temperature) and the solution is cooled to -78 °C. To this solution is added dropwise the organolithium reagent (10.75 mmol) maintaining temperature below -50 °C. The reaction is slowly warmed while monitoring (TLC: SiO₂, 40% Et₂O/CHCl₃) the dissappearance of β -hydroxy α , β -unsaturated sulfone (9) and the appearance of the conjugate addition product (10). The following temperatures and times are typical for the conjugate addition product (10°). The following temperatures and times are typical for the conjugate addition reaction: *n*-butyllithium, $-78 \rightarrow 50$ °C, 1-2 h; phenyllithium and methyl-lithium, $-78 \rightarrow -25$ °C, 1-2 h. After the addition is complete the reaction mixture is cooled to -60 °C, the appropriate alkylating agent is added (6.0-7.5 mmol), and the solution is allowed to warm to room temperature. The THF is removed in vacuo and the reaction mixture is partitioned between ether and saturated ammonium chloride solution. The ether phase (100-200 mL) is transferred to a separate reaction vessel and allowed to react with chromic acid solution⁸ (2.0 M, 30 mmol) at room temperature for 1-2 h with vigorous stirring. After standard extraction⁸ of the ether phase, diazabicycloundecene (10 mmol) is added to the separatory funnel and is occasionally shaken. The elimination reaction is usually complete (TLC) within 0.5-1 h at room temperature. The ether phase is washed with $2 \times 5 \%$ HCl, $2 \times$ saturated NaHCO₃, dried over MgSO₄, and evaporated in vacuo. The crude reaction product may be further purified by filtration through a short plug of SiO₂ (20% THF/hexane, 100–200 mL) to provide pure enones in the *overall* yields⁷ indicated in Table I.

- (12) The use of this reaction in more highly functionalized systems is currently under active investigation.
- (13) The key to this strategy is the organolithium (Grignard¹¹) conjugate addition reaction.¹⁴ The synthesis was designed to use the γ -oxido group of unsaturated sulfone 8 as a "protecting group" to prevent unwanted γ -proton abstraction by the organometallic reagent. We were consequently surprised to find that reaction of phenyllithium or *n*-butyllithium (1.2 equiv, inverse addition) with 1-phenylsulfonylcyclopentene¹⁵ or 1-phenylsulfonylcyclophexene¹⁵ smoothly (>80%) provides the conjugate-addition products (as a mixture of diastereomers) with only a trace of γ -proton abstraction.
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Palladium Catalyzed Amine Exchange Reaction of Tertiary Amines. Insertion of Palladium(0) into Carbon-Hydrogen Bonds

Sir:

Interaction between a carbon-hydrogen bond and a metal center in both heterogeneous¹ and homogeneous systems² are currently the subject of much study. We here wish to report a novel palladium catalyzed exchange reaction of tertiary amines, whose initial step seems to be an insertion of palladium into a carbon-hydrogen bond adjacent to the nitrogen, leading to a highly active intermediate complex of an iminium ion, to which much attention has been paid quite recently.³

The palladium catalyzed amine exchange reaction of tertiary amines occurs at 200 °C, highly efficiently, as depicted below.

$$R^{1}R^{2}R^{3}N + R^{4}R^{5}R^{6}N \xrightarrow{Pd} R^{7}R^{8}R^{9}N \qquad (1)$$

This process may provide a convenient method for the synthesis of unsymmetrical tertiary amines because of high efficiency, simplicity, and facile isolation of the desired products by distillation. In a typical case, a mixture of dibutylhexylamine and a catalytic amount of palladium black was reacted in an autoclave at 200 °C for 16 h. Filtration of the palladium catalyst followed by distillation gave a mixture of four tertiary amines: tributylamine (26%), dibutylhexylamine (37%), butyldihexylamine (24%), and trihexylamine (3%)⁴ (entry 2 in Table I). If tertiary amine $R^{1}_{2}R^{2}N$, for example, is converted into a mixture of tertiary amines whose alkyl groups $(R^1 \text{ and } R^2)$ are distributed statistically, four tertiary amines, $R^{1}_{3}N$, $R^{1}_{2}R^{2}N$, $R^1R^2_2N$, and R^2_3N could be formed, and the product distribution of $R_{m}^{1}R_{3-m}^{2}N$ (m = 0, 1, 2, 3) can be calculated by the equation of $\lim_{n\to\infty} (2nC_m)(nC_{3-m})/3nC_3$ at equilibrium, Surprisingly, the product yields observed are consistent with those calculated by using the equation, as indicated in the parentheses in eq 2. Moreover, when an equimolar mixture of

tributylamine and trihexylamine was reacted under these conditions,⁵ tributylamine (16%), trihexylamine (16%), dibutylhexylamine (31%), and butyldihexylamine (31%) were obtained, and their yields are also consistent with those calculated statistically, 13, 13, 37, and 37%, respectively (entry 4). Other examples⁶ of the exchange reactions of tertiary amines are shown in Table I.

