and polymers of higher nuclearity might be expected to proceed analogously (i.e. via the stepwise methodology used to prepare the trimetallic derivatives or via convergent syntheses in which "arene-poor" complexes are reacted with dilithiated "arene-rich" reagents). Indeed, such studies are currently underway in our group.

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Palladium-Mediated Synthesis of Urethanes from Amines, Carbon Dioxide, and Cyclic Diolefins

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Addition of preformed carbamate anions $RR'NHCO_2^{-+}HBase$, generated from various primary and secondary amines and carbon dioxide, to (norbornadiene)palladium dichloride at −78 °C followed by addition of DIPHOS (bis(diphenylphosphino)ethane) and then reductive cleavage at 0 °C with sodium borohydride gave nortricyclo carbamate esters (**1a–d**) in good yields (75–100% by GC). Cleavage with anhydrous hydrogen chloride also gave nortricyclo carbamate esters. Addition of (dicyclopentadiene)palladium dichloride to the carbamate anion at 0 °C gave the corresponding carbamate esters (**2a–i**) in good yields (53–100% by GC) after reductive cleavage with either sodium borohydride or dihydrogen. Addition of $BuNHCO_2^{-+}H_3NBu$ to 1,4-(cyclooctadiene)palladium dichloride at −35 °C followed by reductive cleavage with sodium borohydride gave cyclooct-4-enyl-1 *N*-butylcarbamate (**3**) in 16% isolated yield. An indication of the nucleophilicity of the carbamate anion was obtained by direct competition studies with the acetate anion on attack on (dicyclopentadiene)palladium dichloride at 0 °C. The relative rate of reaction of $BuNHCO_2^{-+}H_3NBu$ vs $AcO^{-+}H_3NBu$ was determined to be 1:2.66.

Introduction

Urethane and polyurethane materials find many important applications. These materials are historically made by the addition of an alcohol to an isocyanate (eq 1).[1] The isocyanate in turn is constructed by the addition of

$$RN{=}C{=}O + R'OH \rightarrow RNHCO_2R' \quad (1)$$

$$RNH_2 + COCl_2 \rightarrow RN{=}C{=}O + 2HCl \quad (2)$$

phosgene to an amine with elimination of 2 equivalents of hydrogen chloride (eq 2). This method for the production of urethane compounds has the major drawback of using highly toxic raw materials, phosgene and isocyanates. Several publications and patents have dealt with either making isocyanates without the use of phosgene or constructing urethanes without the use of either phosgene or isocyanates.[2] These published results have found only limited success.

The utilization of carbon dioxide in the construction of useful moieties has drawn considerable attention.[3] One strategy for carbon dioxide activation is the addition of either a primary or secondary amine, as shown in eq 3, giving a carbamate salt.[4] Once carbon dioxide has been activated by the amine, the carbamate salt can then be used in further steps to give stable products.[5]

$$2RR'NH + CO_2 \rightleftharpoons RR'NCO_2^{-+}H_2NRR' \quad (3)$$

The use of the carbamate anion as a nucleophile has been investigated, but with only limited success. The carbamate anion has been reported to give two major types of products when used as a nucleophilic agent. The desired product is that which results from oxygen attack on electrophiles giving urethane compounds while the other major reaction mode results from nitrogen attack giving amine products. It is not clear whether the nitrogen attack results from free amine (as a result of the equilibrium established from the reaction of the amine with carbon dioxide, eq 3) or directly from attack at the nitrogen of the carbamate anion.[6] An illustration of this multiple re-

(1) For a discussion of urethane chemistry see: Oertel, G. *Polyurethane Handbood*; Hanser: Munich, 1985.

(2) One recent example appears in U.S. Patent 4713476 issued to Bayer which generates urethanes from amines, alcohols, and urea.

(3) See for example: Inoue, S.; Yamazaki, N. *Organic and Bio-organic Chemistry of Carbon Dioxide*; Kodansha: Tokyo, 1982. Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. Aresta, A.; Forti, G. *Carbon Dioxide as a Source of Carbon*; NATO ASI Series C; Reidel: Dordrecht, The Netherlands, 1987; Vol. 206.

(4) Fichter, R.; Becker, B. *Chem. Ber.* **1911**, *44*, 3481–3485. Jensen, A.; Christensen, R.; Faurholt, C. *Acta Chem. Scand.* **1952**, *6*, 1086–1089 and references therein. Lallau, J. P.; Masson, J.; Guerin, H.; Roger, M.-F. *Bull. Soc. Chim. Fr.* **1972**, 3111–3112.

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Table I. Reaction of Norbornadienepalladium Dichloride with Amine Carbamates

carbamate salt[a]	carbamate product	GC[b] yield, %	isolated yield, %
n-$BuNHCO_2^-{}^+H_3N$(*n*-Bu)	**1a**	87	48
$PhCH_2NHCO_2^-{}^+H_3NCH_2Ph$	**1b**	55	
$PhCH_2NHCO_2^-{}^+HDBN$[c]	**1b**	90	
$PhCH_2NHCO_2^-{}^+H$Quinuclidine[d]	**1b**	88	56
$PhCH_2(Me)NCO_2^-{}^+H_2N(Me)CH_2Ph$	**1c**	8	
$PhCH_2(Me)NCO_2^-{}^+HDBN$[c]	**1c**	100	48
$PhCH_2(Me)NCO_2^-{}^+H$Quinuclidene[d]	**1c**	99.5	
$O(CH_2CH_2)_2NCO_2^-{}^+HDBN$	**1d**	75	56

[a] All reactions were carried out at 1 atm of CO_2 pressure in CH_2Cl_2. The carbamate salt was added to the palladium complex at −78 °C, and after addition the reaction was warmed to −5 °C, after which the reaction was allowed to stir for 15–30 min. All reactions were carried to completion on the basis of the starting palladium diolefin complex. [b] Dodecane was used as an internal standard. [c] DBN = 1,5-diazabicyclo[4.3.0]non-5-ene. [d] Reaction run in THF.

activity comes from the work by Hori and Yoshida.[5k,s] These independent investigators have studied the reaction of the carbamate anion as a nucleophile in direct substitution chemistry using alkyl halides as electrophiles. The poor selectivity obtained, low yields of urethane vs amine, utilizing an alkyl chloride as the electrophile limits the usefulness of their chemistry.

Other examples of the use of the carbamate anion have been reported; however, very few directly use transition-metal complexes to achieve the goal of urethane production. In a series of studies Dixneuf has reported the catalytic conversion of amines, carbon dioxide, and terminal alkynes into *O*-vinylic carbamate esters.[5l-r] These workers suggest that a carbamate anion, generated from the interaction of an amine with carbon dioxide, attacks a metal vinylidine complex giving a metal vinyl species which is subsequently cleaved by protonolysis.

It is well-known that electrophilic metal centers will activate an olefin toward nucleophilic attack.[7] To our knowledge, no one has investigated the nucleophilic attack of the carbamate anion on metal-activated olefins. We wish to report a novel stoichiometric system based on nucleophilic attack of a premade carbamate anion on palladium(II)-activated diolefin complexes. Products derived from this chemistry are potential intermediates in agricultural chemicals and have specialty chemical applications.[8]

Results

Addition of carbon dioxide to a THF or methylene chloride solution of either a secondary or primary amine causes a slightly exothermic reaction, giving the alkylammonium salt of the corresponding carbamate anion. In most cases the salt partially precipitates from solution. Addition of a stoichiometric amount of a tertiary amine base, i.e. quinuclidine or DBN (1,5-diazabicyclo[4.3.0]non-5-ene), gives the corresponding tertiary ammonium salt, as shown in eq 4. The tertiary ammonium carbamate

$$RR'NH + Base + CO_2 \rightleftharpoons RR'NCO_2^-{}^+HBase \quad (4)$$

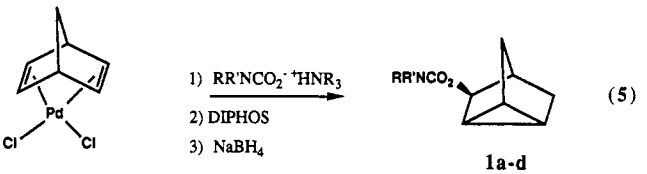
salt solutions are, in general, completely homogeneous.

