difference in the nature of exchange interactions in $LiFe_2F_6$ and $Fe_2F_5{\cdot}2H_2O$, a difference which arises in part from the structural variations, will be considered in a subsequent publication.[11]

Acknowledgment. Work performed at the University of Vermont was supported by the Office of Naval Research. We thank a reviewer for pointing out a mistake in a data table.

Registry No. $Fe_2F_5{\cdot}2H_2O$, 53168-87-9.

Supplementary Material Available: Listing of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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(12) In their initial work,[3] Brauer and Eichner prepared crystalline material using a different route. The unit cell parameters which they determined are in agreement with our work. However, the improper formula used and the apparently incorrect density of 2.43 g/mL (determined pycnometrically in decalin) led to a value of 3 formula units in the unit cell. It should be noted that published powder pattern data for this compound contain several errors.[13]

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(β-Aminoacyl)palladium(II) Complexes: Preparations, Structures, and Reactions

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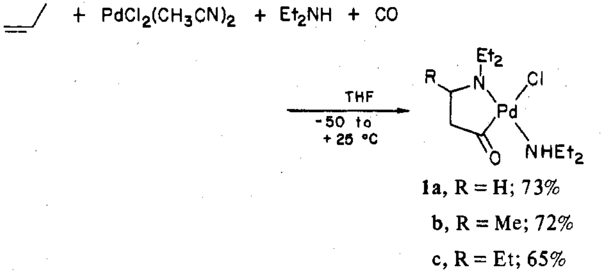
Received March 9, 1977 AIC70188K

The crystal and molecular structure of chloro(3-diethylaminopropionyl)(diethylamine)palladium(II) (**1a**) has been determined from three-dimensional single-crystal x-ray diffraction data, collected by counter techniques. The crystals are orthorhombic, space group *Cmca* (No. 64), with eight formula units in a unit cell of dimensions $a = 12.272$ (3), $b = 8.363$ (2), and $c = 29.445$ (7) Å. The structure was refined by full-matrix least-squares methods to an R of 0.047 ($R_w = 0.053$) for 806 independent reflections with $F^2 > 3\sigma(F^2)$. The monomeric complex exhibits approximately square-planar coordination geometry about the palladium(II) ion, with the chloride ion bonded in a trans configuration with respect to the σ-bonded acyl carbon atom. Bond lengths to palladium are as follows: Pd–C(acyl) = 1.95 (1) Å, $Pd–Cl^-$ = 2.446 (4) Å, Pd–N = 2.09 (1) and 2.11 (1) Å. Oxidative cleavage of this complex and the (3-diethylamino)heptanoyl complex **1d** with Br_2 followed by treatment with methanol, diethylamine, or ammonia resulted in the high-yield production of β-amino esters or amides. Complexes resulting from the replacement of the Et_2NH in complex **1a** by Ph_3P, methyl isocyanide, and (methylamino)(diethylamino)carbene and replacement of both Et_2NH and Cl^- by cyclopentadienyl and methyl isocyanide were synthesized and characterized by ^1H and ^{13}C NMR spectroscopy.

Introduction

Palladium-assisted aminocarbonylation of simple monoolefins produces stable (β-aminoacyl)palladium(II) complexes of structure **1** (eq 1). In an initial publication,[1] the preparation and the infrared and proton NMR spectra of a series of these complexes were reported. In this paper the x-ray crystal structure of complex **1a**, its reactions to form β-amino acid derivatives, and its reactions producing a variety of new palladium(II) complexes containing the β-aminoacyl ligand are presented.



(1)

1a, R = H; 73%

b, R = Me; 72%

c, R = Et; 65%

d, R = *n*-Bu; 70%

Results and Discussion

Structure of Chloro(3-diethylaminopropionyl)(diethylamine)palladium(II). The structure of chloro(3-diethylaminopropionyl)(diethylamine)palladium(II) (**1a**) is displayed in Figure 1, while atomic coordinates, anisotropic thermal parameters, and bond lengths and angles within the complex unit are tabulated in Tables I–III. The complex adopts a square-planar configuration, in which the chloride ion is trans to the acyl carbon of the bidentate 3-diethylaminopropionyl ligand. As described in the Experimental Section of this report,

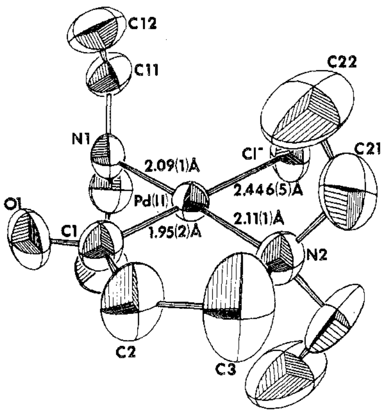


Figure 1. View of the neutral acyl-palladium complex **1a**. Hydrogen atoms are not included, and 50% probability ellipsoids are depicted.

Table I. Atomic Coordinates (Fractional)[a]

Atom	x	y	z
Pd(II)	0.0	0.43547 (12)	0.62129 (4)
Cl⁻	0.0	0.1904 (5)	0.6666 (2)
N1	0.0	0.3028 (14)	0.5611 (4)
N2	0.0	0.5865 (15)	0.6786 (4)
C1	0.0	0.6319 (18)	0.5858 (5)
C2	0.0	0.7850 (20)	0.6151 (7)
C3	0.0	0.7548 (20)	0.6664 (9)
O1	0.0	0.6438 (13)	0.5474 (4)
C11	0.0996 (9)	0.2036 (14)	0.5550 (4)
C12	0.1997 (10)	0.3047 (17)	0.5566 (4)
C21	0.0977 (13)	0.5925 (20)	0.7089 (4)
C22	0.2045 (13)	0.5508 (29)	0.6858 (6)
H(N1)	0.0	0.3784	0.5370
H1(C11)	0.1029	0.1260	0.5785
H2(C11)	0.0960	0.1510	0.5264
H1(C12)	0.2608	0.2425	0.5475
H2(C12)	0.1915	0.3930	0.5366
H3(C12)	0.2104	0.3424	0.5867
H1(C21)	0.1000	0.6323	0.7319
H2(C21)	0.0872	0.4508	0.7227

[a] Standard deviations in least significant digits in parentheses. If no standard deviation is given, the parameter was not refined.

