New Method for the Classification of Nucleophiles in the Palladium-Catalyzed Substitution of Allylic Acetates

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Palladium-catalyzed reactions of nucleophiles were carried out on cyclopent-2-enyl acetate (1), 3a,4,5,6,7,7a-hexahydro-(1α,3aα,4α,7α,7aα)-4,7-methano-1*H*-inden-1-yl acetate (**3b**), and 3a,4,5,6,7,7a-hexahydro-(1β,3aα,4α,7α,7aα)-4,7-methano-1*H*-inden-1-yl acetate (**5b**) to give indications on the mechanism of the reaction and the mode of attack of the nucleophiles. The lack of reactivity of **3b** confirmed that a trans relationship between the approaching Pd(0) complex and the departing acetate is required in the η^3-allyl-forming step. Examination of the reactivity of the nucleophiles with **5b** compared to **1** allowed a decision as to whether the primary attack of the intermediate (η^3-allyl)palladium complex by the nucleophile is directed to η^3-allylic ligand (Nu_1 nucleophiles: sodium dimethyl malonate, sodium cyclopentadienide, lithium thioxodiphenylphosphide, morpholide) or to the metal (Nu_2 nucleophiles: phenylzinc chloride, sodium indenide, ammonium formate).

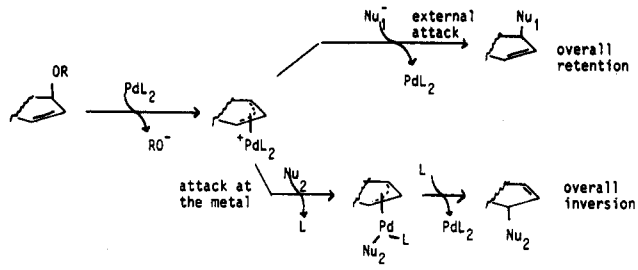
The palladium-catalyzed allylic substitution reaction by various nucleophiles has been thoroughly studied and has received wide applications in organic synthesis.[1] This reaction was regarded to proceed in two steps: the first step involves the oxidative addition of the allylic acetate to a Pd(0) complex; the (η^3-allyl)palladium complex thus formed is further attacked by the nucleophile in a second step (Scheme I).

The usual high stereoselectivities observed for the substitution (overall retention or inversion of configuration) require that both steps are stereoselective. This allows efficient transfer of asymmetry.[2]

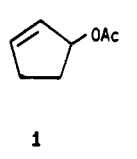
Inversion of configuration in the (η^3-allyl)palladium-forming step (through oxidative addition) was formerly deduced from the overall stereochemistry of substitution[3] and has been recently demonstrated.[2c] This step is subjected to a high stereocontrol and necessitates an antiperiplanar arrangement of the breaking allylic C–O bond and of the C–Pd bond.[4] The stereochemistry of the second step (and hence the stereochemistry of the whole process) has been shown to depend upon the nature of the nucleophile and more precisely upon the mode of attack by the nucleophile of the (η^3-allyl)palladium intermediate complex (Scheme I).

"Nu_1" nucleophiles proceed by external attack of the allylic ligand to give products with overall retention of configuration at the carbon of the acetate. "Nu_2" nucleophiles first attack the metal to give a neutral complex which liberates the product through reductive elimination (coupling of ligands).[5] Two methods are presently used for the classification (Nu_1 or Nu_2) of the nucleophiles. In the first method, the character (Nu_1 or Nu_2) of a nucleophile may be assigned by comparison of the stereochemistries of a stereodefined substrate and of the product of the palladium-catalyzed reaction of this nucleophile. However, this method could not conclude on the origin of the minor inversion observed with amines (either partial behavior of the nucleophile as Nu_2 or isomerization of the substrate prior to oxidative addition).[8a] The second method describes a classification of the nucleophiles according to their regiochemistry selectivity onto a model substrate.[6] Three categories thus correlate with increasing "hardness"[7] of the nucleophiles: (A) soft, (B) intermediate, and (C) hard.

Scheme I



In this work, we describe the use of adequately devised epimeric acetates **3b** and **5b** to gain insight into the stereochemical routes of *both* steps of the Pd-catalyzed substitution of allylic acetates by various nucleophiles. We propose a new, simple method for the classification of the nucleophiles (as Nu_1 or Nu_2) based on their compared reactivity on **5b** and **1**. The alcohol **3a**[10] was prepared by



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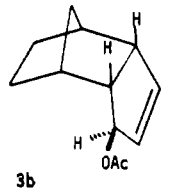

