It appears that the role of the $SnCl_3^-$ ligand is to provide a good leaving group which, in the absence of added ligands including CO, slowly reattacks the platinum center to form a five-coordinate species from which aryl migration to yield the product can occur. This differs from the case wher X = I, which constitutes the only other system studied in which CO insertion readily occurs, to the extent that iodide is a better nucleophile which is less readily displaced but competes effectively with carbon monoxide to form a five-coordinate species from which aryl migration (and probably also phosphine dissociation) can occur. Thus, while tin(II) chloride can be used to catalyze the above carbonylation and decarbonylation reactions, its properties in this situation, at least, are not nearly so unique as has previously been claimed. Consequently, a reexamination of the role of the trichlorostannate ligand in other catalytic systems would appear to be warranted.

Acknowledgment. The continued financial support of the Natural Sciences and Engineering Research Council (to H.C.C.) is gratefully acknowledged. Thanks are expressed to Johnson Matthey Ltd. for a generous loan of platinum salts and to Dr. A. Woon-Fat for certain of the NMR spectra.

Registry No. *trans*-[PtClPh(PPh_3)$_2$], 18421-49-3; *trans*-[PtClPh($PMePh_2$)$_2$], 60772-01-2; *trans*-[Pt($SnCl_3$)Ph(PPh_3)$_2$], 72638-21-2; *trans*-[PtCl(COPh)(PPh_3)$_2$], 18421-48-2; *trans*-[Pt($SnCl_3$)(COPh)(PPh_3)$_2$], 74304-53-3; *trans*-[PtPh(CO)(PPh_3)$_2$]$^+$-$SnCl_3^-$, 78804-26-9; *trans*-[Pt($SnCl_3$)Ph($PMePh_2$)$_2$], 78804-27-0; *trans*-[PtCl(COPh)($PMePh_2$)$_2$], 60742-07-6; *trans*-[Pt($SnCl_3$)-(COPh)($PMePh_2$)$_2$], 78804-28-1; *trans*-[PtPh(CO)($PMePh_2$)$_2$]$^+$-$SnCl_3^-$, 78804-29-2; *trans*-[PtBrPh(PPh_3)$_2$], 41620-24-0; *trans*-[PtIPh(PPh_3)$_2$], 53424-01-4; *trans*-[Pt(N_3)Ph(PPh_3)$_2$], 78804-30-5; *trans*-[PtBr(COPh)(PPh_3)$_2$], 57665-38-0; *trans*-[PtI(COPh)(PPh_3)$_2$], 60751-00-0; *trans*-[Pt(OCOMe)Ph(PPh_3)$_2$], 78804-31-6; *trans*-[Pt-(CN)Ph(PPh_3)$_2$], 78804-32-7; *trans*-[PtIPh($PMePh_2$)$_2$], 78804-33-8; *trans*-[Pt(N_3)Ph($PMePh_2$)$_2$], 78804-34-9; *trans*-[PtI(COPh)-($PMePh_2$)$_2$], 78804-35-0; *trans*-[Pt(OCOMe)Ph($PMePh_2$)$_2$], 78804-36-1.

Catalytic Homogeneous Carbonylation of Azirines by Palladium(0). Important Influence of Catalyst Ligands on the Reaction Pathway

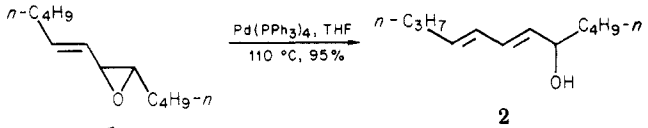
Howard Alper*[1] and Chulangani Perera Mahatantila

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

Received June 25, 1981

The use of soluble palladium(0) catalysts for the carbonylation of azirines results in the novel syntheses of two important classes of compounds. The reaction course is dependent on the nature of the ligands attached to the metal. Tetrakis(triphenylphosphine)palladium(0) catalyzes the conversion of azirines to β-lactams, while vinyl isocyanates are formed in a regiospecific reaction using bis(dibenzylideneacetone)palladium(0) as the catalyst. A mechanism is proposed for these reactions.

