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Synthesis of *β*-Imino Carbonyl Enolato Complexes by Reaction of Nickel(II), Palladium(II), and Copper(II) Acetates with the Enaminodiones (MeOCO)(RCO)CC(R′)NH$_2$ (R = Me, OMe; R′ = Et, EtOCO)

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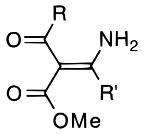
Nickel(II), palladium(II), and copper(II) acetates undertake exchange reaction with the *β*-enaminodiones (MeOCO)(RCO)CC(R′)NH$_2$ (R = Me, OMe; R′ = Et, EtOCO) in ethanol to give the neutral complexes [M((MeOCO)(RCO)CC(R′)NH)$_2$] (**1**−**8**) [R = Me, R′ = Et: M = Ni (**1**), Pd (**2a**,**b**), Cu (**3**); R = Me, R′ = EtOCO: M = Ni (**4**), Pd (**5**), Cu (**6**); R = MeO, R′ = Et, M = Pd (**7a**,**b**); R = MeO, R′ = EtOCO, M = Pd (**8a**,**b**)]. The trifunctional N,O,O ligands act in all cases as bidentate through the imino and one carbonyl group. Complexes **1**−**8** are all monomers with a square planar geometry. Nickel and palladium complexes show more than one form in the solid state. For example the palladium complex **2** has been synthesized in two forms **a** and **b**, which differ in the conformation of the methoxy carbonyl substituent of the chelate ring, while the third isomer or conformer is obtained by thermal treatment at 120 °C. Complexes **7** and **8** also exhibit two forms which differ in the degree of intermolecular hydrogen bonding. Both **7b** and **8b** crystallize in monoclinic unit cells [**7b**: space group $P2_1/n$, $a = 11.963(2)$, $b = 8.438(1)$, $c = 19.637(2)$ Å, $\beta = 94.2(1)°$. **8b**: $P2_1/c$, $a = 10.698(2)$, $b = 14.902(2)$, $c = 13.918(2)$ Å, $\beta = 95.2(1)°$] containing four molecules linked by intermolecular hydrogen bonding [N−H···O=C, 2.14−2.36 Å]. All complexes are thermally stable and volatile. Their mass spectra exhibit intense molecular ion peaks under EI mass conditions.

Introduction

The C−C bond forming reaction between *β*-dicarbonyls and nitriles can be selectively catalyzed by Ni(II), Cu(II), and Zn(II) acetylacetonates instead of the classic, less selective bases.[1,2] This metal-catalyzed approach has been successfully extended to a large variety of C−H acid substrates, such as *β*-ketoamides, nitroacetoesters, phosphonoacetates, *β*-ketophosphonates which react with nitriles to give a large series of substituted *β*-enaminones (RCO)(Z)CC(R′)NH$_2$ (Z and R′ = electron-withdrawing groups) and the corresponding cyclic derivatives.[1] This procedure has been further extended to non activated nitriles (R′ = alkyl, aryl, NH$_2$) using tin tetrachloride as a promoter in stoichiometric quantity.[1]

Despite the great amount of work on the synthetic organic aspects of the C−C bond forming reactions, scarce attention has been paid to the isolation and full characterization of the relevant metal intermediates. Few examples are mainly limited to the reaction of *β*-diketones with cyanogen or benzoyl cyanide catalyzed by nickel(II) or copper(II) acetylacetonates.[3,4] This was partly due to experimental difficulties in obtaining pure complexes by direct reaction of metal(II) *β*-carbonylenolates with nitriles because of the occurrence of side reactions and/or decomposition pathways.

We have found and report here on the synthesis and characterization of the *β*-imino carbonyl enolato complexes of the general formula [M((MeOCO)(RCO)CC(R′)NH)$_2$] [M = Ni(II), Cu(II), Pd(II)]. These complexes can be obtained by reaction of the corresponding metal acetates with *β*-enaminodiones in ethanol at ambient temperature.



The large variety of *β*-enaminodiones with different and tunable steric and electronic properties makes the synthesis of a wide and interesting class of complexes possible through the above-reported approach. These compounds may represent an attractive alternative to the “classical” *β*-diketonates as precursors for the thermal and photochemical production of homogeneous and heterogeneous catalysts and for thin film chemical vapor deposition.[5]

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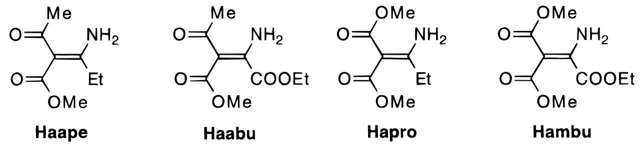
Chart 1



Haape: 2-acetyl-3-amino-2-pentenoic acid, methyl ester;
Haabu: 3-acetyl-2-amino-2-butendioic acid, 1-ethyl 4-methyl ester;
Hapro: 1-aminopropylidene-propandioic acid, dimethyl ester;
Hambu: 2-amino-3-methoxycarbonyl-2-butendioic acid, 1-ethyl 4-methyl ester.

Experimental Section

Reagents and Physical Measurements. Hydrated metal acetates, methyl acetoacetate, dimethylmalonate, propionitrile, ethyl cyanoformate, solvents, and gases were high-purity commercial products and used as received. The following instruments and conditions were employed: Bruker IFS66 FT-IR, Cary 5 UV−vis, single-focus mass spectrometer VG MM16 operating in electron ionization mode at 70 eV electron beam energy and an ion source temperature of 180 °C, Perkin-Elmer TGS-2, DSC-4 equipment for TG-DSC measurements, Bruker AM 250 NMR spectrometer, operating at 250.19 MHz for ^{1}H and at 62.89 for ^{13}C. Typical NMR samples were prepared by dissolving the complexes (20 mg) in the deuterated solvent (0.4 mL). ^{1}H and ^{13}C chemical shifts are reported versus tetramethylsilane and were determined by reference to the residual solvent peaks in the solution spectra. The ^{1}H assignments of Tables 2, 3, 7, and 8 were performed by means of conventional homonuclear 2D COSY or 1D homonuclear decoupling experiments. The ^{13}C assignments were performed by DEPT and 2D ^{1}H,^{13}C HETCORR experiments and by reference to the NMR spectra of the corresponding free ligands. Solid state ^{13}C CP/MAS measurements were carried out according to the procedure previously reported.[4] The ^{13}C shifts are referred to TMS and calculated by reference to the methylene peak at 33.6 ppm of polyethylene, used as internal reference standard.

Synthesis of the Ligands. The β-enaminodiones (MeOCO)(RCO)CC(R′)NH$_2$ (R = Me, R′ = Et (**Haape**), EtOCO (**Haabu**); R = MeO, R′ = Et (**Hapro**), EtOCO (**Hambu**))[6] (Chart 1) were prepared by reaction of the ketoester or diester with the appropriate nitrile in the presence of catalytic quantity of zinc acetylacetonate (**Haabu** and **Hambu**)[6a] or of a stoichiometric quantity of SnCl$_4$ (**Haape** and **Hapro**).[6b] According to this procedure, (MeOCO)$_2$CC(Et)NH$_2$ (**Hapro**) was obtained as white crystals which tend to become a yellowish oil at room temperature (yield 69.5%). IR (KBr): 3588 sh, 3421 m, 3319 m, 3226 m, 1700 s, 1669 s, 1621 vs and 1526 s cm^{-1}; ^{1}H NMR (CDCl$_3$, δ) = 3.75 (s, CH$_3$O), 3.70 (s, CH$_3$O), 2.43 (q, CH$_2$), 1.20 (t, CH$_3$), 5.58 and 8.84 (s, NH$_2$); ^{13}C NMR (CDCl$_3$, δ) = 12.5 (CH$_3$), 28.1 (CH$_2$), 51.O (CH$_3$O), 51.7 (CH$_3$O), 91.5 (C=), 168.6 (C−N), 168.9 (C═O), 169.0 (C═O).

Synthesis of the Complexes. The neutral ML$_2$ complexes have been prepared according to the following general procedure. The metal acetates with the proper ligand (1:2 molar ratio) were dissolved in O$_2$-free ethanol at room temperature under argon atmosphere and the resulting solutions left under stirring for variable times (from minutes to few hours). The ML$_2$ complexes can either precipitate spontaneously from the reaction mixture or be recovered from the solution evaporated to dryness. In many cases the compounds are isolable in two forms distinguished as **a** and **b**, which exhibit identical composition but different spectroscopic properties (Tables 2, 3, 4, 7, and 8). The symbols **a** and **b** only indicate the order in which the complexes have been isolated.