3b

base-induced opening[11] of the exo epoxide **2**.[12] **3a** was then

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(6) Keinan, E.; Roth, Z. *J. Org. Chem.* **1983**, *48*, 1769.
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(8) (a) Trost, B. m.; Keinan, E. *J. Am. Chem. Soc.* **1978**, *100*, 7779. (b) Backvall, J. E.; Nordberg, R. E. *J. Organomet. Chem.* **1985**, *285*, C24.
(9) Experiments with **3a** and its epimer **5a** have been previously carried out to establish that the $Fe(CO)_5$-catalyzed isomerization of allylic alcohols involved a suprafacial 1,3-hydrogen shift occurring—with or without Fe–H bonding—on the same face as the metal atom. (a) Cowherd, F. G.; von Rosenberg, J. L. *J. Am. Chem. Soc.* **1969**, 2157. (b) Strauss, J. U.; Ford, P. W. *Tetrahedron Lett.* **1975**, *33*, 2917.
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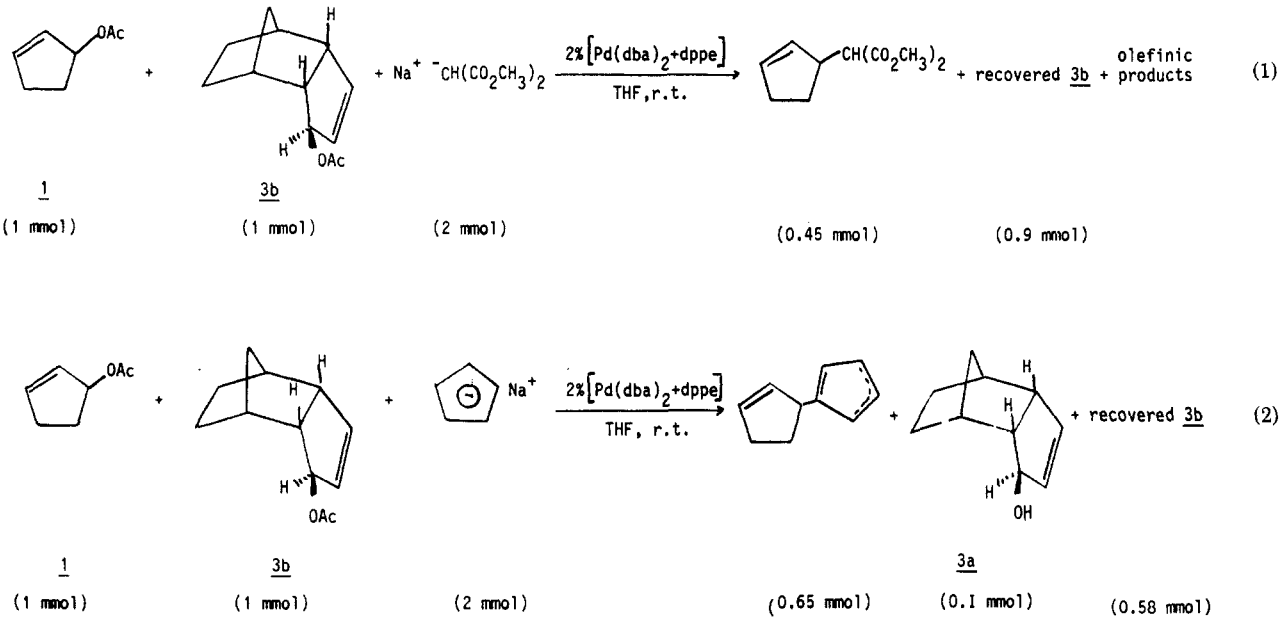
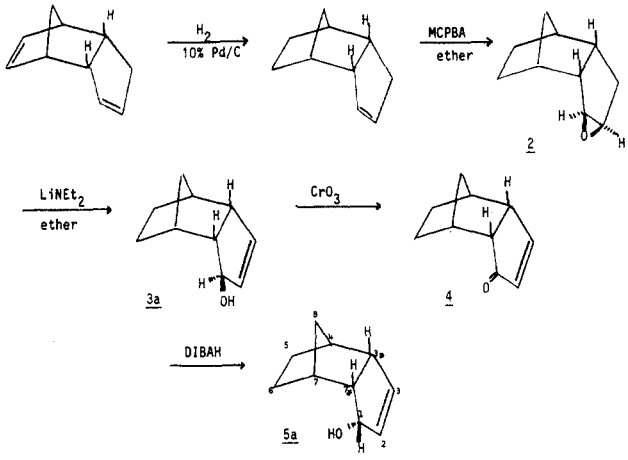


(1) (2)

used as starting material for the preparation of the endo alcohol **5a**[13] obtained by stereoselective reduction of the α,β-unsaturated ketone **4**.[10] The diastereomeric alcohols



3a and **5a** and their corresponding acetates **3b** and **5b** could be easily distinguished and their ratio measured by ^{1}H NMR or GLC. At 110 °C on a 25-m length of CP Sil 19CB capillary column, **3a**, **5a**, **5b**, and **3b** gave completely separated peaks with respectively 4.58, 5.02, 7.23, and 7.82 min as retention times.