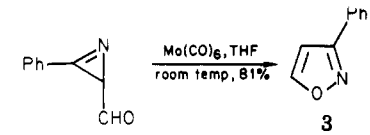
The cleavage of strained ring systems by transition-metal complexes is a topic of considerable recent interest.[2,3] For example, tetrakis(triphenylphosphine)palladium(0) can catalyze the conversion of vinyl epoxides to either allylic alcohols (e.g., 1 → 2) or β,γ-unsaturated ketones, de-



1 2

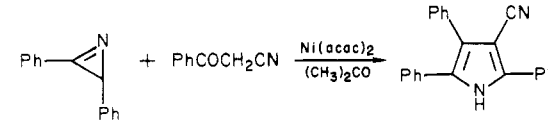
pending on the nature of the organic reactant.[4]

Azirines are another class of three-membered ring compounds which undergo some interesting and useful ring-opening reactions in the presence of organometallic and inorganic compounds.[5-19] For instance, group 6 metal carbonyls can effect intramolecular cycloaddition of appropriately substituted azirines to give five-membered ring heterocycles (e.g., 3) in high yields.[12] Molybdenum hexa-



3

carbonyl induced intermolecular cycloaddition reactions of azirines with alkynes affords 2*H*- or 1*H*-pyrroles, but in low yields.[18] Better product yields can be obtained by the nickel(II)-catalyzed reaction of azirines with activated ketones, leading to pyrroles (e.g., 4).[11] The synthesis of



4

styryl indoles, important intermediates in alkaloid synthesis, can be achieved in fine yields by the cleavage of

(1) E. W. R. Steacie Fellow, 1980–82.
(2) Bishop III, K. C. *Chem. Rev.* **1976**, *76*, 461.
(3) Alper, H. *Isr. J. Chem.*, in press.
(4) Suzuki, M.; Oda, Y.; Noyori, R. *J. Am. Chem. Soc.* **1979**, *101*, 1623.
(5) Hayashi, K.; Isomura, K.; Taniguchi, H. *Chem. Lett.* **1975**, 1011.
(6) Alper, H.; Prickett, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 483.
(7) Alper, H.; Prickett, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 983.
(8) Alper, H.; Prickett, J. E. *Tetrahedron Lett.* **1976**, 2589.
(9) Alper, H.; Prickett, J. E. *Inorg. Chem.* **1977**, *16*, 67.
(10) Komendantov, M. I.; Bekmuchametov, R. R. *Khim. Geterotsikl. Soedin.* **1977**, 1570.
(11) Schuchardt, U.; Faria dos Santos Filho, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 647.
(12) Alper, H.; Prickett, J. E.; Wollowitz, S. *J. Am. Chem. Soc.* **1977**, *99*, 4330.
(13) Isomura, K.; Uto, K.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1977**, 664.
(14) Nakamura, Y.; Bachmann, K.; Heimgartner, H.; Schmid, H.; Daly, J. J. *Helv. Chim. Acta* **1978**, *61*, 589.
(15) Bellamy, F. *J. Chem. Soc., Chem. Commun.* **1978**, 998.
(16) Bellamy, F. *Tetrahedron Lett.* **1978**, 4577.
(17) Alper, H.; Sakakibara, T. *Can. J. Chem.* **1979**, *57*, 1541.
(18) Inada, A.; Heimgartner, H.; Schmid, H. *Tetrahedron Lett.* **1979**, 2983.
(19) Sakakibara, T.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1979**, 458.

0276-7333/82/2301-0070$01.25/0

Table I. Yields, Melting Points, and Analytical Data for 6 [a]

6, R, R'	yield, % [a]	mp, °C	anal. [calcd (found)] % C	% H	% N
p-$CH_3C_6H_4$, H	50	109-111	78.59 (78.51)	6.25 (6.33)	9.65 (9.47)
Ph, H	63	144-146	77.84 (77.87)	5.38 (5.44)	10.68 (10.79)
p-ClC_6H_4, H	37	40-42	61.63 (61.73)	3.65 (3.66)	8.45 (7.86)
p-BrC_6H_4, H	55	145.5-147.0	48.58 (48.71)	2.88 (2.74)	6.67 (6.63)
Ph, CH_3	2.5	oil	78.59 (78.45)	6.25 (6.14)	9.65 (9.06)

[a] Yields are of analytically pure materials. Crude yields were much higher.