Table II. Anisotropic Thermal Parameters[a]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Pd(II)	65 (1)	110 (1)	9.1 (1)	0	0	0 (1)
Cl⁻	172 (5)	162 (7)	12 (1)	0	0	13 (2)
N1	100 (11)	118 (18)	9 (2)	0	0	2 (5)
N2	108 (12)	159 (24)	12 (2)	0	0	−11 (6)
C1	98 (14)	153 (25)	10 (2)	0	0	−8 (6)
C2	258 (28)	140 (27)	17 (3)	0	0	−30 (8)
C3	527 (60)	92 (32)	24 (5)	0	0	−20 (9)
O1	144 (13)	173 (19)	14 (2)	0	0	21 (5)
C11	103 (11)	200 (21)	14 (2)	21 (14)	6 (3)	−11 (5)
C12	98 (10)	330 (29)	20 (2)	34 (16)	11 (4)	−16 (7)
C21	183 (17)	427 (37)	15 (2)	7 (23)	−24 (5)	−38 (8)
C22	103 (14)	884 (79)	35 (3)	−49 (28)	0 (6)	−70 (15)

[a] Estimated standard deviations in the least significant digits are given in parentheses. The form of the anisotropic thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Bond lengths (Å) and Angles (deg)[a]

(a) Lengths

Pd–C1	1.95 (1)	C1–O1	1.13 (2)	N2–C21	1.52 (2)
Pd–N2	2.11 (1)	C1–C2	1.55 (2)	C21–C22	1.48 (2)
Pd–N1	2.09 (1)	C2–C3	1.53 (3)	N1–C11	1.49 (1)
Pd–Cl⁻	2.446 (4)	C3–N2	1.45 (2)	C11–C12	1.49 (2)

(b) Angles

N1–Pd–C1	89.6 (6)	O1–C1–C2	119 (1)
C1–Pd–N2	85.7 (6)	C1–C2–C3	115 (1)
N2–Pd–Cl⁻	93.7 (4)	C2–C3–N2	114 (2)
Cl⁻–Pd–N1	91.0 (3)	C3–N2–C21	109 (1)
		N2–C21–C22	115 (1)
Pd–C1–O1	128 (1)	C21–N2–C21′	104 (1)
Pd–C1–C2	114 (1)	N1–C11–C12	111 (1)
Pd–N2–C3	112 (1)	C11–N1–C11′	110 (1)
Pd–N2–C21	111 (1)		
Pd–N1–C11	113 (1)		

[a] Standard deviations in least significant digits are in parentheses.

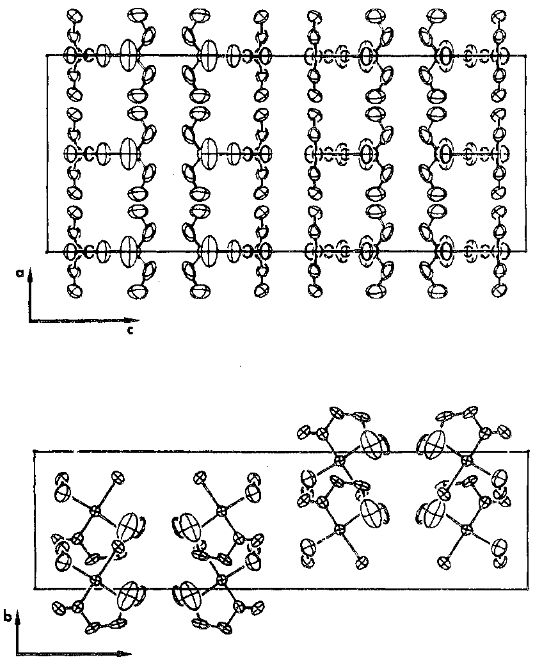


Figure 2. Views of the packing of the acyl-palladium complex **1a** in the unit cell: (top) view down the crystallographic *b* axis; (bottom) view along the crystallographic *a* axis.

all atoms of this complex, with the exception of the *N*-ethyl groups, are constrained to lie in the crystallographic mirror planes at $x = 0$ and $x = {}^1/_2$ (see Figure 2). The coordination geometry, while necessarily perfectly planar on these grounds, is not perfectly square, due primarily to the "bite" of the bidentate 3-diethylaminopropionyl ligand being too small to achieve the idealized 90° angle (C1–Pd–N2 = 85.7 (6)°). The constrained geometry of this ligand chelate ring results in the position of N2 deviating significantly from the expected square-planar position, while other coordinating atoms show essentially no displacement from the idealized coordination positions (as shown by C1–Pd–Cl⁻ 179.4°, N1–Pd–Cl⁻ 91.0 (3)°).

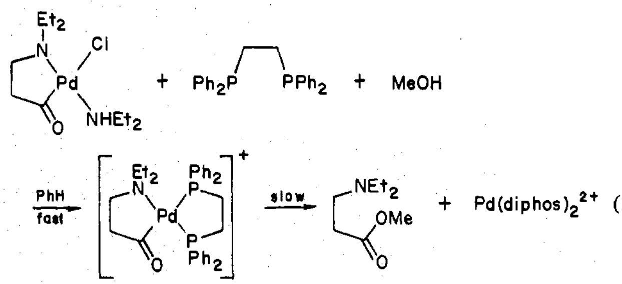
The palladium–nitrogen bond lengths observed for compound **1a** in this study are slightly longer (Pd–N1 = 2.09 (1) Å, Pd–N2 = 2.11 (1) Å) than expected from the results of other studies. For example, in the bis(ethylenediamine)-palladium(II) cation,[2] a Pd–N bond distance of 2.036 (7) Å was observed. The amine nitrogen in the complex [Pd(Me$_3$dpma)Cl]Cl (Me$_3$dpma = methylbis[(6-methyl-2-pyridyl)methyl]amine) was found at the very short distance of 2.018 (8) Å from palladium,[3] although this was probably a consequence of the constraints imposed by the ligand geometry. At the other extreme, the Pd–N(amino) bond length in the complex Pd(Ph$_2$P(CH$_2$)$_3$N(CH$_3$)$_2$)(SCN)(NCS)[4] was observed to be 2.148 (7) Å. This very long bond was felt to be due to the trans influence of the S-bonded thiocyanate group. The Pd–N(amino) bond length in (*N*,*N*-dimethylbenzylamine-2*C*,*N*)(*N*-phenylsalicylaldiminato)palladium(II) was found to be 2.09 (1) Å.[5] This bond, trans to a Pd–N(iminato) bond, is quite comparable in length to the Pd–N(amino) bond lengths in compound **1a** of the present study.

