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Addition of Organic Halides to Alkenes in the Presence of Palladium Complexes and Reducing Agents: 2,3-Dialkenylation of Norbornene and Its Derivatives

Chen-Shun Li, Der-Ching Jou, Chien-Hong Cheng,* Fen-Ling Liao, and Sue-Lein Wang*

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China

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In the presence of Pd(PPh$_3$)$_2$Cl$_2$ and zinc powder, norbornadiene (NBD) reacts catalytically with 3-iodo enones (RI: 3-iodo-2-cyclohexen-1-one (R^{1}I), 3-iodo-5,5-dimethyl-2-cyclohexen-1-one, and 3-iodo-2-cyclopenten-1-one) to give the corresponding *cis-exo*-2,3-disubstituted norbornenes (2,3-R$_2$NBE) **1a–c** in good yields. The structure of **1a** was established by X-ray diffraction. Important crystal data for this compound are as follows: $C_{19}H_{22}O_2$, orthorhombic, space group $Pna2_1$, $a = 30.427(11)$ Å, $b = 5.891(2)$ Å, $c = 8.397(2)$ Å, $V = 1505.1(8)$ Å^3, $Z = 4$. Norbornene (NBE) and cyclopentadiene dimer (CPD) react similarly with 3-iodo-2-cyclohexen-1-one to afford the expected disubstituted (2,3-R$^1_2$) norbornanes **1d,e**. Detailed analysis of the reaction of NBD with 3-iodo-2-cyclohexen-1-one in the presence of Pd(PPh$_3$)$_2$Cl$_2$ and zinc powder leads to the isolation of small amounts of the monosubstituted nortricyclene (2-R^{1}NTC) **2a** and the 7-substituted norbornadiene (7-R^{1}NBD) **3a** in addition to **1a**. Prolonged heating of the reaction mixture resulted in ring opening of **1a** and the formation of the 3,5-disubstituted (*cis*-3,5-CH$_2$R^1)$_2$) cyclopentene product **4a**. When the catalytic reaction of norbornadiene with 3-iodo-2-cyclohexen-1-one was carried out in the presence of triethylamine, the multicyclic compounds **5a** and **6a** were isolated, the structures of which were determined by X-ray diffraction. Crystal data: **5a**, $C_{19}H_{22}O_2$, triclinic, $P\bar{1}$, $a = 11.079(2)$ Å, $b = 11.750(2)$ Å, $c = 13.115(2)$ Å, $\alpha = 75.78(1)°$, $\beta = 98.00(2)°$, $\gamma = 65.55(1)°$, $Z = 4$; **6a**, $C_{19}H_{22}O_2$, monoclinic, $P2_1/c$, $a = 6.582(1)$ Å, $b = 17.926(5)$ Å, $c = 12.696(3)$ Å, $\beta = 98.00(2)°$, $Z = 4$. **1a** was converted to **5a** and **6a** under the same reaction conditions. The palladium intermediates Pd(PPh$_3$)$_2$R′I (**7a**) and Pd(PPh$_3$)(C$_7$H$_8$R′)I (**8a**) from the catalytic reaction of norbornadiene with 3-iodo-2-cyclohexen-1-one in the presence of Pd(PPh$_3$)$_2$Cl$_2$ and zinc powder were detected or isolated. **8a** reacts with Zn and ZnCl$_2$ to give **2a** and with (3-oxocyclohex-1-enyl)zinc iodide (**9a**) to yield **1a**. Mechanisms to account for the formation of **1a**, **2a**, **3a**, **5a**, and **6a** are proposed.

Introduction

The coupling of aryl halides with alkenes to give arylated alkenes is one of the most useful reactions catalyzed by palladium complexes.[1] In general, the catalysis involves oxidative addition of aryl halide to palladium(0) to yield an arylpalladium species, insertion of alkene into the aryl–palladium bond, elimination of palladium hydride, and deprotonation of the palladium hydride to regenerate the palladium(0). β-Hydride elimination to yield a palladium hydride is a key step in this catalytic reaction. In order for the elimination to proceed, the β-hydrogen should be at the syn position relative to the palladium center.[2] However, in some cases there is no suitable β-hydrogen for elimination after the insertion of alkene into the aryl–palladium bond, although β-hydrogen(s) exist in the palladium intermediate. Examples of such alkenes are norbornadiene and norbornene. Either exo or endo addition of arylpalladium species to these olefins would produce intermediates in which the β-hydrogens are not at syn positions for elimination.[3] Thus, in the presence of a nucleophile the intermediates may react further to yield a 1,2-disubstituted product.[4] Several reports on this subject have appeared in the literature.[5] Catellani and Chiusoli showed that norbornadiene (or norbornene) reacted with aryl bromide and sodium tetraphenylborate in the presence of Pd(0) species to yield a 2,3-diarylnorbornene or norbornane.[6] Similarly, the use of Bu$_3$SnCH=CH$_2$ to replace NaBPh$_4$ afforded an aryl vinyl disubstituted product.[7] Earlier, Larock and his co-workers investigated the reaction of norbornadiene with iodobenzene in the presence of Pd(OAc)$_2$ and HCO$_2$K. The hydrogenolysis product *exo*-5-phenylnorborn-2-ene was isolated.[8] In this reaction, HCO$_2$K was the reducing agent and hydrogen donor for the reaction. In a recent study, we observed that aryl iodides react with norbornadiene in

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[1] (a) Heck, R. J. *Palladium Reagents in Organic Syntheses*; Academic Press: New York, 1985. (b) Liebeskind, L. S. *Advances in Metal-Organic Chemistry*; Jai Press: London, 1989; Vol. 1, pp 137–155. (c) Larock, R. C. *Pure Appl. Chem.* **1990**, *62*, 653. (d) Chiusoli, G. P. *J. Organomet. Chem.* **1986**, *300*, 57. (e) 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; pp 720–727.

[2] (a) Dieck, H. A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1133. (b) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146.

[3] (a) Li, C.-S.; Cheng, C. H.; Liao, F.-L.; Wang, S.-L. *J. Chem. Soc., Chem. Commun.* **1991**, 710. (b) Larock, R. C.; Hershberger, S. S.; Takagi, K.; Mitchell, M. A. *J. Org. Chem.* **1986**, *51*, 2450.

[4] (a) Larock, R. C.; Burkhart, J. P.; Oertle, K. *Tetrahedron Lett.* **1982**, 1071. (b) Catellani, M.; Chiusoli, G. P. *Tetrahedron Lett.* **1982**, 4517. (c) Catellani, M.; Chiusoli, G. P.; Peloso, C. *Tetrahedron Lett.* **1983**, 813. (d) Catellani, M.; Chiusoli, G. P.; Mari, A. *J. Organomet. Chem.* **1984**, *275*, 129.

[5] Catellani, M.; Chiusoli, G. P.; Costa, M. *Pure Appl. Chem.* **1990**, *62*, 623.

[6] Catellani, M.; Chiusoli, G. P.; Concari, S. *Tetrahedron* **1989**, *45*, 5263.