In compound **3b**, the face of the double-bond distal to the acetate group is hindered, thus precluding its approach by reagents. This is not the case in the epimeric compound **5b**.

Oxidative addition of the allylic acetates to the palladium(0) complex requires coordination of the complex by a distofacial[15] route (relative to the acetate group). We thus anticipated that no Pd-catalyzed substitution of the acetate group in **3b** could be achieved. Indeed, when equimolecular amounts of **1** and **3b** were brought in a competitive catalyzed reaction with sodium dimethyl malonate, **3b** was found to be unreactive and was recovered in a quantitative yield (eq 1). The main product formed from **3b** and sodium cyclopentadienide was the alcohol **3a** arising from the noncatalyzed nucleophilic attack on the carbonyl of the acetate group (eq 2). On prolonged reaction with bulky nucleophiles (sodium indenide) **3a** was isolated is good (67%) yield. The lack of reactivity of **3b** in Pd-catalyzed reaction of nucleophiles thus confirms the stereochemistry of the oxidative addition of the allylic acetates to palladium(0) complex.

In contrast to compound **3b**, **5b** would be expected to coordinate the palladium(0) complex by a distofacial[14] route (relative to the acetate group) and then ionize and form a (η^3-allyl)palladium intermediate **6**. Nucleophiles able to attack at the metal would give the neutral complex **7** and after coupling of ligands the product **8**. In contrast, nucleophiles that would attack the η^3-allylic ligand anti to the metal should be unreactive.

Nucleophiles that are unreactive with **5b** but reactive with **1** (considered as a nonhindered analogue of **5b**) would be defined as Nu_1 nucleophiles. Nucleophiles that react with **5b** may therefore be classified as Nu_2 nucleophiles. Competitive experiments were carried out by reacting 2 mol equiv of nucleophile with a 1:1 mixture of **1** and **5**. Yields for products are collected in Table I.

In agreement with the above expectation, the malonate anion did not react. The thiophosphide anion was unreactive too, thus confirming the stereochemistry of the attack of the nucleophile.[16]

In conditions with which a product was formed in good yield in the reaction of **1**, reaction of **5b** with morpholine afforded no expected product. This result is a strong indication that amines behave as soft or "A"[6] nucleophiles. The loss of stereochemistry reported for the reaction of amines with stereodefined substrates[8] would thus be more likely due to some isomerization of the allylic acetate, as shown by Backvall.[8b]

In the catalytic conditions used for the substitution (2% catalyst), either in the absence of any added nucleophile or in the presence of added acetate (2 mol equiv of tetraethylammonium/substrate) little (<2%) isomerization of **5b** into **3b** was detected (GLC). This latter isomer would, however, not lead to a substitution product (vide supra). The formation of a nonreactive η^3-allylic complex from **5b** should result in a decrease of the concentration

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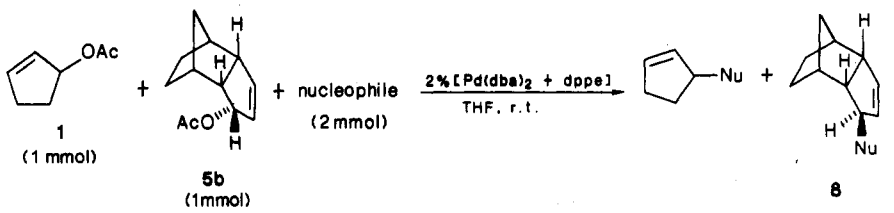
Table I. Classification of Nucleophiles



nucleophile	Nu	isolated products after 24-h reaction, mmol: Nu	recovered 5b	8	class of nucleophile (cf. Scheme II)
$Na^+C^-H(CO_2CH_3)_2$	$-CH(CO_2CH_3)_2$	0.55	1.0		Nu_1
		0.55	0.78		Nu_1
$Li^+P^-(S)Ph_2$	$-P(S)Ph_2$	0.81	0.76		Nu_1
		0.50	0.50[a]		Nu_1
				0.65[d]	Nu_2
$PhZnCl^b$	-Ph			0.50	Nu_2
$HCOONH_4{}^{b,c}$	-H			0.54	Nu_2

[a] 0.1 mmol of alcohol **5a** was also produced. [b] The reaction was carried out on 1 mmol of **5b** alone. [c] $Pd(OAc)_2$ as catalyst in dioxane as solvent. [d] 0.15 mmol of alcohol **5a** was also produced, and 0.08 mmol of acetate **5b** was recovered.

of the palladium catalyst. It thus could be responsible for the moderate yields in products obtained from 1 in the competitive experiments of nucleophiles between 1 and **5b**.