[Ni(aape)$_2$] (1). Ni(OAc)$_2$·4H$_2$O (0.250 g, 1.0 mmol) and **Haape** (0.344 g, 2.0 mmol) were dissolved in ethanol (50 mL), and the resulting orange solution was stirred for 1 h at room temperature under argon. The solvent was subsequently evaporated at reduced pressure with the external bath thermostated at 40 °C in order to remove the acetic acid produced in the reaction. The solid mixture was redissolved in ethanol (30 mL) and permitted to react for one more hour under stirring at room temperature. The above-reported procedure was repeated 10 times and yielded a reddish solid. The pure complex **1** could be obtained by recrystallization of the reddish solid with ethyl ether (0.260 g, 65%): mp 183 °C. UV−vis (in KBr, nm): 244, 270, 338, 360. Magnetic moment: $\mu_{\text{eff}} = 0.5\ \mu_{\text{B}}$. Anal. Calcd for C$_{16}H_{24}N_2NiO_6$: C, 48.15; H, 6.06; N, 7.02. Found: C, 48.22; H, 6.20; N, 7.05.

[Pd(aape)$_2$] (2a,b). Pd(OAc)$_2$ (0.225 g, 1.0 mmol) and **Haape** (0.344 g, 2.0 mmol) were dissolved in ethanol (30 mL) and the solution was left for 18 h under stirring in argon atmosphere. The color of the solution slowly turned from amber to green. A small amount of metallic palladium was filtered off, and the resulting yellow solution was evaporated to dryness to give a pale-yellow solid. This solid was washed with ethyl ether (10 mL) and dried in vacuo to yield pure **2a** (0.240 g, 54%): mp > 250 °C. UV−vis (in KBr, nm): 250, 345.

The ether filtrate contained some **2a** and the most soluble form **2b**. The solution was concentrated, and the addition of hexane led to the precipitation of a mixture from which the complex **2b** could be obtained pure by repeated recrystallization (ethyl ether/hexane) (0.051 g, 11%): mp > 250 °C. UV−vis (in KBr, nm): 244, 336. Anal. Calcd for C$_{16}$H$_{24}$N$_2$O$_6$Pd (**2**): C, 43.01; H, 5.41; N, 6.27. Found for **2a**: C, 43.10; H, 5.42; N, 6.04. Found for **2b**: C, 43.22 H, 5.52; N, 6.17.

[Cu(aape)$_2$] (3). Cu(OAc)$_2$·H$_2$O (0.189 g, 1.0 mmol) and **Haape** (0.344 g, 2.0 mmol) were dissolved in ethanol (50 mL), and the resulting blue solution was stirred for 4 h at room temperature under argon. The solvent was then evaporated at reduced pressure with the external bath thermostated at 40 °C in order to remove the acetic acid produced in the reaction. The solid mixture was redissolved in ethanol (30 mL) and permitted to react for four more hours under stirring at room temperature. This procedure was repeated five times to give a blue solid mixture which contained some unreacted copper acetate. The pure complex **3** could be obtained as violet needles by recrystallization of the reaction mixture with hexane (0.285 g, 71%): mp 105 °C. UV−vis (in KBr, nm): 250, 300, 320. Magnetic moment: $\mu_{\text{eff}} = 1.9\ \mu_{\text{B}}$. Anal. Calcd for C$_{16}H_{24}CuN_2O_6$: C, 47.58; H, 5.99; N, 6.94. Found: C, 47.91; H, 5.96; N, 6.84.

[Ni(aabu)$_2$] (4). Ni(OAc)$_2$·4H$_2$O (0.250 g, 1.0 mmol) and **Haabu** (0.430 g, 2.0 mmol) were dissolved in ethanol (80 mL) and the solution was stirred for 2 h at room temperature under argon. A red solid started to precipitate from the orange solution in a few minutes. The ethanol unsoluble reaction product was isolated by filtration, washed with ethanol, and dried under vacuum (0.410 g, 84%): mp 236 °C (dec). UV−vis (in KBr, nm): 256, 272, 320 sh, 370; UV−vis (in CHCl$_3$, nm, ϵ in parentheses): 253 (31 700), 273 (33 500), 320 sh, 370 (2600), 534 (78). Magnetic moment: $\mu_{\text{eff}} = 0.6\ \mu_{\text{B}}$. Anal. Calcd for C$_{18}H_{24}N_2NiO_{10}$: C, 44.38; H, 4.97; N, 5.75. Found: C, 44.27; H, 5.27; N, 5.76.

[Pd(aabu)$_2$] (5). Pd(OAc)$_2$ (0.225 g, 1.0 mmol) and **Haabu** (0.430 g, 2.0 mmol) were dissolved in ethanol (50 mL), and the solution was stirred at room temperature under argon. In a few minutes a greenish solid started to precipitate from the amber solution. It was filtered off after 10 h and recrystallyzed as yellow prisms from dichloromethane (0.454 g, 85%): mp 240 °C (dec). UV−vis (in KBr, nm): 258, 348; UV−vis (in CHCl$_3$, nm, ϵ in parentheses): 258 (36 100), 350 (5200). Anal. Calcd for C$_{18}$H$_{24}$N$_2$O$_{10}$Pd: C, 40.43; H, 4.52; N, 5.24. Found: C, 40.64; H, 4.50; N, 5.08.

[Cu(aabu)$_2$] (6). Cu(OAc)$_2$·H$_2$O (0.100 g, 0.5 mmol) and **Haabu** (0.215 g, 1.0 mmol) were dissolved in ethanol (50 mL), and the solution was stirred at room temperature under argon. In a few minutes a pale blue solid started to precipitate from the blue solution. It was filtered off after 4 h and washed with ethanol (0.220 g, 89%): mp 197 °C (dec). UV−vis (in KBr, nm): 248, 296; UV−vis (in CHCl$_3$, nm, ϵ in parentheses): 250 (26 200), 289 (24 300), 570 (73). Magnetic moment: $\mu_{\text{eff}} = 1.8\ \mu_{\text{B}}$. Anal. Calcd for C$_{18}H_{24}CuN_2O_{10}$: C, 43.95; H, 4.92; N, 5.69. Found: C, 44.17; H, 5.09; N, 5.79.

[Pd(apro)$_2$] (7a,b). Pd(OAc)$_2$ (0.270 g, 1.2 mmol) and **Hapro** (0.450 g, 2.6 mmol) were dissolved in ethanol (30 mL), and the solution was stirred for 3 h at room temperature under argon. The amber-green solution was then filtered to separate traces of metallic palladium and

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Table 1. Crystallographic Data for Complexes **7b** and **8b**

	7b	**8b**
empirical formula	$C_{16}H_{24}N_2O_8Pd$	$C_{18}H_{24}N_2O_{12}Pd$
fw	478.77	566.79
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	11.963(2)	10.698(2)
b, Å	8.438(1)	14.902(2)
c, Å	19.637(2)	13.918(2)
β, deg	94.2(1)	95.2(1)
V, Å^3	1976.9(5)	2219.7(7)
Z	4	4
T, K	293	293
λ, Å	0.710 69	0.710 69
ρ_{calcd}, g cm^{-3}	1.61	1.70
μ, cm^{-1}	9.67	8.87
R $(F_o)^a$	0.041	0.035
R_w $(F_o)^b$	0.047	0.034

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = 1/(\sigma^2(F) + 0.009245F^2)$ (**7b**) or $1/(\sigma^2(F) + 0.000682F^2)$ (**8b**).

evaporated almost to dryness to give, on standing for 1 day, a pale yellow solid, which was recrystallyzed from ethanol (**7a**, 0.380 g, 66%): mp 176 °C. UV−vis (in KBr, nm): 254, 304.

Complex **7a** (0.239 g, 0.5 mmol) was dissolved in dichloromethane (20 mL) and the resulting gold yellow solution left under stirring for 20 h. The solvent was then removed to give a yellow solid, which was treated with ethanol (3 mL) and filtered (**7b**, 0.210 g, 88%): mp 199 °C (dec). UV−vis (in KBr, nm): 236, 300, 400 sh. Anal. Calcd for $C_{16}H_{24}N_2O_8Pd$ (**7**): C, 40.14; H, 5.05; N, 5.85. Found (**7a**): C, 40.30; H, 5.04; N, 5.69. Found (**7b**): C, 40.25; H, 5.15; N, 5.77.

[Pd(ambu)$_2$] (8a,b). Pd(OAc)$_2$ (0.225 g, 1.0 mmol) and **Hambu** (0.462 g, 2.0 mmol) were dissolved in ethanol (50 mL) and the solution was stirred for 4 h at room temperature under argon. The greenish precipitate was then filtered off and recrystallized as a yellow solid from acetone (**8a**, 0.260 g, 55%): mp 228 °C (dec). UV−vis (in KBr, nm): 348, 330.