[7] Kosuki, M.; Tamura, H.; Sano, H.; Migita, T. *Tetrahedron* **1989**, *45*, 961.

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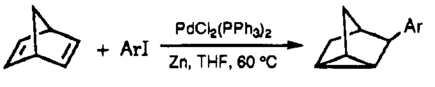
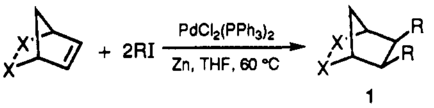
the presence of zinc metal and a palladium phosphine complex to give aryl-substituted nortricyclenes (eq 1).[9] In



(1)

an attempt to prepare a similar compound from norbornadiene and 3-iodo-2-cyclohexen-1-one (RI), a 2,3-disubstituted norbornene was isolated. This reaction was found to be general for cyclic 3-iodo enones (eq 2). Due to the



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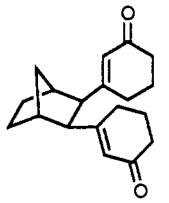
(2)

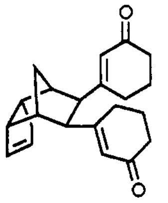
inherent eclipsed conformation at the two substituted carbons, and the relatively large group of the cyclic substituents, these products exhibit some unusual properties. We report herein the scope of reaction 2 and the synthesis, characterization, and properties of the products.

Results and Discussion

The reactions of norbornadiene (NBD) with 3-iodo enones were performed in THF in the presence of Pd(PPh$_3$)$_2$Cl$_2$ and zinc powder at 60 °C. In general, the maximum yield of product **1** was obtained if the reaction was terminated as soon as 3-iodo enone was consumed. Thus, all reactions were monitored by ^{1}H NMR spectroscopy to determine the time required for 3-iodo enone to disappear completely. Under these conditions, 3-iodo-2-cyclohexen-1-one, 3-iodo-5,5-dimethyl-2-cyclohexen-1-one, and 3-iodo-2-cyclopenten-1-one all reacted with NBD to give the disubstituted norbornene products (**1a–c**) in 50–76% isolated yields. Other substrates which possess activated carbon–carbon double bonds such as norbornene and cyclopentadiene dimer also reacted with 3-iodo-2-cyclohexen-1-one to afford the expected products **1d,e**,



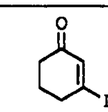
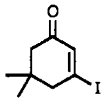
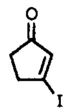
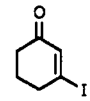
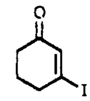
1d



1e

respectively. The yields and the detailed reaction conditions are presented in Table I. These products exhibit spectral data characteristic of the proposed cis-2,3-disubstituted structure. In the mass spectrum (see Experimental Section) of **1a**, the *m/e* ratio of the parent ion is in agreement with the proposed formula of two 3-oxocyclohex-1-enyl and one norbornenyl group. Although the mass spectrum reveals the presence of 19 carbon atoms in **1a**, there are only 10 signals in the ^{13}C NMR spectrum, including 4 sp^3 secondary and 2 sp^3 tertiary, 2 sp^2 tertiary, and 2 sp^2 quaternary carbon resonances. The characteristic absorptions for α,β-unsaturated enone groups in the IR spectrum appear at 1662 and 1604 cm^{-1}, and the proton resonances for the two olefinic protons come at δ 6.00 (s) and 6.32 (s). All these results support the proposed structure having two cis 3-oxocyclohex-1-enyl groups. For a trans-2,3-disubstituted structure, the number of resonances in the ^{13}C and ^{1}H NMR spectra are expected to be greater than the present observed values. Although these spectral data clearly demonstrate cis geometry for the two 3-oxocyclohex-1-enyl groups, the stereochemistry of the two groups relative to the bridging carbon cannot be established on the basis of the observed spectral data. Either an exo or an endo arrangement of the two 3-oxocyclohex-1-enyl groups appears to agree with the coupling patterns and the number of resonances in the NMR spectra of **1a**. Both exo and endo addition of organic groups to norbornadiene has been documented.[3-6,10]

Table I. Results of Reaction of Alkenes with 3-Iodo 2-En-1-ones in the Presence of Pd(PPh$_3$)$_2$Cl$_2$ and Zinc Powder[a]

entry no.	alkene	iodo enone	product	time (h)	yield (%)[b]
1	NBD		**1a**	5	82 (75)
2	NBD		**1b**	13	79 (56)
3	NBD		**1c**	5	85 (76)
4	NBE[c]		**1d**	6	(55)
5	CPD[d]		**1e**	6	(50)

[a] All reactions were carried out in THF at 60 °C; the reaction conditions are described in the Experimental Section. [b] Yields were determined by ^{1}H NMR. Isolated yields are recorded in parentheses. [c] Norbornene. [d] Cyclopentadiene dimer.

To determine the stereochemistry of the proposed structure, an X-ray structural study of compound **1a** was undertaken. The molecular structure with selected bond distances and angles is displayed in Figure 1. The results of the X-ray analysis unambiguously establish an exo and cis arrangement of the two 3-oxocyclohex-1-enyl groups in **1a**. One particularly interesting aspect of the structural results is the observation of an exceptionally long bond length of 1.60 Å between C2 and C3. This bond distance is approximately 0.06 Å longer than an average carbon single-bond distance of 1.54 Å. Due to the special conformational requirement of the norbornene group, the two 3-oxocyclohex-1-enyl groups on C2 and C3 are eclipsed with each other. Presumably, the required eclipsed conformation as well as the presence of two bulky substituents leads to the unusual long carbon–carbon length between C2 and C3.

In addition to compound **1a**, two other minor products, the nortricyclene derivative **2a** and the 7-substituted norbornadiene **3a**, were also isolated in 5 and 9% yields, respectively, from the reaction of 3-iodo-2-cyclohexen-1-

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(8) Larock, R. C.; Johnson, P. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1368.

(9) Li, C.-S.; Cheng, C.-H.; Cheng, S.-S.; Shaw, J.-S. *J. Chem. Soc., Chem. Commun.* **1990**, 1774.

(10) (a) Vedejs, E.; Weeks, P. D. *Tetrahedron Lett.* **1974**, 3207. (b) Larock, R. C.; Takagi, K.; Hershberger, S. S.; Mitchell, M. A. *Tetrahedron Lett.* **1981**, 5231. (c) Vedejs, E.; Salomon, M. F.; Weeks, P. D. *J. Organomet. Chem.* **1972**, *40*, 221.