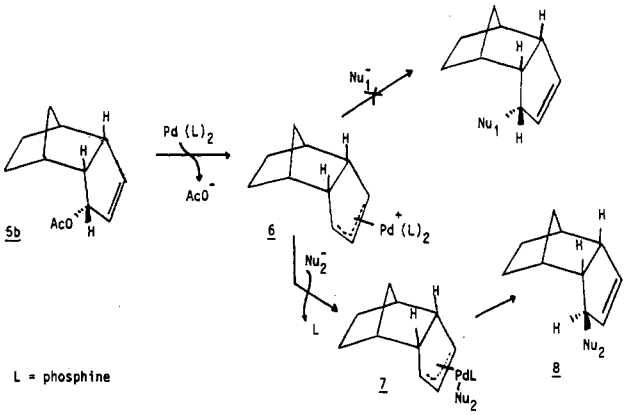
We have shown by ^{31}P [^1H] NMR examination that oxidative addition of **5b** was immediately obtained when mixing equimolecular amounts of dppe and $Pd(dba)_2$ in THF. Monitoring of the decrease in intensity of the ^{31}P signal (δ = 31.1 ppm relative to 85% H_3PO_4) of $Pd(dppe)_2$ after addition of 1 or **5b** revealed that reaction of 1 with $Pd(dppe)_2$ was 10 times faster than reaction of **5b**. This result allows us to explain that relatively slow oxidative addition of **5b** did not rapidly poison the catalyst but lowered the yields in products of nucleophiles with 1.

The palladium-catalyzed reaction of **5b** with phenylzinc chloride (known to proceed with inversion of configuration)[5b] did afford a phenyl-substitution single product. To the phenyl was assigned the exo stereochemistry, as the ^1H NMR spectrum showed no aliphatic proton shifted by the proximity of the phenyl group.

Whereas the cyclopentadienide anion behaves as a soft nucleophile, the indenide anion acts as a "hard" nucleophile, to give moderate yield of product. These behaviors may be correlated to the pk_A of the conjugate acids (respectively 15 for the cyclopentadiene[16] vs. 21 for indene).[17] The stereochemistry of the Pd-catalyzed reduction of allylic acetates with ammonium formates[18] has not yet been described and is not easy to determine with a stereochemical model. Our results account for the attack of the formate ion at the palladium followed by reductive coupling of ligands in the (η^3-allyl)palladium complex obtained after decarboxylation (Scheme II).

Our experiments with **3b** indicate that a definite trans stereochemical relationship between the approaching palladium(0) complex and the departing acetate is required to ensure the oxidative addition occurs. Examination of the reactivity of nucleophiles with **5b** compared to 1 allowed us to decide whether the primary attack of the nucleophile to the (η^3-allyl)palladium complex is directed to the η^3-allylic ligand (trans to the metal) (Nu_1 nucleophiles)

Scheme II[a]



[a] All compounds are racemic.

or to the metal (Nu_2 nucleophiles).

Use of **5b** in competitive reactions with 1 would constitute an easy, straightforward method for the classification of nucleophiles according to their mode of attack in metal-catalyzed substitution of allylic acetates.

Experimental Section

Instrumentation and Materials. ^1H NMR spectra were recorded by using either Perkin-Elmer R32 (90 MHz) or Bruker WM-250 (250 MHz) spectrometers in $CDCl_3$ unless otherwise stated; chemical shifts are reported in parts per million downfield from an internal standard (Me_4Si). GC analyses were performed on a Carlo Erba 4130 capillary gas chromatography using a 25-m CP Sil 19 CB capillary column connected with a computing integrator. Mass spectral (MS) (70 eV) data were determined on an R-10 gas chromatograph/mass spectrometer. Silica gel 60 (230–400 mesh) supplied by Merck was used for flash column chromatography.[19] In vacuo distillation refers to the use of a Kugelrohr GK 50 Buchi apparatus. Reactions involving palladium catalysis were run under an argon atmosphere. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon. The following materials were prepared by the methods reported in the literature: cyclopent-2-enol[20] and diphenylphosphine sulfide.[21]

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General Procedure for Pd-Catalyzed Reactions. In the Experimental Section the catalyst refers to a solution prepared by dissolving equimolecular amounts of $Pd(dba)_2$ (23 mg, 0.04 mmol) and dppe (16 mg, 0.04 mmol) in THF (2 mL) and stirring the resulting solution for 15 min at room temperature. An appropriate amount (2 mol %) of this catalyst solution was added to 1, **3b**, **5b** (1 mmol), or a mixture of two among them (competitive reaction) in THF (10 mL).

The substrate–catalyst solution was stirred for 15 min, and an equimolecular amount of nucleophile, previously prepared as an approximately 0.2 M solution in THF (sodium dimethyl malonate, sodium cyclopentadienide or indenide, lithium thiophenylphosphide), was then added. After being stirred overnight at room temperature, the reaction mixture was hydrolyzed (saturated NH_4Cl aqueous solution) and extracted with pentane or ether. The organic layer was dried, the solvent removed, and the residue purified by Kugelrohr distillation or flash column chromatography. Product mixtures were analyzed by GLC or NMR.

