the bicyclo[2.1.0]pentane system.[9,10] We have previously uncovered an extraordinary reactivity of 3,5-dehydronoriceane (1),[11] a strained cage molecule incorporating a bicyclo[2.1.0]pentane system in its rigid structure: with silver(I) catalyst, a formal [$_\sigma 2_a + _\sigma 2_a$] rearrangement of 1 into 2,4-ethenonoradamantane (2) was observed.[12] In the present paper, we wish to report a reaction of 1 with $Rh_2(CO)_4Cl_2$, providing the first experimental evidence for the *oxidative addition* of Rh(I) complex to a bicyclo[2.1.0]pentane system.



Results and Discussion

Preparation and Reaction of an Acylrhodium Complex (3). When 1 was treated with a catalytic amount of $Rh_2(CO)_4Cl_2$ in chloroform at 55 °C for 48 h, no substantial change was observed by ^1H NMR. On the other hand, a pale yellow precipitate appeared within 10 min when a *stoichiometric* solution of 1 and $Rh_2(CO)_4Cl_2$ in hexane was kept at ambient temperature. The precipitate was collected to give an acylrhodium complex (3) in 83% yield. The structure of 3 was elucidated by IR (2025 and 1740 cm^{-1}) and elemental analysis. Furthermore, hydride reductions of 3 were undertaken in order to confirm the structure of 3 (vide infra).



The successful isolation of 3 is probably attributed to its cage structure, because bicyclo[2.1.0]pentane itself undergoes a rearrangement to cyclopentene with a *catalytic* amount of $Rh_2(CO)_4Cl_2$.[3,4] Wiberg and Bishop supposed a mechanism involving (a) an oxidative addition of Rh(I) complex to the central bond, (b) an abstraction of the *exo*-β-hydrogen, forming an allylrhodium hydride, and (c) a decomposition to cyclopentene and the Rh(I) complex.[4] In the present case, however, the abstraction of an *exo*-β-hydrogen (H_e) in a probable intermediate complex (4) must be strongly impeded by a bridghead olefin (5) formation. Hence, 4 may undergo the well-known migrative insertion of a carbonyl group[13] to give 3. Thus, the formation of 3 provides experimental evidence for the

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[1] Trivial nomenclatures are used for simplicity. The IUPAC names are given in the Experimental Section.

[2] Reviews: (a) Bishop, K. C., III *Chem. Rev.* **1976**, *76*, 461. (b) Greenberg, A., Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; pp 245-277.

[3] Gassman, P. G.; Atkins, T. J.; Lumb, J. T. *Tetrahedron Lett.* **1971**, 1643; *J. Am. Chem. Soc.* **1972**, *94*, 7757.

[4] Wiberg, K. B.; Bishop, K. C., III *Tetrahedron Lett.* **1973**, 2727.

[5] An oxidative addition mechanism has been also proposed for nickel(0)-catalyzed reactions of bicyclo[2.1.0]pentane with electron deficient olefins: Takaya, H.; Suzuki, Y.; Kumagai, Y.; Yamakawa, M.; Noyori, R. *J. Org. Chem.* **1981**, *46*, 2846.

[6] Cassar, L.; Halpern, J. *J. Chem. Soc., Chem. Commun.* **1970**, 1082.

[7] Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515.

[8] Blum, J.; Zlotogorski, C.; Zoran, A. *Tetrahedron Lett.* **1975**, 1117.

[9] Sohn, M.; Blum, J.; Halpern, J. *J. Am. Chem. Soc.* **1979**, *101*, 2694.

[10] It has been reported that bicyclo[2.1.0]pentane derivatives give acyliron complexes upon treatment with $Fe(CO)_5$ under irradiated conditions: Aumann, R.; Aberbeck, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 610.

[11] Katsushima, T.; Yamaguchi, R.; Kawanisi, M. *J. Chem. Soc., Chem. Commun.* **1975**, 692; *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3245.

[12] Katsushima, T.; Yamaguchi, R.; Kawanisi, M.; Ōsawa, E. *J. Chem. Soc., Chem. Commun.* **1976**, 39; *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3313.

[13] Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 260-315.