These reactions can be rationalized by assuming Scheme I, in which palladium coordinates to nitrogen and undergoes insertion into the adjacent C-H bond to give 2, which then comes to rapid equilibrium with a key intermediate, an iminium ion complex (3). In support of insertion of palladium into the C-H bond of the α position of tertiary amines, recovered (S)-(+)-N,N-dimethyl-sec-butylamine (10) was found to have \sim 15% of the optical rotation of the starting amine upon

Table I. Product Yields Obtained by Palladium Catalyzed	Exchange Reaction of Tertiary Amines (Eq 1)
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	$NR^{1}R^{2}R^{3}$		NR ⁴ R ⁵ R ⁶		$NR^{7}R^{8}R^{9}$ b (% yield, c % calculated yield ^d)									
Entry	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	R ⁷	R ⁸	R ⁹		R ⁷	R ⁸	R ⁹	
1	CH_3	C ₄ H ₉	C ₄ H ₉				CH ₃	CH3	CH ₃	(-,4)	CH3	CH ₃	C₄H9	(18, 22)
	<u> </u>	~	~				CH ₃	C₄H9	C₄H9	(48, 44)	C₄H9	C₄H ₉	C₄H9	(25, 30)
2	C ₄ H ₉	C ₄ H ₉	$C_{6}H_{13}$				C ₄ H ₉	C ₄ H ₉	C ₄ H ₉	(26, 30)	C ₄ H ₉	C ₄ H ₉	$C_{6}H_{13}$	(37, 44)
							C4H9	$C_{6}H_{13}$	$C_{6}H_{13}$	(24, 22)	$C_{6}H_{13}$	$C_{6}H_{13}$	$C_{6}H_{13}$	(3, 4)
3	C_3H_7	C₄H9	$C_{6}H_{13}$				C_3H_7	$C_{3}H_{7}$	C_3H_7	(3, 4)	C_3H_7	C_3H_7	C₄H9	(10, 11)
							C_3H_7	C₄H9	C4H9	(10, 11)	C4H9	C4H9	C₄H9	(3, 4)
							C_3H_7	C_3H_7	$C_{6}H_{13}$	(10, 11)	C_3H_7	C₄H9	$C_{6}H_{13}$	(29, 22)
							C ₄ H ₉	C ₄ H ₉	C_6H_{13}	(10, 11)	C_3H_7	C ₆ H ₁₃	C ₆ H ₁₃	(10, 11)
							C ₄ H ₉	$C_{6}H_{13}$	$C_{6}H_{13}$	(10, 11)	$C_{6}H_{13}$	$C_{6}H_{13}$	$C_{6}H_{13}$	(3, 4)
4	C ₄ H ₉	C ₄ H ₉	C4H9	$C_{6}H_{13}$	C ₆ H ₁₃	C ₆ H ₁₃	C ₄ H ₉	C₄H9	C ₄ H ₉	(16, 13)	C ₄ H ₉	C ₄ H ₉	$C_{6}H_{13}$	(31, 37)
							C₄H9	$C_{6}H_{13}$	$C_{6}H_{13}$	(31, 37)	C_6H_{13}	$C_{6}H_{13}$	$C_{6}H_{13}$	(16, 13)
5	C ₄ H ₉	C₄H ₉	C₄H ₉	C_8H_{17}	$C_{8}H_{17}$	$C_{8}H_{17}$	C ₄ H ₉	C ₄ H ₉	C ₄ H ₉	(18, 13)	C ₄ H ₉	C₄H ₉	C_8H_{17}	(30, 37)
							C ₄ H ₉	C_4H_{17}	C_8H_{17}	(30, 37)	C_8H_{17}	C ₈ H ₁₇	C_8H_{17}	(18, 13)

^a Reaction was carried out at 200 °C for 16 h. ^b Satisfactory IR and ¹H NMR was obtained for all compounds. ^c Yield is based upon starting amines. All yields are determined by GLC analysis vs. eicosane or tridecane as an internal standard. d Yield in italics is calculated based upon the statistical calculation at complete equilibrium.



