Table I. Products of the Reactions of Primary and Secondary Amines (Eq 1)

Amines $R^1CH_2NHR^2$		Temp, °C	Time, hr	Product yield (%)[a]		Conversion (%)[d]
R^1	R^2			$(R^1CH_2)_2NR^2$	$R^1CH{=}NCH_2R^1$	
C_6H_5	H	80	5	45	45	90
$CH_2{=}CH$	H	25	5		95[b]	95
C_6H_5	CH_3	120	20	85		28
H	C_6H_5	120	20	98		7
CH_3	C_6H_5	150	48	98		5
$n\text{-}C_3H_7$	CH_3	160	5	85[c]		70

[a] Yields based on unrecovered amines. [b] $CH_3CH_2CH{=}NCH_2CH{=}CH_2$. [c] Another product was $(n\text{-}C_4H_9)_3N$ (8%). [d] Conversions based on unrecovered amines are easily improved by prolonged reaction time or higher temperature.

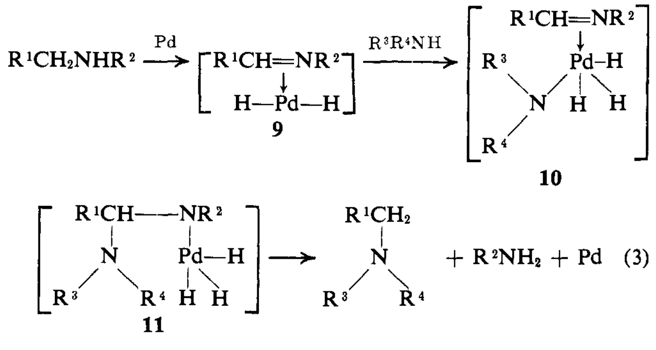
Table II. Reactions of Secondary Amines with Either Primary Amines or Secondary Amines (Eq 2)

Amines				Temp, °C	Time, hr	Product yield (%)[a]		Conversion (%)[b]
$R^1CH_2NHR^2$		R^3NHR^4				R^1CH_2-NHR^3R^4	$R^1CH{=}NR^3$	
R^1	R^2	R^3	R^4					
C_6H_5	CH_3	$n\text{-}C_6H_{13}$	H	120	10	55	30	37
C_6H_5	CH_3	C_6H_{11}	H	120	10	10	90	40
C_6H_5	CH_3	C_6H_5	H	120	20	48	52	40
C_6H_5	CH_3	$H_2N(CH_2)_2$	H	120	10	95		24
H	C_6H_5	$n\text{-}C_6H_{13}$	H	120	40	98		5
$n\text{-}C_3H_7$	CH_3	$n\text{-}C_6H_{13}$	H	160	7	75		45
C_6H_5	CH_3	$n\text{-}CH_3(CH_2)_3$	CH_3	120	10	80		55
C_6H_5	CH_3	$(CH_2)_5$		130	10	97		90
C_6H_5	CH_3	$(CH_2)_4$		130	10	75		75
$n\text{-}C_3H_7$	CH_3	$(CH_2)_5$		160	5	98		85

[a] Yields based on unrecovered amines. [b] Conversions based on unrecovered amines are easily improved by prolonged reaction time or higher temperature.

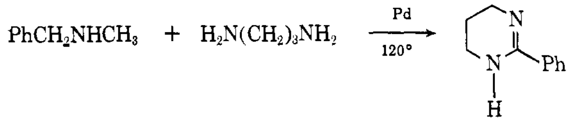
benzylamine (95%), and on treatment of *N*-methylpropylamine with pyrrolidine led to *N*-propylpyrrolidine (98%).

Secondary and tertiary amines are simply synthesized by reaction of various amines using a palladium catalyst. The conversion of these reactions is improved by using more active catalysts such as π-allylpalladium complexes or Wilkinson catalyst, although side reactions appear. The reaction can be envisioned as follows. The key step is the formation of a palladium π complex of Schiff base bearing a Pd–H bond (**9**) by dehydrogenation by palladium. Oxidative addition of an amine (R^3R^4NH) into **9** leading to **10**, followed by addition of the Pd–N across the N=C bond, would form **11** which subsequently cleaves to form products



reductively.[6] The palladium(II)-catalyzed additions of amines across carbon–carbon[7] or carbon–nitrogen[8] double bonds have been demonstrated.

Variations of this reaction can open new routes to heterocyclic compounds. For example, palladium-catalized reaction of *N*-methylbenzylamine with 1,3-propanediamine at 120° affords 2-phenyl-1,4,5,6-tetrahydropyrimidine (**12**) in 75% yield. Furthermore,



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treatment of allylamine with 1,3-propanediamine gives 2-ethylhexahydropyrimidine in 82% yield. We are currently exploring other applications of this reaction.