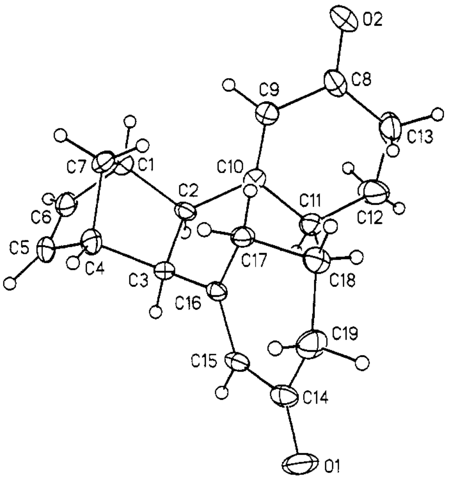
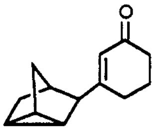
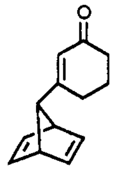


Figure 1. Molecular structure of **1a** showing the atom-labeling scheme. Selected bond distances (Å) and angles (deg): C2–C3 = 1.603(9), C2–C10 = 1.511(10), C9–C10 = 1.366(10), C8–O2 = 1.226(11), C3–C16 = 1.507(10), C15–C16 = 1.352(10), C14–O1 = 1.214(9), C5–C6 = 1.336(12); C2–C3–C16 = 119.2(6), C3–C2–C10 = 117.8(6), C3–C16–C15 = 118.4(6), C2–C10–C9 = 124.9(7), C14–C15–O1 = 122.1(7), C9–C8–O2 = 119.9(8).

one with norbornadiene in the presence of Pd(PPh$_3$)$_2$Cl$_2$ and zinc powder. The structures of both **2a** and **3a** are assigned on the basis of the spectral data of these compounds. The number of ^{13}C NMR signals as well as the coupling patterns of **2a** are all in agreement with the proposed structure. Key resonances include the three enone carbon signals at δ 125.67 (d), 166.81 (s), and 200.58 (s) and the signals for the cyclopropane ring at δ 9.59 (d), 11.17 (d), and 12.37 (d), which are approximately 20 ppm more upfield relative to the normal tertiary sp^3 carbon signal.[11] In the IR spectrum, characteristic absorptions for the substituted cyclopropane ring at 3058 and 807 cm^{-1} and for the enone group at 1668 and 1621 cm^{-1} were observed. For compound **3a**, the three olefinic proton signals appear at δ 5.67, 6.59, and 6.87 with an intensity ratio of 1:2:2. The last two signals are very close to that of norbornadiene, indicating that **3a** is a substituted norbornadiene in nature. The number of resonances and coupling patterns in the ^{13}C NMR spectrum and the mass spectral data also support the indicated structure, in which the 3-oxocyclohex-1-enyl group is attached to the bridging carbon of the norbornadiene group.

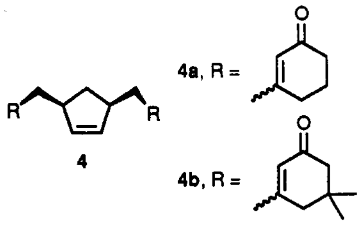


2a



3a

Interestingly, prolonged heating of the reaction mixture of norbornadiene with 3-iodo-2-cyclohexen-1-one in THF in the presence of Pd(PPh$_3$)$_2$Cl$_2$ and zinc powder leads to the isolation of the cis-3,5-disubstituted cyclopentene product **4a** in 56% isolated yield. The same product was also isolated by heating **1a** in THF in the presence of Pd(PPh$_3$)$_2$Cl$_2$ and zinc powder. As indicated by its mass spectrum, this product contains two more hydrogens than **1a**. In addition, in its ^{1}H NMR spectrum only two olefinic resonances with equal intensity were observed. The results strongly indicated that the two extra hydrogens were added to C2 and C3 carbons of **1a**. If hydrogenation occurred at one of the enone carbon–carbon double bonds, the resulting product would contain three different olefinic protons of equal intensity. Another possibility with hydrogenation at the double bond of the norbornene group of **1a** would reduce the number of olefinic proton signals in the product to only one. The cis-disubstituted nature of this product gains support from the observation in its ^{1}H NMR spectrum that the two methylene protons on the cyclopentene ring are different in chemical shift with one at δ 0.97 (d of t) and the other being buried in the region δ 2.16–2.40. The two methylene protons would be equal in chemical shift if the two substituents on the ring were trans to each other. In the ^{13}C NMR spectrum of **4a**, the number of carbon signals and coupling patterns also support the proposed structure. The ready cleavage of the C2–C3 bond in **1a** conforms to a weak and long bond between these two carbon atoms, although the mechanism for this hydrogenolysis reaction is unknown at the present time. Prolonged heating of the reaction mixture of norbornadiene with 3-iodo-2-cyclopenten-1-one or with 5,5-dimethyl-3-iodo-2-cyclohexen-1-one under the conditions for reaction 2 also led to ring opening of the products **1b,c** and the formation of the corresponding hydrogenolysis products **4b,c**, respectively, as indicated by the ^{1}H NMR spectra of reacting solutions. However, due to difficulty in separation of these compounds from other side products, they were not isolated in pure form.



Reaction of NBD with 3-Iodo-2-cyclohexen-1-one in the Presence of Base. The reaction of norbornadiene with 3-iodo-2-cyclohexen-1-one depends greatly on the reaction conditions. Addition of NEt$_3$ to the catalytic solution for the preparation of **1a** led to the isolation of the two multiple-ring products **5a** and **6a** (Scheme I). During the course of the reaction, **1a** was observed, but it disappeared at the end of the reaction. The structures of these two products were determined by singe-crystal X-ray diffraction methods. As indicated by the molecular structure drawings shown in Figures 2 and 3, each compound contains in total six rings, including three five-membered and three six-membered rings. In agreement with the X-ray structure results, the ^{13}C NMR spectra of the two products all exhibit 19 signals with expected chemical shifts and coupling patterns. With **5a** as the example, several characteristic resonances include δ 215.9 (s) for the carbon, δ 72.0 (s) for the carbon to which the hydroxyl group is attached, and δ 116.4 (d), 138.6 (d), 139.2 (d), and 140.7 (s) for the four carbons on the carbon–carbon double bonds. The presence of the hydroxyl and carbonyl groups in the compound is further evidenced by the observation of IR absorptions at 3387 and 1712 cm^{-1}, respectively.

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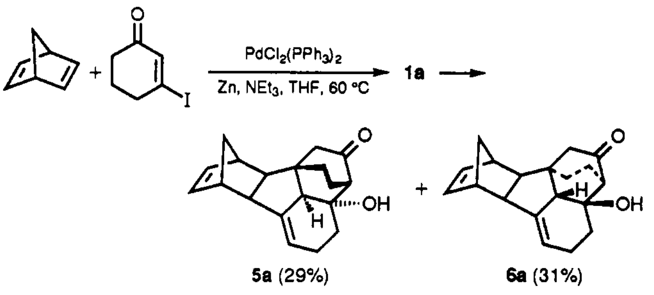
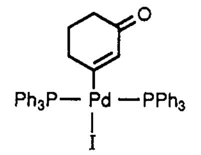
[11] (a) Franzus, B.; Wu, S.; Baird, W. C., Jr.; Scheinbaum, M. L. *J. Org. Chem.* **1972**, *37*, 2759. (b) Neale, R. S.; Whipple, E. B. *J. Am. Chem. Soc.* **1964**, *86*, 3130. (c) Morris, D. G.; Murray, A. M. *J. Chem. Soc., Perkin Trans. 2* **1975**, 734.