The novel palladium–acyl linkage of **1a** exhibits a Pd–C1(acyl) bond length of 1.95 (1) Å. This is significantly shorter than most other reported Pd–C bond lengths, indicating the formation of a very strong bond between the palladium(II) ion and the acyl carbon. As would be expected, Pd–C σ bonds, where C is an sp^3 hybridized carbon, are much longer than the Pd–C(sp^2) bond length reported here, with reported values ranging from 2.02 (1)[6] to 2.16 (5) Å[7] and clustering in the range 2.02–2.07 Å.[8-10] When the carbon attached to palladium(II) is sp^2 hybridized, however, much shorter Pd–C bonds are observed. For example, σ-bonded aryl complexes of palladium(II) have exhibited Pd–C(phenyl) bond lengths of 1.99 (2) Å in *trans*-chloro-2-(phenylazo)phenylbis(triethylphosphine)palladium(II),[11] 1.981 (7) Å in (*N*,*N*-dimethylbenzylamine-2*C*,*N*)(*N*-phenylsalicylaldiminato)palladium(II),[5] and 1.94 (2) Å in the biacetyl bis(*N*-methyl-*N*-phenyl)osazone complex of palladium(II).[12] As has been pointed out previously,[5] these Pd–C(sp^2) distances are significantly shorter than the value of 2.05 Å predicted for these bond lengths from the sum of the σ covalent radii [1.31 Å (Pd(II)) + 0.74 Å (C(sp^2))]. This would seem to indicate that the very short Pd–C1(acyl) bond in the present study possesses partial double-bond character, arising from "back-donation" of d electrons from the metal into the empty π-antibonding orbital of the acyl group. This interpretation of the bonding in this Pd–C system gains support from the observed infrared spectrum of compound **1a**.[1]

The large trans influence of σ-bonded carbon is well established.[13] The consequence of this in the present structure is that the Pd–Cl^- bond trans to Pd–C1(acyl) is among the longest Pd–Cl^- bonds known, with an observed bond length of 2.446 (4) Å. The normal range for terminal Pd–Cl^- bond lengths is 2.25–2.33 Å.[14] When trans to P(phosphine), however, Pd–Cl^- bond lengths are typically in the range 2.34–2.37 Å,[15-17] and the observed range of palladium(II)–chloride bond lengths is extended to include Pd–Cl^- bond lengths of 2.382 (5)[11] and 2.413 (1) Å[8] when trans to σ-bonded carbon. The extremely long Pd–Cl^- bond length observed in the present study is thus a natural consequence of the extremely short and strong Pd–C1(acyl) bond in the trans position.

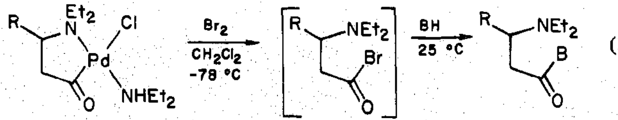
All of the light-atom positions in the 3-diethylaminopropionyl ligand, with the exception of the coordinating atoms C1 and N2, are influenced by the presence of a small unresolvable disorder effect, as described in the Experimental Section. Thus, although the values of bond lengths and angles observed within this ligand are not greatly different from the expected values, the authors feel that a detailed analysis of these bond lengths and angles is not justified. All bond lengths and angles for the nondisordered diethylamine ligand appear normal. No significant intermolecular contacts were found involving the palladium ion.

Synthesis of β-Amino Acid Derivatives. The amination–carbonylation sequence described in eq 1 results in the difunctionalization of the olefinic substrate and affords a potential synthesis of β-amino acid derivatives by cleavage of the metal from the β-aminoacyl ligand. Direct nucleophilic displacement of the β-aminoacyl ligand was unsuccessful. Weak nucleophiles such as excess methanol, diethylamine, and sodium acetate failed to react under a variety of conditions. Stronger nucleophiles, such as sodium methoxide, lithium diethylamide, methyllithium, phenyllithium, vinyllithium and allyllithium, led to a rapid deposition of metallic palladium, but little if any of the corresponding β-amino acid derivative. In these cases, abstraction of the relatively acidic hydrogens α to the acyl group and/or on the coordinated diethylamine probably occurred and led to decomposition. Fair yields of β-amino acid derivatives were obtained by treatment of a benzene solution of the complex with diphos ($Ph_2PCH_2CH_2PPh_2$) in the presence of excess methanol or diethylamine. Two equivalents of diphos was required, the first equivalent being complexed almost immediately with no production of β-amino acid derivative (TLC), while the second equivalent was slowly consumed (16 h) yielding the β-amino acid derivative in the process (eq 2). The use of diphos produced the best yields of β-amino acid derivatives. Other ligands including Ph_3P, EtO_3P, TMEDA, EDTA, and pyridine were considerably less efficient in this process. While diphos-induced cleavage of the β-aminoacyl ligand produced good crude yields of the desired β-amino acid derivatives, separation of these products from remaining diphos- and palladium-containing materials proved to be difficult. The product β-amino esters and amides were prone to β elimination of diethylamine, producing acrylic acid derivatives that partially polymerized. Acceptable yields of pure material could be obtained by column chromatography on neutral alumina.



(2)

The most efficient conversion of (β-aminoacyl)palladium(II) complexes to β-amino acid derivatives was achieved by treatment of a CH_2Cl_2 solution of the complex with 1 equiv of Br_2 at −78 °C, followed by addition of excess methanol, diethylamine, or ammonium hydroxide and warming to room temperature (eq 3).[18] (This cleavage was shown by IR spectral data to produce acyl bromide as an intermediate.) This procedure led to essentially quantitative yields of crude β-amino esters or amides which were greater than 95% pure by NMR but were slightly colored. Colorless material was obtained by molecular distillation or chromatography on neutral alumina, although some loss of material through elimination of diethylamine was always experienced.



(3)

"quantitative" yield

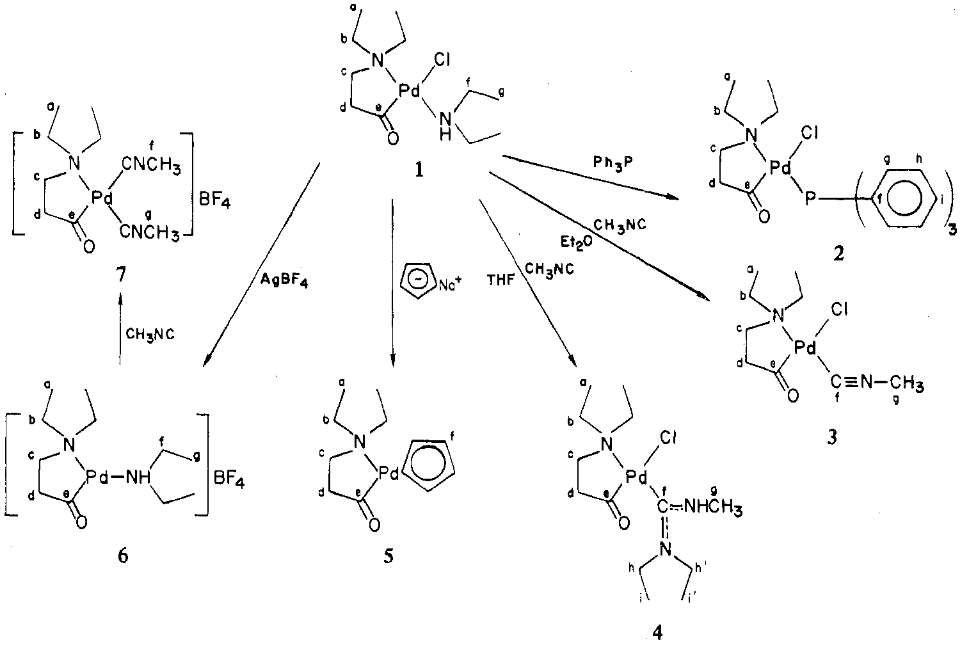
R = H, *n*-Bu

B = OMe, NEt_2, NH_2

Since the (β-aminoacyl)palladium(II) complexes are available in 65–70% overall yield from olefin and amine, this cleavage reaction completes a facile and high-yield difunctionalization sequence for conversion of olefins to β-amino acid derivatives[19,20] and is presently being developed for use in the synthesis of natural products.