3a,4,5,6,7,7a-Hexahydro-(1α,3aα,4α,7α,7aα)-4,7-methano-1*H*-inden-1-ol (3a). Dicyclopentadiene was hydrogenated in EtOH over 10% Pd/C to give a 90:10 mixture (GLC) of dihydrocyclopentadiene and tetrahydrocyclopentadiene. The solvent was distilled, and the residue was treated by *m*-chloroperoxybenzoic acid (MCPBA) (1 mol equiv) in ether to give the exo epoxide **2**,[12] which was used without further purification in the next step.

To a cooled (−20 °C) 1.6 M solution of *n*-BuLi in hexane (69 mL, 110 mmol) was added dropwise a solution of diisopropylamine (15.4 mL, 110 mmol) in ether (50 mL). This solution was allowed to warm to room temperature, and a mixture of 38 mL (220 mmol) hexamethylphosphoramide (HMPA) and 6.6 g (44 mmol) of epoxide **2** in 50 mL) ether was added dropwise. After being stirred overnight, the reaction mixture was diluted with ether (100 mL), washed with 10% HCl and water, and dried ($MgSO_4$), and the solvent was removed. Distillation of the residue afforded 4.6 g (70%) of **3a**: bp 70–80 °C (1 mmHg); NMR 1.06–1.30 (4 H, m), 1.47–1.55 (2 H, m, H_8), 2.2–2.4 (3 H, m, H_4, H_7, H_{7a}), 3.15 (1 H, m, H_{3a}), 4.68 (1 H, br s, H_1), 5.82 (1 H, ddd, J = 6, 2, 2 Hz, H_2), 5.90 (1 H, ddd, J = 6, 2, 2 Hz, H_3).

3a,4,5,6,7,7a-Hexahydro-(1α,3aα,4α,7α,7aα)-4,7-methano-1*H*-inden-1-yl Acetate (3b). To a cooled (0 °C) mixture of **3a** (1.5 g, 10 mmol), Et_3N (1.65 mL, 12 mmol), and DMAP (122 mg, 1 mmol) in 20 mL of ether was added dropwise Ac_2O (1.05 mL, 11 mmol). After being stirred for 2 h, the solution was washed with 10% HCl and saturated $NaHCO_3$ and dried ($MgSO_4$). Evaporation of the solvent and distillation of the residue gave 1.8 g (94%) of **3b** as an oil: bp 90–100 °C (1 mmHg); NMR 1.1–1.6 (6 H, m), 2.05 (3 H, s, CH_3CO), 2.35 (2 H, m), 2.45 (1 H, m), 3.15 (1 H, m, H_{3a}), 5.6 (1 H, m, H_1), 5.8 (1 H, ddd, J = 6, 2, 2 Hz, HC=), 6.05 (1 H, m, HC=); GC–MS (m/e) 192 (M^+), 150, 132, 131, 104, 91, 83, 66, 54, 43. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.90; H, 8.46.

3a,4,5,6,7,7a-Hexahydro-(3aα,4α,7α,7aα)-4,7-methano-1*H*-inden-1-one (4). To 2.0 g (13.3 mmol) of **3a** dissolved in acetone (15 mL) was added dropwise a solution of 2.32 g of CrO_3 in 1.1 mL of concentrated H_2SO_4 and 4.4 mL of H_2O. This mixture was stirred for 0.1 h and then diluted with 80 mL of H_2O and extracted with ether. The ethereal layer was separated, washed with water, and dried ($MgSO_4$). Removal of the solvent gave the enone **4** (1.93 g, 98%): mp 33–35 °C (lit.[10] 34–36 °C); NMR 1.15 (2 H, m), 1.40 (2 H, br s), 1.60 (2 H, m), 2.46 (1 H, br s), 2.57 (2 H, br s), 3.19 (1 H, m, H_{7a}), 6.05 (1 H, dd, J = 5.7, 1.6 Hz, H_2), 7.55 (1 H, dd, J = 5.7, 2.65 Hz, H_3).

3a,4,5,6,7,7a-Hexahydro-(1β,3aα,4α,7α,7aα)-4,7-methano-1*H*-inden-1-ol (5a). To an ice-cooled solution of **4** (1.48 g, 10 mmol) in hexane (50 mL) under an argon atmosphere was introduced (syringe) 1.5 equiv of diisobutylaluminum hydride (DIBAH). The mixture was stirred for 2 h, and methanol (50 mL) and then tartaric acid were added until total dissolution of aluminum salts was achieved. Ether (100 mL) was added, the organic layer separated and dried, and the solvents removed to leave **5a** (0.95 g, 63%): NMR 1.1–1.7 (6 H, m), 2.3 (2 H, m), 2.59 (1 H, m), 2.80 (1 H, m), 4.85 (1 H, dd, J = 9, 1.8 Hz, H_1), 5.71 (1 H, m, C=CH), 5.76 (1 H, m, =CH).