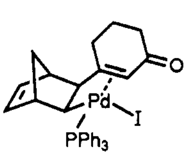
Scheme I



Catalyst Intermediates and Their Chemical Properties. One interesting question about reaction 2 is how the two alkenyl groups are added to NBD to give the observed product 1. To understand the mechanism of the catalysis, catalyst intermediates were isolated and characterized. During the catalytic reaction of NBD with 3-iodo-2-cyclohexen-1-one, both **7a** and **8a** were observed by ^{1}H NMR spectroscopy. The former may be isolated from the direct reaction of 3-iodo-2-cyclohexen-1-one with the Pd(PPh$_3$)$_2$Cl$_2$–Zn system or with Pd(PPh$_3$)$_4$.[12] The reaction of this intermediate with NBD led to the isolation of insertion product **8a**. The structure of **8a** is assigned on the basis of the observed spectral data and elemental analysis. Key evidence for the coordination of the carbon–carbon double bond to the palladium center includes the observations of a doublet for the α-proton and a doublet for the α-carbon in the ^{1}H and ^{13}C{^{1}H} NMR spectra, respectively. This structure and its spectral data are similar to those of the complexes Pd(PPh$_3$)(C$_7$H$_8$Ar)I isolated from the reaction of Pd(PPh$_3$)$_2$(Ar)I with NBD.[3a] As indicated by the X-ray results of one of these complexes, the Ar group is coordinated to the palladium center via a η^2 mode.



7a



8a

The reduction of **8a** by zinc metal powder in the presence of zinc dichloride in THF at ambient temperature yields the nortricyclene **2a** as the sole product. This reduction is extremely slow in the absence of zinc halide. To our surprise, heating **8a** in the presence of a mixture of 3-iodo-2-cyclohexen-1-one and zinc powder in THF failed to give the expected product **1a**.[13] However, when 3-iodo-2-cyclohexen-1-one was allowed to react with activated zinc powder for 20 min at room temperature and was then added to a THF solution of **8a**, the cis-2,3-disubstituted product **1a** was obtained in good yield. The results appear to indicate that 3-iodo-2-cyclohexen-1-one first reacts with zinc metal to give the organozinc iodide **9a**, which then reacts with **8a** to afford the expected product. According to a recent report, the organozinc halide **9a** may be generated from the reaction of 3-halo-2-cyclohexen-1-one.[14] Thus, by following the reported procedure, we prepared **9a** and the addition of 1 equiv of this organozinc halide to a THF solution of **8a** afforded the cis-2,3-disubstituted product in high yield, confirming the notion that **9a** was generated during the course of the catalysis of reaction 2.

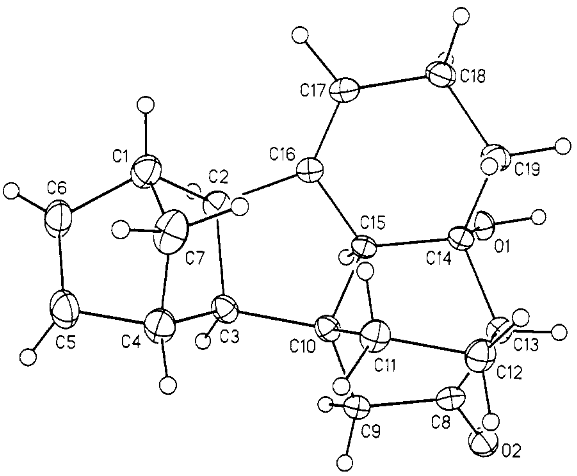


Figure 2. Molecular structure of **5a** showing the atom-labeling scheme. Selected bond distances (Å) and angles (deg): C2–C3 = 1.576(4), C5–C6 = 1.321(5), C16–C17 = 1.322(4), C8–O2 = 1.226(5), C14–O1 = 1.434(4); C1–C2–C16 = 120.8(3), C4–C3–C10 = 121.4(2), C9–C8–O2 = 122.2(3), C15–C14–O1 = 106.6(2).

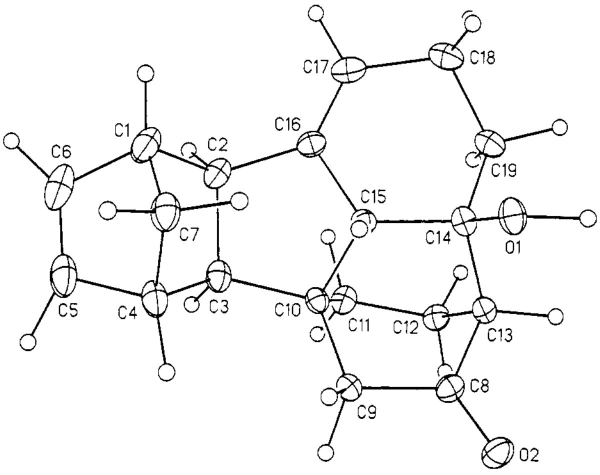
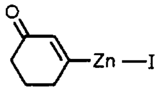


Figure 3. Molecular structure of **6a** showing the atom-labeling scheme. Selected bond distances (Å) and angles (deg): C2–C3 = 1.571(6), C5–C6 = 1.320(8), C16–C17 = 1.321(5), C8–O2 = 1.220(5), C14–O1 = 1.445(5); C1–C2–C16 = 114.7(4), C4–C3–C10 = 119.8(4), C9–C8–O2 = 121.8(4), C15–C14–O1 = 104.9(3).



9a

Mechanistic Considerations. On the basis of the above observations and the well-established principles for palladium-catalyzed reactions, a mechanism using NBD and 3-iodo-2-cyclohexen-1-one as the reagents is proposed as shown in Scheme II to account for the catalysis of reaction 2. The first step of the catalytic reaction is expected to be the reduction of Pd(PPh$_3$)$_2$Cl$_2$ to Pd(PPh$_3$)$_2$, followed by the oxidative addition of 3-iodo enone to Pd(PPh$_3$)$_2$ of the palladium(0) species, insertion of norbornadiene into the resulting Pd(II) complex to yield **8a**, and

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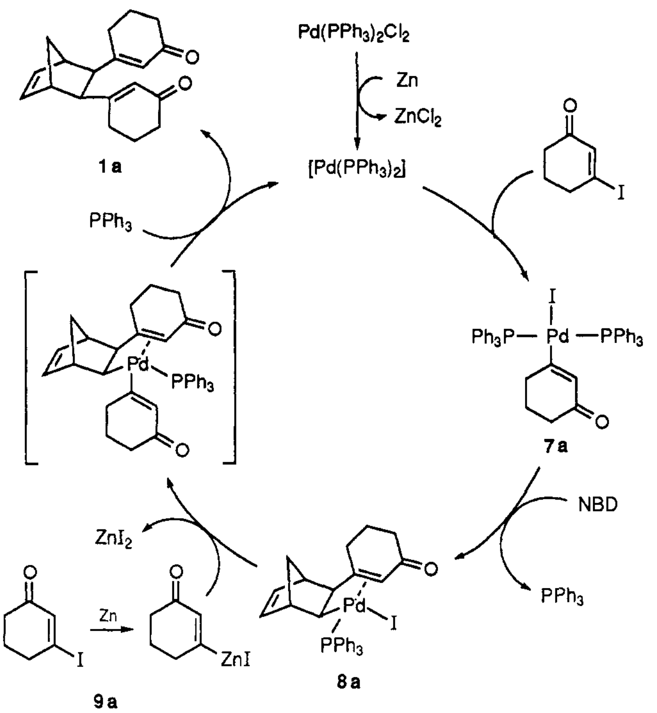
[12] Onishi, M.; Yamamoto, H.; Hiraki, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1856.