The ethanol filtrate was evaporated to dryness and the resulting yellow solid treated with ether (10 mL) and filtered (**8b**, 0.155 g, 33%): mp 235 °C (dec). UV−vis (in KBr, nm): 244, 316, 344 sh. Complex **8b** may be also obtained by slow recrystallization of **8a** from dichloromethane. Anal. Calcd for $C_{18}H_{24}N_2O_{12}Pd$ (**8**): C, 38.14; H, 4.27; N, 4.94. Found for **8a**: C, 38.25; H, 4.23; N, 4.84. Found for **8b**: C, 38.27; H, 4.24; N, 4.81.

X-ray Data Collection and Structure Determination of [Pd(apro)$_2$] (7b) and [Pd(ambu)$_2$] (8b). Crystals of **7b** and **8b** suitable for X-ray analysis were obtained by recrystallization from ethanol and dichloromethane−ethanol, respectively. The intensities were collected on a Philips PW 1100 four-circle diffractometer, operating in the $\theta - 2\theta$ scan mode, using the Mo Kα monochromatized radiation. The positional parameters of the non-hydrogen atoms were determined by direct methods using the *SIR92* phasing program[7] (**7b**) or *SHELXS*86 (**8b**) (see Table 1). After a few cycles of full-matrix least-squares refinement (using anisotropic thermal parameters), all the H atoms of **7b** and **8b** were calculated and refined with isotropic thermal parameters.

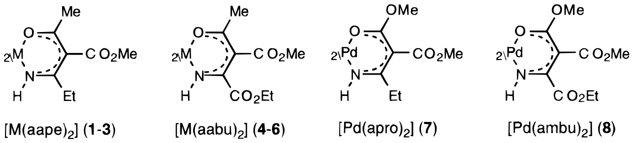
Results and Discussion

Metal(II) acetates of nickel, palladium, and copper react very selectively in ethanol with β-enaminoketoesters and -diesters to give the corresponding bis(imino carbonyl enolato) complexes (**1**−**8**) (Chart 2) in high yields (eq 1).

$$M(OAc)_2 + 2(MeOCO)(RCO)CC(R')NH_2 \rightarrow [M((MeOCO)(RCO)CC(R')NH)_2]\ (\mathbf{1}-\mathbf{8}) + 2HOAc \quad (1)$$

In the most cases the complexes precipitate spontaneously or after partial evaporation of the reaction solvent. Only in the case of the [M(aape)$_2$] complexes **1** and **3** the reaction is forced toward the desired products by codistillation of the acetic acid produced in the ligand exchange process with the solvent from the reaction mixture. Palladium acetate reacts with all four ligands, whereas nickel and copper acetates are reactive only with the two β-enaminoketoesters (R = Me, **Haape**, **Haabu**). Attempts to apply this synthetic procedure to zinc acetate were unsuccessful.

Chart 2



[M(aape)$_2$] (**1**-**3**) [M(aabu)$_2$] (**4**-**6**) [Pd(apro)$_2$] (**7**) [Pd(ambu)$_2$] (**8**)

M = Ni (**1**,**4**), Pd (**2**,**5**), Cu (**3**,**6**)

The ligand exchange reaction is always complete and the trifunctional β-imino carbonyl enolato ligand acts in all cases as bidentate to give monomeric square planar neutral ML$_2$ complexes. The palladium complexes **2**, **7**, and **8** have been isolated in two forms, labeled **a** and **b**.

[M(aape)$_2$] Complexes (M = Ni (1), Pd (2a,b), Cu (3)). The nickel complex **1** was obtained as red needles with a visible spectrum diagnostic of a square planar coordination. However the weak paramagnetism of the metal center produces a broadening of the C1, C4, and C5 resonances observed at 180.5, 31.7, and 12.3 ppm in the ^{13}C NMR solution spectrum of this sample, respectively (Table 2). In addition, the carbonyl C1 signal (180.5 ppm) is upfield shifted in comparison to the signal of the corresponding carbon in the free ligand (197.1 ppm). These features suggest the N,O coordination of the **aape** ligand to Ni as pictured in the sketch of Table 2.[8] Unfortunately the chemical shifts of the C=N and C(O)OMe carbons are very close to those found for the same carbons in the free ligand and they do not appear furtherly informative of the type of coordination. In the ^{13}C NMR solution spectra of the samples **2a** and **2b** the chemical shifts of the C1, C3, and C6 carbons are very close to those observed for the same atoms in the spectrum of sample **1** suggesting the same type of coordination (N,O) of the **aape** ligand to the palladium. However, some small differences between the NMR spectra of samples **2a** and **2b** have been detected (see Table 2). NOE experiments carried out on the sample **2a** revealed a strong dipolar interaction between the protons of the C8 methyl and the protons of the C7 methyl indicating that the acetyl and methyl ester groups are spatially very close to each other. A weaker dipolar interaction between the protons of C5 and C7 has been also observed in the same experiment. These results suggest that the rotation of the ester group is hindered and that C7 is preferentially faced to C8 (conformation **a** in Table 2). This conformation is similar to that determined by X-rays on related complexes [M((MeCO)$_2$CC(R)NH)$_2$] (M = Ni, Cu, R = CN; M = Ni, R = PhCO).[3] The oxo and methoxy substituents are turned on **2b**, where the methyl ester is preferentially faced toward the ethyl group (conformation **b** in Table 2). Thus the small differences observed in the solution NMR spectra of **2a** and **2b** can be easily attributed to these conformational changes of the ester substituent of the chelate ring.

The solid state ^{13}C CP/MAS NMR spectra of samples **1**, **2a**, and **2b** are in close agreement with the solution spectra, suggesting that the same coordination and possibly the same conformation are also present in the solid state.

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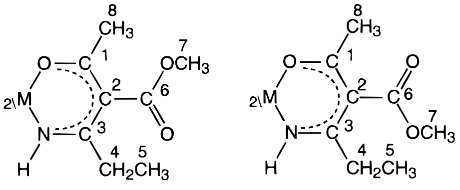
Table 2. ^{1}H and ^{13}C NMR Data for the [M(aape)$_2$] Complexes (M = Ni (**1**), Pd (**2a**, **2b**))[a]



conformation **a** conformation **b**

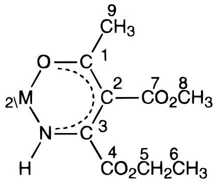
	1		**2a**		**2b**	
	solution	solid state	solution	solid state	solution	solid state
C atom						
1	180.5	181.7	180.4	177.9	178.9	180.4
2	106.0	104.2	105.9	106.4	106.5	104.3
3	173.1	173.1[b]	170.7	168 sh[b]	170.5	170.3[b]
4	31.7	32.8	32.6	32.1	31.7	32.1
5	12.3	12.4	13.0	12.6	12.5	11.9
6	170.4	171.5	171.2	170.1	171.3	172.6
7	51.3	52.3	51.6	51.8	51.6	52.3
8	25.5	27.0	25.5	24.9	25.2	26.7
H atom						
4	2.41		2.41		2.49	
5	1.04		1.08		1.12	
7	3.68		3.70		3.72	
8	1.89		2.05		2.04	
NH	6.06		7.55		7.60	

[a] In $(CD_3)_2CO$ at 25 °C (δ in ppm from TMS) and in the solid state; the drawing indicates the numbering scheme adopted and the proposed coordination (see also text). NMR data for the free ligand in $CDCl_3$: ^{1}H resonances at 1.21 (H5), 2.26 (H8), 2.53 (H4), 3.77 (H7), 5.95 and 11.25 (NH_2); ^{13}C resonances at 12.3 (C5), 29.0 (C4), 29.9 (C8), 51.3 (C7), 102.5 (C2), 170.2 (C6), 171.6 (C3), 197.1 (C1). [b] This attribution, which can be interchanged with C6, is based on the assumption that a broad signal is expected for an imino carbon atom.