Synthesis of Other (β-Aminoacyl)palladium(II) Complexes. The stability of the chelating β-aminoacyl ligand in complex **1** toward displacement allowed the preparation of a variety of unusual complexes resulting from displacement of Cl^- and/or diethylamine (Scheme I). The diethylamino group was readily exchanged with dibutylamine or piperidine by stirring a THF solution of complex **1** with excess amine for several hours and then evaporating to dryness. Exchange of

Scheme I[a]



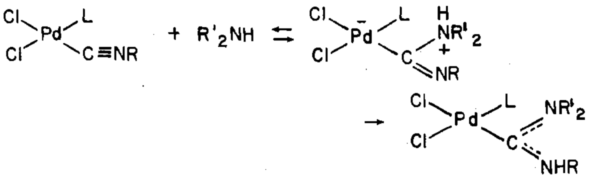
[a] Lower case letters refer to ^{1}H and ^{13}C chemical shifts reported in Table V.

this amine ligand caused little change in the infrared frequency of the acyl group or the NH group. In contrast, tri-*n*-propylamine did *not* exchange with coordinated diethylamine, perhaps because of steric problems. However, the rather bulky triphenylphosphine also readily replaced diethylamine to produce complex **2**, a pale yellow, quite stable crystalline solid. The shift of the acyl stretching frequency to 1680 cm^{-1} indicates that in this complex triphenylphosphine is less of a donor (more of an acceptor) than is diethylamine. The ^{13}C NMR spectrum of the aminoacyl ligand (Table V) shows virtually no change in going from amine to phosphine complex. The ^{13}C absorptions of the coordinated triphenylphosphine have C–P coupling constants characteristic of phosphonium salts.[21] The ^{1}H NMR spectrum of pure complex **2** has two distinct signals for the two $-CH_2-N$ (b) (δ 3.0, 3.6) groups, indicating nonequivalence, and a complex AA′BB′ pattern for the $-CH_2CH_2-$ (c,d) bridge in the aminoacyl ligand. Addition of a very small excess of triphenylphosphine caused the b proton signals to coalesce into a broad peak at δ 3.23 and the c,d proton pattern to simplify. Addition of a large excess of triphenylphosphine caused the b protons to appear as a quartet ($J = 7$ Hz) at δ 3.10 and the c,d protons as two doublets at δ 2.36 and 2.60 ($J = 5$ Hz). This simplification of the proton NMR spectrum is a result of rapid exchange of bound phosphine with free phosphine, making the *N*-ethyl groups magnetically equivalent in the process.

Complex **1** reacted with 1 equiv of methyl isocyanide in ether to produce **3**, a white crystalline solid which slowly darkened at room temperature and rapidly decomposed when exposed to vacuum. The acyl band in the IR spectrum appears at 1705 cm^{-1}, indicating that isocyanide is a weaker donor than either diethylamine or triphenylphosphine in similar complexes.[22] The isocyanide CN stretching frequency is 2255 cm^{-1}, a substantial shift to higher wavenumber from free isocyanide (2170 cm^{-1}).[23] Typically palladium-coordinated isocyanide appears in the range 2195–2260 cm^{-1}, and the shift to higher frequency is thought to be caused by σ donation of the carbon atom lone pair with little concomitant π back-donation.[24] The ^{13}C NMR spectrum again shows little change in the aminoacyl ligand absorptions, with the exception of a slight (~5 ppm) upfield shift of the carbonyl carbon. The isocyanide carbon appears at 158.7 ppm, in comparison with that of free methyl isocyanide (156.3 ppm) and t-BuNCBMe$_3$ (157.8 ppm).[25] The ^{13}C chemical shift of transition metal bound isocyanide ranges from 117.2 ppm in $Pd(CHC_6H_{11})_2I_2$ to 170.4 ppm in $Mn(CO)(CNC_6H_{11})_4Br$.[26] The ^{1}H NMR spectrum of this material is unremarkable.

Treatment of complex **1** with 1 equiv of methyl isocyanide in THF led to the very stable colorless carbene complex **4**, resulting from attack of coordinated isocyanide by the initially displaced diethylamine. Attack of palladium-coordinated isocyanide by amines to form carbene complexes is well established,[27–32] and palladium complexes containing diaminocarbene ligands similar to that in complex **4** have been well characterized. The infrared spectrum of **4** has bands at 3260, 3220 (ν_{N-H}), and 1560 cm^{-1} ($\nu_{N\cdots C\cdots N}$) characteristic of an aminocarbene ligand, as well as acyl bands at 1678 and 1660 cm^{-1}. The observation of two N—H bands and two acyl bands suggests complex **4** is a mixture of isomers. This is confirmed by the proton NMR, which has two singlets of equal intensity at δ 3.44 and 3.51 due to the N—CH$_3$ group. Restricted rotation[29,30] around the carbenoid $C\cdots N(H)Me$ bond allows for two *N*-methyl isomers, which are obtained in roughly equal amounts. Similarly, restricted rotation about the $C\cdots NEt_2$ bond of the aminocarbene ligand results in the observation of two distinct NCH_2CH_3 absorptions (h, i, h′, i′; Table V).[33] Both the IR and ^{1}H NMR spectra of complex **4** are strictly comparable to those obtained for a series of Pd(II) complexes containing the C(NH-t-Bu)(NEt$_2$) diaminocarbene ligand.[31] Again the ^{1}H and ^{13}C NMR spectra of the aminoacyl ligand showed little change in going from complex **1** to complex **4**. The observation that isocyanide complex **3** is formed in ether while carbene complex **4** is formed in THF may be due to the insolubility of **3** in ether and its rapid precipitation before reattack of diethylamine to form complex **4** can occur. In addition, it has been shown that carbene formation proceeds through a charged intermediate[34] (eq 4) and hence should be favored by polar solvents.