3a,4,5,6,7,7a-Hexahydro-(1β,3aα,4α,7α,7aα)-4,7-methano-1*H*-inden-1-yl Acetate (5b). Prepared as for **3b**: NMR 1.1–1.7 (6 H, m), 2.05 (3 H, s, CH_3CO), Hz, 2.1 (1 H, br s), 2.3 (1 H, br s), 2.85 (2 H, m), 5.6 (1 H, d of m, J = 8.8 Hz, H_1), 5.7 (1 H, ddd, J = 5.8, 1.8, 1.8 Hz, C=CH), 5.9 (1 H, ddd, J = 5.75, 2.2 Hz, C=CH). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.17; H, 8.64.

Reactions with Sodium Dimethyl Malonate. The sodium dimethyl malonate was prepared by addition of an equimolecular amount of dimethyl malonate in a suspension of dry NaH in THF.

a. A reaction was carried out with 126 mg (1 mmol) of 1 and 1 mmol of sodium dimethyl malonate, in THF, in the presence of 2 mol % catalyst. After workup, distillation of the residue afforded 109 mg (55%) of the dimethyl cyclopent-2-enylmalonate as an oil: NMR 1.4–1.75 (2 H, m), 2.0–2.4 (3 H), 3.34 (1 H, d, J = 8 Hz, $CH(CO_2Me)_2$), 3.7 (6 H, s, CO_2CH_3), 5.55–5.85 (2 H, m, C=CH); GC–MS (m/e) 198 (M^+) (6), 139 (14), 138 (53), 133 (14), 132 (45), 107 (26), 106 (16), 101 (34), 100 (20), 79 (44), 78 (13), 77 (22), 67 (100), 66 (32), 41 (18).

b. The same reaction as above was performed on a mixture of 126 mg (1 mmol) of **1**, 192 mg (1 mmol) of **5b**, and dimethyl malonate (2 mmol). Fractional distillation afforded 110 mg (55%) of dimethyl cyclopent-2-enylmalonate and 189 mg (98.5% recovery) of **5b**.

c. The reaction performed on a mixture of 126 mg (1 mmol) of 1 and 192 mg (1 mmol) of **3b** gave 262 mg of a 2:1 (NMR) mixture of **3b** and dimethyl cyclopent-2-enylmalonate. This latter compound (91 mg, 45%) was isolated by distillation while 170 mg (90%) of **3b** was recovered.

Reactions with Morpholine. a. A reaction was carried out with 126 mg of **1** (1 mmol) and 87 μL (1 mmol) of morpholine in the presence of 2 mol % catalyst. After workup, the residue was distilled to give 100 mg (65%) of *N*-(cyclopent-2-enyl)-morpholine as an oil: bp 60 °C (1 mmHg); NMR 1.7–2 (2 H, m), 2.1–2.5 (6 H, series of m, CH_2N and $=CCH_2$), 3.5–3.8 (5 H, series of m, CH_2O and =CCHN), 5.6–5.9 (2 H, =CH); GC–MS (m/e) 153 (M^+), 138, 124, 108, 94, 86, 67, 56, 41. Anal. Calcd for $C_9H_{15}NO$: C, 70.54; H, 9.87; N, 9.14. Found: C, 70.37; H, 9.93; N, 8.93.

b. A competitive reaction was carried out between 126 mg of 1 (1 mmol), 192 mg of **5b** (1 mmol), and 175 μL of morpholine (2 mmol) in the presence of 2 mol % catalyst. The reaction mixture was stirred overnight and diluted with ether (50 mL). The ethereal layer was washed successively with 10% HCl and water and dried ($MgSO_4$). After removal of the solvent, the residue was distilled (Kugelrohr) to give 150 mg (78% recovery) of pure **5b** (TLC and GLC). The aqueous phase was made basic (10% NaOH) and extracted with ether to afford, after removal of the solvent, 85 mg (55%) of *N*-(cyclopent-2-enyl)morpholine.

Reactions with Cyclopentadienylsodium. a. The reaction of CpNa (10 mL of a 0.2 M solution in THF, 2 mmol) with 1 (252 mg, 2 mmol) in 5 mL of THF in the presence of 1 mol % catalyst afforded, after workup and column chromatography (SiO_2, pentane), a colorless oil (168 mg, 64%) as a mixture (GLC) of the two isomers (1- and 2-(cyclopent-2-enyl)cyclopentadiene: NMR (CCl_4) 1.2–1.9 (2 H, m, CH_2), 2.0–2.5 (2 H, m, $C=CCH_2$), 2.75–2.85 (2 H, 2 br s, $=CCH_2C=$), (1 H, m, =CCHC=), 5.6–6.4 (5 H, =CH); GC–MS (m/e) 132 (M^+), 131, 117, 91, 78, 67, 51, 38. Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.78; H, 9.19.