Table 3. Infrared Data of the [M((MeOCO)(RCO)CC(R′)NH)$_2$] Complexes (**1**−**8**) (KBr, cm^{-1})

M complex	R R′	ν(N−H)	ν(MeOCO)	ν(MeCO)	ν(EtOCO)
Ni **1**	Me Et	3306m	1686s	1575s	
Pd **2a**	Me Et	3297m	1719s	1581s	
Pd **2b**	Me Et	3307m	1682s	1579s	
Cu **3**	Me Et	3365m	1697s	1590s	
Ni **4**	Me EtOCO	3267m	1709s	1565s	1733s
Pd **5**	Me EtOCO	3261m	1711s	1571s	1731s
Cu **6**	Me EtOCO	3276m	1704s	1563s	1733s
Pd **7a**	MeO Et	3320m, 3287m	1705s 1662s 1580vs		
Pd **7b**	MeO Et	3344m 3276m	1699s 1668s 1580vs		
Pd **8a**	MeO EtOCO	3217m	1709s 1582vs		1746s
Pd **8b**	MeO EtOCO	3320m 3260m	1724s 1683s 1580vs		1744s

Table 4. ^{1}H and ^{13}C NMR Data for the [M(aabu)$_2$] Complexes (M = Ni (**4**), Pd (**5**))[a]



	4		**5**	
	solution	solid state	solution	solid state
C atom				
1	186.2	189.0	185.8	186.9
2	103.0	101.6	102.8	102.0
3	161.6	163.7[b]	159.5	162.0[b]
4	163.7	165.4	164.1	165.6
5	62.6	62.6	62.9	62.8
6	13.9	14.6	13.9	14.2, 15.4
7	167.9	166.6	168.6	167.2
8	51.4	51.6	51.6	51.4, 52.2
9	26.2	27.7	26.4	26.7
H atom				
5	4.25		4.28	
6	1.30		1.33	
8	3.63		3.66	
9	2.14		2.32	
NH	6.14		7.63	

[a] In $CDCl_3$ at 25 °C (δ in ppm from TMS) and in the solid state; the drawing indicates the numbering scheme adopted and the proposed coordination (see also text). NMR data for the free ligand in $CDCl_3$ (less abundant species in parentheses): ^{1}H resonances at 1.26 (H6), 2.36 (2.42) (H9), 3.58 (3.80) (H8), 4.22 (H5), 6.20 and 10.5 (NH_2); ^{13}C resonances at 14.3 (C6), 30.6 (31.5) (C9), 52.3 (51.8) (C8), 63.4 (63.2) (C5), 102.2 (101.5) (C2), 156.9 (158.7) (C3), 164.6 (165.5) (C4), 168.8 (169.3) (C7), 199.2 (197.7) (C1). [b] This attribution, which can be interchanged with C4, is based on the assumption that a broad signal is expected for an imino carbon atom.

The IR spectra in KBr (Table 3) of the complexes **1**, **2a**, and **2b** are consistent with the proposed picture. The band at 1575−1581 cm^{-1} is easily attributed to the coordinated acetyl carbonyl,[4,9] whereas the absorption in the range 1682−1719 cm^{-1} is due to the C═O stretching vibration of the uncoordinated ester. In fact, the wavenumber values for O,O′-chelation in β-ketoester and β-diester complexes are always close to 1600 cm^{-1}, as an effect of electronic delocalization which occurs in the metallocycle ring.[10] The remarkable difference in the stretching frequency of the carbonyl ester in **2a** (1719 cm^{-1}) and **2b** (1682 cm^{-1}) arises from the different conformation of the ester group in the two cases and suggests a slightly more extended bond delocalization in the second one.

The IR spectrum of the copper complex **3** is similar to that of **1**, with the only difference beeing the N−H stretching band observed at higher wavenumbers. It is reasonable to propose for complex **3** the same N,N,O,O square planar coordination.

[M(aabu)$_2$] Complexes (M = Ni (4), Pd (5), Cu (6)). The compounds are all obtained in only one form and in almost quantitative yields. The NMR data in solution and in the solid state of complexes **4**−**6** are reported in Table 4. The N,O coordination of the **aabu** ligand to the metal centers was inferred from the NMR data following the approach described for samples **1** and **2**. Indeed, replacement of ethoxy carbonyl substituent for the ethyl group at the imino carbon does not influence the type of coordination.

However, the solid state ^{13}C CP/MAS NMR spectrum of complex **5** shows two couples of signals for the methyl carbons C6 and C8 and only one signal for each of the other carbons.

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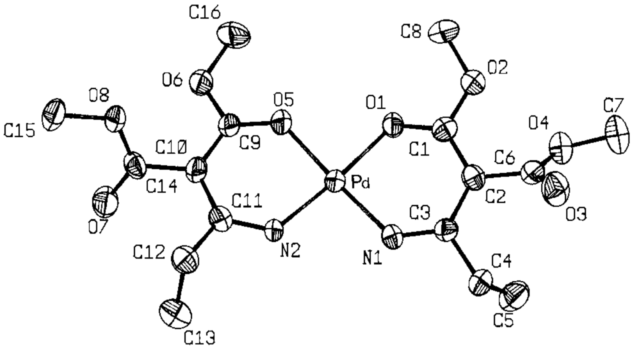


Figure 1. Crystal structure of [Pd(apro)$_2$] (**7b**). Hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex **7b**

Pd−O(1)	1.993(4)	Pd−O(5)	2.005(3)
Pd−N(1)	1.965(3)	Pd−N(2)	1.952(4)
O(1)−C(1)	1.277(5)	O(2)−C(1)	1.343(5)
O(2)−C(8)	1.435(5)	O(3)−C(6)	1.203(5)
O(4)−C(6)	1.359(5)	O(4)−C(7)	1.437(6)
O(5)−C(9)	1.251(5)	O(6)−C(9)	1.342(5)
O(6)−C(16)	1.436(6)	O(7)−C(14)	1.220(6)
O(8)−C(14)	1.319(5)	O(8)−C(15)	1.462(5)
N(1)−C(3)	1.331(5)	N(2)−C(11)	1.334(6)
C(1)−C(2)	1.412(5)	C(2)−C(3)	1.421(5)
C(2)−C(6)	1.480(6)	C(3)−C(4)	1.508(6)
C(4)−C(5)	1.503(7)	C(9)−C(10)	1.417(6)
C(10)−C(11)	1.429(6)	C(10)−C(14)	1.481(5)
C(11)−C(12)	1.532(7)	C(12)−C(13)	1.500(7)
N(1)−Pd−N(2)	92.9(2)	O(5)−Pd−N(2)	90.5(2)
O(5)−Pd−N(1)	176.1(2)	O(1)−Pd−N(2)	174.0(2)
O(1)−Pd−N(1)	91.2(2)	O(1)−Pd−O(5)	85.6(1)
Pd−O(1)−C(1)	124.6(3)	C(1)−O(2)−C(8)	118.1(4)
C(6)−O(4)−C(7)	115.8(4)	Pd−O(5)−C(9)	126.6(3)
C(9)−O(6)−C(16)	116.3(4)	C(14)−O(8)−C(15)	116.0(4)
Pd−N(1)−C(3)	127.5(3)	Pd−N(2)−C(11)	128.4(3)
O(1)−C(1)−O(2)	116.1(4)	O(2)−C(1)−C(2)	116.3(4)
O(1)−C(1)−C(2)	127.6(4)	C(1)−C(2)−C(6)	118.0(3)
C(1)−C(2)−C(3)	122.8(4)	C(3)−C(2)−C(6)	119.1(3)
N(1)−C(3)−C(2)	123.9(4)	C(2)−C(3)−C(4)	119.4(4)
N(1)−C(3)−C(4)	116.5(4)	C(3)−C(4)−C(5)	114.3(4)
O(4)−C(6)−C(2)	111.7(4)	O(3)−C(6)−C(2)	126.7(4)
O(3)−C(6)−O(4)	121.6(5)	O(5)−C(9)−O(6)	116.6(4)
O(6)−C(9)−C(10)	115.4(4)	O(5)−C(9)−C(10)	128.0(4)
C(9)−C(10)−C(14)	120.0(4)	C(9)−C(10)−C(11)	122.5(4)
C(11)−C(10)−C(14)	117.6(4)	N(2)−C(11)−C(10)	123.2(5)
C(10)−C(11)−C(12)	120.9(4)	N(2)−C(11)−C(12)	115.6(4)
C(11)−C(12)−C(13)	114.1(4)	O(8)−C(14)−C(10)	114.3(4)
O(7)−C(14)−C(10)	123.6(4)	O(7)−C(14)−O(8)	122.1(5)

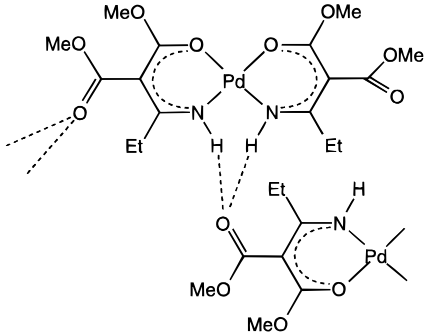
All chemical shifts of the signals observed in the solid state spectrum are roughly close to those of the corresponding carbons in the solution spectrum. These results were assumed as indicative of similar structure of the complex **5** in the solid state and CDCl$_3$ solution (N,O coordination of the **aabu** ligand) and the splitting of the methyl carbons C6 and C8 can be mainly attributed to packing effects of the complexes in the solid state.