Table II. Reaction of Dicyclopentadienepalladium Dichloride with Amine Carbamates

carbamate salt[a]	carbamate product	GC yield, % $NaBH_4$ quench (H_2 quench)[b]	isolated yield, %
n-$BuNHCO_2^-{}^+H_3N$(*n*-Bu)	**2a**	100 (100)	72
sec-$BuNHCO_2^-{}^+H_3N$(*sec*-Bu)	**2b**	69	41
t-$BuNHCO_2^-{}^+H_3N$(*t*-Bu)	**2c**	54	
t-$BuNHCO_2^-{}^+H_3N$(*t*-Bu)[c]	**2c**	80	26
t-$BuNHCO_2^-{}^+HDBN$[d]	**2c**	60	
$PhCH_2NHCO_2^-{}^+H_3NHCH_2Ph$	**2d**	83	54
$PhCH_2NHCO_2^-{}^+HDBN$[d]	**2d**	68 (72)	
$CH_2(CH_2CH_2)_2NCO_2^-{}^+H_2N$-$(CH_2CH_2)_2CH_2$	**2e**	55	20
$CH_2(CH_2CH_2)_2NCO_2^-{}^+HDBN$[d]	**2e**	48–53	
$O(CH_2CH_2)_2NCO_2^-{}^+H_2N$-$(CH_2CH_2)_2O$	**2f**	27	
$O(CH_2CH_2)_2NCO_2^-{}^+HDBN$[d]	**2f**	79 (65)	54
$Et_2NCO_2^-{}^+H_2NEt_2$	**2g**	44 (40)	28
$Et_2NCO_2^-{}^+HDBN$[d]	**2g**	53	
$PhCH_2(Me)NCO_2^-{}^+H_2N(Me)$-$CH_2Ph$	**2h**	40	
$PhCH_2(Me)NCO_2^-{}^+HDBN$[d]	**2h**	83	37
$PhNHCO_2^-{}^+H_3NPh$[c]	**2i**	0	
$PhNHCO_2^-{}^+HDBN$[c,d]	**2i**	47	
$PhNHCO_2^-{}^+HNEt(i\text{-}Pr)_2$[d]	**2i**	70.5	29

[a] All reactions were carried out at −5 °C using CH_2Cl_2 as solvent. Reaction time was 15–30 min after addition of olefin complex was complete. All reactions under 1 atm of CO_2 unless stated otherwise. All reactions carried to completion on the basis of the palladium diolefin complex. [b] Yields determined using dodecane as internal standard. Sodium borohydride used as reductant. (Dihydrogen used as reductant.) [c] Under 80 psig of CO_2 pressure. [d] DBN = 1,5-diazabicyclo-[4.3.0]non-5-ene.

Addition of the carbamate salt solution to (norbornadiene)palladium dichloride −78 °C followed by warming to ca. −5 °C under a carbon dioxide atmosphere (ca. 1 atm) gave a light yellow solution. Addition of DIPHOS (bis(diphenylphosphino)ethane) followed by sodium borohydride, in aqueous 2.5 N NaOH, gave a clear solution and a black precipitate (Pd^0). After workup the carbamate esters **1a–d** shown in eq 5 were isolated. Table I gives the



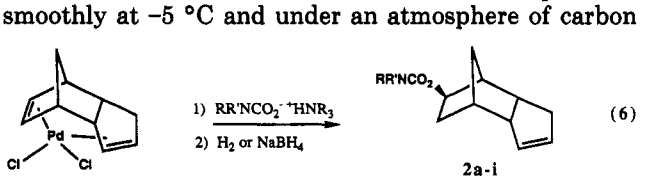
(5)

1a-d

1a: R = *n*-Bu, R' = H
1b: R = CH_2Ph, R' = H
1c: R = CH_2Ph, R' = Me
1d: R,R' = $O(CH_2CH_2)_2$

results of various amines utilized in this reaction. Quenching the reaction in eq 5, using benzylcarbamate as the nucleophile, with an ethereal solution of HCl in place of sodium borohydride gave the urethane product **1b** in 62% yield by GC.

Equation 6 shows the results of addition of (dicyclopentadiene)palladium dichloride to a premade solution of various carbamate salts. In this case the reaction proceeds smoothly at −5 °C and under an atmosphere of carbon



(6)

2a-i

2a: R = *n*-Bu, R' = H
2b: R = *s*-Bu, R' = H
2c: R = *t*-Bu, R' = H
2d: R = CH_2Ph, R' = H
2e: R, R' = $(CH_2)_5$
2f: R, R' = $O(CH_2CH_2)_2$
2g: R, R' = Et
2h: R = CH_2Ph, R' = Me
2i: R = Ph, R' = H

(6) For a review of chemistry of *N,N*-dimethyl carbamate and a discussion of nitrogen vs oxygen reactivity see: Schroth, V. W.; Andersch, J.; Schadler, H.-D.; Spitzner, R. *Chem. Z.* **1989**, *113*, 261–271.

(7) For a general discussion see: 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 433–458. Braterman, P. S. *Reactions of Coordinated Ligands*; Plenum Press: New York, 1987.

(8) For an example of the use of carbamate products as insecticides see: Khur, R. J.; Dorough, H. W. *Carbamate Insecticides: Chemistry, Biochemistry and Toxicology*; CRC Press: Cleveland, OH, 1976.