Table II. Pertinent Spectral Data for 6

6, R, R'	IR, [a] ν_{CO}, cm^{-1}	NMR, [b] δ ^1H	NMR, [b] δ ^{13}C	MS, *m/e*
p-$CH_3C_6H_4$, H	1780	2.35 (s, 6 H, methyl protons), 3.55 (s, 2 H, CH_2), 3.95, 5.00 (d each, 2 H, CH_2, J = 16 Hz), 7.05-7.90 (m, 8 H, aromatic protons)	21.11 (CH_3), 21.54 (CH_3), 53.23 (CH_2), 55.97 (CH_2), 92.66 (→C-N), 125.53, 128.34, 128.78, 129.17, 129.48, 136.90, 137.96, 142.42 (aromatic carbons), 170.19 (CO), 179.37 (CN)	290
Ph, H	1780	3.59 (s, 2 H, CH_2), 4.00, 5.10 (d each, 2 H, CH_2, J = 16 Hz), 7.20-7.90 (m, 10 H, aromatic protons)	53.46 (CH_2), 56.09 (CH_2), 92.91 (→C-N), 125.57, 128.40, 128.59, 131.44, 131.98, 139.68 (aromatic carbons), 170.50 (CO), 179.21 (CN)	262
p-ClC_6H_4, H	1780	3.53 (s, 2 H, CH_2), 3.93, 5.30 (d each, 2 H, CH_2, J = 16 Hz), 7.20-7.90 (m, 8 H, aromatic protons)	53.71 (CH_2), 56.01 (CH_2), 92.64 (→C-N), 127.07, 128.83, 129.23, 129.71, 134.37, 138.04, 138.41 (aromatic carbons), 169.75 (CO), 178.71 (CN)	
p-BrC_6H_4, H	1783	3.53 (s, 2 H, CH_2), 3.92, 4.98 (d each, 2 H, CH_2, J = 16 Hz), 7.30-7.80 (m, 8 H aromatic protons)	53.63 (CH_2), 55.95 (CH_2), 92.68 (→C-N), 127.35, 129.82, 130.12, 131.79, 132.19, 135.46 (aromatic carbons), 169.87 (CO), 178.66 (CN)	420
Ph, CH_3	1763	1.35, 1.62 (dd each, 6 H, methyl protons), 3.78 (m, 1 H, CH), 4.63 (m, 1 H, CH), 7.08-7.78 (m, 10 H, aromatic protons)		290

[a] $CHCl_3$ solution. [b] $CDCl_3$ with Me_4Si as internal standard. ^{13}C assignments made with the aid of fully and partially decoupled spectra.

azirines by cobalt[8] or rhodium[6] carbonyls.

Several years ago, one of us initiated a study of the metal complex catalyzed carbonylation of azirines using soluble metal complexes. It was hoped that one could ring-expand the azirine to a four-membered ring heterocycle and thus realize the synthesis of β-lactam derivatives, an important class of compounds. Although carbonylation of azirines did occur by the use of stoichiometric quantities of rhodium(I) compounds (e.g., chlorodicarbonylrhodium(I) dimer), the ring-opened vinyl isocyanates were obtained and not any heterocyclic compounds.[19] We now wish to report that the carbonylation of azirines in the presence of catalytic quantities of tetrakis(triphenylphosphine)palladium(0) does indeed result in the formation of β-lactams. Furthermore, the ligands attached to the zerovalent metal have a very significant effect on the reaction course. A preliminary communication has appeared on part of this research.[20]

Results and Discussion

Carbonylation of an azirine (5) with a catalytic amount of tetrakis(triphenylphosphine)palladium(0) in benzene affords the fused β-lactam, 6. This homogeneous process

5 6

occurs under mild conditions (1 atm, 40 °C) using a 10:1 ratio of 5/$Pd(PPh_3)_4$. The yields, melting points, and analytical data for 6 are listed in Table I, and pertinent spectral data are given in Table II. The structure of the product was determined from analytical and spectral data. A single-crystal X-ray determination of 6, R = *p*-$CH_3C_6H_4$, R' = H, was also made.[20,21]

Consistent with the presence of a β-lactam ring in 6 was the appearance of a carbonyl stretching band at 1763–1783 cm^{-1} ($CHCl_3$) in the infrared spectrum. In the proton magnetic resonance spectra of 6, R = aryl, R' = H, the two methylene groups displayed different magnetic properties, with the occurrence of a singlet (δ 3.53–3.59) for the protons of the four-membered ring and two doublets (δ 3.92–4.00, δ 4.98–5.30, J = 16 Hz) for the methylene protons of the five-membered ring. The methylene carbons of 6, R = aryl, R' = H, occurred at δ 53.23–56.09 in the carbon magnetic resonance spectra, and the carbon at the ring juncture appeared at δ 92.64–92.91. The signal at δ 169.75–170.50 was assigned to the carbonyl carbon by comparison with shifts for the analogous carbon in related penam systems.[22] The unsaturated carbon of the imidazoline ring gave a signal at δ 178.66–179.37. All of the mass spectra displayed a molecular ion peak, the primary fragmentation of which was the extrusion of carbon monoxide.

The effect of added ligands, polar solvents, and hydrogen on the carbonylation reaction always resulted in reduced

(20) Alper, H.; Perera, C. P.; Ahmed, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 1289.

(21) Details of the X-ray analysis will be published separately by F. R. Ahmed.

(22) Bose, A. K.; Srinivasan, P. R. *Org. Magn. Reson.* **1979**, *12*, 34.