b. CpNa (2 mmol in 10 mL of THF) was reacted with 1 (126 mg, 1 mmol) and **5b** (192 mg, 1 mmol) in the presence of the catalyst in 10 mL of THF. After workup, the crude product was purified by column chromatography (SiO_2). Elution with pentane afforded the above products 1- and 2-(cyclopent-2-enyl)cyclopentadiene (67 mg, 51%; further elution (pentane/EtOAc 1:1) gave 127 mg of a 3:1 mixture of **5b** and **5a** (GLC).

c. A similar reaction with **3b** (instead of **5b**) afforded 83 mg (63%) of (cyclopent-2-enyl)cyclopentadienes and 130 mg of a 7:1 mixture of **3a** and **3b** (GLC).

Reactions with Indenylsodium. a. 1 (126 mg, 1 mmol) was reacted with indenylsodium (1 mmol) in THF (5 mL) in the presence of 2 mol % catalyst. Evaporation of the solvent and distillation of the residue gave 95 mg (52%) of 1-(cyclopenten-2-yl)indene: bp 130 °C (1 mmHg); NMR 1.6–2.3 (2 H, m, aliphatics), 2.3–2.6 (2 H, m, $CH_2C=C$), 3.2 (2 H m, $ArCH_2C=$), 3.9

(21) Peters, G. *J. Am. Chem. Soc.* **1960**, *82*, 4751.

(1 H, m, = CCHC=), 5.9-6.1 (3 H, m, =CH), 7.0-7.5 (4 H, m, Ar); GC-MS (*m/e*) 182 (M^+), 167, 152, 141, 128, 116, 91, 89, 67, 51, 41. Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.54; H, 7.88.

b. **5b** (384 mg, 2 mmol) was reacted with indenylsodium (2 mmol) in THF (10 mL) in the presence of 2 mol % catalyst. Column chromatography (SiO_2, cyclohexane) of the crude mixture gave an oil from which excess indene was removed by distillation, to afford as a residue the 1-substituted indene (320 mg, 65%): NMR 1.25-1.55 (6 H, m, aliphatics), 2.3 (1 H), 2.4 (2 H), 3.15 (1 H, m, =C CH), 3.3 (2 H, m, $ArCH_2C$=), 3.75 (1 H, m, =CCHC=), 5.8 (2 H, =CH), 6.1 (1 H, m, =CH), 7.1-7.5 (4 H, Ar); GC-MS (*m/e*) 248 (M^+), 233, 220, 205, 191, 181, 165, 152, 133, 118, 115, 91, 79, 67, 51, 45. Further elution (80:20 cyclohexane/EtOAc) afforded two fractions: 30 mg (0.16 mmol) of recovered acetate **5b** and 50 mg (0.33 mmol) of alcohol **5a**.

Attempt at Isomerization of 5b. **5b** (192 mg, 1 mmol) was mixed with tetraethylammonium acetate (523 mg, 2 mmol) in THF (10 mL) in the presence of 4 mol % catalyst. After 72 h of reaction, no isomerization was detected by GC analysis. Distillation of the residue afforded 145 mg (75%) of recovered **5b**.

Reactions with PhZnCl. Phenylzinc chloride was prepared through addition of an equimolecular amount of phenylmagnesium chloride to a cooled (0 °C), stirred solution of zinc chloride in THF.

a. A reaction was carried out with 126 mg of **1** (1 mmol) and 1 mmol of a PhZnCl mixture in THF, in the presence of 2 mol % catalyst. After workup, the product was distilled to give a mixture of biphenyl and 3-phenylcyclopentene, from which this latter compound was isolated by column chromatography (44 mg, 30%): NMR 1.4-2.6 (4 H, m), 3.85 (1 H, m, CHPh), 5.7-6.0 (2 H, m, CH=), 7.2 (5 H, aromatics); GC-MS (*m/e*) 144 (M^+), 129, 125, 91, 77, 66, 51, 39.

b. A reaction performed with 192 mg (1 mmol) of **5b** and 1 mmol of PhZnCl in the presence of 2 mol % catalyst afforded, after removal of the biphenyl by distillation, the phenyl-substituted dihydrocyclopentadiene (101 mg, 48%) as an oil: NMR 1.2-1.6 (m, 6 H, aliphatics), 2.3 (m, 3 H), 3.15 (m, 1 H, CHC=), 3.68 (m, 1 H, CHPh), 5.67 (ddd, 1 H, =CH), 5.74 (ddd, J = 5.6, 1.6, 1.4 Hz, 1 H, =CH), 7.0-7.3 (m, 5 H, aromatics); GC-MS (*m/e*) 210 (M^+), 167, 153, 143, 128, 115, 91, 77, 67, 51, 41.