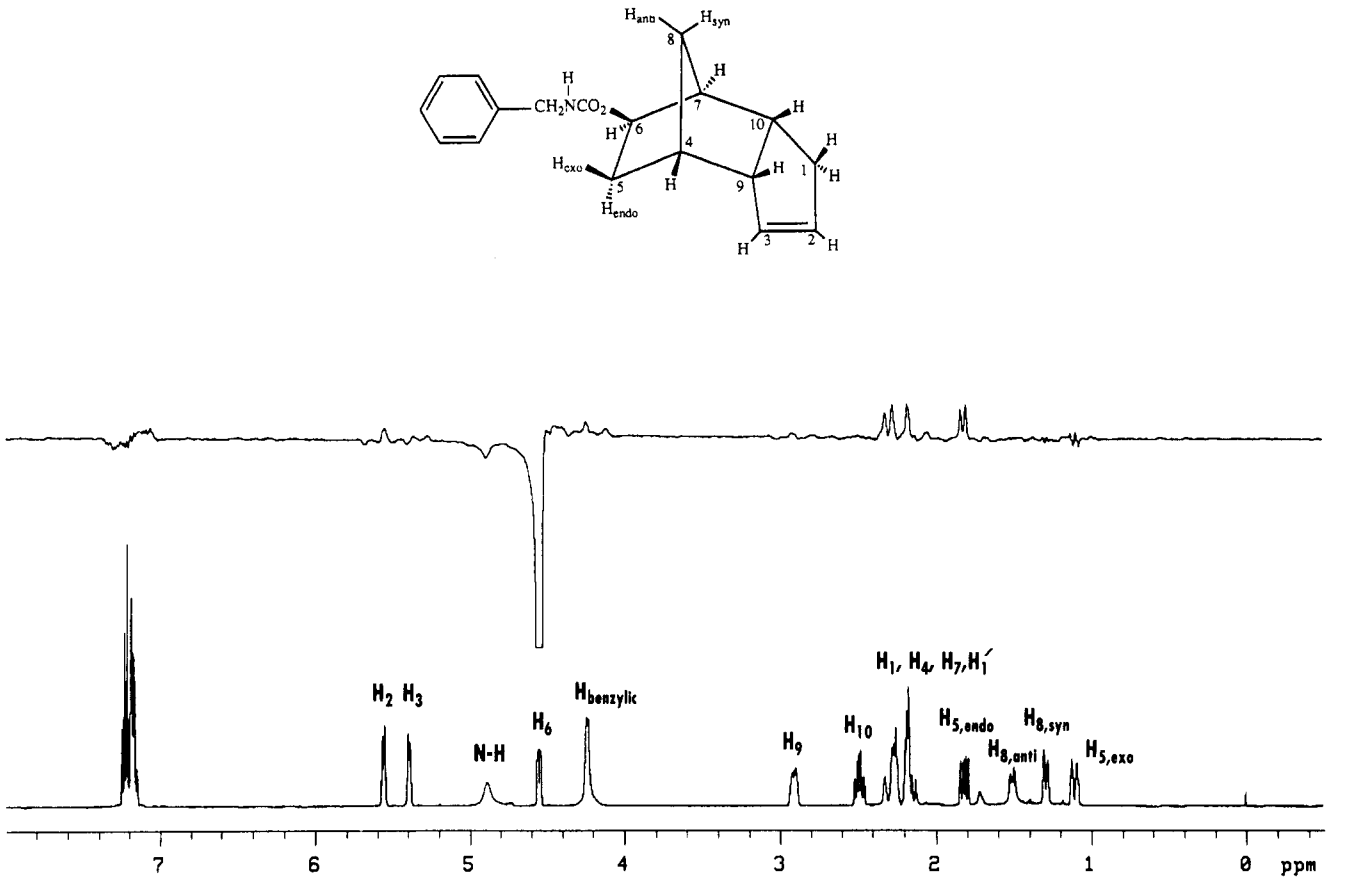
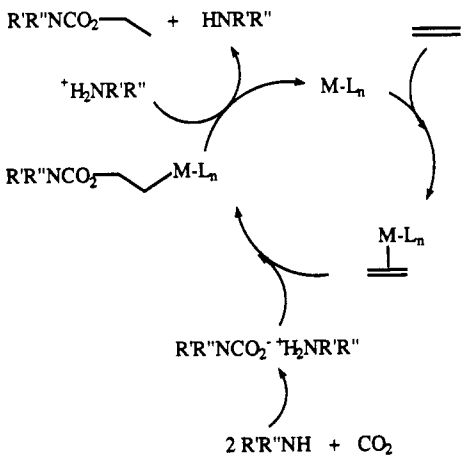


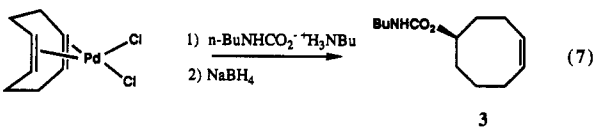
Figure 1. Double quantum filtered COSY-NMR spectrum of carbamate ester **2d**.

Scheme I



dioxide. The reaction appears to be instantaneous as the yellow-orange color of the palladium complex decolorizes upon addition to the carbamate solution. Again, quenching the reaction with aqueous 2.5 N NaOH gives the carbamate esters **2a–i** in good isolated yields (Table II). Quenching the reaction by the addition of hydrogen also gives urethanes in high yields (Table II). The stereochemistry of the resulting urethane product was determined by 2-D COSY, heteronuclear carbon–hydrogen and NOE NMR experiments (See Figures 1–3).[9] These experiments gave the stereo- and regiochemistry consistant with the structure shown above.

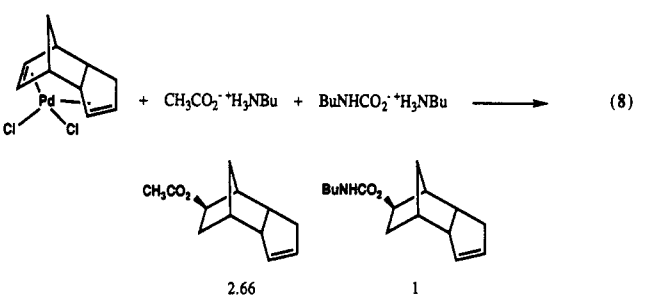
Addition of a THF solution of (1,5-cyclooctadiene)palladium dichloride to a premade solution of *N*-butylcarbamate at −35 °C and then quenching by the addition of sodium borohydride in 2.5 N NaOH gave the urethane **3** in 16% isolated yield, eq 7.



(7)

3

The addition of a solution of (dicyclopentadiene)palladium dichloride to a 1:1 mixture of acetate anion and *N*-butylcarbamate anion (both as their corresponding butylammonium salts) followed by quenching with 2.5 N NaOH gave a ratio of 2.66:(1 ± 0.11), acetate to urethane products (eq 8).



(8)

2.66 1

Addition of (dicyclopentadiene)palladium dichloride to a methylene chloride solution of acetate anion, as the butylammonium salt, gave a clear solution (GC analysis showed 100% yield of acetate product after quenching an aliquot with sodium borohydride). To this was added an excess of butylcarbamate (as butylammonium salt) at 0 °C, and after 45 min an aliquot was taken and quenched with sodium borohydride. Analysis by GC showed only acetate product with no urethane production.[10] Similarly,

(9) 2-D NMR work performed by Bill Wise of Monsanto's PSC department.