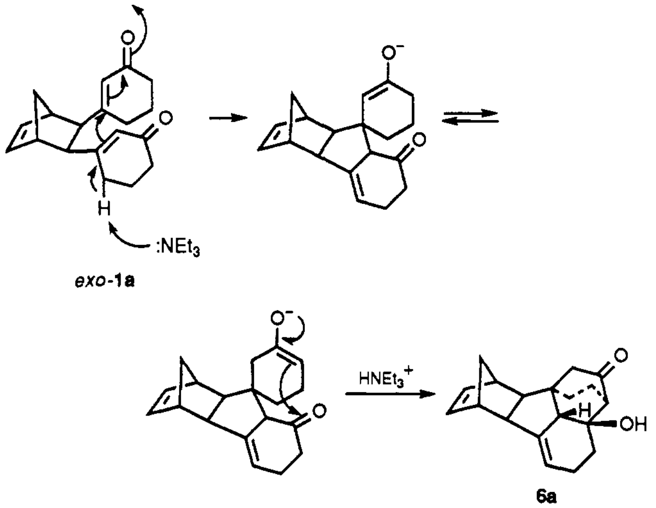
[13] A different product, 3,5-bis(*exo*-3-oxocyclohex-1-enyl)nortricyclene, was obtained under the reaction conditions. The results will be published separately.

[14] Knochel, P.; Rao, C. J. *Tetrahedron* **1993**, *49*, 29.

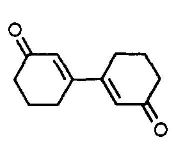
Scheme II



Scheme III

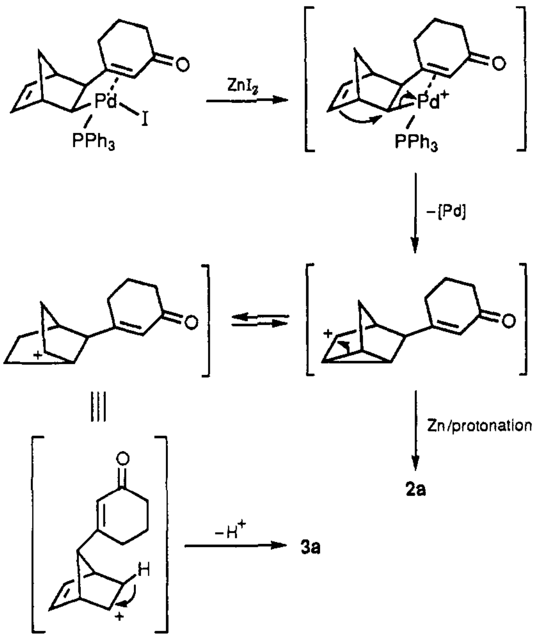


attack of **8a** by the alkenylzinc iodide to afford the final product **1a** and to regenerate Pd(PPh$_3$)$_2$. Although the alkenylzinc iodide **9a** is expected to be involved in the nucleophilic attack at the intermediate **8a** to give **1a**, the reaction of equal molar ratios of **9a**, NBD, and **7a** yielded only a trace of **1a**. The major product was the coupling product **10a** between 3-iodo-2-cyclohexen-1-one and the alkenylzinc iodide **9a**. Apparently, the presence of a substantial amount of **9a** resulted in the rapid attack of **7a** by **9a** prior to the NBD insertion into the Pd–carbon bond in **7a**. The formation of **1a** as the major product from reaction 2 is likely due to the slow generation in situ of **9a** during the catalytic reaction, allowing the NBD insertion to proceed before nucleophilic attack.

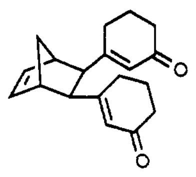


10a

Scheme IV



The detailed mechanism for the formation of the multiple-ring compounds **5a** and **6a** is unknown, but it is possible, on the basis of the known organic discipline and the observation that **1a** is the intermediate, to propose a mechanism to account for the reactions. Scheme III shows the reaction pathways for the formation of **6a**. The first step involves deprotonation of the γ-methylene group of **1a**, followed by nucleophilic attack at the β-carbon of the other 3-oxocyclohex-1-enyl group, proton shift, another nucleophilic attack, and the final protonation to complete the reaction. The two 3-oxocyclohex-1-enyl groups of **1a** are in an exo conformation (the position of oxo groups relative to the bridging carbon) during the first nucleophilic attack. A mechanism similar to Scheme II for the formation of **6a** is expected, except that an endo conformation for the two 3-oxocyclohexyl-1-enyl groups of **1a** is employed for the first nucleophilic attack. The isolated yields for **5a** and **6a** are approximately the same, indicating *endo*-**1a** that both the endo and exo attacks are about equal in chance for this ring closure reaction. Under the reaction conditions, free rotation of the two 3-oxocyclohex-1-enyl groups around the C–C bonds connected to the norbornenyl group are expected. Surprisingly, the observed conformation in the solid state with one oxo group at the endo position and the other occupying the exo site (see Figure 1) can yield no diastereomers. Model studies indicate that this exo–endo conformation cannot lead to ring closure as shown in the last step of Scheme III. The distance between the two carbons for ring closure is too long for interaction.



endo-1a

The formation of substituted nortricyclene **2a** (Scheme IV) in the catalytic solution is likely from the reduction of the catalyst intermediate **8a**, as supported by the results of the direct reaction of **8a** with zinc metal in the presence of $ZnCl_2$ (*vide supra*). Although the intimate mechanism by which **8a** is converted to **2a** is not clear at the present, the requirement of zinc halide in the reduction appears to indicate that zinc halide acts as a Lewis acid, removing the iodide ligand on **8a** during the reaction to give a cationic palladium(II) complex. The Pd(II) cation, which is known to be strongly electron-withdrawing,[15] likely induces the formation of a substituted NBD cation. Attack of the carbon–carbon double bond at the cationic carbon in the proposed substituted NBD cation yields a nortricyclene cation. The subsequent trapping by zinc metal to yield an organic zinc iodide followed by protonation leads to the product **2a**. The same substituted NBD cation is also likely involved in the production of **3a** from the catalytic reaction. Skeletal rearrangement of the NBD cation as shown in Scheme IV yields 7-substituted NBD. Such a rearrangement of NBD cation has been extensively studied previously.[16]

Conclusion

We have observed the rich chemistry of palladium-catalyzed addition of alkenyl groups to NBD. It is possible to synthesize various 2,3-disubstituted norbornenes and nortricyclenes by adjusting the reaction conditions. The 2,3-disubstituted norbornene **1a** readily undergoes either cyclization to give multicyclic compounds or ring opening to yield a cis-3,5-disubstituted cyclopentene. These catalytic reactions provide an efficient method for multiple carbon–carbon bond formation, which is generally a difficult step in organic synthesis. The application of this addition method to other olefins is currently under investigation.