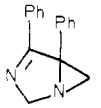
Table III. Yields and Pertinent Spectral Data for 15

15, R, R¹	yield, %	IR,[a] cm⁻¹ ν_{NCO} (14)	IR,[a] cm⁻¹ ν_{NH}	IR,[a] cm⁻¹ ν_{CO}	¹H NMR,[b] δ	MS, m/e
p-$CH_3C_6H_4$, H	83	2285	3400	1735	2.28 (s, 3 H, CH_3), 3.63 (s, 3 H, $COOCH_3$), 4.92, 5.57 (s each, 2 H, CH_2=), 6.6 (s(br), 1 H, NH), 7.12, 7.30 (d each, 4 H, J = 9 Hz, aromatic protons)	191
Ph, H	77	2260	3415	1740	3.65 (s, 3 H, $COOCH_3$), 4.97, 5.63 (s each, 2 H, CH_2=), 6.8 (s(br), 1 H, NH), 7.10-7.60 (m, 5 H, aromatic protons)	177
p-ClC_6H_4, H	99		3400	1735	3.69 (s, 3 H, $COOCH_3$), 4.95, 5.55 (s each, 2 H, CH_2=), 6.50 (s(br), 1 H, NH), 7.25-7.55 (m, 4 H, aromatic protons)	
p-BrC_6H_4, H	96	2270	3397	1735	3.68 (s, 3 H, $COOCH_3$), 4.94, 5.53 (s each, 2 H, CH_2=), 6.60 (s(br), 1 H, NH), 7.23, 7.43 (d each, 4 H, J = 9 Hz, aromatic protons)	256
Ph, CH_3	98	2260[c]	3400	1728	1.68 (d, 3 H, J = 8 Hz, CH_3), 3.65 (s, 3 H, $COOCH_3$), 5.99 (q, 1 H, CH=), 7.27 (s, 5 H, C_6H_5)	

[a] $CHCl_3$ solution. [b] $CDCl_3$ with Me_4Si as internal standard. [c] NMR of 14, R = Ph, R¹ = CH_3: 1.67 (d, 3 H, J = 8 Hz, CH_3), 5.63 (q, 1 H, CH=), 7.33 (s, 5 H, C_6H_5). These data are in excellent accord with those reported for the same compound (i.e., the E isomer) synthesized by an independent route (ref 24).

yields of the β-lactam, with the recovery of increased amounts of **5**. For example, the carbonylation of 2-phenylazirine (**5**, R = Ph, R′ = H) by $Pd(PPh_3)_4$ and 2,2′-bipyridyl (1:1 ratio of the catalyst and 2,2′-bipyridyl) in benzene gave **6** in 29% yield. The latter was formed in only 16% yield when the $Pd(PPh_3)_4$-catalyzed carbonylation of **5** (R = Ph, R′ = H) was run in the dipolar aprotic solvent, *N,N*-dimethylacetamide. Treatment of the same azirine with synthesis gas (1:1 CO/H_2) and the palladium catalyst in benzene afforded **6** in 25% yield. It is also worth noting that the nickel [$Ni(PPh_3)_4$] and platinum [$Pt(PPh_3)_4$] analogues of $Pd(PPh_3)_4$ were ineffective as catalysts for the azirine carbonylation reaction.

In a preliminary communication[20] we proposed, as a working hypothesis, a mechanism for the $Pd(PPh_3)_4$ catalyzed carbonylation reaction which involved ring opening of the azirine (e.g., **5**, R = Ph, R′ = H) by the in situ generated $Pd(PPh_3)_3CO$ (**7**) to give **8** (Scheme I). Intermolecular reaction of **8** with additional reactant and subsequent ring closure and decomplexation of **9** would afford the diazabicyclohexene **10**. Conversion of **10** to **6** may then occur by oxidative addition (to **11**), ligand migration (**12**), and reductive elimination. If **10** were an intermediate, then one would expect the palladium catalyst to promote the carbonylation of an aziridine to a β-lactam. However, no reaction occurred when *N*-*n*-butyl-2-phenylaziridine exposed to carbon monoxide and $Pd(PPh_3)_4$. In addition, the photodimer (**13**)[23] of 2-phenylazirine is an isomer of

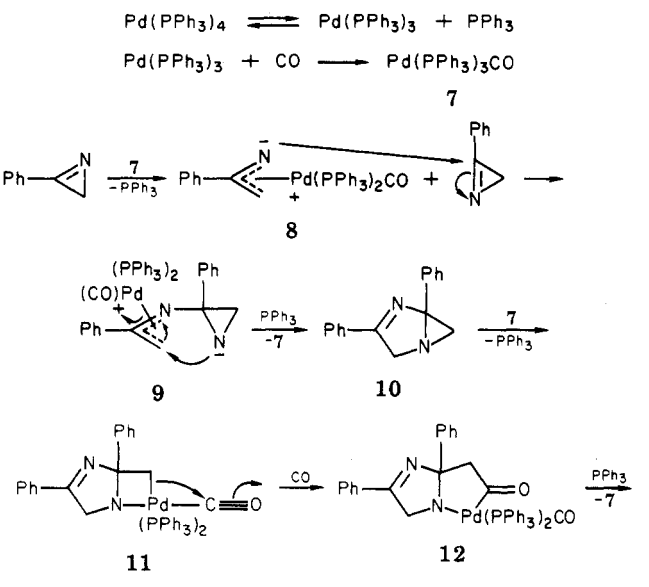


13

10, and it also failed to undergo carbonylation under conditions identical with those described for **5**, R = Ph, R′ = H. These results provide evidence against the intermediacy of **10** in the carbonylation reaction.