Sodium cyclopentadienide reacted with complex **1** at 25 °C in THF to produce the coffee brown cyclopentadienyl complex **5**. Although this complex was only moderately stable, de-



(4)

composing after several days in the solid state, but rather rapidly in solution, it was well characterized. The acyl band appeared at 1680 cm^{-1} in the IR spectrum, only a small shift from complex **1**. The ^{1}H NMR spectrum had the typical aminoacyl pattern, as well as a sharp singlet at δ 5.50 due to the cyclopentadienyl protons. The ^{13}C NMR spectrum was recorded after only 110 pulses since the complex decomposed after longer periods. Hence, the carbonyl carbon signal was not observed. The cyclopentadienyl carbons appeared as a sharp peak at δ 96.09. These values compare favorably with those of (π-allyl)Pd(C_5H_5), which had a singlet at δ 5.71 in ^{1}H NMR and a ^{13}C absorption at δ 94.7 for the cyclopentadienyl ring.[35] Since complex **1** reacted cleanly with sodium cyclopentadienide as well as thallium acetylacetonate,[1] the reactions of other types of carbanions were studied. Treatment of complex **1** under a variety of conditions with allyllithium, vinyllithium, phenyllithium, and methyllithium led in all cases to dark, intractable, uncharacterized materials. The triphenylphosphine complex **2** behaved in a similar manner toward the same organolithium reagents, indicating the relatively acidic proton on the coordinated diethylamine in complex **1** was not the problem. Since these organolithium reagents are considerably stronger bases than either acetylacetonate or cyclopentadienide, they may react with complex **1** by abstraction of a proton α to the acyl or by direct attack on the acyl group. Whatever the case, decomposition of **1** was the result.

Treatment of a THF solution of complex **1** with silver tetrafluoroborate resulted in immediate precipitation of silver chloride[30,36] and production of complex **6**, a pale yellow, slightly hygroscopic crystalline solid. The shift of the carbonyl band at 1710 cm^{-1} in the IR spectrum is consonant with a reduction of electron density of Pd relative to complex **1**. The ^{1}H and ^{13}C NMR spectra were as expected, with the carbonyl carbon appearing at slightly higher field (δ 212) compared to the other complexes in the series (δ 216–227). Treatment of **6** with sodium cyclopentadienide produced **5**. Reaction of **6** with allyl-, vinyl-, phenyl-, or methyllithium again resulted in production of black intractable materials, with no evidence for formation of discreet alkyl–acyl complexes or discreet organic coupling products. Complex **6** was inert to a variety of unsaturated acceptor type ligands such as butadiene, ethylene, and carbon monoxide under a variety of conditions. NMR spectra of **6** in the presence of butadiene showed no evidence for interaction. Attempts to form β-amino acid derivatives by treatment of **6** with excess amine or alcohol (vide supra) led to slow decomposition of the complex but produced only intractable organic material.

Methyl isocyanide (2 equiv) reacted with **6** to produce the bis(isocyanide) complex **7**, a white solid that slowly darkened at room temperature. Use of only 1 equiv of methyl isocyanide led to a 1:1 mixture (by NMR) of complex **7** and starting material, with no evidence for formation of a monoisocyanide complex. The infrared spectrum of **7** had two bands due to the two cis isocyanides (2240, 2260 cm^{-1})[24] and the acyl band appeared at 1698 cm^{-1}. The ^{1}H NMR confirmed the presence of two slightly different methyl isocyanide groups having two singlets δ 3.61 and 3.64. This complex lacked sufficient stability in solution to obtain a ^{13}C NMR spectrum, undergoing extensive decomposition within the time required for measurement. The absence of carbene complex formation in the reaction of **6** with methyl isocyanide is consistent with the observation[30] for platinum complexes that as the positive charge on the metal increases, so does the difficulty in obtaining carbene complexes.

Experimental Section

General Procedure. Melting points are uncorrected. Infrared (IR) spectra were measured with a Perkin-Elmer Model 267 or a Beckman Model 1200 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were measured with a Varian Associates Model T-60 or with a JEOL Model JNMH100 spectrometer in deuteriochloroform with Me_4Si internal standard. Layer chromatography was performed using Brinkmann silica gel F254 analytical plates and UV light or iodine. Microanalyses were performed by Midwest Microanalytical Laboratory, Indianapolis, Ind. All manipulations of palladium–olefin complexes were carried out under argon.

Materials. THF was freshly distilled from $LiAlH_4$ and stored under an argon atmosphere. Petroleum ether (technical grade) was distilled prior to use. Methanol, chloroform, and benzene (Fisher, reagent grade) were used without further purification. Ethene and carbon monoxide were purchased from Matheson. Diethylamine (Baker Reagent) was used without further purification. Dichlorobis(acetonitrile)palladium(II) was prepared by stirring anhydrous $PdCl_2$ in acetonitrile for 12 h at 25 °C and collecting the gold precipitate by filtration.

Preparation of Chloro(3-diethylaminopropionyl)(diethylamine)palladium(II) (1a). This procedure is a modification of a previously reported[1] procedure and is superior for large-scale preparations. The $PdCl_2(CH_3CN)_2$ (2.69 g, 10 mmol) was dissolved in 130 mL of THF in a 12-oz Fischer-Porter aerosol compatibility tube and was stirred for 10 min at 25 °C under 25 psi ethene pressure. The pressure vessel was then slowly cooled to −50 °C (dry ice–acetonitrile), the ethene pressure released, and diethylamine (5.0 mL, 50 mmol) added dropwise over 4 min. The vessel was repressured with ethene to 40 psi, and the reaction mixture was stirred for 0.5 h at −50 °C. The temperature was then slowly raised to 0 °C, the ethene pressure released, and carbon monoxide (100 psi) added. The mixture immediately turned black. After being stirred for 6 h, the reaction mixture was filtered and evaporated to dryness at 0 °C under vacuum. The crude material was taken up in absolute ethanol, filtered, and evaporated to give 2.6 g (73%) of pale yellow crystals. Colorless material was obtained by recrystallizing from absolute EtOH/petroleum ether.

Complexes **1b** and **1c** were prepared in a similar manner. Complex **1d** was prepared using a fivefold excess of olefin relative to $PdCl_2$.

Data Collection and Structure Determination for Chloro(3-diethylaminopropionyl)(diethylamine)palladium(II). Crystal data are as follows: for $Pd(C_{11}H_{25}N_2OCl)$ (mol wt 343.2), orthorhombic, $a = 12.272\ (3)$ Å, $b = 8.363\ (2)$ Å, $c = 29.445\ (7)$ Å, $V = 3022$ Å^3, $\rho_{obsd} = 1.52$ g cm^{-3}, $\rho_{calcd} = 1.51$ g cm^{-3} for $Z = 8$, and $F(000) = 1408$; space group *Cmca* (No. 64), Mo Kα radiation λ_1 0.709 30 Å, λ_2 0.713 59 Å, μ(Mo Kα) = 13.7 cm^{-1}.