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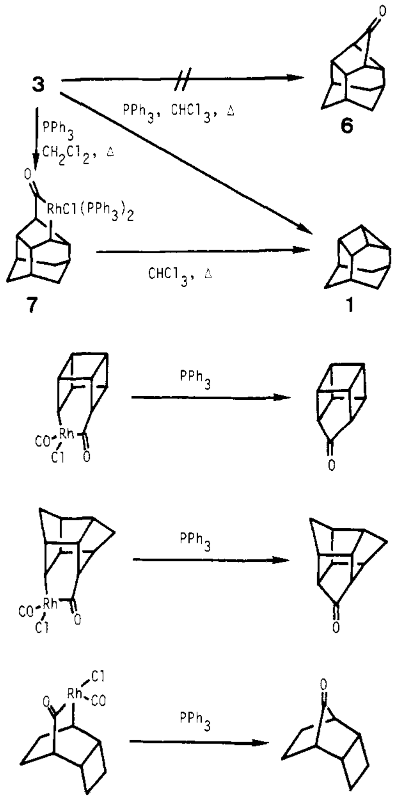
Table I. Hydride Reductions of 3

hydride	solvent	yield,[a] %	ratio of 8:9:10[b]
$NaBH_4$	pyridine	73	89:8:3
$NaBH_4$	THF	79	82:14:4
$LiAlH_4$	THF	82	71:11:18

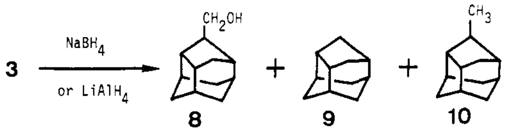
[a] Isolated yield. [b] Determined by GLC.

oxidative addition mechanism.

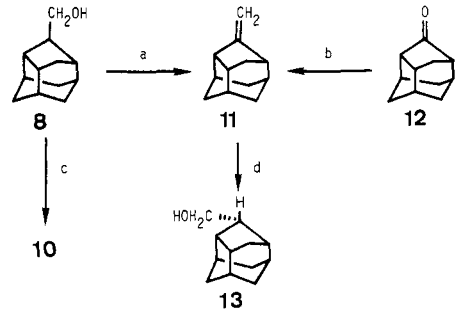
When **3** was heated under reflux in the presence of 2 equiv of triphenylphosphine in chloroform, the expected ketone (**6**)[14] was not detected. Instead, **1** was obtained in 89% isolated yield, along with $Rh(CO)Cl(PPh_3)_2$ (quantitative yield). This contrasts markedly with the reported reactions of the acylrhodium complexes derived from cubane,[7] 1,3-bisomocubane,[8] and *syn*-tricyclo[4.2.0.0^{2,5}]octane[9] with triphenylphosphine to yield the corresponding ketones. On the other hand, when **3** and 2 equiv of triphenylphosphine were heated under reflux in dichloromethane for 30 min, a yellow precipitate (**7**) was obtained. The structure of **7** was deduced to be the bis(triphenylphosphine)acylrhodium complex,[15] since the IR spectrum of **7** showed an absorption due to the acyl carbonyl (1635 cm^{-1}) but not due to the terminal carbonyl and, upon further heating under reflux in chloroform, **7** gave **1** and $Rh(CO)Cl(PPh_3)_2$. Thus, there is a definite difference in behavior between the acylrhodium complex (**3**) derived from the bicyclo[2.1.0]pentane system and those derived from other strained systems mentioned above.[16]



Hydride Reduction of 3. In order to acertain the structure of **3**, hydride reduction of **3** was conducted.[17] A reduction of **3** with sodium borohydride in pyridine gave *exo*-3-(hydroxymethyl)noriceane (**8**), along with a small amount of two hydrocarbons, noriceane (**9**)[11] and *exo*-3-methylnoriceane (**10**). Similarly, reductions of **3** with sodium borohydride or lithium tetrahydroaluminate in tetrahydrofuran also gave the same three products as above. The results are summarized in Table I.



The structures of **8** and **10** were determined by the following chemical transformations. Dehydration of **8** with hexamethylphosphoric triamide[18] gave 3-methylenenoriceane (**11**), which was identical with that prepared by methylenation[19] of 3-noriceanone (**12**).[20] Hydroboration of **11** took place from the sterically less hindered exo side to give *endo*-3-(hydroxymethyl)noriceane (**13**), which is isomeric to **8**. Finally, tosylation of **8** followed by reduction with lithium triethylborohydride gave **10**.