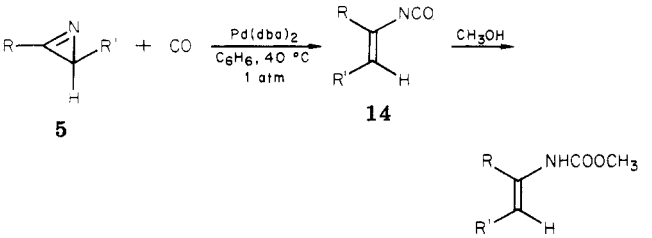
The influence of different ligands attached to zerovalent palladium was also examined in order to gain some insight into the pathway for the carbonylation reaction. Replacement of two triphenylphosphine ligands of $Pd(PPh_3)_4$ by a dimethyl acetylenedicarboxylate ligand (i.e., $Pd(PPh_3)_2(COOCH_3C{\equiv}CCOOCH_3)$) resulted in β-lactam

Scheme I



6, R = Ph, R′ = H

formation from 2-phenylazirine, but in somewhat lower yield than in the case of $Pd(PPh_3)_4$. The use of a bidentate donor ligand such as 1,2-bis(diphenylphosphine)ethane (i.e., $Pd(diphos)_2$) instead of triphenylphosphine resulted in the complete inhibition of the reaction. Much more interesting were the results obtained with the catalyst $Pd(dba)_2$ (dba = dibenzylideneacetone), which contains an acceptor bidentate ligand. This metal-catalyzed azirine carbonylation reaction proved to be an exceedingly clean one leading to vinyl isocyanates (**14**) in high yields.



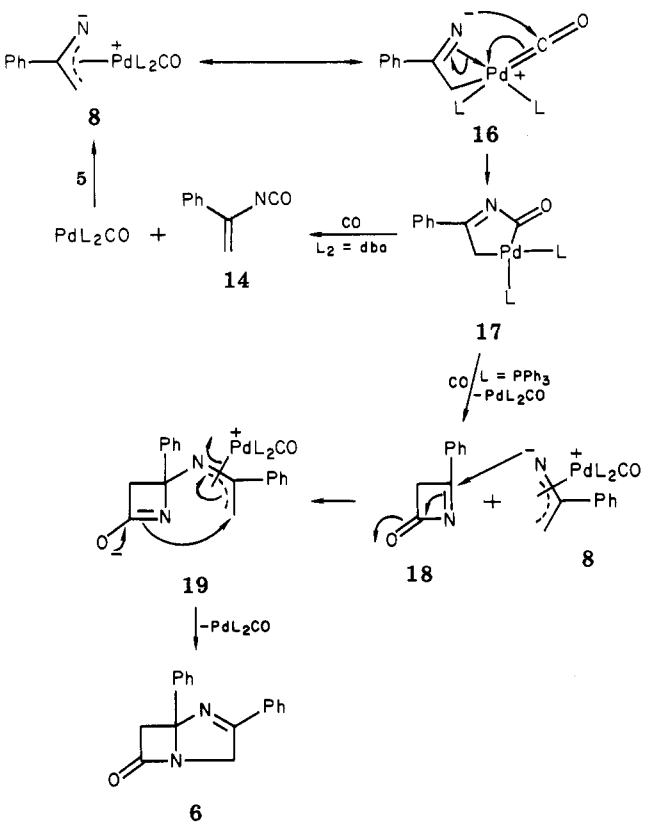
5 **14**

15

Product characterization was made either on the vinyl isocyanate itself or on the carbamate ester (**15**), formed by simple addition of methanol to **14**. The yields (77–99%)

(23) Padwa, A.; Dharan, M.; Smolanoff, J.; Wetmore, Jr., S. I. *J. Am. Chem. Soc.* **1973**, *95*, 1954.