Preliminary Weissenberg and precession photographs revealed Laue symmetry *mmm* and exhibited the following conditions for observation of reflections: hkl, $h + k = 2n$; $h0l$, $l = 2n$; $hk0$, $h = 2n$. These conditions are consistent with space groups *Cmca* (No. 64) and *C2cb* (a variant of the noncentric *Aba*2 (No. 41)).[37]

The small, yellow crystal chosen for data collection was mounted on the Enraf-Nonius CAD-3 diffractometer, with the c axis approximately coincident with the diffractometer ϕ axis. After accurate centering, the orientation matrix for data collection, together with the unit cell parameters reported above, was obtained from least-squares calculations on the automatically determined[38] 2θ, χ, and ϕ settings of 25 reflections (at ambient temperature, 20 (±1) °C) with 2θ values in the range 20–35°.

The intensities of all reflections for which $2.5 < \theta < 25.0°$ and $h, k, l \geq 0$ were measured by θ–2θ scans, employing Zr-filtered Mo Kα radiation. The scan range employed was 1° to either side of the calculated K$\bar{\alpha}$ peak position, at a constant scan rate of 10° min^{-1}. The number of times a given reflection was scanned varied according to the intensity, with weak reflections being scanned a maximum of five times. Background was counted at both ends of the scan, for a total time equal to the scan time. The takeoff angle was 3.5°, and zirconium foil attenuators were inserted automatically (to avoid coincidence losses) if the peak count rate exceeded 2500 counts s^{-1}. The intensity of one of three reference reflections (400, 0,0,12, and 049) was measured every 25 reflections. These control reflections showed no significant or systematic changes in intensity during the course of data collection.

The reflection data were inspected by hand, and all systematically extinct reflections (see conditions above) were removed from the data set. None of these systematically extinct reflections exhibited a net intensity greater than 3 times the estimated standard deviation for that reflection (from counting statistics, see below). Lorentz and polarization corrections were applied to the remainder of the data (1395 unique reflections). The uncertainty parameter g, in the formula used for the standard deviation in the intensity[39,40] was taken as 0.04. Reflections for which $F^2 > 3\sigma(F^2)$ were judged to be observed, and the 806 reflections which met this criterion were employed in the solution and refinement of the structure. Due to the low absorption coefficient and the small size of the data collection crystal (approximate dimensions 0.1 × 0.1 × 0.2 mm), no absorption correction was performed.

The position of the palladium(II) ion was assigned from the Patterson map in a position consistent with the crystallographically required m symmetry ($Z = 8$, no special reflection conditions).[37] The positions of all other nonhydrogen atoms were then obtained from Fourier syntheses phased by the atoms in known positions. Scattering factors for palladium(II), oxygen, nitrogen, carbon, and the chloride ion were taken from ref 41. Scattering factors for spherically bonded hydrogen atoms[42] were also taken from ref 41, as were correction terms $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to palladium and chlorine.

Full-matrix least-squares refinement[43] (on F) was carried to convergence with all atoms (hydrogen not included) refined anisotropically. In this model (the planar model) all atoms except those of the ethyl groups were restricted to positions in the mirror plane of symmetry ($x = 0$). At this point, large components of thermal motion were observed perpendicular to the mirror plane for methylene carbon atoms C2 and C3 of the chelate ring (see Figure 1), suggesting a slight amount of either static or dynamic disorder relative to this plane. This effect is supported by the higher than normal amplitudes of thermal motion observed for the acyl oxygen atom (O1) and the carbon atoms (C21 and C22) of the ethyl group on N2 of the bidentate ligand. The normal appearance of the thermal parameters for the atoms (C1 and N2) bonded directly to palladium suggests that these atoms do not participate directly in this disorder. Attempts were made to resolve this apparent disorder problem (a) by refinement of a "nonplanar" model in which atoms O1, C2, and C3 of the bidentate ligand were allowed to take partially occupied positions slightly out of the mirror plane and (b) by refinement in the noncentric space group *C2cb*, where no requirement of crystallographic symmetry is imposed on the molecule. Neither of these alternative models led to results significantly better (in terms of bond length patterns and R factor ratio test)[41] than the planar model described above, and the planar model was used for the final refinement stages of the determination. Hydrogen atoms were included in this model when they could be clearly seen (0.3–0.5 e Å^{-3}) in a difference Fourier based on the refined heavy-atom positions. Hydrogen atoms were placed in fixed, idealized positions 0.95 Å from carbon, with isotropic thermal parameters 1 Å^2 larger than the carbon atom to which they were attached. With hydrogen atom positions established in this manner, refinement of the nonhydrogen atom positions and thermal parameters was continued (with necessary adjustments in H atom positions after each cycle) until all shifts in parameters were less than 15% of the estimated standard deviation for that parameter. The final R value ($R = \sum||F_o| - |F_c||/\sum|F_o|$) was 0.047 (unobserveds not included), while the final R_w ($= [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$) was 0.053. The error in an observation of unit weight was 1.37. The NUCLS refinement program minimizes $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factor amplitudes, respectively, and w is the weight for each reflection ($=4F_o^2/\sigma^2(F_o^2)$). Correction for secondary extinction was not deemed necessary. In the final difference Fourier electron density map, all peaks were below 0.4 e Å^{-3}, with the exception of two peaks (~0.7 e Å^{-3}) in the immediate vicinity of the palladium ion.

Final atomic positional parameters are listed in Table I, while Table II lists the anisotropic thermal parameters obtained for the nonhydrogen atoms.

Preparation of β-Amino Acid Derivatives from Complex 1. (1) Diphos-Induced Cleavages. Complex **1a** (343 mg, 1 mmol) was dissolved in 20 mL of benzene, and diphos ($Ph_2P-CH_2CH_2PPh_2$) (800 mg, 2 mmol) was added, followed by methanol (1 mL, 25 mmol). The mixture was stirred at 25 °C until analytical TLC (neutral alumina, 20:1 petroleum ether–methanol) showed no complex **1** remained (16–24 h). Solvent was removed under vacuum, and the desired β-amino ester was separated from the Pd–diphos residue by column chromatography on neutral alumina, eluting with ether. Identical procedures were used to prepare the amino ester from complex **1d** and the amino–diethylamide from complexes **1a** and **1d**. Pure material was obtained in 30–50% yield after column chromatography.

Table IV. Infrared Spectra of Complexes **1–8**[a]

Complex	ν_{NH}, cm^{-1}	ν_{CO}, cm^{-1}	$\nu_{C\equiv N}$, cm^{-1}	Other
1	3240	1665		
2		1680		
3		1705	2255	
4	3260, 3220	1678, 1660		1560 (C–N)
5		1680		
6	3250	1710		
7		1698	2244, 2260	

[a] Infrared spectra recorded as Nujol mulls on NaCl plates.