The infrared spectra of the complexes **4**−**6** (Table 3) are very similar to each other, with narrow ranges for the stretching frequencies of the N−H (3261−3276 cm^{-1}), EtOC=O (1731−1733 cm^{-1}), MeOC=O (1704−1711 cm^{-1}), and MeC$\overset{\cdots}{-}$O (1563−1571 cm^{-1}) groups.

***β*-Imino Diesterato Complexes [Pd(apro)$_2$] (7a,b) and [Pd(ambu)$_2$] (8a,b).** Palladium complexes **7** and **8** are both isolable in two forms (**a** and **b**) in the solid state. The molecular structures of **7b** and **8b** have been determined by X-ray analysis. Complex **7b** crystallizes as monoclinic with four molecules per unit cell (Figure 1, Table 5).

The N(1), N(2) imino hydrogens are involved in an intermolecular hydrogen bond with the oxygen atom O(7) of the methoxy carbonyl group of a different molecule in the elementary cell [N(1)⋯O(7), 3.094(5) Å, N(2)⋯O(7), 3.000(5) Å, N−H⋯O, 152.3−152.1 °] (Chart 3). This interaction produces some slight deviations from the ideal square planar geometry.

Chart 3. Intermolecolar Hydrogen Bonds, in the Solid State, of Complex **7b**



The Pd−N bond distances [1.965(3) and 1.952(4) Å] are only slightly shorter than those normally observed in Shiff base palladium complexes [2.037(40) Å][11] and in the related N-substituted imino carbonyl enolato platinum complex *trans*-[Pt(N(COMe)C(Ph)CH(COMe))$_2$] [2.01(1) Å].[12] The Pd−O distances are normal [1.993(4) and 2.005(3) Å] and compare well with those found in [Pd(acac)$_2$] [1.96(1) and 1.974−1.985 Å][13] and in *cis*-[Pd(bzac)$_2$] [1.973(5)−1.980(4) Å].[14] The palladium center is on the square plane defined by N(1)N(2)O(1)O(5). The N−Pd−N angle is much greater than the O−Pd−O angle [92.9(2) vs 85.6(1)°] probably as a consequence of the mutual repulsion of the two imino hydrogen atoms. The complex adopts a saddle-shaped conformation in which the ligands are both on one of the two half-spaces defined by the coordination plane. The deviation from planarity is greater for the ligand not involved in intermolecular bonding so that the dihedral angle formed by C(1)C(2)C(3) with the plane PdN(1)N(2)O(1)O(5) is greater than that formed by C(9)C(10)C(11) [21.1(3) against 6.1(2)°]. At the same time the two uncoordinated methoxy carbonyl groups exhibit similar torsion angles with respect to the coordination plane [47.1(1) and 43.6(1)°]; the two oxo atoms point both toward the imino nitrogens but are situated one above and one below them. Bond distances are not significantly different in the two ligands and show an extended bond delocalization; in fact the values of *r*(CC) [1.412(5)−1.429(5) Å], *r*(CO) [1.251(5) and 1.277(5) Å], and *r*(CN) [1.331(5) and 1.334(6) Å] in the chelate part are intermediate between single and double bond and close to those found in nickel and copper β-imino carbonyl enolato complexes.[3]

According to the structure defined for the **7b** form, the solid state ^{13}C CP/MAS NMR spectrum of this sample exhibits almost single broad signals for the two imino carbons and the two metal coordinated carbonyls at 175.7 and 170.5 ppm, respectively (Figure 2, Table 6). Despite the symmetry of the complex, well-defined couple of signals, with approximately the same relative intensity, are detected for the remaining types of carbon of the complex. This spectral feature confirms the not equivalence of the two ligands binding the same palladium center. The inspection of the solid state ^{13}C CP/MAS NMR spectrum of

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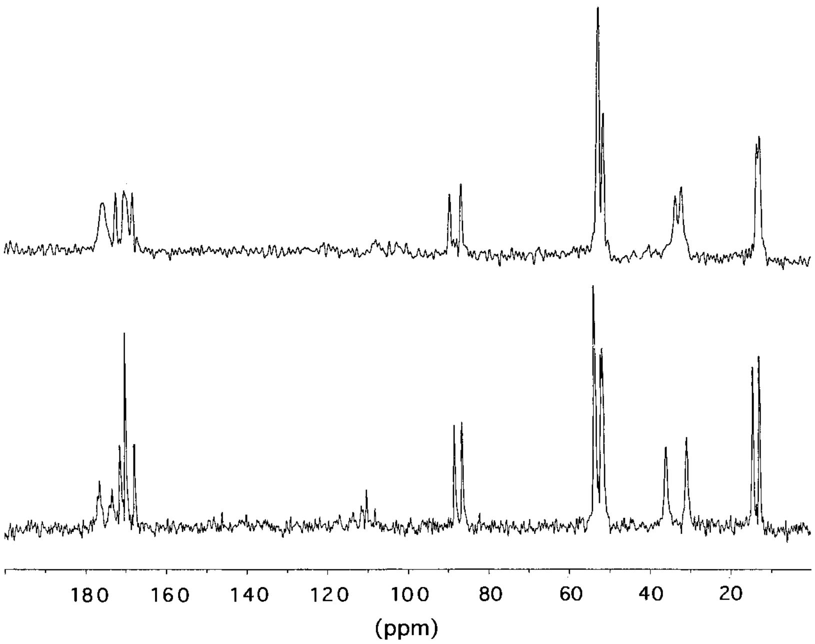


Figure 2. ^{13}C CP/MAS NMR spectra of the two forms of [Pd(apro)$_2$] (**7**) (**7a** bottom, **7b** top).

Table 6. ^{1}H and ^{13}C NMR Data for the [Pd(apro)$_2$] Complex (**7a**, **7b**)[a]

	solution	solid state	
	7a and **7b**	**7a**	**7b**
C atom			
1, 9	168.9[b]	169.8	170.5
2, 10	89.5	86.6, 88.4	86.9, 89.7
3, 11	174.6	173.3, 176.3	175.7
4, 12	32.5	30.9, 35.8	32.4, 33.8
5, 13	13.6	12.8, 14.4	13.0, 13.5
6, 14	169.7[b]	167.7, 171.3	168.4, 172.6
7, 8, 15, 16	51.6, 52.5	51.6, 52.0, 53.6	51.8, 53.0
H atom			
8	3.62		
7	3.68		
4	2.33		
5	1.07		
NH	6.50		

[a] Atom labeling as in Figure 1; in (CD$_3$)$_2$CO at 25 °C (δ in ppm from TMS) and in the solid state. NMR data for the free ligand in CDCl$_3$. ^{1}H resonances at 1.20 (H5), 2.43 (H4), 3.70 (H8), 3.75 (H7), 5.54 and 8.84 (NH$_2$); ^{13}C resonances at 12.5 (C5), 28.1 (C4), 51.0 (C8), 51.7 (C7), 91.5 (C2), 168.6 (C3), 168.9 (C1), 169.0 (C6). [b] Tentative attributions which can be exchanged.

sample **7a** reveals the same pattern of signals observed for sample **7b** but a greater chemical shift differences in each couple of signals, particularly those regarding the imino groups. As a matter of fact, two distinct resonances attributable to the imino carbons are detected at 173.3 and 176.3 ppm and well distinguished resonances for the methyl (C5 and C13) and methylene (C4 and C12) carbons are also observed.

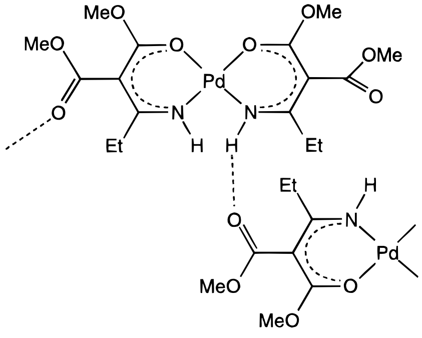
The infrared spectra in KBr of **7a** and **7b** are very similar as the whole, being characterized by a couple of N−H stretching bands (at 3320 and 3287 for **7a** and 3344 and 3276 cm^{-1} for **7b**) and by three bands in the CO region (1705, 1662, and 1580 for **7a**; 1699, 1668, and 1580 cm^{-1} for **7b**). The splitting of the absorptions is attributable to different degrees of hydrogen bond interactions between the carbonyl and the two imino groups. At the same time the band of the coordinated ester is unique and unchanged at 1580 cm^{-1} in the two forms. The IR spectra of **7a** and **7b** in CHCl$_3$ solution are identical (the maximum of the fairly large band at 1704 appears shifted at 1700 cm^{-1} in the spectrum of **7a** registered immediately after dissolution) and are much simpler showing bands at 3324 [ν(N−H)], 1704 [ν(C=O)] and 1582 [ν(C$\overset{\cdot\cdot\cdot}{-}$O)] cm^{-1}, thus indicating the absence of hydrogen bonding and rapid conversion of **7a** to **7b** in the chloroform solution.