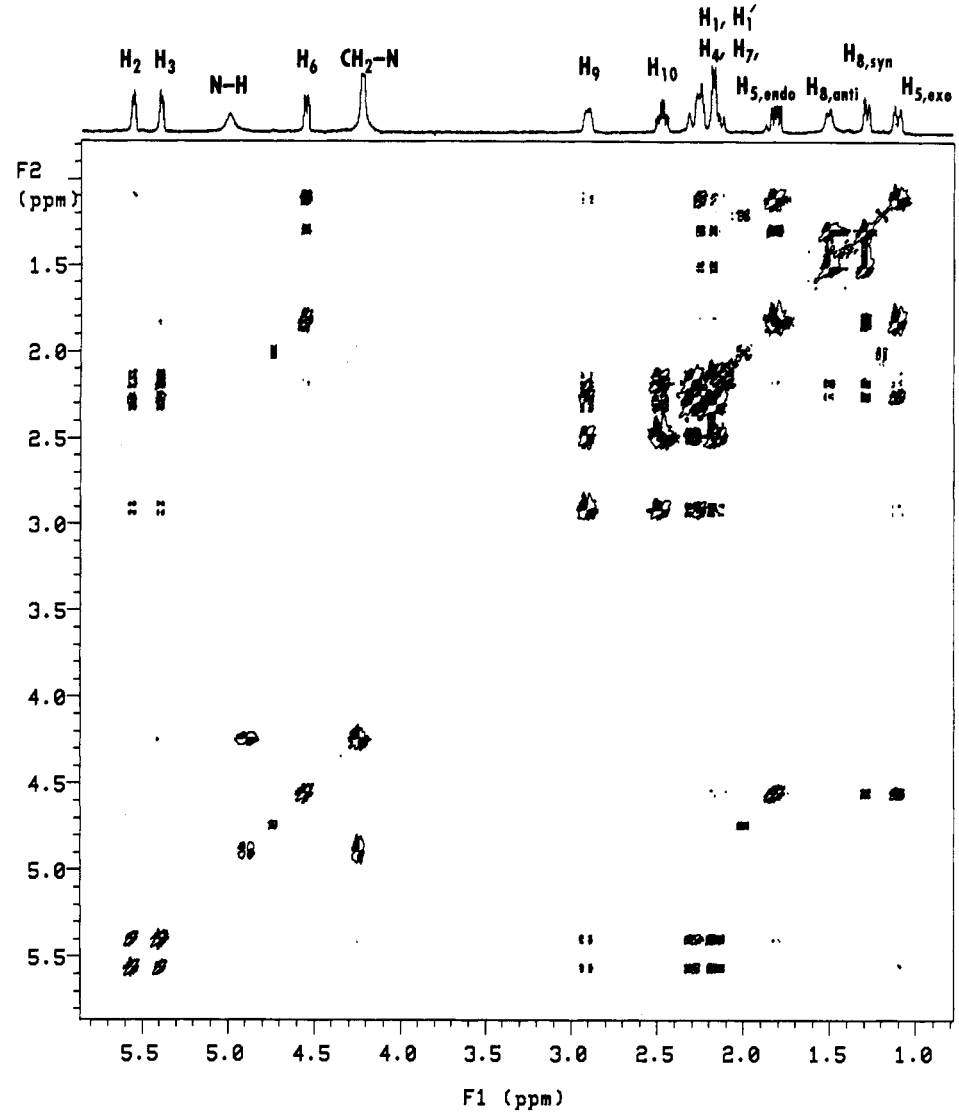


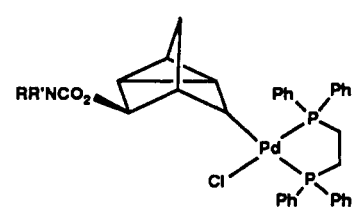
Figure 2. Proton–carbon correlated 2-dimensional NMR spectrum of carbamate ester **2d**.

addition of (dicyclopentadiene)palladium dichloride to a methylene chloride solution of butylcarbamate (as the butylammonium salt), gave a clear solution (GC analysis showed 100% yield of urethane product after quenching an aliquot with sodium borohydride). To this was added an excess of acetate anion, as butyl ammonium salt, at 0 °C, and after 45 min an aliquot was taken and quenched with sodium borohydride. Analysis by GC showed only urethane product with no acetate production.

Discussion

The utilization of carbon dioxide as a building block in chemical synthesis has drawn considerable attention.[3] Our approach has been to take advantage of the activation of carbon dioxide by either a primary or secondary amine giving the corresponding carbamate salt. This method for the fixation of carbon dioxide has been well documented.[4] The utilization of the carbamate anion has also been reported; however, the chemistry is dominated by the loss of carbon dioxide resulting in amine products, in which chemistry occurs at the nitrogen center.

The results given in this account demonstrate that we can successfully obtain high yields and high selectivities of urethane products (oxygen-centered chemistry) under very mild conditions. To achieve this, we have made use of another well-studied system to activate our substrate toward nucleophilic attack by the carbamate anion. The use of palladium(II) to activate diolefins toward nucleophilic attack has ample precedent.[7] We have found that under atmospheric pressure of carbon dioxide and at subambient temperatures the carbamate anion will add to the palladium-coordinated diolefin. With norbornadiene as the coordinating diolefin, addition of the premade carbamate anion to a slurry of the palladium complex at −78 °C followed by warming to ice temperature gives a homogeneous light yellow solution. Quenching of this complex by the addition of $NaBH_4$ gives rise to different isomers of the norbornylurethane. Addition of DIPHOS to the intermediate palladium complex prior to reductive cleavage gives a slightly darker yellow solution of (DIPHOS)Pd(Cl)(nortricyclo urethane), A. Quenching of this



A

(10) Heating the reaction mixture does give slow exchange of the acetate, giving rise to urethane product.

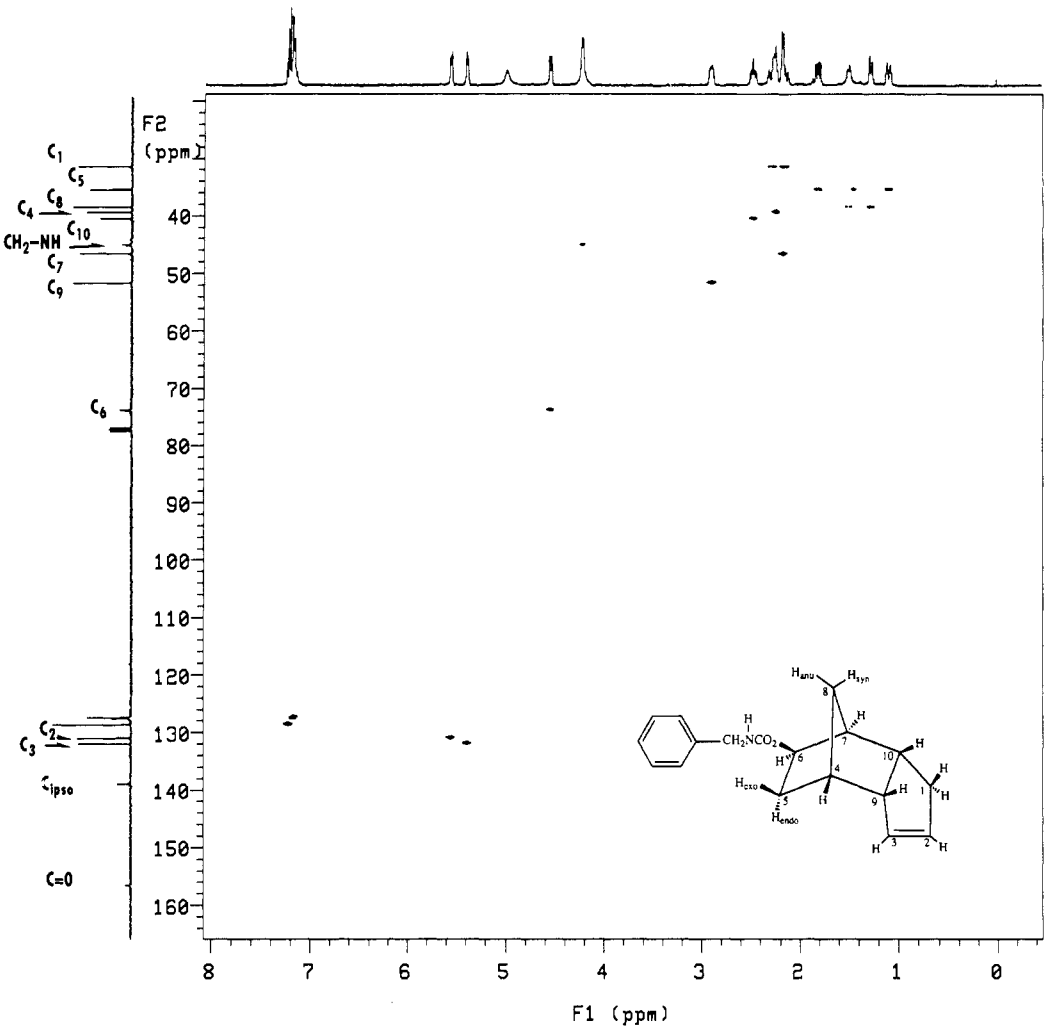


Figure 3. NOE-NMR difference spectrum of carbamate ester **2d**, irradiation of H_6.

species by sodium borohydride gives the urethanes **1a–d** in high yields exclusively with the nortricyclic framework, eq 5 (Table I). Cleavage of the intermediate A by the addition of anhydrous HCl also gives the nortricyclo urethane and (DIPHOS)$PdCl_2$.

The combination of steps demonstrated in the conversion of norbornadiene, carbon dioxide, and amines to nortricyclic urethane esters using palladium, models a potential catalytic cycle, as shown in Scheme I, in which the conjugate acid $H_2NR'R''^+$ protonates the metal alkyl liberating urethane.

This cycle can be envisioned as a process requiring three key steps: first is the activation of carbon dioxide by an amine giving the carbamate anion salt followed by nucleophilic attack of this species on a metal olefin complex generating a metal-bound urethane species which is finally cleaved to free urethane by protonolysis. In modeling of this cycle, the activation of carbon dioxide by amines has been demonstrated to be facile and has ample precedent in the literature. We have shown that the second step, nucleophilic attack at the metal-activated olefin, is also facile giving high yields and selectivities of urethane moieties bound to palladium. The final step (protonolysis), however, could only be shown to be successful by the use of strong acid, HCl. This indicates that the palladium–carbon bond in intermediate A is too strong for protonolysis by ammonium ion, which is required for the cycle in Scheme I to be completed. Other metal ligand environments may prove to be more anemable toward all the steps necessary for catalysis to occur.