(2) Bromine-Induced Cleavages. (a) Preparation of Methyl (3-Diethylamino)propionate. Complex **1a** (211 mg, 0.67 mmol) in 10 mL of CH_2Cl_2 was cooled to −78 °C, and Br_2 (98 mg, 0.62 mmol) in 3 mL of CH_2Cl_2 at −78 °C was added. The mixture was stirred at −78 °C for 30 min; then methanol (2 mL) was added and the mixture was allowed to warm to 25 °C. The reaction mixture was evaporated to dryness, dissolved in 10 mL of $CHCl_3$, and washed with 20 mL of Na_2SO_3 solution. The aqueous phase was washed with 3 × 10 mL of $CHCl_3$, and the combined organic extracts were dried over anhydrous $MgSO_4$ and evaporated to dryness. The resulting semisolid was triturated with 20 mL of petroleum ether and filtered and the filtrate was evaporated to dryness to produce a yellow oil (86 mg, 96%) identical in all respects with authentic material prepared by a different method.[44] Infrared spectrum (neat): 2980, 2940, 2875, 2820 (CH), 1740 (C=O), 1490, 1380, 1260, 1220 (br), 1050 (br) cm^{-1}. NMR spectrum ($CDCl_3$–Me_4Si): δ 1.05 (t, J = 7 Hz, 6, CH_3), 2.52 (q, J = 7 Hz, 4, CH_2N), 2.6 (m, 4, $-CH_2CH_2-$), 3.63 (s, 3, OCH_3).

(b) *N,N*-Diethyl(3-diethylamino)propionamide. The above procedure was followed using 408 mg (1.19 mmol) of complex **1a**, 190 mg (1.19 mmol) of Br_2, and 2 mL of diethylamine to produce 239 mg (100%) of the desired product, >95% pure by NMR when compared to material prepared by a different method.[22] Infrared spectrum (neat): 2980, 2940, 2880, 2820 (CH), 1622 (C=O), 1480, 1460, 1448, 1432, 1380, 1360, 1250 cm^{-1}. NMR spectrum ($CDCl_3$–Me_4Si): δ 1.05 (t, J = 7 Hz, 6, CH_3), 1.10 (t, J = 7 Hz, 6, CH_3), 2.4–2.8 (m, 8, CH_2N and $-CH_2CH_2$), 3.40 (q, J = 7 Hz, 4, CH_2NCO).

(c) 3-Diethylaminopropionamide. Complex **1a** (160 mg, 0.465 mmol) and bromine (75 mg, 0.465 mmol) were allowed to react and then were treated with 1 mL of concentrated NH_4OH, to produce 66 mg (79%) of the desired product. Infrared spectrum (neat): 3340, 3180 (NH), 2960, 2920, 2860, 2800 (CH), 1665 (C=O), 1620 (amide II), 1450, 1405, 1380, 1290, 1250, 1210 cm^{-1}. NMR spectrum ($CDCl_3$–Me_4Si): δ 1.05 (t, J = 7 Hz, 6, CH_3), 2.60 (m, 8, $-CH_2N$ and NCH_2CH_2CO). Mass spectrum: parent *m/e* 134.

(d) Methyl (3-Diethylamino)heptanoate. The above procedure was followed using 340 mg (0.85 mmol) of complex **1d**, 136 mg (0.85 mmol) of Br_2, and 1 mL of methanol to produce 187 mg (86%) of the desired product >95% pure by NMR. Infrared spectrum (neat): 2980, 2940, 2880, 2820 (CH), 1735 (C=O), 1470, 1460, 1450, 1440, 1382, 1290, 1272, 1235 cm^{-1}. NMR spectrum ($CDCl_3$–Me_4Si): 1.00 (t, J = 7 Hz, 3, CH_3), 1.05 (t, J = 7 Hz, 6, CH_3, CH_2N), 1.36 (m, 6 H, CH_2 of C_4 group), 2.50 (m, 7, $-CH_2N$ and $N-CH_2CH_2CO$), 3.68 (s, 3, OCH_3). Mass spectrum: parent *m/e* 215.

(e) *N,N*-Diethyl(3-diethylamino)heptanoamide. Complex **1d** (204 mg, 0.51 mmol) and bromine (82 mg, 0.51 mmol) were reacted as above to produce 129 mg (98%) of the desired product >95% pure by NMR. Infrared spectrum (neat): 2960, 2930, 2870, 2810 (CH), 1630 (C=O), 1460, 1436, 1380, 1260 cm^{-1}. NMR spectrum ($CDCl_3$–Me_4Si): δ 0.70–1.50 (m, 21, all CH_3's, CH_2's of C_4 group), 2.50, (m, 4 H, CH_2-N, $NCH-CH_2CO$), 3.20 (m, 4, CH_2NCO). Mass spectrum: parent *m/e* 256.

(f) 3-Diethylaminoheptanoamide. Complex **1d** (233 mg, 0.59 mmol) and Br_2 (93 mg, 0.59 mmol) were reacted as above and treated with

Table V. ^{13}C and ^{1}H NMR Spectra of Complexes 1–8[a]

Complex	Solvent	Nucleus	a	b	c	d	e	f	g	h	i	h′	i′	
1	$CDCl_3$	^{13}C	12.75	55.00	52.80	49.80	221.30	47.60	15.44					
	$CDCl_3$	^{1}H	1.46 (t, *J* = 7)	2.7–3.8 (m)	2.63 (t, *J* = 4)			2.7–3.8 (m)	1.57 (t, *J* = 7)					
2	$CDCl_3$	^{13}C	13.08	54.35	57.92	48.03	221.03	131.85 (J_{CP} = 41.2)	134.51 (J_{CP} = 11.3)	128.00 (J_{CP} = 9.6)	130.10 (J_{CP} = 0)			
	$CDCl_3$	^{1}H	1.50 (t, *J* = 7)	3.0, 3.5 (m)	2.5–2.8 (m)			7.5 (m)						
3	$CDCl_3$	^{13}C	12.62	54.26	55.71	49.02	216.11	158.70	29.18					
	$CDCl_3$	^{1}H	1.50 (t, *J* = 7)	2.9–3.8 (m)	2.75 (d, *J* = 4)	2.66 (d, *J* = 4)			3.42 (s)					
4	$CDCl_3$	^{13}C	11.82	52.77	52.77	48.84	227.08	201.50	35.93	40.28	11.82	54.19	13.94	
	$CDCl_3$	^{1}H	1.50 (t, *J* = 7)	2.9–3.6 (m)	2.56 (t, *J* = 4)				3.44 3.51	2.9–3.6 (m)	1.20 (t, *J* = 7)	4.17 (q, *J* = 7)	1.33 (t, *J* = 7)	5.5 (br) (NH)
5	$CDCl_3$	^{13}C	12.67	54.61	53.65	53.30		96.09						
	Acetone-d_6	^{1}H	1.36 (t, *J* = 7)	2.90 (q, *J* = 7)	2.61 (s)			5.50 (s)						
6	Acetone-d_6	^{13}C	11.90	53.62	51.00	50.42	212.14	47.14	15.14					
	Acetone-d_6	^{1}H	1.45 (t, *J* = 6.3)	3.14 (q, *J* = 6.3)	2.82 (m)			3.16 (q, *J* = 6.3)	1.54 (t, *J* = 6.3)					
7	Acetone-d_6	^{1}H	1.50 (t, *J* = 7)	3.27 (q, *J* = 7)	2.89 (m)			3.61 (s)	3.64 (s)					

[a] Chemical shifts are reported in ppm downfield from internal standard Me_4Si. Coupling constants are reported in Hz. The ^{13}C NMR spectra were obtained in natural abundance in the pulse Fourier transform mode at 22.635 Hz using a Bruker HFX 90 spectrometer and a Digilab FTX/NMR 3 data system.