Experimental Section

All reactions were performed under dry nitrogen, and all solvents were dried by standard methods. The ^1H and ^{13}C NMR spectra were recorded on Bruker AM-400 or Varian Gemini 300 instruments at 400 and 300 MHz, respectively, while infrared spectra were obtained from a Bomem MB-100 spectrometer. JEOL JMS-D100 and JMS-HX110 instruments were used to measure low- and high-resolution mass spectra, respectively.

Materials. All chemicals were obtained from commercial suppliers and used without further purification unless otherwise noted. Zinc dust (>230 mesh) was purchased from Merck Chemical Co. The following starting materials were prepared according to the literature: $PdCl_2(PPh_3)_2$,[1a] $Pd(PPh_3)_4$,[17] 3-iodocyclohexen-1-one,[18] 5,5-dimethyl-3-iodocyclohexen-1-one,[18] 3-iodocyclopenten-1-one,[18] (3-oxo-1-cyclohexen-1-yl)zinc iodide (**9a**).[14]

Isolation of Compounds 1a, 2a, and 3a. A mixture of $Pd(PPh_3)_2Cl_2$ (0.250 mmol), 3-iodo-2-cyclohexen-1-one (5.00 mmol), zinc powder (50.0 mmol), norbornadiene (10.0 mmol), and THF (30 mL) was heated under nitrogen with stirring at 60 °C until 3-iodo-2-cyclohexen-1-one was completely consumed, as indicated in the ^1H NMR spectrum of the solution. The time required to complete the reaction was ca. 5 h. The mixture was filtered through Celite and then evaporated. The residue was dissolved in dichloromethane and washed with saturated aqueous sodium chloride solution. The dichloromethane solution, after being dried over Na_2SO_4, was concentrated and then separated on a silica gel column. Elution with a mixture of hexane and ethyl acetate (5/1) gave the first portion, which contained a mixture of **2a** and **3a**. Further elution with a mixture of hexane and ethyl acetate (1/3) afforded 0.529 g of compound **1a** in 75% yield. Separation of the first portion on a TLC plate using hexane/ethyl acetate (5/1) as the eluent gave **2a** (0.047 g) in 5% yield and **3a** (0.084 g) in 9% yield. The important spectral data for these compounds are shown below.

Compound 1a. ^1H NMR (300 MHz, $CDCl_3$): δ 1.61 (d, J = 9.2 Hz, 1 H), 1.83–1.92 (m, 5 H), 2.19–2.36 (m, 8 H), 2.61 (s, 2 H), 2.94 (s, 2 H), 6.00 (s, 2 H), 6.32 (s, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 22.46 (t), 30.27 (t), 36.95 (t), 45.29 (t), 46.10 (d), 50.97 (d), 127.20 (d), 139.18 (d), 167.14 (s), 199.32 (s). IR (KCl): 3062, 2988, 2949, 2876, 1662, 1604, 1326, 1254, 719 cm^{-1}. Mp: 137–139 °C. MS (*m/e* (relative intensity)): 282 (M^+, 8), 217 (100). HRMS: $C_{19}H_{22}O_2$, calcd 282.1620, found 282.1624.

Compound 2a. ^1H NMR (300 MHz, $CDCl_3$): δ 1.08–1.24 (m, 5 H), 1.42 (br s, 2 H), 1.93–2.02 (m, 3 H), 2.20–2.43 (m, 5 H), 5.98 (d, J = 1.4 Hz, 1 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 9.59 (d), 11.17 (d), 12.37 (d), 22.64 (t), 29.08 (t), 29.29 (t), 32.60 (d), 34.75 (t), 37.41 (t), 51.72 (d), 125.67 (d), 166.81 (s), 200.58 (s). IR (neat): 3058, 2941, 2866, 1668, 1621, 807 cm^{-1}. HRMS: $C_{13}H_{16}O$, calcd 188.1202, found 188.1219.

Compound 3a. ^1H NMR (300 MHz, $CDCl_3$): δ 1.92 (m, 2 H), 2.10 (t, J = 5.8 Hz, 2 H), 2.30 (t, J = 6.7 Hz, 2 H), 3.24 (s, 1 H), 3.69 (m, 2 H), 5.67 (m, 1 H), 6.59 (t, J = 1.9 Hz, 2 H), 6.87 (t, J = 2.1 Hz, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 22.29 (t), 28.82 (t), 36.97 (t), 51.62 (d), 89.11 (d), 127.08 (d), 140.15 (d), 144.23 (d), 164.16 (s), 200.56 (s). IR (neat): 3065, 2978, 2929, 1667, 1651, 1618, 1545, 737 cm^{-1}. MS (*m/e* (relative intensity)): 186 (M^+, 40), 129 (100). HRMS: $C_{13}H_{14}O$, calcd 186.1045, found 186.1032.

Compounds **1b–e** were prepared from the reaction of norbornadiene, norbornene, and cyclopentadiene dimer with the corresponding 3-iodo enone. The reaction conditions and the isolation methods were similar to those for compound **1a**. Important spectral data for these compounds are listed below.

Compound 1b. ^1H NMR (300 MHz, $CDCl_3$): δ 0.96 (s, 6 H), 1.00 (s, 6 H), 1.63 (d, J = 9.3 Hz, 1 H), 1.85 (d, J = 9.3 Hz, 1 H), 1.95–2.23 (m, 8 H), 2.55 (s, 2 H), 2.91 (s, 2 H), 6.01 (s, 2 H), 6.32 (s, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 27.91 (q), 28.53 (q), 33.05 (s), 44.59 (t), 45.68 (t), 46.32 (d), 50.64 (t), 51.11 (d), 126.43 (d), 139.19 (d), 164.37 (s), 199.80 (s). IR (KCl): 3063, 2954, 2876, 1657, 1626, 1279, 902, 721 cm^{-1}. Mp: 120–123 °C. MS (*m/e* (relative intensity)): 338 (M^+, 8), 273 (100). HRMS: $C_{23}H_{30}O_2$, calcd 338.2246, found 338.2253.

Compound 1c. ^1H NMR (300 MHz, $CDCl_3$): δ 1.69 (d, J = 9.3 Hz, 1 H), 1.83 (d, J = 9.3 Hz, 1 H), 2.34 (m, 4 H), 2.47 (m, 4 H), 2.83 (s, 2 H), 3.03 (s, 2 H), 6.04 (s, 2 H), 6.35 (s, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 32.26 (t), 34.97 (t), 45.27 (t), 47.38 (d), 47.61 (d), 131.16 (d), 138.67 (d), 183.28 (s), 209.29 (s). IR (KCl): 3071, 2965, 2940, 1695, 1630, 1179, 727 cm^{-1}. Mp: 140–141 °C. MS (*m/e* (relative intensity)): 254 (M^+, 4), 189 (100). HRMS: $C_{17}H_{18}O_2$, calcd 254.1307, found 254.1322.