Scheme II



and spectral data for the carbamate esters are given in Table III. Not only are the yields of **14** and **15** consistently higher with $Pd(dba)_2$ than with the chlorodicarbonylrhodium(I) dimer[19] but the reaction is catalytic in palladium(0), while a serious disadvantage of the rhodium reaction is its stoichiometric nature. Another valuable feature of the palladium-catalyzed reaction is its regiospecificity, exemplified by the conversion of 3-methyl-2-phenyl-1-azirine (**5**, R = Ph, R′ = CH_3) to (*E*)-1-phenyl-1-propenyl isocyanate (**14**, R = Ph, R′ = CH_3) and to the carbamate ester **15** (R = Ph, R′ = CH_3) on reaction of the isocyanate with methanol. No *Z* isomer of **14** or **15** was detected.

What is remarkable about the results described above is the complete selectivity exhibited by the palladium catalysts. While $Pd(PPh_3)_4$ catalyzes the conversion of azirines to β-lactams (**6**) with no vinyl isocyanate (**14**) product being detected, compound **14** is the only product obtained when $Pd(dba)_2$ is used as the catalyst.

How can one rationalize the formation of β-lactams and vinyl isocyanates in these reactions? It is conceivable that both products arise via a common intermediate (Scheme II; illustrated for **5**, R = Ph, R′ = H). Structure **16** is a contributor to the resonance hybrid of **8**. Intramolecular cyclization of **16** would afford **17**. Decomplexation of the palladocycle can occur in one of two ways. For L_2 = dba, elimination of Pd(dba)CO occurs in the presence of carbon monoxide to give the vinyl isocyanate (**14**). Reaction of the palladium species with azirine will regenerate **8**. For L = PPh_3, reductive elimination takes place to give the azetinone **18** and $Pd(PPh_3)_2CO$, the latter again forming **8** on treatment with additional azirine (**5**). Nucleophilic addition of **8** to **18** would afford **19** which on ring closure and elimination of $Pd(PPh_3)_2CO$ would give the β-lactam (**6**).

(24) Tanaka, C.; Kurauchi, T.; Nishida, M. *Yakugaku Zasshi* **1976**, *96*, 962.

In conclusion, $Pd(PPh_3)_4$ and $Pd(dba)_2$ are highly selective catalysts for the novel synthesis of β-lactams and vinyl isocyanates, respectively. These two classes of compounds are of considerable importance in medicinal (β-lactams) and polymer (vinyl isocyanates) chemistry. Other features of these reactions include the use of mild conditions and the simplicity in the workup of the reactions. The remarkable ligand effects observed in this investigation are rather unusual in homogeneous catalysis.

Experimental Section

General Data. Melting point determinations were made by using a Fisher-Johns apparatus and are uncorrected. Infrared spectra were obtained by use of a Unicam SP-1100 spectrometer equipped with a calibration standard. Mass spectra were determined on an AEI MS902 spectrometer. Varian T60 and HA100 spectrometers were used for proton magnetic resonance determinations, and carbon magnetic resonance spectra were recorded in the fully and partially decoupled modes with a Varian FT-80 spectrometer. Elemental analyses were carried out by Canadian Microanalytical Service, Vancouver, Canada.

The azirines were synthesized following literature procedures.[25,26] *N*-*n*-Butyl-2-phenylaziridine prepared by first treating styrene oxide with *n*-butylamine[27] and then reacting the resultant β-butylamino-α-phenethyl alcohol with chlorosulfonic acid followed by potassium hydroxide.[28] Irradiation of 2-phenylazirine in benzene afforded 4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**13**).[23]

Tetrakis(triphenylphosphine)palladium(0) was either purchased from Aldrich Chemical Co. or synthesized following the procedure of Coulson.[29] Tetrakis(triphenylphosphine)nickel(0) and tetrakis(triphenylphosphine)platinum(0) were obtained from Strem Chemicals, Inc. Literature methods were used to prepare (dimethyl acetylenedicarboxylate)bis(triphenylphosphine)palladium[30] and bis(dibenzylideneacetone)palladium(0).[31] Dr. T. Izumi kindly donated $Pd(diphos)_2$. Solvents were purified and dried by standard methods.

General Procedure for the $Pd(PPh_3)_4$-Catalyzed Carbonylation of Azirines. A slow stream of carbon monoxide was bubbled through a benzene (50 mL) solution of the azirine (10 mmol) and $Pd(PPh_3)_4$ (1.0 mmol) at 40 °C and atmospheric pressure. The reaction was followed by thin-layer chromatography, and when complete (usually overnight), the reaction mixture was concentrated by using a rotary evaporator. The pure β-lactam (**6**) was obtained by column chromatography (silica gel) using benzene–chloroform or ether–hexane as the eluant. The yields and analytical data for **6** are given in Table I.

Attempted Carbonylation of 2-Phenylazirine (5, R = Ph, R′ = H) Catalyzed by $Ni(PPh_3)_4$ or $Pt(PPh_3)_4$. Substitution of $Ni(PPh_3)_4$ or $Pt(PPh_3)_4$ for $Pd(PPh_3)_4$ in the previous procedure did not result in β-lactam formation, even after a reaction time of 5 days.