1 mL of concentrated NH_4OH to produce 110 mg (100%) of the desired product >95% pure by NMR. Infrared spectrum (neat): 3340, 3180 (NH), 2960, 2940, 2840, 2800 (CH), 1668 (C=O), 1625 (amide II), 1460, 1390, 1300, 1250, 1200 cm^{-1}. NMR spectrum ($CDCl_3$–Me_4Si): δ 1.05 (m, 9, CH_3), 1.40 (m, 6, $-CH_2-$), 2.3–3.0 (m, 7, CH_2N, CH_2CO), 6.10 (br s, 2, NH).

Although NMR spectra of the above materials were identical in all respects with those of pure materials, the compounds were colored, from yellow to orange. Colorless materials could be obtained by column chromatography on neutral alumina eluting with ether, with losses of 15–30% of the materials, and no change in spectra.

Chloro(3-diethylaminopropionyl)(triphenylphosphine)palladium(II) (2). Complex **1a** (215 mg, 0.62 mmol) was dissolved in 55 mL of ether, and triphenylphosphine (167 mg, 0.63 mmol) was added. Within 1 min a fine yellow precipitate began to form. After 3 h the mixture was filtered and the precipitate air-dried to give 311 mg (94%) of complex **2**, a pale yellow crystalline solid: mp 109–112 °C dec; infrared spectrum, Table IV; NMR spectra, Table V. Anal. ($C_{25}H_{29}ClNOPPd$) C, H, N, Cl.

Chloro(3-diethylaminopropionyl)(methyl isocyanide)palladium(II) (3). Complex **1a** (121 mg, 0.35 mmol) was dissolved in 20 mL of ether, cooled to 0 °C, and CH_3NC (18.5 μL, 0.39 mmol) was added. A white precipitate formed immediately. After 20 min at 0 °C, the mixture was filtered and the white precipitate was air dried (vacuum drying led to decomposition), giving 108 mg (98%) of a fine white powder: mp 146–150 °C dec; infrared spectrum, Table IV; NMR spectra, Table V. Anal. ($C_9H_{17}ClN_2OPd$) C, H, N, Cl.

Chloro(3-diethylaminopropionyl)diethylamino(methylamino)carbenepalladium(II) (4). Complex **1** (130 mg, 0.38 mmol) was dissolved in 20 mL of THF and cooled to 0 °C, and methyl isocyanide (19 μL, 0.40 mmol) was added. The mixture was stirred at 0 °C an additional 15 min and then at 25 °C for 3.5 h. The solvent was removed under vacuum and the white crystalline residue (146 mg, 100%) was dried under vacuum: mp 148 °C; infrared spectrum, Table IV; NMR spectra, Table V. Anal. ($C_{13}H_{28}ClN_3OPd$) C, H, N, Cl.

Cyclopentadienyl(3-diethylaminopropionyl)palladium(II) (5). Complex **1** (416 mg, 1.21 mmol) was dissolved in 55 mL of THF and cooled to 0 °C, and sodium cyclopentadienide (6.0 mL of a 0.2 M solution in THF, 1.21 mmol; prepared from cyclopentadiene and NaH in THF) was added dropwise. The initial orange color of the solution became coffee brown while stirring 2 h at 25 °C. This solution was evaporated to dryness at 0 °C (vacuum); the solid was taken up in benzene; the mixture was filtered to remove NaCl and evaporated to dryness at 0 °C to produce 325 mg (89%) of a coffee brown solid: mp 96–102 °C dec; infrared spectrum, Table IV; NMR spectra, Table V. This complex was too unstable to obtain an elemental analysis.

(3-Diethylaminopropionyl)(diethylamine)palladium(II) Tetrafluoroborate (6). Complex **1** (275 mg, 0.80 mmol) was dissolved in 3 mL of THF in a test tube containing a stirring bar. A solution of silver tetrafluoroborate (156 mg, 0.80 mmol) in 3 mL of THF was added and the mixture was stirred for several minutes. The AgCl precipitate was removed by decanting the supernatant after centrifugation at low rpm. The AgCl was washed with two 2-mL portions of THF. The combined THF fractions could be used directly for reactions of complex **6**. For isolation, 110 mL of dry petroleum ether was added to the THF solution of **6**, and the resulting white crystalline material was collected by filtration (320 mg, 100%): mp 80–81 °C dec (this complex is moderately hygroscopic); infrared spectrum, Table IV; NMR spectra, Table V. Anal. ($C_{11}H_{25}BF_4N_2OPd$) C, H, N.

(3-Diethylaminopropionyl)bis(methyl isocyanide)palladium(II) (7). Complex **6** (0.20 mmol) prepared from **1** (60 mg, 0.20 mmol) and $AgBF_4$ (39 mg, 0.20 mmol) in 10 mL of THF was cooled to 0 °C and CH_3NC (19 μL, 0.40 mmol) was added. After 15 min at 0 °C the resulting solution containing a fine white precipitate was evaporated to dryness (0 °C) and the white crystalline residue was dried under vacuum: 84 mg (100%); mp 134–138 °C dec; infrared spectrum, Table IV; NMR spectra, Table V. This material decomposed slowly at 25 °C becoming dark gray in 1 day.

Acknowledgment. This investigation was supported by Grant No. GP-43626 awarded by the National Science Foundation and by Grant No. R01 CA 18680 awarded by the National Cancer Institute (x-ray structure determination). Mr. K. C. Van Horne is acknowledged for providing technical assistance with the structure determination. Computer funds were supplied in part by Colorado State University and the

Colorado State University Computing Center.

Registry No. 1a, 62776-24-3; **1d**, 62708-12-7; **2**, 62708-11-6; **3**, 62708-10-5; **4**, 62708-09-2; **5**, 62708-08-1; **6**, 62708-17-2; **7**, 62708-07-0; methyl (3-diethylamino)propionate, 5351-01-9; *N*,*N*-diethyl(3-diethylamino)propionamide, 27945-00-2; 3-diethylaminopropionamide, 3813-27-2; methyl (3-diethylamino)heptanoate, 62682-89-7; *N*,*N*-diethyl(3-diethylamino)heptanoamide, 62682-88-6; 3-diethylaminoheptanoamide, 62682-87-5; ^{13}C, 14762-74-4; Pd-$Cl_2(CH_3CN)_2$, 14592-56-4.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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