Compound 1d. ^1H NMR (300 MHz, $CDCl_3$): δ 1.32 (d, J = 8.6 Hz, 2 H), 1.39 (d, J = 9.9 Hz, 1 H) 1.66 (d J = 8.6 Hz, 2 H), 1.82–1.93 (m, 5 H), 2.20–2.34 (m, 8 H), 2.40 (s, 2 H), 2.70 (s, 2 H), 5.99 (s, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 22.27 (t), 29.76 (t), 30.18 (t), 36.86 (t), 37.05 (t), 40.65 (d), 55.84 (d), 126.98 (d), 166.89 (s), 199.77 (s). IR (KCl): 2946, 2873, 1664, 1615, 902, 731 cm^{-1}. Mp: 98–102 °C. MS (*m/e* (relative intensity)): 284 (M^+, 100), 215 (54). HRMS: $C_{19}H_{24}O_2$, calcd 284.1776, found 284.1786.

Compound 1e. ^1H NMR (300 MHz, $CDCl_3$): δ 1.54 (d, J = 10.4 Hz, 1 H), 1.70–1.97 (m, 5 H), 2.08–2.30 (m, 12 H), 2.42 (d, J = 4.9 Hz, 1 H), 2.56 (d, J = 10.1 Hz, 1 H), 2.66 (d, J = 10.1 Hz, 1 H), 3.13 (br s, 1 H), 5.49 (br s, 1 H), 5.74 (br s, 1 H), 5.92 (s, 1 H), 5.89 (s, 1 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 22.25 (t, 2 C), 29.92 (t), 30.79 (t), 32.02 (t), 37.00 (t), 37.08 (t), 39.68 (t), 42.41 (d), 43.00 (d), 45.64 (d), 47.33 (d), 50.37 (d), 53.04 (d), 126.58 (d), 127.16 (d), 131.72 (d), 132.51 (d), 167.13 (s), 167.30 (s), 199.76

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(15) (a) Lai, T.-W.; Sen, A. *J. Am. Chem. Soc.* **1981**, *103*, 4627. (b) Lai, T.-W.; Sen, A. *J. Am. Chem. Soc.* **1982**, *104*, 3520. (c) Lai, T.-W.; Sen, A. *Organometallics* **1982**, *1*, 415.

(16) (a) Akhtar, M. N.; Rooney, J. J.; Samman, N. G.; Hügel, H. M.; Jackson, W. R.; Nicolson, D. M.; Rash, D. *Aust. J. Chem.* **1977**, *30*, 1509. (b) Sorenson, T. S.; Ranganayakulu, K. *Tetrahedron Lett.* **1972**, 2447.

(17) Cotton, F. A. *Inorg. Synth.* **1972**, *13*, 121.

(18) (a) Piers, E.; Grierson, J. R.; Lau, C. K.; Nagakura, I. *Can. J. Chem.* **1982**, *60*, 210. (b) Piers, E.; Nagakura, I. *Synth. Commun.* **1975**, *5*, 193.

Table II. Crystal and Data Collection Parameters

	1a	**5a**	**6a**
empirical formula	$C_{19}H_{22}O_2$	$C_{19}H_{22}O_2$	$C_{19}H_{22}O_2$
fw	282.4	282.4	282.4
cryst size, mm	0.60 × 0.34 × 0.08	0.66 × 0.28 × 0.24	0.44 × 0.18 × 0.16
cryst syst	orthorhombic	triclinic	monoclinic
space group	$Pna2_1$	$P\bar{1}$	$P2_1/c$
a, Å	30.427(11)	11.079(2)	6.582(1)
b, Å	5.891(2)	11.750(2)	17.926(5)
c, Å	8.397(2)	13.115(2)	12.696(3)
α, deg		75.78(1)	
β, deg		74.68(1)	98.00(2)
γ, deg		65.55(1)	
cell vol. Å^3	1505.1(8)	1480.8(4)	1483.4(7)
Z	4	4	4
D(calcd), Mg/m^3	1.246	1.267	1.264
abs coeff, mm^{-1}	0.079	0.080	0.075
F(000)	608	608	608
scan type	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
scan speed, deg/min	variable; 2.93–14.65	variable; 2.93–14.65	variable; 2.93–14.65
2θ range, deg	2.5–50.0	2.5–45.0	2.5–45.0
ω-scan range, deg	0.82 + Kα separation	1.00 + Kα separation	1.00 + Kα separation
index ranges	$0 \le h \le 36, 0 \le k \le 6, -10 \le l \le 0$	$-11 \le h \le 11, -11 \le k \le 12, 0 \le l \le 12$	$-7 \le h \le 7, 0 \le k \le 19, 0 \le l \le 13$
rflns collected	1638 (908 > 3.0$\sigma(I)$)	5433 (3923 > 3.0$\sigma(I)$)	3569 (1256 > 3.0$\sigma(I)$)
no. of indep rflns	1357 (634 > 3.0$\sigma(I)$)	3899 (2447 > 3.0$\sigma(I)$)	1945 (1074 > 3.0$\sigma(I)$)
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0002F^2$	$w^{-1} = \sigma^2(F) + 0.0016F^2$	$w^{-1} = \sigma^2(F) + 0.0003F^2$
R	0.0464	0.0449	0.0438
R_w	0.0423	0.0458	0.0418
goodness of fit	1.57	1.05	1.50
largest diff peak/hole, e Å^{-3}	+0.17/−0.14	+0.20/−0.18	+0.15/−0.17

(s), 199.84 (s). IR (KCl): 3038, 2928, 1663, 1551, 1340, 1109, 838, 709 cm^{-1}. MS (*m/e* (relative intensity)): 322 (M$^+$, 100), 155 (49). HRMS: $C_{22}H_{26}O_2$, calcd 322.1933, found 322.1941.

Isolation of Compound 4a. A mixture of $Pd(PPh_3)_2Cl_2$ (0.25 mmol), 3-iodo-2-cyclohexen-1-one (5.00 mmol), zinc powder (50.0 mmol), norbornadiene (10.0 mmol), and THF (30 mL) was heated under nitrogen with stirring at 60 °C for 11 h. The mixture was filtered through Celite and then evaporated. The residue was dissolved in dichloromethane and washed with saturated aqueous sodium chloride solution. The dichloromethane solution was dried over anhydrous Na_2SO_4, concentrated, and then separated on a flash silica gel column. Elution with a mixture of hexane and ethyl acetate (3/1) gave two portions. Further separation of the second portion on a longer column using hexane/ethyl acetate (3/1) as the eluent gave **4a** (0.398 g) in 56% yield and **1a** (0.0282 g) in 4% yield. Important spectral data for **4a** are as follows. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (dt, J = 12.5, 7.6 Hz, 1 H), 2.00 (m, 4 H), 2.16–2.40 (m, 13 H), 2.94 (m, 2 H), 5.66 (s, 2 H), 5.89 (br s, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 22.47 (t), 29.74 (t), 36.95 (t), 37.16 (t), 43.02 (d), 45.01 (t), 126.72 (d), 134.65 (d), 104.88 (s), 200.21 (s). MS (*m/e* (relative intensity)): 284 (M$^+$, 4), 175 (100), 110 (67). HRMS: $C_{19}H_{24}O_2$, calcd 284.1778, found 284.1776.