Carbonylation of 2-Phenylazirine Catalyzed by $Pd(PPh_3)_4$ and 2,2′-Bipyridyl. To a mixture of 0.254 g (0.220 mmol) of $Pd(PPh_3)_4$ and 0.037 g (0.24 mmol) of 2,2′-bipyridyl in benzene (50 mL) was added **5**, R = Ph, R′ = H (0.263 g, 2.25 mmol). The reaction mixture was stirred overnight at 40 °C under a carbon monoxide atmosphere. Removal of benzene (rotary evaporation) gave an oil which was chromatographed on silica gel. Elution with ether–hexane (1:4) gave 0.0866 g (29%) of **6**, R = Ph, R′ = H.

Carbonylation of 2-Phenylazirine Catalyzed by $Pd(PPh_3)_4$ in *N,N*-Dimethylacetamide. The general procedure was applied to the $Pd(PPh_3)_4$ (0.21 mmol) catalyzed carbonylation of **5**, R =

(25) Hortmann, A. G.; Robertson, D. A.; Gillard, B. K. *J. Org. Chem.* **1972**, *37*, 322.
(26) Hassner, A.; Fowler, F. W. *J. Am. Chem. Soc.* **1968**, *90*, 2869.
(27) Emerson, W. S. *J. Am. Chem. Soc.* **1945**, *67*, 516.
(28) Wells, J. N.; Shirodkar, A. V.; Knevel, A. M. *J. Med. Chem.* **1966**, *9*, 195.
(29) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
(30) Greaves, E. O.; Lock, C. J. L.; Maitlis, P. M. *Can. J. Chem.* **1968**, *46*, 3879.
(31) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065.

Ph, R′ = H (2.18 mmol) in *N,N*-dimethylacetamide (50 mL) instead of benzene. Workup gave **6**, R = Ph, R′ = H, in 16% yield.

Reaction of 2-Phenylazirine with 1:1 CO/H_2 Catalyzed by $Pd(PPh_3)_4$. A 1:1 carbon monoxide–hydrogen gas mixture was bubbled through a benzene (50 mL) solution containing **5**, R = Ph, R′ = H (0.531 g, 4.54 mmol), and $Pd(PPh_3)_4$ (0.58 mmol). Workup in the usual manner (silica gel chromatography) gave 0.15 g (25%) of **6**, R = Ph, R′ = H, and 0.024 g (4.5%) of 4,5-diphenylpyrimidine.

Reaction of *N*-*n*-Butyl-2-phenylaziridine with CO and $Pd(PPh_3)_4$. The heterocycle (0.602 g, 3.44 mmol) and $Pd(PPh_3)_4$ (0.403 g, 0.349 mmol) in benzene (50 mL) were stirred under an atmosphere of carbon monoxide at 40 °C for 2 days. Workup gave recovered starting material.

Reaction of 4,5-Diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (13) with CO and $Pd(PPh_3)_4$. Starting material was recovered when a mixture of 4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (0.207 g, 0.884 mmol) and $Pd(PPh_3)_4$ (0.117 g, 0.102 mmol) in benzene (50 mL) was exposed to carbon monoxide for 2 days at 40 °C.

(Dimethyl acetylenedicarboxylate)bis(triphenylphosphine)palladium-Catalyzed Carbonylation of 2-Phenylazirine (5, R = Ph, R′ = H). A benzene (50 mL) solution of **5**, R = Ph, R′ = H (0.510 g, 4.36 mmol), and the palladium catalyst (0.337 g, 0.436 mmol) was stirred overnight at 40 °C under a CO atmosphere. Workup gave 0.20 g (35%) of **6**, R = Ph, R′ = H.

General Procedure for the $Pd(dba)_2$-Catalyzed Carbonylation of Azirines. This reaction was effected in a manner identical with that described for the $Pd(PPh_3)_4$ reaction, except for the change in catalyst. The vinyl isocyanate (**14**) can be isolated by distillation[19] of the oil obtained after rotary evaporation. The following procedure was used to obtain pure carbamate ester (**15**): hexane (20–80 mL) was added to the oil, and the solution was filtered. Excess (10–20 mL) methanol was added to the filtrate, and the solution was stirred at room temperature for approximately 2 h. After removal of hexane–methanol (rotary evaporation), the residue was chromatographed on silica gel. The product yields are listed in Table III.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council for support of this research. We thank Dr. John Krause and Raj Capoor for recording mass and carbon-13 magnetic resonance spectra, respectively.