Reactions with $LiP(S)Ph_2$. Lithium thioxodiphenylphosphide (2 mmol, prepared by addition of equimolecular amount of *n*-BuLi to $HP(S)Ph_2$ in THF) was added to a mixture of **5b** (192 mg, 1 mmol) and **1** (126 mg, 1 mmol) in the presence of 2 mol % catalyst. After workup, the crude mixture was distilled (90-100 °C, 1 Torr) to give **5b** (146 mg, 76% recovery). The residue purified by column chromatography to afford 280 mg (81%) of (cyclopent-2-enyl)diphenylphosphine sulfide: NMR 2-2.25 (2 H, m, aliphatics), 2.3 (2 H, m, CH_2 C=), 4.0 (1 H, m, PCH), 5.43 (1 H, m, CH=), 5.98 (1 H, m, CH=), 7.45 (6 H, m, aromatics), 7.85 (4 H, m, aromatics); GC-MS (*m/e*) 284 (M^+), 218, 183, 152, 139, 107, 97, 77, 63, 51, 41. Anal. Calcd for $C_{17}H_{17}PS$: C, 71.80; H, 6.03; S, 11.28; P, 10.89. Found: C, 71.91; H, 5.97; S, 11.40; P, 11.15.

Reaction with Ammonium Formate. To **5b** (192 mg, 1 mmol) and ammonium formate (126 mg, 2 mmol) dissolved in dioxane (10 mL) were added $Pd(OAc)_2$ (5 mg, 0.02 mmol) and PPh_3 (26 mg, 0.1 mmol). After 12 h of stirring, water (50 mL) was added and the resulting mixture was extracted with pentane (2 × 50 mL). The pentane layer was dried, the solvent removed, and the residue purified by column chromatography (pentane as eluent) to give 3a,4,5,6,7,7a-hexahydro-(3aα,4α,7α,7aα)-4,7-methano-1*H*-indene (72 mg, 54%).

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Registry No. **1**, 20657-21-0; **2**, 65437-13-0; **3a**, 58616-86-7; **3b**, 102935-87-5; **4**, 5019-96-5; **5a**, 19926-79-5; **5b**, 107407-81-8; **8**, 107407-83-0; dimethyl cyclopent-2-enylmalonate, 88444-66-0; *N*-(cyclopent-2-enyl)morpholine, 6284-13-5; 1-(cyclopent-2-enyl)cyclopentadiene, 5202-73-3; 2-(cyclopent-2-enyl)cyclopentadiene, 24667-77-4; 1-(cyclopenten-2-yl)indene, 107407-82-9; biphenyl, 92-52-4; 3-phenylcyclopentene, 37689-22-8; (cyclopent-2-enyl)diphenylphosphine sulfide, 107407-84-1; 3a,4,5,6,7,7a-hexahydro-(3aα,4α,7α,7aα)-4,7-methano-1*H*-indene, 2825-86-7; dicyclopentadiene, 77-73-6; sodium dimethyl molonate, 18424-76-5; morpholine, 110-91-8; cyclopentadienylsodium, 4984-82-1; indenylsodium, 23181-84-2; phenylzinc chloride, 28557-00-8; lithium thioxodiphenylphosphide, 54572-97-3; ammonium formate, 540-69-2; palladium acetate, 3375-31-3; triphenylphosphine, 603-35-0; $Pd(dba)_2$, 32005-36-0; dppe, 1663-45-2.

Heterogeneous Catalysis in Organic Chemistry. 6.[1] An Experimental Description of the Nature of the Hydrogenation Sites Present on Dispersed Pt Catalysts

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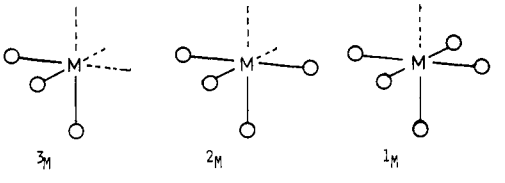
Ten Pt/controlled pore glass (CPG) catalysts having different reactive site densities as determined by single turnover (STO) characterizations were used to catalyze the dehydrogenation of cyclohexane to benzene under conditions previously used for the Pt single-crystal catalysis of this same reaction. It was found that the extent of benzene formation was related to the number of STO hydrogenation sites present on the catalyst. Since the single-crystal study showed that this dehydrogenation reaction occurred over corner atoms, it is concluded that the hydrogenation sites on the dispersed Pt catalysts are corner atoms as previously implied on mechanistic considerations.

One of the problems associated with the use of heterogeneous catalysts is the frequent lack of selectivity encountered in reactions promoted by such species. One reason for this problem is the presence on the catalyst of a number of different types of surface atoms having varying degrees of coordinative unsaturation and, thus, differing reaction characteristics.[2] In order to more fully utilize these catalytic species, it is necessary to have some understanding of the types of reactions promoted by these

Scheme I



(1) For Part 5, see: Augustine, R. L.; Lenczyk, M. E. *J. Catal.* **1986**, *97*, 269.

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