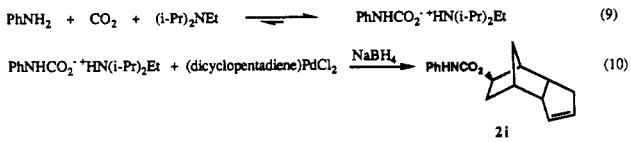
We also made use of (dicyclopentadiene) as the chelating diolefin, and this gives the urethane products (**2a–i**), after addition of the carbamate anion followed by reductive cleavage (Table II). Addition of the palladium complex to the premade carbamate proceeds smoothly at −5 °C in methylene chloride. The reaction appears to be instantaneous as the orange color of the diolefin complex decolorizes immediately upon addition to the carbamate solution. Quenching of the reaction with sodium borohydride gives high yields of urethane products using standard purification techniques, eq 6. The urethane complex can also be obtained in high yield by reductive cleavage with dihydrogen at room temperature. This method for the reductive cleavage of a palladium–alkyl bond has ample president in the literature.[11] The stereochemistry of the resulting tricyclic urethane was determined by two dimensional and NOE–NMR techniques (Figures 1–3) and is consistent with exo substitution.[12]

In some cases (see Tables I and II) the use of a tertiary amine as the proton scavenger in the production of the carbamate anion, eq 4, substantially improves the yields of urethane product. The most dramatic improvement is seen in the utilization of aniline. Without added tertiary

(11) For example in an analogous palladium system see: (a) Stille, J. K.; Morgan, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 5135–5141. (b) Akermark, B.; Backvall, J. E.; Hegedus, L. S.; S.-Hansen, K.; Sjoberg, K. *J. Organomet. Chem.* **1974**, *72*, 127–138.

(12) Exo-substitution is consistent with the results discussed in ref 11.

amine base only nitrogen-based products are obtained (0% urethane). The addition of a stoichiometric amount of added cobase, diisopropylethylamine gives dramatic increases in the amount of urethane products (70.5%). The nature of this reversal of selectivity may be accounted for by a shift in equilibrium in the formation of the carbamate anion with added base, eqs 9 and 10.



2i

The use of 1,5-cyclooctadiene as the chelating diolefin also produces urethane products. This system is considerably more sensitive to the reaction conditions. Addition of the diolefin complex to the carbamate at −35 °C gave a clear solution. Quenching of the solution at −35 °C with sodium borohydride gave 20–30% yields of cyclooct-4-enyl-1 carbamates (by GC), eq 7. Warming the solution to −5 °C prior to quenching gave poor yields (<5%) of urethane products.

The literature gives no indication of the relative nucleophilicity of the carbamate anion (this may be a reflection of the poor yields of oxygen-derived products in reported systems). The determination of the carbamate's nucleophilicity would give us a handle on what types of reaction pathways might be kinetically feasible. We chose to investigate the relative reactivity of the carbamate generated from butylamine (high yield and high selectivity of oxygen attack; see Table II) versus the acetate anion. The counterion in both cases was the butylammonium cation, thereby eliminating counterion effects. The results of this study, eq 8, gave a relative ratio of acetate attack to carbamate attack of 2.66:(1 ± 0.11). Control experiments were carried out to confirm the kinetic nature of the ratio of reaction products. This difference in reactivity between butylcarbamate and acetate in a direct competition study indicates that the carbamate anion, in this particular reaction, is only slightly less nucleophilic than the acetate anion.

Conclusion

The results of these studies have successfully demonstrated that each step in the proposed metal-mediated route to urethanes from amines, carbon dioxide, and olefins shown in Scheme I is indeed feasible. The key to this demonstration is (1) the activation of carbon dioxide by an amine, (2) activation of an olefin substrate by a metal center toward nucleophilic attack by the carbamate anion, and (3) cleavage of the resulting metal–carbon bond by protonolysis. Work is in progress toward the development of catalytic systems which make it possible to produce urethanes from amines and carbon dioxide.

Experimental Section

Materials. All amines and diolefins used in this account were obtained either from Aldrich Chemical Co. or Kodak Chemical Co. and were used as received. Anhydrous THF (tetrahydrofuran) under nitrogen and anhydrous methylene chloride under nitrogen were obtained from Aldrich Chemical Co. Bis(benzonitrile)-palladium dichloride and bis(diphenylphosphino)ethane (DIPHOS) were obtained from Aldrich Chemical Co. Norbornadiene-palladium dichloride, (dicyclopentadiene)palladium dichloride, and cyclooctadienepalladium dichloride were prepared according to the literature.[13]

Analytical Procedure. Gas chromatographic analysis was performed on a Varian Model 3400 gas chromatograph with a Model 8000 autosampler using a 30-m Megabore DB-1 (3 μm) J & W Scientific column. Urethane products were purified and were identified by ^{1}H NMR, ^{13}C NMR, mass spectroscopy, IR, and elemental analysis. Nuclear magnetic resonance spectra were obtained on a Varian VXR-300 or VXR-400 spectrometer. Mass spectra were obtained by chemical ionization techniques using isobutane as reagent gas or by FAB techniques. Infrared spectra were obtained on a Nicolet FT-IR system. Melting points of solid products were taken on a Haake Buchler melting point apparatus and are uncorrected. Elemental analysis were performed by Galbraith Laboratories Inc.

Synthesis. Tricyclo[2.2.1.0^{2,6}]heptyl-3 *N*-(phenylmethyl)carbamate (1b). Into a 500-mL three-neck flask was weighed 500 mg (1.86 mmol) of (norbornadiene)palladium dichloride. The flask was fitted with an addition funnel, a gas inlet and a rubber septum. The apparatus was pump-filled with nitrogen followed by the addition of 30 mL of dry THF and 144 mg (0.85 mmol) of dodecane (as internal GC standard). This yellow slurry was cooled to −78 °C using a dry ice/IPA bath.

Into a 50-mL round-bottomed flask was weighed 800 mg (7.5 mmol) of benzylamine and 880 mg (9.8 mmol) of quinuclidine. To this was added 15 mL of dry THF followed by the addition of carbon dioxide. The clear solution was cooled to 0 °C, and CO_2 was bubbled through the solution for 15 min. At the end of this time a small amount of solid had appeared. The carbamate slurry was added to the Pd^{II} complex at −78 °C. After addition was complete the reaction mixture was warmed to 0 °C (ice bath) and was allowed to stir for 6 h at 0 °C. After the 6 h a solution of 760 mg (1.91 mmol) of bis(diphenylphosphino)ethane (DIPHOS) in 10 mL of THF was added and the ice bath removed. The resulting reaction mixture was allowed to stir overnight at room temperature. To the reaction mixture was added 570 mg (15 mmol) of $NaBH_4$ in 1 mL of NaOH (2.5 N) and 10 mL of THF, giving a black suspension. The reaction mixture was allowed to stir at room temperature for 1 h and was then filtered through Celite using THF to wash the Celite. The clear filtrate was concentrated leaving an oily residue. By GC a yield of 80% was calculated. The crude product was chromatographed on silica gel using 44% CH_2Cl_2/hexane. Upon concentration of the desired fractions 235 mg (0.97 mmol, 52%) of the urethane **1b** was obtained as a white solid: mp = 97–98.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.4–7.27 (overlapping m, 5 H), 4.98 (br, 1 H, N–H), 4.70 (s, 1 H), 4.39 (d, J = 5.8 Hz, 2 H), 2.09 (s, 1 H), 1.79 (d, J = 9.9 Hz, 1 H), 1.52 (d, J = 10.4 Hz, 1 H), 1.34–1.27 (overlapping m, 5 H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 157.1, 139.2, 129.1, 128.0, 80.9, 34.1, 30.9, 30.7, 13.4, 11.7; IR (Nujol): 1680, 3312 ($CHCl_3$), 1711, 3449 cm^{-1}; MS (CI, isobutane) m/z = 244 (MH^+). Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.04; H, 7.05; N, 5.76. Found: C, 74.27; H, 7.14; N, 5.61.