In fair agreement with the latter findings, forms **7a** and **7b** exhibit the same ^{1}H and ^{13}C NMR spectra in deuterioacetone solution (Table 6). A single set of resonances has been detected for both ligands under this condition, indicating that the solid-state effects described above are removed by dissolution process and that the two ligands are equivalent in deuterioacetone solution. 2D ^{1}H,^{13}C HETCORR analysis permitted the attribution of the ^{13}C signal at 174.6 to the imino carbons and established that the carbonyls at 168.9 and 169.7 ppm bind the methoxy carbons observed at 52.5 and 51.6, respectively. Unfortunately the attribution of these signals to the coordinated and uncoordinated ester moieties does not appear viable. NOESY experiments carried out on the deuterioacetone solution of samples **7a** and **7b** showed only dipolar correlations (cross-peaks) between imino proton and ethyl protons. No cross-peaks for the methyl protons of the ester moieties were detected.

These results can be explained assuming the same type of coodination of the **apro** ligand to palladium in both **7a** and **7b** forms. The **7a** form, kinetically favored and isolated by precipitation from ethanol solution, could be constituted in the solid state by a net of molecules joined by hydrogen bonding between the carbonyl oxygen of one ligand and the hydrogen of only one imino group (Chart 4). According to this picture and assuming the same numbering scheme of **7b**, the ^{13}C signals at 167.7, 171.3, and 169.8 ppm observed in the solid state ^{13}C CP/MAS NMR spectrum of sample **7a** with relative intensity ratio 1:1:2, could be attributed to the carbonyl group involved in the H-bonding (C14), the "free" carbonyl (C6), and the metal-coordinated (C1 and C9) carbonyls, respectively. The two imino signals detected at 173.3 and 176.3 ppm could be also assigned to the "free" group and to the imino group involved in the hydrogen bonding.

The complex [Pd(ambu)$_2$] is also obtained in two forms. The most stable **8b** can be isolated as pure compound, whereas **8a** always contains small amount of **8b**, under our experimental conditions. The structure of **8b**, determined by X-ray analysis

Chart 4. Proposed Intermolecolar Hydrogen Bonds, in the Solid State, of Complex **7a**



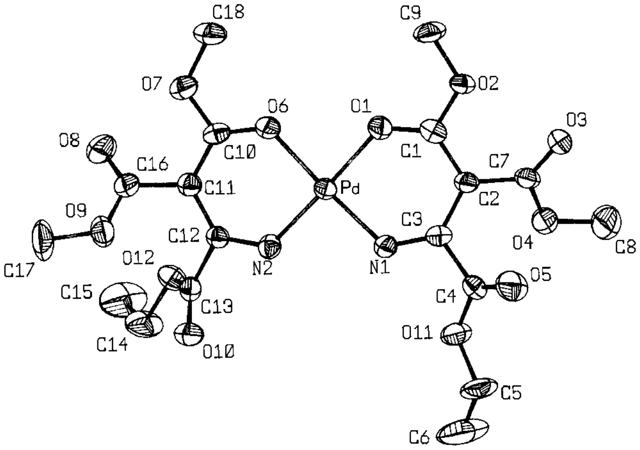


Figure 3. Crystal structure of [Pd(ambu)$_2$] (**8b**). Hydrogen atoms are omitted for clarity.

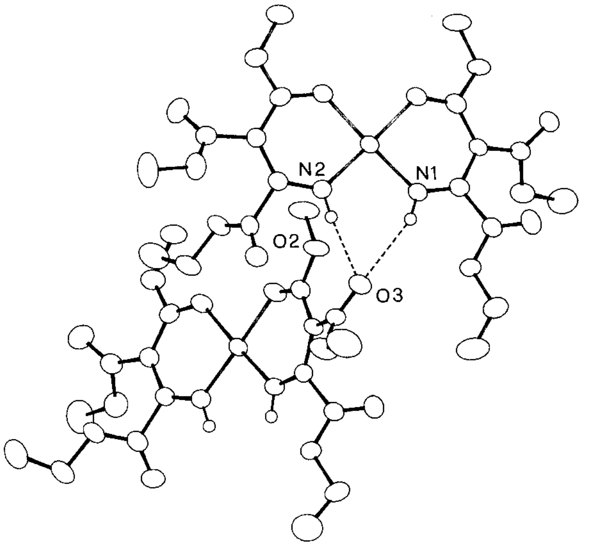


Figure 4. Partial view of the unit cell of **8b**, showing the intermolecular hydrogen bonding.

Table 7. Selected Bond Distances (Å) and Angles (deg) for Complex **8b**

Pd−O(1)	1.983(3)	Pd−O(6)	1.980(3)
Pd−N(1)	1.939(3)	Pd−N(2)	1.926(3)
O(1)−C(1)	1.237(5)	O(2)−C(1)	1.312(5)
O(2)−C(9)	1.428(6)	O(3)−C(7)	1.197(5)
O(4)−C(7)	1.336(5)	O(4)−C(8)	1.419(7)
O(5)−C(4)	1.172(5)	O(6)−C(10)	1.248(5)
O(7)−C(10)	1.316(5)	O(7)−C(18)	1.431(6)
O(8)−C(16)	1.184(6)	O(9)−C(16)	1.331(5)
O(9)−C(17)	1.427(7)	O(10)−C(13)	1.172(5)
O(11)−C(4)	1.305(5)	O(11)−C(5)	1.442(5)
O(12)−C(13)	1.315(6)	O(12)−C(14)	1.442(6)
N(1)−C(3)	1.286(5)	N(2)−C(12)	1.289(5)
C(1)−C(2)	1.413(6)	C(2)−C(3)	1.401(5)
C(2)−C(7)	1.449(6)	C(3)−C(4)	1.520(6)
C(5)−C(6)	1.397(9)	C(10)−C(11)	1.389(6)
C(11)−C(12)	1.391(6)	C(11)−C(16)	1.478(6)
C(12)−C(13)	1.511(6)	C(14)−C(15)	1.460(9)

N(1)−Pd−N(2)	92.5(2)	O(6)−Pd−N(2)	90.7(2)
O(6)−Pd−N(1)	176.4(1)	O(1)−Pd−N(2)	177.9(2)
O(1)−Pd−N(1)	89.7(2)	O(1)−Pd−O(6)	87.1(2)
Pd−O(1)−C(1)	127.0(3)	C(1)−O(2)−C(9)	116.7(4)
C(7)−O(4)−C(8)	115.6(4)	Pd−O(6)−C(10)	126.9(3)
C(10)−O(7)−C(18)	118.2(4)	C(16)−O(9)−C(17)	116.5(5)
C(4)−O(11)−C(5)	117.0(4)	C(13)−O(12)−C(14)	116.0(4)
Pd−N(1)−C(3)	126.6(3)	Pd−N(2)−C(12)	126.5(3)
O(1)−C(1)−O(2)	117.4(5)	O(2)−C(1)−C(2)	116.0(4)
O(1)−C(1)−C(2)	126.6(4)	C(1)−C(2)−C(7)	120.1(4)
C(1)−C(2)−C(3)	120.1(4)	C(3)−C(2)−C(7)	119.8(4)
N(1)−C(3)−C(2)	126.8(5)	C(2)−C(3)−C(4)	118.1(4)
N(1)−C(3)−C(4)	114.6(4)	O(11)−C(4)−C(3)	111.3(4)
O(5)−C(4)−C(3)	123.3(4)	O(5)−C(4)−O(11)	125.3(6)
O(11)−C(5)−C(6)	110.3(6)	O(4)−C(7)−C(2)	110.7(4)
O(3)−C(7)−C(2)	127.8(4)	O(3)−C(7)−O(4)	121.4(4)
O(6)−C(10)−O(7)	117.1(4)	O(7)−C(10)−C(11)	116.5(5)
O(6)−C(10)−C(11)	126.4(5)	C(10)−C(11)−C(16)	119.9(4)
C(10)−C(11)−C(12)	122.3(4)	C(12)−C(11)−C(16)	117.6(4)
N(2)−C(12)−C(11)	126.5(4)	C(11)−C(12)−C(13)	120.6(5)
N(2)−C(12)−C(13)	112.6(5)	O(12)−C(13)−C(12)	109.8(4)
O(10)−C(13)−C(12)	124.4(5)	O(10)−C(13)−O(12)	125.6(4)
O(12)−C(14)−C(15)	106.9(4)	O(9)−C(16)−C(11)	110.5(5)
O(8)−C(16)−C(11)	126.6(5)	O(8)−C(16)−O(9)	122.9(5)