(a) HMPT, Δ; (b) CH_2Br_2, Zn-$TiCl_4$; (c) 1, TsCl/Py, 2, $LiEt_3BH$; (d) 1, BH_3/THF, 2, H_2O_2-NaOH

Hydride reductions of acylrhodium complexes derived from cyclopropanes and quadricyclane were claimed to give the corresponding alcohols.[14,15] Hence, the formation of **8** from **3** is justifiable and confirms the structure of **3**, while the detection of two hydrocarbons, **9** and **10**, is a novel observation. Although precise mechanistic pathways leading to **9** and **10** are not clear, rhodium hydride derivatives probably produced under the reaction conditions may be responsible for their formation.

Experimental Section

All the temperatures were uncorrected. The IR spectra were obtained on a Shimadzu IR-27 or a Hitachi 215 spectrometer. The mass spectra were taken by using a Hitachi RMS-4 mass spectrometer. The ^1H and ^{13}C NMR spectra were obtained on Varian EM-390 and CFT-20 spectrometers, Me_4Si being chosen as the internal standard. Analytical GLC was carried out on a Shimadzu GC-4C gas chromatograph with 10% SE-30 and 10% PEG-20M columns, and preparative GLC separation was accomplished on a Varian Aerograph 920 chromatograph. The microanalyses were performed by Kyoto University Elemental Analysis Center. All reactions were performed under an inert atmosphere of nitrogen or argon.

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(14) Synthesis of **6** has been accomplished in this laboratory by an alternative way: Yamaguchi, R.; Tokita, T.; Kawanisi, M., unpublished results.

(15) It has been reported that an acylrhodium complex derived from phenylcyclopropane, upon treatment with triphenylphosphine, gives a bis(triphenylphosphine)acylrhodium complex similar to **7**. However, upon heating the complex gives 1-phenylpropene but not phenylcyclopropane: McQuilline, F. J.; Powell, K. C. *J. Chem. Soc., Dalton Trans.* **1972**, 2129.

(16) It should be noted that an acylrhodium complex derived from bicyclo[2.2.0]hexane, upon treatment with triphenylphosphine, gives 3-cyclohexene-1-carboxaldehyde but not 7-norbornanone.[9]

(17) Hydride reduction has been used for the purpose of the confirmation of the structure of the acylrhodium complex derived from quadricyclane: Gassman, P. G.; Nikora, J. A. *J. Organomet. Chem.* **1975**, *95*, 81. See also the literature quoted in ref 15.

(18) For dehydration of alcohols by means of HMPT: Monson, R. S. *Tetrahedron Lett.* **1971**, 567.

(19) Takai, K.; Hotta, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1978**, 2417.

(20) Katsushima, T.; Yamaguchi, R.; Kawanisi, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3318.

Preparation of the Acylrhodium Complex (3). To a solution of $Rh_2(CO)_4Cl_2$ (1000 mg, 2.57 mmol) in hexane (80 mL) was added pentacyclo[5.3.1.$0^{2,6}$.$0^{3,5}$.$0^{4,9}$]undecane (**1**)[11] (760 mg, 5.21 mmol) at ambient temperature. After 10 min, a pale yellow precipitate began to appear. After 4 h, the mixture was concentrated in vacuo to ca. 20 mL. The pale yellow precipitate was collected, washed with hexane, and dried in vacuo to give **3** (1458 mg, 83%): mp 198 °C dec; IR (KBr) 2025, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.73–3.60 (m, 14 H). Anal. Calcd for $C_{13}H_{14}ClO_2Rh$: C, 45.84; H, 4.14. Found: C, 46.07; H, 4.10.

Reactions of 3 with Triphenylphosphine. (a) A solution of **3** (170 mg, 0.5 mmol) and triphenylphosphine (288 mg, 1.1 mmol) in $CHCl_3$ (5 mL) was heated under reflux for 5 h. The solvent was evaporated and the yellow residue was washed with pentane. The yellow precipitate was collected by filtration, washed with pentane thoroughly, and dried in vacuo to give Rh(CO)-Cl$(PPh_3)_2$ (341 mg, 99%). The combined pentane solution was concentrated and the residue was chromatographed on silica gel. Elution by pentane gave **1** (65 mg, 89%).

(b) A solution of **3** (170 mg, 0.5 mmol) and triphenylphosphine (262 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) was heated under reflux for 0.5 h. The solvent was evaporated and the residue was dissolved in CH_2Cl_2 (1 mL). Addition of hexane (12 mL) to the solution gave a yellow precipitate, which was collected by filtration and washed with hexane to give **7** (316 mg, 76%): mp 170 °C dec; IR (KBr) 1635, 1575, 1475, 1425, 1095, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.10–8.00 (m, 30 H), 0.55–2.67 (m, 14 H). Anal. Calcd for $C_{48}H_{44}ClOP_2Rh$: C, 68.87; H, 5.30. Found: C, 68.58; H, 5.12.