Reaction of 3-Iodo-2-cyclohexen-1-one with Norbornadiene in the Presence of Triethylamine. A mixture of $Pd(PPh_3)_2Cl_2$ (0.25 mmol), 3-iodo-2-cyclohexen-1-one (5.00 mmol), zinc powder (50.0 mmol), norbornadiene (10.0 mmol), triethylamine (0.505 g, 5.0 mmol), and THF (20 mL) was heated under nitrogen with stirring at 60 °C for 12 h. The mixture was filtered through Celite and then evaporated. The residue was dissolved in dichloromethane and was washed with saturated aqueous sodium chloride solution. The dichloromethane solution, after being dried over anhydrous Na_2SO_4, was concentrated and separated on a flash silica gel column. Elution with a mixture of hexane and ethyl acetate (2/1) gave two portions. The first portion contained a mixture of **2a** and **3a**. Further separation of the second portion with a silica gel column using a mixture of hexane and ethyl acetate (2/1) afforded **5a** and **6a** in 29% (0.204 g) and 31% (0.219 g) yields, respectively. The important spectral data for these compounds are shown below.

Compound 5a. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35–1.40 (m, 2 H), 1.51–1.70 (m, 6 H), 1.84–1.93 (m, 2 H), 2.05–2.29 (m, 6 H), 2.56–2.68 (m, 2 H), 2.89 (s, 1 H), 5.71 (m, 1 H), 6.15 (s, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 19.11 (t), 20.04 (t), 20.07 (t), 30.44 (t), 40.89 (s), 41.28 (d), 41.72 (d), 44.86 (t), 49.23 (d), 51.54 (d), 51.73 (t), 55.16 (d), 60.11 (d), 72.03 (s), 116.41 (d), 138.60 (d), 139.24 (d), 140.74 (s), 215.92 (s). IR (KCl): 3387, 3053, 2960, 2923, 2884, 2842, 1712, 1561, 1308, 1215, 717 cm^{-1}. Mp: 177–178 °C. MS (*m/e* (relative intensity)): 282 (M$^+$, 3), 216 (100). HRMS: $C_{19}H_{22}O_2$, calcd 282.1620, found 282.1612.

Compound 6a. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17–1.44 (m, 5 H), 1.56–1.69 (m, 4 H), 1.77–1.87 (m, 1 H), 2.05–2.15 (m, 2 H), 2.26 (m, 2 H), 2.38 (s, 2 H), 2.63 (d, J = 6.6 Hz, 1 H), 2.75 (d, J = 8.9 Hz, 2 H), 5.71 (m, 1 H), 6.16 (br s, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 19.20 (t), 20.23 (t), 27.41 (t), 31.29 (t), 42.72 (s), 42.82 (d), 43.77 (t), 45.26 (t), 48.21 (d), 49.88 (d), 51.17 (d), 55.45 (d), 57.26 (d), 72.84 (s), 122.62 (d), 138.67 (d), 139.57 (d), 141.92 (s), 215.43 (s). IR (KCl): 3367, 3051, 2954, 2886, 1713, 1562, 1300, 715 cm^{-1}. Mp: 177–179 °C. MS (*m/e* (relative intensity)): 282 (M$^+$, 4), 216 (100). HRMS: $C_{19}H_{22}O_2$, calcd 282.1620, found 282.1618.

Reaction of Tetrakis(triphenylphosphine)palladium with 3-Iodo-2-cyclohexen-1-one and Norbornadiene. A round-bottom flask (100 mL) containing $Pd(PPh_3)_4$ (1.154 g, 1.00 mmol) was purged with nitrogen gas three times. To the flask was added degassed THF (10 mL) and 3-iodo-2-cyclohexen-1-one (0.222 g, 1.00 mmol). The solution was then stirred for 2 h at ambient temperature. White precipitate was observed at the end of the reaction. To the solution was added NBD (0.92 g, 10 mmol), and the mixture was heated at 60 °C for 6 h. The orange-red solution was evaporated in vacuo, and the solid was washed under nitrogen with ether (30 mL). The crude compound was recrystallized from dichloromethane and hexane to give the desired orange precipitate *cis-exo*-$[Pd(C_7H_8Ph)(PPh_3)I]$ (**8a**; 0.768 g, 0.90 mmol) in 90% yield. The important spectral data for the compound are as follows. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.15 (dd, J = 15.0, 6.4 Hz, 1 H), 1.27 (d, J = 9.3 Hz, 1 H), 1.98 (d, J = 9.3 Hz, 1 H), 2.08–2.78 (m, 8 H), 2.86 (s, 1 H), 5.42 (dd, J = 5.5, 3.0 Hz, 1 H), 5.84 (br s, 1 H), 6.10 (dd, J = 5.3, 3.0 Hz, 1 H), 7.45 (m, 9 H), 7.72 (m, 6 H). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, −60 °C): δ 11.88 (d, J_{PC} = 6.0 Hz, attached to Pd metal), 20.21, 33.23, 35.52 (cyclohexenone, CH_2), 45.50, 46.08 (norbornenyl bridgehead), 47.33 (norbornenyl bridge), 47.55 (attached to cyclohexenone), 104.16 (d, J_{PC} = 16.1 Hz, cyclohexenone, sp^2 tertiary C), 128.86 (cyclohexenone, sp^2 quaternary C), 136.27 (d, J_{PC} = 11.1 Hz, norbornenyl CH═CH), 137.65 (norbornenyl CH═CH), 198.25

(=CO), 127.75 (d, J_{PC} = 11.1 Hz), 129.93 (d, J_{PC} = 50.6 Hz), 130.45 (s), 134.60 (d, J_{PC} = 11.1 Hz, PPh$_3$). $^{31}P\{^1H\}$ NMR (40.25 MHz, CDCl$_3$): 31.09 (s) ppm. IR (KCl): 3050, 2980, 1674, 1653, 1568, 1433, 750, 693 cm^{-1}. Mp: 175 °C dec. MS (FAB): 555 (M$^+$ – I). Anal. Calcd for $C_{31}H_{30}IOPPd$: C, 54.55; H, 4.40. Found: C, 54.71; H, 4.52.

X-ray Structure Determinations. All data were collected at room temperature on a Siemens R3m/V diffractometer using Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator. The structures were solved by direct methods and refined by a full-matrix least-squares method based on F values. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were positioned on geometric grounds (C–H = 0.96 Å), and an overall hydrogen atom thermal parameter was refined to a value of 0.087 Å^2. All calculations were performed on a Micro VAX II computer system using SHELXTL-Plus programs. Relevant crystallographic parameters are assembled in Table II.

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Supplementary Material Available: Tables of atomic coordinates, complete bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1a**, **5a**, and **6a** (15 pages). Ordering information is given on any current masthead page.

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