(Figures 3 and 4, Table 7), shows the usual N,O coordination through the imino nitrogen and the carbonyl oxygen atoms. The Pd−O [1.983(3) and 1.980(3) Å] and Pd−N [1.939(3) and 1.926(3) Å] distances are slightly shorter than in **7b**, with the palladium atom at the center of a distorted square plane [N(1)−Pd−N(2), 92.5(2)°, and O(1)−Pd−O(6) 87.1(2)°]. The carbonyl oxygens O(3) and O(8) are both faced toward the corresponding methoxy oxygen atoms [O(2) and O(7)] of the coordinated ester in this case, so that the intermolecular hydrogen bonding of the two imino groups with one oxo atom [N(1)···O(3), 3.128(4) Å; N(2)···O(3), 2.944(5) Å; N−H···O, 147.5−156.2°] is reinforced by a positive donor acceptor interaction of N(2) with O(2) [2.896(4) Å; N(2)−H···O(2), 94.1°] (Figure 4). The atoms of the chelate ring not involved in hydrogen bonds are almost coplanar with the N(1)N(2)O(1)O(6) coordination plane, which, by contrast, forms marked angles with N(1)O(1)C(1)C(3) [11.0(1)°] and C(1)C(2)C(3) [21.7(3)°].

The ^{1}H and^{13}C NMR data of **8a** and **8b** in CDCl$_3$ solution are reported in Table 8. The spectra of these samples are as the whole very similar, suggesting the same type of coordination of the **ambu** ligand to the palladium. The ^{1}H coupled ^{13}C NMR spectrum of **8b** presents two quartets ($^3J_{CH} = 3$ Hz) at 169.3 and 167.0 ppm, which can be attributed to the methyl ester carbonyl "long-range coupled" with the corresponding methyl protons. In addition, the doublet of triplets centered at 163.0 ppm (2H, $^3J_{CH} = 3$ Hz; 1H, $^3J_{CH} = 7$ Hz) would arise from the coupling of the ethoxy carbonyl with the methylene protons of the ethoxy group and the imino proton. The signal at 164.0 ppm can be finally assigned to the imino carbon. The ROESY experiment showed intense cross-peaks between the imino proton and the ethoxyl protons and, as well, the methyl protons of both methyl ester groups, indicating the relative steric proximity of these protons.

The solid state ^{13}C CP/MAS spectrum of **8b** shows as expected a double set of signals corresponding to the different chemical environment of the two ligands. The relative intensities of the peaks in the range 160.2−169.4 ppm are also in this case

Table 8. ^{1}H and ^{13}C NMR Data for the [Pd(ambu)$_2$] Complex (**8a**, **8b**)[a]

	8a		**8b**	
	solution	solid state	solution	solid state
C atom				
1, 10	169.6[b]	169.7[b]	169.3[b]	169.4
2, 11	88.2	86.4	88.6	86.0, 88.1
3, 12	164.1	164.7	164.0	164.5
4, 13	162.6	163.9	163.0	164.5
5, 14	62.8	62.4	63.0	62.7
6, 15	13.8	12.3	13.7	13.7, 14.4
7, 16	167.0[b]	166.8[b]	167.0[b]	160.2, 167.9
8, 9, 17, 18	51.7, 53.7	52.9, 54.0	51.7, 53.3	50.8, 52.6, 53.9
H atom				
5, 14	4.28		4.28	
6, 15	1.33		1.33	
8, 17	3.67		3.67	
9, 18	3.81		3.84	
NH	6.44		6.22	

[a] Atom labeling as in Figure 3; in CDCl$_3$ at 25 °C (δ in ppm from TMS) and in the solid state; the two forms **a** and **b** are present in the solution of sample **8a**, with approximate **a**/**b** ratio 1/1 in the ^{1}H (after 15 min) and 2/3 in the ^{13}C spectrum (after 1 h). NMR data for the free ligand: ^{1}H resonances at 1.21 (H6), 3.76 (H8, H9), 4.32 (H5), 5.80 and 8.42 (NH$_2$). ^{13}C resonances at 13.8 (C6), 52.4 and 51.8 (C8, C9), 63.1 (C5), 95.5 (C2), 150.4 (C3), 163.1 (C4), 168.0, and 167.2 (C1, C7). [b] Tentative attributions which can be exchanged.

useful for the attributions. The resonances at 160.2 and 167.9 ppm can be attributed to C(7) and C(16) carbons (see Figure 3) and the signal at 169.4 ppm, with a relative intensity ratio 2:1 with the latter, can be assigned to the C(1) and C(10) equivalent carbons. The solid state ^{13}C CP/MAS spectrum of sample **8a** is quite similar, albeit with a single set of signals. This feature indicates the equivalence of the two ligands and rules out the presence of intermolecular interactions. As a consequence, we suggest for the fairly unstable compound **8a** a square planar N,N,O,O coordination not stabilized by hydrogen bonds.

The infrared data of **8a** in KBr, reported in Table 3, are obtained by subtracting from the experimental spectrum the contribution of **8b**. The presence of bands at 3217 [ν(N$-$H)], 1746 [ν(EtOC$=$O)], 1709 [ν(MeOC$=$O)], and 1582 [ν(MeOC$\overset{\cdots}{-}$O)] cm^{-1} is consistent with coordination of the imino group and one of the two ester carbonyls, without any hydrogen bonding. By opposite reasons, the two N$-$H and MeOC$=$O absorptions in **8b** support the intermolecular hydrogen bonding revealed by the X-ray analysis. The same behavior is maintained in the chloroform solution. In particular the initial spectrum of **8a** shows one band at 3216 and bands at 3341 and 3282 cm^{-1} due to **8b**. The latter bands increase with time while the signal at 3216 cm^{-1} decreases. The IR spectrum of pure **8b**, characterized by bands at 3341, 3282 sh, 1727, 1668 sh, and 1580 cm^{-1}, can be obtained after 2 h.

The spectroscopic data of **8b** suggest that it retains in chloroform solution the same intermolecular hydrogen bonding observed in the solid state (Figure 4). This allows a fast, in the NMR time scale, exchange of the N(1), N(2) positions, via 180° rotation of the coordination plane, so that the proton in the two imino groups becomes magnetically equivalent (only one signal at 6.22 ppm) and can give cross-peaks with the protons of both C(8) and (C9) methyl esters in the ROESY experiment.

Mass Spectra and TG-DSC Measurements of Complexes 1−8. The complexes are volatile and remarkably stable (Table 9) as it appears evident from the presence of very intense molecular ions in the mass spectra of all compounds **1**−**8**. Furthermore, the EI mass spectra of forms **a** and **b** are identical, indicating the presence of the same molecular ion in the gas phase.

Many different primary fragmentations are present. They can be divided in two main categories: fragmentations of the ligand moiety of the complexes without metal−ligand bond cleavage and those that necessarily involve this cleavage. The fragmentation processes belonging to the first category (ML$_2$ − CH$_3$, ML$_2$ − CH$_3$O, ML$_2$ − CH$_3$OH, ML$_2$ − C$_2$H$_5$O, and ML$_2$ − C$_2$H$_5$OCO) are expected to be R and R′ dependent, whereas those of the second kind (ML$_2$ − R′CN) depend on the nature of the metal center.

“R loss” (ML$_2$ − CH$_3$ for **1**−**6** and ML$_2$ − CH$_3$O for **7** and **8**) represents the α-cleavage typical of carbonyl groups. The occurrence of such a fragmentation is sufficiently clear in the case of the complexes with R = CH$_3$. In fact we can observe the CH$_3$ loss in the spectra of all the compounds with the exception of those with R $\neq$ CH$_3$ (**7** and **8**). This behavior allows in addition to exclude, even in the case of complexes **1**−**6**, the contribution of alternative CH$_3$ sources such as the C$_2$H$_5$ groups of the two different R′ substituents or the CH$_3$O groups. Methoxy loss in compounds **7** and **8** cannot be on the other hand surely attributed to the α-bond cleavage of the R group owing to the occurrence for all the compounds **1**−**8** of a CH$_3$O loss clearly due to the fragmentation of the methoxy carbonyl substituent in C2. Analogously to this last fragmentation, loss of C$_2$H$_5$O (and of R′) occurs from the ethoxy carbonyl groups in compound **4**−**6** and **8** with R′= EtOCO. A particular case among the primary fragmentation processes of the first kind is represented by the CH$_3$OH loss which takes place significantly only in the case of Cu complexes **3** and **6** showing an unexpected specificity toward the metal center.