Tricyclo[2.2.1.0^{2,6}]heptyl-3 *N*-Butylcarbamate (1a): oil; ^{1}H NMR ($CDCl_3$) δ 4.6 (br, 1 H, N–H), 4.64 (s, 1 H), 3.18 (t, J = 6.7 Hz, 2 H), 2.06 (br s, 1 H), 1.79 (d, J = 10.3 Hz, 1 H), 1.52–1.25 (overlapping m, 10 H), 0.94 (t, J = 7.2 Hz, 3 H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 157.0, 80.6, 41.2, 34.1, 32.6, 30.9, 30.7, 20.4, 14.3, 14.2, 13.4, 11.6; IR (film) 1695, 3333 cm^{-1}; MS (CI, isobutane) m/z = 210 (MH^+). Anal. Calcd for $C_{12}H_{19}NO_2$: C, 68.85; H, 9.16; N, 6.7. Found: C, 68.63; H, 9.28; N, 6.97.

Tricyclo[2.2.1.0^{2,6}]heptyl-3 *N*-(Phenylmethyl)-*N*-methylcarbamate (1c): oil, ^{1}H NMR ($CDCl_3$) δ 7.4–7.2 (m, 5 H), 4.73 (s, 1 H), 4.48 (br s, 2 H), 2.88 (br s, 3 H), 2.09 (br s, 1 H), 1.7–1.9 (br m, 1 H), 1.53 (d, J = 10.5 Hz, 1 H), 1.30 (br m, 5 H); IR (film) 1703 cm^{-1}; MS (FAB, *n*-BuOH) m/z = 258 (MH^+). Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.67; H, 7.45; N, 5.45. Found: C, 74.50; H, 7.56; N, 5.50.

Tricyclo[2.2.1.0^{2,6}]heptyl-3 *N*-Morpholinylcarbamate (1d): oil, ^{1}H NMR ($CDCl_3$) δ 4.66 (s, 1 H), 3.66 (t, J = 4.9, 4 H), 3.46 (t, J = 4.9, 4 H), 2.05 (br s, 1 H), 1.76 (d, J = 10.2 Hz, 1 H), 1.50 (d, J = 10.3 Hz, 1 H), 1.34–1.25 (overlapping m, 5 H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 155.8, 81.3, 67.1, 44.5, 34.1, 30.8, 14.4, 13.5, 11.7. IR (film) 1699 cm^{-1}; MS (FAB, *n*-BuOH) m/z = 224 (MH^+). Anal. Calcd for $C_{12}H_{17}NO_3$: C, 64.55; H, 7.67; N, 6.27. Found: C, 64.00; H, 7.78; N, 6.35.

3a,4,5,6,7,7a-Hexahydro-*endo*-4,7-methanoindenyl-6-*exo* *N*-*sec*-Butylcarbamate (2b): Into a three-neck 500-mL round-bottomed flask was added 700 mg (9.6 mmol) of *sec*-butylamine and 20 mL of methylene chloride. The flask was fitted

(13) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 3413–3416.

with an addition funnel, a gas inlet, and a rubber stopper. The clear solution was cooled to 0 °C and carbon dioxide was bubbled through the solution. Into a glass vial was weighed 500 mg (1.62 mmol) of (dicyclopentadiene)palladium dichloride and 218 mg (1.28 mmol) of dodecane (as GC internal standard). To this was added 25 mL of methylene chloride, and the resulting orange solution was transferred to the addition funnel. After 15 min of CO_2 addition, the palladium complex was added dropwise to the carbamate solution over a 30-min period. Upon addition the palladium solution decolorized. After addition was complete the reaction mixture was stirred at 0 °C for 15 min. The reaction was quenched by adding 480 mg (12.7 mmol) of $NaBH_4$ in 2 mL of 2.5 N NaOH to the solution. The reaction was allowed to stir at 0 °C for 10 min during which time it deposited a black precipitate (Pd^0). The reaction mixture was filtered through Celite using methylene chloride to wash the Celite. A GC trace of the clear filtrate was taken (69%). The crude filtrate was washed with 1 × 50 mL of H_2O, 1 × 100 mL of 0.6 M HCl, and 1 × 50 mL of H_2O. The aqueous washes were each extracted with 1 × 50 mL of CH_2Cl_2. The combined organic layers were dried over sodium carbonate, filtered, and then concentrated, leaving an oily residue. This residue was chromatographed on silica gel using 50% CH_2Cl_2/hexane (TLC plates developed using phosphomolybdic acid). Upon concentration of the desired fractions 164 mg (0.66 mmol 41%) of the urethane **2b** was isolated as a white solid: mp = 78–79.5 °C; ^1H NMR ($CDCl_3$) δ 5.68 (m, 1 H), 5.52 (m, 1 H), 4.62 (d, J = 6 Hz, 1 H), 4.35, (br s, N–H), 3.6 (br m, 1 H), 3.02 (m, 1 H), 2.60 (m, 1 H), 2.45–2.26 (overlapping m, 4 H), 1.91 (ddd, J = 13.2, 7.2, 2.6 Hz, 1 H), 1.63 (d, J = 9.7 Hz, 1 H), 1.47 (overlapping m, 3 H), 1.21 (br d, J = 14 Hz, 1 H), 1.14 (d, J = 6.3 Hz, 3 H), 0.93 (t, J = 6.4 Hz, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.5, 132.4, 131.4, 73.7, 52.1, 48.8, 47.0, 40.9, 39.8, 35.9, 31.9, 30.5, 21.2, 10.8; IR (Nujol) 1701, 3327 ($CHCl_3$), 1700, 3442 cm^{-1}; MS (CI, isobutane) m/z = 250 (MH^+). Anal. Calcd for $C_{15}H_{23}NO_2$: C, 72.24; H, 9.30; N, 5.62. Found: C, 71.74; H, 9.47; N, 5.49.

3a,4,5,6,7,7a-Hexahydro-*endo*-4,7-methanoindenyl-6-*exo* *N*-Butylcarbamate (2a). Into a three-neck 500-mL round-bottomed flask was added 720 mg (9.86 mmol) *n*-butylamine and 20 mL of methylene chloride. The flask was fitted with an addition funnel, a gas inlet, and a rubber stopper. The clear solution was cooled to 0 °C and carbon dioxide was bubbled through the solution. In a glass vial was added 496 mg (1.60 mmol) of (dicyclopentadiene)palladium dichloride and 195 mg (1.15 mmol) of dodecane (as GC internal standard), to this was added 25 mL of methylene chloride, and the resulting orange solution was transferred to the addition funnel. After 15 min of CO_2 addition, the palladium complex was added dropwise to the carbamate solution over a 30-min period. Upon addition the palladium solution decolorized. After addition was complete the reaction mixture was stirred at 0 °C for 15 min. The reaction was quenched by bubbling hydrogen through the solution. The reaction was allowed to warm to room temperature with the continuous addition of hydrogen, during which time the reaction slowly deposited a black precipitate. After 1.5 h the reaction mixture was filtered through Celite using methylene chloride to wash the Celite. A GC trace of the clear filtrate was taken (100%). The crude filtrate was washed with 1 × 50 mL of H_2O, 1 × 100 mL of 0.6 M HCl, and a 1 × 50 mL of H_2O. The aqueous washes were each extracted with 1 × 50 mL of CH_2Cl_2. The combined organic layers were dried over sodium carbonate, filtered, and then concentrated, leaving an oily residue. This residue was chromatographed on silica gel using 50% CH_2Cl_2/hexane (TLC plates developed using phosphomolybdic acid). Upon concentration of the desired fractions 285 mg (1.15 mmol, 72%) of the urethane, **2a** was isolated as a white solid: mp = 46–48 °C; ^1H NMR ($CDCl_3$) δ 5.65 (m, 1 H), 5.49 (m, 1 H), 4.6 (br s, N–H), 4.59 (br d, J = 5.4 Hz, 1 H), 3.15 (t, J = 6.7 Hz, 2 H), 3.0 (m, 1 H), 2.58 (m, 1 H), 2.43–2.23 (overlapping m, 4 H), 1.90 (ddd, J = 13.1, 7.3, 2.6 Hz, 1 H), 1.61 (d, J = 9.7 Hz, 1 H), 1.5–1.3 (overlapping m, 5 H), 1.20 (d, J = 13 Hz, 1 H), 0.93 ppm (t, J = 7.2 Hz, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 157.1, 132.4, 131.4, 73.9, 52.1, 47.0, 41.2, 40.9, 39.8, 38.9, 35.9, 32.7, 31.9, 20.4, 14.2; IR (nujol) 1684, 3304 ($CHCl_3$), 1709, 3453 cm^{-1}; MS (CI, isobutane) m/z = 250 (MH^+). Anal. Calcd for $C_{15}H_{23}NO_2$: C, 72.24; H, 9.30; N, 5.62. Found: C, 72.47; H, 9.66; N, 5.19.