Registry No. 5 (R = *p*-$CH_3C_6H_4$, R′ = H), 32687-33-5; **5** (R = Ph, R′ = H), 7654-06-0; **5** (R = *p*-ClC_6H_4, R′ = H), 32687-35-7; **5** (R = *p*-BrC_6H_4, R′ = H), 17631-26-4; **5** (R = Ph, R′ = CH_3), 16205-14-4; **6** (R = *p*-$CH_3C_6H_4$, R′ = H), 77329-86-3; **6** (R = Ph, R′ = H), 77329-87-4; **6** (R = *p*-ClC_6H_4, R′ = H), 77329-88-5; **6** (R = *p*-BrC_6H_4, R′ = H), 77329-89-6; **6** (R = Ph, R′ = CH_3), 77329-90-9; **13**, 36879-67-1; **14** (R = *p*-$CH_3C_6H_4$, R′ = H), 79152-64-0; **14** (R = Ph, R′ = H), 4737-17-1; **14** (R = *p*-ClC_6H_4, R′ = H), 79152-65-1; **14** (R = *p*-BrC_6H_4, R′ = H), 72328-09-7; **14** (R = Ph, R′ = CH_3), 60995-85-9; **15** (R = *p*-$CH_3C_6H_4$, R′ = H), 79152-66-2; **15** (R = Ph, R′ = H), 72328-04-2; **15** (R = *p*-ClC_6H_4, R′ = H), 79152-67-3; **15** (R = *p*-BrC_6H_4, R′ = H), 72328-10-0; **15** (R = Ph, R′ = CH_3), 79152-68-4; $Pd(PPh_3)_4$, 14221-01-3; $Ni(PPh_3)_4$, 15133-82-1; $Pt(PPh_3)_4$, 14221-02-4; $Pd(PPh_3)_2(COOCH_3C{\equiv}CCOOCH_3)$, 15629-88-6; $Pd(dba)_2$, 32005-36-0; $Pd(diphos)_2$, 31277-98-2.

Mercury in Organic Chemistry. 22. Carbon–Carbon Bond Formation via Organocopper–Organomercury Cross-Coupling Reactions

Richard C. Larock* and Douglas R. Leach

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received June 30, 1981

Aryl-, alkenyl-, and alkylmercurials undergo carbon–carbon bond formation with primary and secondary alkyl- and alkenylcuprate reagents to give fair to excellent yields of cross-coupled products. The reaction tolerates certain functional groups and proceeds stereospecifically with retention. Mixed diorganocuprates appear to be intermediates in these reactions as evidenced by their ability to add 1,4 to α,β-unsaturated ketones.

Cross-coupling reactions of organometallic reagents have become an increasingly important tool in the formation of carbon–carbon bonds. Attention has recently focused on the development of mild, new chemo-, regio-, and stereoselective organometallic reagents for application in organic synthesis. The ability of organomercurials to accommodate essentially all important organic functional groups and the ease with which they undergo a variety of mild carbon–carbon bond forming reactions make organomercurials increasingly attractive as synthetic intermediates in organic synthesis. Of late, a variety of synthetically interesting reactions of these compounds have been reported.[1]

Unfortunately, the direct alkylation of organomercurials is not easily effected. In general, organomercurials are inert toward alkyl halides. Only under forcing conditions[2-5] or in the presence of aluminum bromide[6] can low to modest yields of cross-coupled products be obtained. We have recently observed that organorhodium(III) compounds can be employed to effect cross-coupling of alkenyl-, alkynyl-, and arylmercurials and that the reaction can even be carried out by using only catalytic amounts of rhodium (eq 1).[7] However, the catalyst turnover is generally quite low.

$$CH_3I \xrightarrow{ClRh(PPh_3)_3} CH_3RhI_2(PPh_3)_2 \xrightarrow{RHgCl} R\text{–}CH_3 \qquad (1)$$

Bergbreiter and Whitesides have reported that the reaction of primary and secondary alkylmercurials, iodo(tri-*n*-bu-

(1) Larock, R. C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 27–37.
(2) Kekulé, A.; Franchimont, A. *Chem. Ber.* **1872**, *5*, 906–908.
(3) Whitmore, F. C.; Thurman, E. N. *J. Am. Chem. Soc.* **1929**, *51*, 1491–1503.
(4) Schroeder, W. X.; Brewster, R. Q. *J. Am. Chem. Soc.* **1938**, *60*, 751–753.
(5) Gilman, H.; Wright, G. F. *J. Am. Chem. Soc.* **1933**, *55*, 3302–3314.
(6) Beletskaya, I. P.; Vol'eva, V. B.; Reutov, O. A. *Dokl. Akad. Nauk SSSR* **1972**, *204*, 93–95; *Dokl. Chem. (Engl. Transl.)* **1972**, *204*, 383–385.
(7) Larock, R. C.; Hershberger, S. S. *Tetrahedron Lett.* **1981**, 2443.

0276-7333/82/2301-0074$01.25/0