The primary fragmentation involving the metal−ligand bond cleavage is represented by the R′CN loss (C$_2$H$_5$CN and C$_2$H$_5$OCOCN). This process, which may be considered a retrosynthetic reaction, is tightly depending on the metal center and has only been observed with Pd complexes. This behavior is consistent with the impossibility of synthesizing these complexes by the straightforward reaction of the proper palladium β-carbonylenolate with the corresponding nitrile.

The mass spectra of all the complexes are also characterized by the presence of HML ions containing only one coordinated ligand and their fragmentation ions.

TG-DSC measurements have been limited to the nickel and palladium [M(aape)$_2$] complexes **1** and **2**, and to [Pd(apro)$_2$] (**7**). The thermal behavior of these compounds is rather complicated and only the main features will be outlined here.

Complex **1** undergoes at 126 °C a transformation (ΔH = 17 kJ mol^{-1}, scan rate 40° min^{-1}) into an isomer, whose infrared spectrum (3291 m, 1707 s, 1570 s, 1456 m cm^{-1}) is very similar to that of the related palladium complex **2a**. It evaporates at temperatures around 300 °C (ΔH = 96 kJ mol^{-1}) to leave a very negligible residue (ca. 1% at 900 °C). Complex **1** sublimes at 115−120 °C and 5 × 10^{-2} mbar to give a red sublimate, which is characterized by a new set of infrared bands (3358 w, 3339 w, 1703 vs, 1595 sh, 1582 s, and 1458 m cm^{-1}). This suggests the possibility of at least three different forms for complex **1**.

Complex **2a** does not sublime even at 180 °C and 10^{-1} mbar and decomposes above 300 °C leaving a residue of palladium metal (24.7% at 420 °C). The thermal behavior of **2b** is markedly different and closely resembles that of complex **1**. Also in this case an endothermic peak at 117 °C (ΔH = 20 kJ mol^{-1}) reveals the formation of an isomer more stable at higher temperature. Complex **2b** sublimes at 155 °C and 5 × 10^{-2} mbar to give a sublimate, which is a mixture of **2b** and of a

Table 9. Selected EI Mass Data for the $[M((MeOCO)(RCO)CC(R')NH)_2]$ Complexes (**1**−**8**)[a]

	R = Me, R′ = Et			R = Me, R′ = EtOCO			R = OMe, R′ = Et	R = OMe, R′ = EtOCO
ionic species	**1** (Ni)	**2** (Pd)	**3** (Cu)	**4** (Ni)	**5** (Pd)	**6** (Cu)	**7** (Pd)	**8** (Pd)
$[ML_2]^+$	398(100)	446(55)	403(38)	486(100)	534(100)	491(55)	478(100)	566(100)
$[ML_2 - CH_3]^+$	383(5)	431(3)	388(1)	471(12)	519(34)	476(3)		
$[ML_2 - CH_3O]^+$	367(16)	415(10)	372(8)	455(13)	503(14)	460(9)	447(29)	535(19)
$[ML_2 - CH_3OH]^+$	366(4)		371(29)			459(14)		
$[ML_2 - C_2H_5O]^+$				441(6)	489(8)	446(4)		521(11)
$[ML_2 - C_2H_5CN]^+$		391(10)					423(81)	
$[ML_2 - C_2H_5OCO]^+$				413(11)	461(8)	418(3)		493(11)
$[ML_2 - CH_3O - C_2H_5CN]^+$	312(6)							
$[ML_2 - CH_3OH - C_2H_5CN]^+$	311(8)	359(13)					391(85)	
$[ML_2 - CH_3OH - C_2H_5CN - CH_3]^+$	296(3)	344(4)						
$[ML_2 - C_2H_5OCOCN]^+$					435(5)			467(30)
$[ML_2 - C_2H_5OCO - CH_3O]^+$						387(10)		
$[ML_2 - C_2H_5OCO - CH_3OH]^+$				381(22)	429(5)	386(3)		461(24)
$[ML_2 - C_2H_5OCOCN - CH_3OH]^+$					403(23)			435(89)
$[ML_2 - 2C_2H_5OCO]^+$					388(14)	345(64)		
$[HML]^+$	229(11)	277(20)	234 (29)	273(8)	321(25)	278(23)	293(89)	337(51)
$[HML - H]^+$	228(8)		232 (78)	272(13)	320(16)		292(37)	336(30)
$[HML - 2H]^+$	227(97)	275(100)	202(100)		319(96)	276(14)	291(85)	335(81)
$[HML - CH_3]^+$		262(33)		258(11)				
$[HML - H - CH_3]^+$					305(39)	262(10)		
$[HML - CH_3O]^+$	198(13)			242(19)				
$[HML - CH_3OH]^+$	197(20)	245(2)			289(45)	246(48)	261(42)	305(92)
$[HML - CH_3CO]^+$		234(13)						
$[HML - H - CH_3CO]^+$					277(84)			
$[HML - C_2H_5OH]^+$						232(23)		
$[HML - H - CH_3OCO]^+$		217(7)			261(43)			
$[HML - H - C_2H_5OCO]^+$					247(65)			
$[HML - CH_3CO - CH_3OCO]^+$					219(62)			
$[HL]^+$	171(46)	171(6)	171(47)	215(4)	215(10)	215(40)	187(9)	231(34)
$[HL - H]^+$		170(39)						
$[HL - CH_3]^+$					200(35)	200(100)		
$[HL - CH_3O]^+$							156(32)	
$[HL\text{-}C_2H_5OCO - CH_3OH]^+$								126(73)
$[C_2H_5O]^+$				45(9)	45(9)	45(33)		45(4)
$[CH_3CO]^+$	43(44)	43(18)	43(90)	43(18)	43(21)	43(22)	43(9)	43(11)

[a] The *m*/*z* values are referred to the ions containing the most abundant isotope of each element (for the metals: ^{58}Ni, ^{106}Pd, and ^{63}Cu). Relative intensities of ions containing metals have been calculated by summing all the isotopic contributions. Forms **a** and **b** of the various complexes exhibit the same mass spectra. Complete data are in the Supporting Information.

new form with characteristic infrared bands at 3254 m, 1717 s, 1584 vs, and 1451 m cm^{-1}.

Complex **7b** sublimes at 155 °C and 5×10^{-2} mbar before its isomerization to **7a** at 176 °C ($\Delta H = 13$ kJ mol^{-1}). The sublimate is however pure **7a**.

Conclusions

There are many ML_2 complexes having N,O coordination and most of them are derived from classical salicylaldiminato Shiff bases. Rather less common are examples of the same type of complexes derived from deprotonated β-ketoamines.[15] The reported synthetic procedure opens the way to a potentially wide class of N,O β-imino carbonyl enolato complexes characterized by a bulky methoxy carbonyl substituent in the α-position. In all cases, the imino nitrogen is coordinated to the metal center and coordination of the oxygen of the keto group is preferred to that of the ester. The reduced ligating ability of the ester carbonyl is confirmed by the lack of reactivity of nickel and copper acetate toward β-enaminodiesters. In this regard it is worth noting that zinc acetate, which is unreactive toward both the β-enaminoketoesters and the -diesters investigated here, reacts easily with the β-enaminodiketone $(MeCO)_2CC(CCl_3)NH_2$.[16] The synthesis of the β-enaminodione ligands is easy and the scope of the possible substituents very large. In fact they can be obtained from the reaction of β-diketones, β-ketoesters, β-diesters, β-ketoamides with nitriles bearing either electron-withdrawing or electron-donating groups, without apparent limitations on the chain length.[1,17] All complexes are monomeric, thermally and hydrolitically stable and volatile. Furthermore the availability of β-enaminodiones with different steric and electronic properties (different size and ligating ability) makes viable the synthesis of complexes of various metals with tunable volatility and stability.

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Supporting Information Available: Complete EI mass data of complexes **1**−**8** are available (5 pages). X-ray crystallographic files in CIF format for the structure of complexes **7b** and **8b** are available on the Internet only. Access and ordering information is given in any current masthead page.

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