3a,4,5,6,7,7a-Hexahydro-*endo*-4,7-methanoindenyl-6-*exo* *N*-*tert*-Butylcarbamate (2c): mp 82–85 °C; ^1H NMR ($CDCl_3$) δ 5.66 (m, 1 H), 5.50 (m, 1 H), 4.6 (br s, N–H), 4.57 (br m, 1 H), 3.0 (m, 1 H), 2.59 (m, 1 H), 2.45–2.22 (overlapping m, 4 H), 1.91 (ddd, J = 13.0, 7.2, 2.6 Hz, 1 H), 1.62 (d, J = 9.6 Hz, 1 H), 1.40 (d, J = 9.1 Hz, 1 H), 1.33 (s, 9 H), 1.19 ppm (d, J = 12.8 Hz, 1 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.5, 132.4, 131.4, 73.2, 52.1, 50.7, 47.0, 40.9, 39.8, 35.9, 32.0, 29.6; IR ($CHCl_3$) 1713, 3451 cm^{-1}; MS (CI, isobutane) m/z = 250 (MH^+). Anal. Calcd for $C_{15}H_{23}NO_2$: C, 72.24; H, 9.30; N, 5.62. Found: C, 72.57; H, 9.48; N, 5.58.

3a,4,5,6,7,7a-Hexahydro-*endo*-4,7-methanoindenyl-6-*exo* *N*-(Phenylmethyl)carbamate (2d): mp = 70–71 °C; ^1H NMR ($CDCl_3$) δ 7.39–7.27 (m, 5 H), 5.68 (m, 1 H), 5.51 (m, 1 H), 5.02 (br s, N–H), 4.67 (br d, J = 7 Hz, 1 H), 4.36 (d, J = 5.5 Hz, 2 H), 3.03 (m, 1 H), 2.61 (m, 1 H), 2.45–2.29 (overlapping m, 4 H), 1.94 (m, 1 H), 1.63 (br d, J = 9.1 Hz, 1 H), 1.41 (br d, J = 9.3 Hz), 1.23 ppm (br d, J = 13.2 Hz, 1 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 157.1, 138.7, 131.8, 130.7, 128.4, 127.4, 127.2, 73.6, 51.4, 46.4, 45.5, 40.3, 39.2, 38.3, 35.2, 31.3; IR (Nujol) 1684, 3314 ($CHCl_3$), 1711, 3451 cm^{-1}; MS (CI, isobutane) m/z = 284 (MH^+). Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.28; H, 7.47; N, 4.95. Found: C, 76.16; H, 7.53; N, 4.93.

3a,4,5,6,7,7a-Hexahydro-*endo*-4,7-methanoindenyl-6-*exo* *N*-Piperadinylcarbamate (2e): mp = 61–62 °C; ^1H NMR ($CDCl_3$) δ 5.67 (m, 1 H), 5.51 (m, 1 H), 4.63 (d, J = 7 Hz, 1 H), 3.41 (t, J = 5.2 Hz, 4 H), 3.01 (m, 1 H), 2.61 (m, 1 H), 2.46–2.25 (overlapping m, 4 H), 1.92 (ddd, J = 13.2, 7.2, 2.6 Hz, 1 H), 1.64 (d, J = 9.5 Hz, 1 H), 1.53–1.60 (overlapping m, 5 H), 1.42 (d, J = 9.6 Hz, 1 H), 1.23 (br d, J = 13.2 Hz, 1 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.0, 132.4, 131.4, 74.3, 52.1, 47.1, 45.2, 40.9, 39.8, 39.0, 35.9, 31.9, 26.2, 25.0; IR ($CHCl_3$) 1670 cm^{-1}; MS (CI, isobutane) m/z = 262 (MH^+). Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.51; H, 8.88; N, 5.36. Found: C, 73.72; H, 9.04; N, 5.36.

3a,4,5,6,7,7a-Hexahydro-*endo*-4,7-methanoindenyl-6-*exo* *N*-Morpholinylcarbamate (2f): mp = 53–55 °C; ^1H NMR ($CDCl_3$) δ 5.66 (m, 1 H), 5.50 (m, 1 H), 4.63 (br d, J = 6.5 Hz, 1 H), 3.65 (t, J = 4.8 Hz, 4 H), 3.44 (t, J = 4.8 Hz, 4 H), 3.0 (m, 1 H), 2.59 (m, 1 H), 2.42–2.25 (overlapping m, 4 H), 1.92 (ddd, J = 13.2, 7.1, 2.6 Hz, 1 H), 1.61 (d, J = 9.5 Hz, 1 H), 1.41 (d, J = 9.6 Hz, 1 H), 1.21 (br d, J = 13.3 Hz, 1 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.9, 132.4, 131.4, 74.9, 67.1, 52.0, 47.0, 44.5, 40.9, 39.8, 38.9, 35.9, 31.9; IR (Nujol) 1709 ($CHCl_3$) 1688 cm^{-1}; MS (CI, isobutane) m/z = 264 (MH^+). Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.40; H, 8.04; N, 5.32. Found: C, 68.28; H, 8.17; N, 5.06.

3a,4,5,6,7,7a-Hexahydro-*endo*-4,7-methanoindenyl-6-*exo* *N*,*N*-diethylcarbamate (2g): oil; ^1H NMR ($CDCl_3$) δ 5.63 (m, 1 H), 5.47 (m, 1 H), 4.61 (br d, J = 7.3 Hz, 1 H), 3.23 (br m, 4 H), 2.98 (m, 1 H), 2.6 (m, 1 H), 2.44–2.18 (overlapping m, 4 H), 1.89 (ddd, J = 13, 7.2, 2.5 Hz, 1 H), 1.62 (d, J = 9.6 Hz, 1 H), 1.38 (d, J = 9.6 Hz, 1 H), 1.20 (d, J = 13.2 Hz, 1 H), 1.10 (t, J = 7 Hz, 6 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.3, 132.4, 131.4, 74.0, 52.1, 47.1, 41.9 (br), 40.9, 39.8, 39.0, 35.8, 31.9, 14.4 (br); IR (film) 1699 cm^{-1}; MS (CI, isobutane) m/z = 250 (MH^+).