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^{207}Pb Pulse Fourier Transform Nuclear Magnetic Resonance. A Promising New Tool for Studies in Lead Chemistry

Sir:

The recent development of pulse Fourier transform approaches has made ^{13}C nmr spectroscopy a powerful, popular, and convenient tool for a wide range of chemical studies. We wish to report here that virtually the same techniques used for ^{13}C are also applicable to ^{207}Pb resonances and provide some preliminary data illustrating the promise and characteristics of high-resolution ^{207}Pb nmr. Although there have been earlier nmr studies of ^{207}Pb (21.1% naturally abundant, 9.13×10^{-3} as sensitive as ^1H for equal numbers of

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Table I. Typical High-Resolution ^{207}Pb Nmr Data[a]

Compound	Solvent (molar concn)	Line width, Hz	Chemical shift,[b] ppm	T_1, sec
$Pb(CH_3)_4$	Toulene (3.7)	2	0	0.6
$Pb(C_2H_5)_4$	Neat	6	70.6	1.2
$Pb_2(C_6H_5)_6$	Carbon disulfide 87% (0.2) benzene 17%	4	−73.2	
$Pb(CH_3)_3OCOCH_3$	Acetic acid (0.8)	6	408.1	
$Pb(C_2H_5)_3OCOCH_3$	Acetic acid (2.0)	8	412.0	
$Pb(n\text{-}C_3H_7)_3OCOCH_3$	Acetic acid (1.0)	12	428.8	
$Pb(n\text{-}C_4H_9)_3OCOCH_3$	Acetic acid (2.0)	12	424.0	
$Pb(i\text{-}C_4H_9)_3OCOCH_3$	Acetic acid (2.0)	9 (320°) 5 (270°)	432.0	0.08 (270°)
$Pb(C_6H_5)_3C_2H_5$	Carbon tetrachloride (0.5)	11	−114.5	
$Pb(OCOCH_3)_2$	Water (1.1)	100	−1337.0	
$Pb(OCOCH_3)_2$	Acetic acid (2.1)	100	−1519.0	
$Pb(NO_3)_2$	Water (1.0)	12	−2961.2	1.1

[a] Results obtained at 304 ± 4°K, unless otherwise indicated. [b] Chemical shifts given with respect to 3.7 *M* $Pb(CH_3)_4$; higher values correspond to lower shielding.

nuclei, $I = {}^1/_2$),[1–9] mainly by wide-line or INDOR methods, there are no previous reports of the application of modern, high-resolution, on-line pulse Fourier transform approaches to this nuclide.

Spectra were obtained in natural abundance at 18.83 MHz, using a Bruker HFX-90 spectrometer and Digilab FTS/NMR-3 data system and 400-S pulser. Details of the spectrometer configuration that permits observation of the nmr spectra of ^{207}Pb and many other nuclides will be presented elsewhere.

Table I summarizes some of the chemical shifts that have been determined by this technique. The data show that even rather minor structural variations give rise to large chemical shifts, which shows the great structural selectivity that ^{207}Pb offers for chemical studies. Considered together with the very large structural sensitivity of ^{207}Pb chemical shifts from the earlier wide-line and INDOR work on ^{207}Pb,[1–7] these data demonstrate the promise of ^{207}Pb chemical shift measurements for studies of structure and dynamics in lead compounds and for analytical applications. In addition, very large effects of solvent and temperature variation (about 0.5 ppm decrease in shielding per degree increase in temperature for 2 *M* triisobutyllead acetate in acetic acid) on the ^{207}Pb chemical shifts of the acetates have been observed in this work, implying that significant changes in species identity and/or environment accompany such variations. Systematic studies of these phenomena should elucidate the detailed nature of structural alterations and the dynamics and thermodynamics of complexation equilibria in these and other systems.

Spin–lattice relaxation times have been determined by a $180°\text{–}\tau\text{–}90°$ method for some of the samples indicated in Table I. These T_1 values range typically from about 0.1 to 2 sec. These values are remarkably short, in view of the generally larger T_1's for ^{13}C and ^{29}Si, especially the latter, in analogous compounds.[10,11] With no possibility of quadrupole relaxation mechanisms, this implies substantial contributions to spin–lattice relaxation from mechanisms such as chemical exchange, chemical shift anisotropy, and spin rotation. It should be emphasized that the T_1 values reported here are properties of *typical samples*, not scrupulously purified materials. Hence, they are representative of the parameters one encounters in optimizing experimental procedures, but are not necessarily characteristic of the intrinsic properties of the indicated species.

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Alkylation of Acid Halides by Alkylrhodium(I) Complexes

Sir:

As part of our studies directed toward transition metal catalyzed functionalization of olefins, we have examined the reactions of alkylrhodium(I) complexes with acid halides to produce ketones. The general reaction as well as the proposed mechanism for the transformation are detailed in Scheme I. The results, collected in Table I, demonstrate the range of unsymmetrical ketones available by this method.

Organolithium reagents and organomagnesium halides are equally useful for the production of the necessary alkylrhodium(I) complexes. These complexes react smoothly with alkoyl, benzoyl, and cinnamoyl chlorides, as well as those of greater complexity, to produce unsymmetrical ketones in high yield. Furthermore, the alkylrhodium(I) complexes do *not* react with