(C) A solution of **7** (167 mg, 0.25 mmol) in $CHCl_3$ (5 mL) was heated under reflux for 5 h. The solvent was evaporated and the residue was washed with pentane. The yellow precipitate was collected by filtration, washed with pentane, and dried in vacuo to give Rh(CO)Cl$(PPh_3)_2$ (136 mg, 98%). The combined pentane solution was concentrated to give **1** (24 mg, 83%).

Hydride Reductions of 3. (a) To a solution of **3** (170 mg, 0.5 mmol) in pyridine (2 mL) was slowly added $NaBH_4$ (500 mg) under ice bath cooling. The mixture was stirred for 25 h at room temperature and then diluted with ether (ca. 30 mL). After addition of H_2O (ca. 1.5 mL) to quench the excess hydride, the ether layer became clear and was secured by decantation. The residue was washed twice with ether. The combined ethereal solution was washed thoroughly with 10% aqueous HCl and brine, and dried (Na_2SO_4). After evaporation of the solvent, the residue was chromatographed on silica gel. Elution by pentane gave a mixture (6 mg, 8%) of **9**[11] and **10** in a ratio of 8:3 (GLC). Each of **9** and **10** was isolated by preparative GLC and identical with the authentic sample (vide infra). Further elution by CH_2Cl_2 gave **8** (58 mg, 65%). The total yield was 73% and the ratio of **8**:**9**:**10** resulted in 89:8:3.

***exo*-3-Tetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecanemethanol (8)**: mp 57–59 °C; MS, *m/e* (%) 178 (M^+, 35), 79 (100); IR (neat) 3200, 2900, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.50 (d, J = 7 Hz, 2 H), 0.70–2.67 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 65.4 (t), 45.0 (d), 42.1 (d), 41.3 (d), 41.1 (d), 38.3 (d) 38.1 (d), 35.4 (d), 31.4 (d), 31.1 (t), 31.0 (t), 24.0 (t). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.73; H, 10.38.

(b) A similar reduction of **3** (170 mg, 0.5 mmol) with $NaBH_4$ (200 mg) in THF (5 mL) to the above gave a mixture of **9** and **10** (11 mg, 14%) and **8** (59 mg, 65%). The total yield was 79% and the ratio of **8**:**9**:**10** was 82:14:4.

(c) A similar reduction of **3** (170 mg, 0.5 mmol) with $LiAlH_4$ (150 mg) in THF (5 mL) to the above gave a mixture of **9** and **10** (20 mg, 24%) and **8** (52 mg, 58%). The total yield was 82% and the ratio of **8**:**9**:**10** was 71:11:18.

Dehydration of 8 with HMPT. A solution of **8** (63 mg, 0.35 mmol) in HMPT (0.5 mL) was heated at 230–240 °C for 5 h under Ar.[18] The mixture was poured into ice–water and extracted with hexane. The hexane solution was washed with water and dried (Na_2SO_4). After evaporation of the solvent, the residue was chromatographed on silica gel. Elution by hexane gave **11** (21 mg, 37%), which was identical with an authentic sample described below.

3-Methylenetetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecane (11). To a suspension of Zn dust (588 mg, 9.0 mmol) and CH_2Br_2 (522 mg, 3.0 mmol) in THF (30 mL) was added a 1 M solution of $TiCl_4$ in CH_2Cl_2 (2.2 mL, 2.2 mmol) under ice bath cooling. After 20 min, a solution of tetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecan-3-one (**12**)[20] (162 mg, 1 mmol) in THF (1 mL) was added to the above mixture. The reaction mixture was stirred for 18 h at room temperature, poured into water, and extracted with hexane. The hexane solution was washed with water and dried (Na_2SO_4). The solvent was evaporated and the residue was chromatographed on silica gel to give **11** (116 mg, 73%): mp 73–75 °C; MS, *m/e* (%) 160 (M^+, 36), 82 (100); IR (KBr) 2880, 2810, 1660, 1450, 865 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.63 (d.d, J = 9 and 2 Hz, 2 H), 0.73–2.90 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 157.6 (s), 100.0 (t), 49.5 (d), 42.9 (d), 42.5 (d), 41.9 (d), 40.9 (t), 38.1 (d), 32.7 (d), 32.4 (t), 30.4 (t), 25.7 (t). Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.74; H, 10.13.