3a,4,5,6,7,7a-Hexahydro-*endo*-4,7-methanoindenyl-6-*exo* *N*-(Phenylmethyl)-*N*-methylcarbamate (2h): oil; ^1H NMR ($CDCl_3$) δ 7.39–7.26 (m, 5 H), 5.69 (m, 1 H), 5.52 (m, 1 H), 4.70 (br m, 1 H), 4.46 (br s, 2 H), 3.02 (br m, 1 H), 2.86 (br s, 3 H), 2.62 (m, 1 H), 2.48–2.27 (overlapping m, 4 H), 1.97 (m, 1 H), 1.6 (br m, 1 H), 1.42 (br m, 1 H), 1.25 ppm (br m, 1 H); IR (film) 1699 cm^{-1}; MS (CI, isobutane) m/z = 298 (MH^+). Anal. Calcd for $C_{19}H_{23}NO_2$: C, 76.74; H, 7.80; N, 4.71. Found: C, 76.81; H, 8.15; N, 5.21.

3a,4,5,6,7,7a-Hexahydro-*endo*-4,7-methanoindenyl-6-*exo* *N*-Phenylcarbamate (2i): mp = 113.5–115.5 °C; ^1H ($CDCl_3$) δ 7.42–7.3 (m, 4 H), 7.08 (t, J = 7 Hz, 1 H), 6.59 (s, N–H), 5.69 (m, 1 H), 5.54 (m, 1 H), 4.74 (br m, 1 H), 3.05 (m, 1 H), 2.64 (m, 1 H), 2.47–2.30 (overlapping m, 4 H), 1.98 (m, 1 H), 1.68 (d, J = 9.8 Hz, 1 H), 1.46 (d, J = 9.6 Hz, 1 H), 1.29 (br d, J = 13.4 Hz, 1 H); $^{13}C\{^1H\}$ ($CDCl_3$) δ 153.9, 138.6, 132.5, 131.4, 129.5, 123.7, 119.0, 74.8, 52.0, 47.0, 41.0, 39.9, 35.9, 32.0; IR (Nujol) 1705, 3238 ($CHCl_3$), 1730, 3436 cm^{-1}; MS (CI, isobutane) m/z = 270 (MH^+). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.80; H, 7.11; N, 5.20. Found: C, 75.89; H, 7.22; N, 4.99.

Cyclooct-4-enyl-1 *N*-Butylcarbamate (3). Into a three-neck 500-mL round-bottomed flask was added 1.115 g (15.3 mmol) of *n*-butylamine and 40 mL of methylene chloride. The flask was fitted with an addition funnel, a glass inlet, and a rubber stopper. The clear solution was cooled to −35 °C, and carbon dioxide was bubbled through the solution. Into a glass vial was weighed 755 mg (2.65 mmol) of (1,5-cyclooctadiene)palladium dichloride. To this was added 30 mL of methylene chloride, and the resulting yellow-orange solution was transferred to the addition funnel.

After 15 min of CO_2 addition, the palladium complex was added dropwise to the carbamate solution over a 30-min period. Upon addition the palladium solution decolorized. After addition was complete the reaction mixture was stirred at −35 °C for 15 min. The reaciton was quenched by adding 760 mg (20 mmol) of $NaBH_4$ in 2 mL of 2.5 N NaOH to the solution. The reaction mixture was stirred at −35 °C for 10 min during which time it deposited a black precipitate (Pd^0). The reaction mixture was filtered through Celite using methylene chloride to wash the Celite. The crude filtrate was washed with 1 × 50 mL of H_2O, 2 × 100 mL of 0.6 M HCl, and 1 × 50 mL of H_2O. The aqueous washes were each extracted with 1 × 50 mL of CH_2Cl_2. The combined organic layers were dried over sodium carbonate, filtered, and then concentrated leaving an oily residue. This residue was chromatographed on silica gel using 50% CH_2Cl_2/hexane (TLC plates developed using phosphomolybdic acid). Upon concentration of the desired fractions 96 mg (0.42 mmol, 16%) of the urethane **3** was isolated as a clear oil: ^1H NMR ($CDCl_3$) δ 5.64 (m, 2 H), 4.73 (overlapping m, 2 H), 3.16 (q, J = 6.5 Hz, 2 H), 2.4–1.3 (overlapping m, 14 H), 0.93 (t, J = 7.2 Hz, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.8, 130.2, 76.3, 41.1, 34.6, 34.4, 32.7, 26.1, 25.3, 22.9, 20.4, 14.2; IR (film) 1696, 3335 cm^{-1}; MS (CI, isobutane) m/z = 226 (MH^+). Anal. Calcd for $C_{13}H_{23}NO_2$: C, 69.29; H, 10.29; N, 6.22. Found: C, 69.39; H, 10.46; N, 6.46.

Competition Study (Butylcarbamate vs Acetate). Into a three-neck 100-mL round-bottomed flask was added 120 mg (2 mmol) of acetic acid, 438 mg (6 mmol) of *n*-butylamine, and 10 mL of methylene chloride. The flask was fitted with an addition funnel and a rubber stopper. The clear solution was cooled to −5 °C, and carbon dioxide was added to the solution. Into a glass vial was weighed 100 mg (0.33 mmol) of (dicyclopentadiene)-palladium dichloride and 58 mg (0.34 mmol) of dodecane (as GC internal standard). To this was added 10 mL of methylene chloride, and the resulting orange solution was added to the addition funnel.

After 15 min of CO_2 addition, the palladium complex was added to the carbamate solution over a 10-min period. Upon addition the palladium solution decolorized. After addition was complete the reaction mixture was quenched by adding $NaBH_4$ (upon addition of borohydride the reaction deposited a black precipitate). A GC trace of the clear filtrate was taken, giving a calculated ratio of acetate product to urethane product of 2.75:1. The reaction was repeated three more times, giving a calculated ratio of products of 2.66:(1 ● 0.11) (mean value of four runs).

Control Experiments. Into a three-neck 100-mL round-bottomed flask was added 150 mg (2.05 mmol) of *n*-butylamine, 121 mg (2.02 mmol) of acetic acid, and 10 mL of methylene chloride. The flask was fitted with an addition funnel and a rubber stopper. The clear solution was cooled to −5 °C. Into a glass vial was weighed 101 mg (0.33 mmol) of (dicyclopentadiene)palladium dichloride and 57 mg (0.34 mmol) of dodecane (GC internal standard). To this was added 10 mL of methylene chloride, and the resulting orange solution was added to the addition funnel. The palladium complex was added dropwise to the acetate solution over a 10-min period. Upon addition the palladium solution decolorized. After addition was complete an aliquot was taken and was quenched with sodium borohydride. GC analysis of the aliquot showed a 100% yield of acetate product. To a solution of 293 mg (4 mmol) of *n*-butylamine in 5 mL of methylene chloride was added carbon dioxide. This carbamate solution was then added to the above reaction mixture under carbon dioxide. The reaction was allowed to stir for 45 min at −5 °C. An aliquot was taken, quenched with sodium borohydride, and filtered. GC analysis showed only acetate product.

Into a three-neck 100-mL round-bottomed flask was added 303 mg (4.15 mmol) of *n*-butylamine and 10 mL of methylene chloride. The flask was fitted with an addition funnel and a rubber stopper. The clear solution was cooled to −5 °C, and carbon dioxide was bubbled through the solution. Into a glass vial was weighed 99 mg (0.32 mmol) of (dicyclopentadiene)palladium dichloride and 58 mg (0.34 mmol) of dodecane (GC internal standard). To this was added 10 mL of methylene chloride, and the resulting orange solution was added to the addition funnel. The palladium complex was added dropwise to the acetate solution over a 10-min period. Upon addition the palladium solution decolorized. After addition was complete an aliquot was taken and was quenched with sodium borohydride. GC analysis of the aliquot showed a 100% yield of urethane product. To the reaction mixture was added 249 mg (4.15 mmol) of acetic acid in 5 mL of methylene chloride. The reaction was allowed to stir for 30 min at −5 °C. An aliquot was taken, quenched with sodium borohydride, and filtered. GC analysis showed only urethane product.

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