treatment with palladium.^{7,8} When (S)-(+)-N,N-dimethyl-2-methylbutylamine (11) was treated with palladium,⁵ N-



methyldi(2-methylbutyl)amine and trimethylamine were each obtained in 6% yield, as expected. In this case, however, the recovered starting amine retained its optical rotation. Therefore, the conversion of 2 to 4 must be faster than the β -elimination of palladium hydride species, leading to an enamine. Since iminium ions present an extremely electrophilic carbon for nucleophilic attack,⁹ the second tertiary amine attacks 3 to give 4, from which the exchange amines, 6-9, or the starting amine 5 are, for example, produced as a result of alkyl group migration. The alternative mechanism which involves a palladium insertion into a carbon-nitrogen bond followed by alkyl or amide group exchange and reductive elimination seems unlikely because of the following facts. When trioctylamine was allowed to react with palladium, even trace amounts of octene-1 or dioctylamine¹⁰ could not be detected. The presence of an α -C-H bond is required in the substrate tertiary amines. Indeed, only tertiary amines having α -C-H bonds underwent the exchange reaction, and tertiary amines such as N,Ndimethyl-1-methyl-1-phenylpropylamine, N,N-dimethyl-1ethyl-1-methylbutylamine, and N-(1-methyl-1-phenylpropyl)tetrahydropyrimidine retained their optical activity.⁵ The deuterium exchange of the hydrogen attached to the α carbon took place upon treatment with palladium under the reaction condition. Thus, when a mixture of N,N-dimethylbutylamine and N_N -dimethyl-1,1-dideuteriobutylamine was allowed to react with palladium, the recovered N,N-dimethylbutylamines consisted of d_0 , d_1 , and d_2 amines.¹¹ Consequently, the mechanism of the tertiary amine reactions is in contrast to that of primary or secondary amines where a complex of Schiff base (12) formed by insertion of palladium into the N-H bond is suggested to be involved.¹²

We have discovered that the palladium catalyzed reaction of 1,3-propanediamine does not give the ordinary expected triamines such as N-(3-aminopropyl)trimethylenediamine but propylamine (22%), N-propyl-1,3-propanediamine (13, 19%), N,N-dipropyl-1,3-propanediamine (14, 8%), and 2-ethyltetrahydropyrimidine (15, 43%), all of which curiously contain *n*-propyl units (eq 3).¹³ These unusual results should be pointed



out in relation to the exchange reaction of tertiary amines, since 13-15 seem to be formed from propylamine or allylamine which are formally derived from the insertion of palladium into the carbon-nitrogen bond.¹⁴

While it is not yet possible to provide definitive mechanistic information about the palladium catalyzed exchange reaction of tertiary amines, the data are suggestive of insertion of palladium into the C-H bond adjacent to nitrogen. Related work is now in progress.

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Cyclopropene, Alkene, Alkyne, and Carbonyl Complexes of Cyclopentadienylniobium Species and **Reduction of Cyclopropene**

Sir:

Catalytic reduction of unsaturated hydrocarbons by homogeneous catalysis¹ and by biological² means have become subject of increasing interest. Mechanisms of such reactions have been elucidated by isolation of related stable metalhydrocarbon complexes and careful investigation of their reduction chemistry.^{3,4} We wish to report a new series of complexes derived from a $(\eta^5 - C_5 H_5)_2 NbCl$ species and describe the reduction chemistry of a novel cyclopropene complex,

Generation of the $(C_5H_5)_2NbCl$ species seems to proceed smoothly when 200 mg of $(C_5H_5)_2NbCl_2^5$ dissolved in 40 mL of toluene is stirred with sodium amalgam in the presence of a substrate molecule. The resulting air-sensitive solution can then be filtered and the solvent removed in vacuo and purified by sublimation. In this manner, treatment of $(C_5H_5)_2NbCl_2$ with carbon monoxide yields a new chlorocarbonyl complex, $(C_5H_5)_2NbCl(CO)$ as well as the known $(\eta^5-C_5H_5)Nb-$ (CO)₄:

$$(C_5H_5)_2NbCl_2 \xrightarrow[CO]{Na/Hg} (C_5H_5)_2NbCl(CO) + (C_5H_5)Nb(CO)_4 \quad (1)$$
88%