***exo*-3-Methyltetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecane (10).** A solution of **8** (100 mg, 0.56 mmol) and tosyl chloride (213 mg, 1.1 mmol) in pyridine (1 mL) was kept in a refrigerator overnight. The reaction mixture was poured into water and extracted with ether. The ethereal solution was washed with 5% aqueous HCl and brine and dried (Na_2SO_4). The solvent was evaporated to give the corresponding tosylate (216 mg) as a colorless oil. To a solution of the tosylate in THF (3 mL) was added a 1 M solution of $LiEt_3BH$ in THF (1 mL, 1 mmol) and the mixture was heated under reflux for 2 h. To the cooled solution were added H_2O (1 mL), 3 N aqueous NaOH (1 mL), and then 30% H_2O_2 (1 mL). The mixture was stirred for 20 min, poured into water, and extracted with pentane. The pentane solution was washed with water and dried (Na_2SO_4). The solvent was evaporated and the residue was distilled from Kugelrohr to give **10** (90 mg, 77%): bp 130 °C (12 mmHg); MS, *m/e* (%) 162 (M^+, 100); IR (neat) 2880, 1470, 1450 cm^{-1}; ^{1} NMR ($CDCl_3$) δ 0.67–2.65 (m, 15 H), 0.82 (d, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 49.4 (d), 41.3 (t), 41.0 (d), 39.5 (d), 38.5 (d), 38.0 (d), 32.4 (d), 31.9 (d), 31.3 (t), 31.0 (t), 23.4 (t), 18.4 (q). Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.84; H, 11.43.

***endo*-3-Tetracyclo[5.3.1.$0^{2,6}$.$0^{4,9}$]undecanemethanol (13).** To a solution of **11** (49 mg, 0.31 mmol) in THF (1 mL) was added a 1 M solution of BH_3–THF (2 mL, 2 mmol) and the mixture was heated under reflux for 5 h. To the cooled reaction mixture were added H_2O (0.5 mL), 3 M aqueous NaOH (0.7 mL), and then 30% H_2O_2 (0.5 mL) and the mixture was additionally stirred at 40–50 °C for 1 h. The reaction mixture was poured into water and extracted with ether. The ethereal solution was washed with brine and dried (Na_2SO_4). The solvent was evaporated and the residue was chromatographed on silica gel. Elution by hexane–CH_2Cl_2 (8:2) gave **13** (40 mg, 72%), along with a small amount of an unidentified compound. An analytical sample of **13** was obtained by preparative GLC. **13**: mp 76–79 °C; MS, *m/e* (%) 178 (M^+, 2), 160 (100); IR (KBr): 3200, 2880, 1010 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.88 (d.d, J = 3 and 5 Hz, 2 H), 0.77–2.60 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 64.8 (t), 50.2 (d), 43.7 (d), 42.5 (d), 41.4 (t), 37.8 (d), 37.2 (d), 36.3 (d), 32.6 (t), 31.9 (t), 30.4 (d), 29.9 (t). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.62; H, 10.36.

Acknowledgment. We thank Dr. T. Katsushima for the preliminary work. Thanks are also due to Drs. P. G. Gassman and H. Takaya for their helpful discussions. This work was partially supported by a Grant-in-Aid for Science and Culture, Ministry of Education, Japan (No. 57750745) and Kawakami Science Foundation.

Note Added in Proof. Although quadricyclane appears to be a derivative of a bicyclo[2.1.0]pentane system in a formal sense, this compound has not been regarded as a bicyclo[2.1.0]pentane system because of the large difference between their reactivities. Hence, we consider that the present paper provides the first experimental evidence for the oxidative addition of Rh(I) complex to a genuine bicyclo[2.1.0]pentane system. We thank Dr. P. G. Gassman for brinding our attention to this point.

Registry No. 1, 58008-63-2; 3, 92285-08-0; 7, 92314-27-7; 8, 92285-09-1; 9, 58008-54-1; 10, 92285-10-4; 11, 92285-11-5; 12, 77419-12-6; 13, 92344-81-5; $Rh_2(CO)_4Cl_2$, 14523-22-9; PPh_3, 603-35-0.