Niobocene chlorocarbonyl is characterized by a sharp singlet in its ¹H NMR at 5.01 ppm due to the cyclopentadienyl protons and a strong infrared absorption at 1900 cm⁻¹ due to the carbonyl group.⁶ $(C_5H_5)Nb(CO)_4$ was identified by its mass spectrum and previously reported infrared spectrum.⁷ If the reduction of $(C_5H_5)_2NbCl_2$ is carried out under high pressure carbon monoxide, $(C_5H_5)Nb(CO)_4$ is obtained in higher yields and by simpler procedures than previously reported⁷ and a new complex $(C_5H_5)_3Nb(CO)$ is generated:

$$(C_{5}H_{5})_{2}NbCl_{2} \xrightarrow{Na/Hg}_{CO, 130 atm} (C_{5}H_{5})Nb(CO)_{4} + (C_{5}H_{5})_{3}Nb(CO)$$
(2)
 30%

 $(C_5H_5)_3Nb(CO)$ is characterized by a strong carbonyl infrared absorption at 1890 cm⁻¹ and a ¹H NMR exhibiting singlet absorptions at 4.4 and 6.20 ppm integrating 10:4.8, suggesting two η^5 -C₅H₅ and one η^1 -C₅H₅ ligands.⁶

Niobocene chlorocarbonyl may be used to synthesize new carbonyl or alkene complexes (eq 3 and 4). $(C_5H_5)_2$ -Nb(CH₃)(CO) is characterized by ¹H NMR absorptions at 4.67 and -0.38 ppm integrating 10:3 and a strong carbonyl infrared absorption at 1890 cm^{-1,7} (C₅H₅)₂Nb(Cl)(C₂H₄) is characterized by ¹H NMR absorptions showing a singlet at



6.01 ppm due to cyclopentadienyl protons and broad overlapping multiplets at 1.33 and 1.45 ppm (integration 10:4.8) due to the inequivalent ends of the ethylene ligand.⁶ Related olefin complexes⁸ have displayed similar NMR spectra.

Coordination of alkynes by the niobocene monochloride fragment also proceeds smoothly under the conditions shown in eq 5. $(C_5H_5)_2Nb(CF_3C \equiv CCF_3)Cl$ is characterized by a ¹H NMR absorption at 5.28 ppm due to cyclopentadienyl



protons, a mass spectrum with (C₅H₅)₂Nb(CF₃=CCF₃)Cl⁺ as the present ion, and an infrared absorption at 1790 cm⁻¹ due to the C=C stretch. $(C_5H_5)_2Nb(HC=CCH_3)Cl$ is characterized by a strong infrared absorption at 1740 cm^{-1} due to the C=C stretch, a satisfactory mass spectrum, and a ¹H NMR spectrum with absorptions at 5.30, 2.83, 2.37, and 7.98 ppm integrating 10:1,25:1.67:0.9. The two methyl absorptions at 2.83 and 2.37 ppm are due to the two possible isomers of $(C_5H_5)_2Nb(HC \equiv CCH_3)Cl.^6$ Similar complexes of tantalum have been prepared, but only with disubstituted alkynes.⁹ Synthesis of $(C_5H_5)_2Nb(HC \equiv CCH_3)Cl$ by displacement of carbon monoxide from $(C_5H_5)_2Nb(Cl)CO$ does proceed at 1 atm, although very slowly, as followed by NMR.10

Having demonstrated the ability of the $(C_5H_5)_2NbCl$ species to readily coordinate ordinary alkenes and alkynes, a new substrate of intermediate multiple bond character, cyclopropene,¹¹ was investigated. A moss-green cyclopropene complex was readily isolated (eq 6). This compound is char-

$$(C_{5}H_{5})_{2}NbCl(C_{3}H_{4})$$
(6)

acterized by a ¹H NMR with a sharp singlet at 5.87 ppm due to cyclopentadienyl protons and a broad multiplet due to cyclopropene protons at 1.43 ppm integrating 10:4.9. The mass spectrum and infrared spectrum were in agreement with the proposed structure and treatment of the complex with HCl yielded almost pure cyclopropane, providing additional support for the structure (eq 7). This is the first reported reduction of cyclopropene via an isolable metal complex. One other monomeric cyclopropene complex has been reported,13 but no investigation of its chemistry was undertaken. Reduction of cyclopropene by the nitrogenase enzyme to a mixture of cyclopropane and propene has been recently reported.¹⁴ While our results do suggest that cyclopropane formation from