Configuration of Imino Carbon Pailadated Pyridine-2-carbaldimines. Crystal and Molecular Structure of trans-Chlorobis(dimethylphenylphosphine){[(p-methoxyphenyl)imino](2-pyridyl)methyl{palladium(II)

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Reaction of trans- $[PdCl(2-C_5H_5N)(L)_2]Cl(2-C_5H_5N = N-protonated 2-pyridyl; L = PMe_2Ph, PEt_3)$ with an equimolar amount of isocyanide, CNR ($R = C_6H_4OMe_p$, Me), followed by deprotonation with NEt₃, yields the imino(2-pyridyl)methyl complexes trans- $[PdCl(C(2-C_5H_4N)=NR)(L)_2]$. These compounds have been characterized by usual spectroscopic techniques and by reaction with ZnCl₂, which gives 1:1 binuclear adducts containing the α -dimino group σ, σ' -N,N' chelated to the zinc center. ¹H NMR spectra in CD₂Cl₂ indicate a predominant E-trans conformation in the temperature range -80-30 °C for the imino carbon palladated organic moiety, when not involved in chelation. This is also the only configuration present in the solid state, as shown by an X-ray crystal structure determination of trans- $[Pd\tilde{C}](C(2-C_5H_4N) = 0)$ $NC_6H_4OMe_p$ (PMe₂Ph)₂]. This compound crystallizes in the monoclinic system: space group $P2_1/n$ and cell constants a = 16.520 (2) Å, b = 10.953 (1) Å, c = 16.544 (2) Å, $\beta = 97.46$ (2)°, and Z = 4. A total of 3969 reflections have been used in the refinement, resulting in a final R value of 0.029. The structure is characterized by a planar N=C-C-N α -dimino skeleton, which is perpendicular to the palladium coordination plane (dihedral angle of 86.4 (2)°) and coplanar with the 2-pyridyl ring (dihedral angle of 1.9 (2)°), whereas the phenyl ring of the $C_6H_4OMe_p$ substituent is rotated by 19.5 (2)°. The coordination around palladium is essentially square-planar, with Pd-C(1) = 2.006 (4), Pd-Cl = 2.430 (2), Pd-P(1) = 2.4302.323 (2), and Pd-P(2) = 2.331 (2) Å.

Introduction

In the last few years much attention has been paid to the coordination chemistry of α -diimino ligands of the type $RN=C(R_1)-C(R_1)=NR$, because of their versatile ligating properties.¹ These compounds are also interesting for their flexible N=C-C=N skeleton, which may give rise to different conformational isomers, when not involved in chelation. Spectroscopic studies have led to the conclusion that free α -difference are predominantly present in solution with a "trans" N=C-C=N arrangement and with E(anti) substituents at both imino nitrogen atoms:²⁻⁴



The "trans" conformation is the most stable one, according to quantum chemical calculations (which give a rotational barrier of 22-26 kJmol⁻¹ for trans \rightarrow cis conversion when $R_1 = H$ ^{5,6} and is the only one observed in the solid state for RN=CH-CH=NR (R = $c-C_6H_{11}$).⁷

A similar conformational behavior is shown by the 1,2bis(imino)alkyl group in the complexes trans-[MCl{C(= $NRC(R_1) = NR_2 (PPh_3)_2 (M = Pd, Pt)$ both in solution and in the solid, in spite of the bulky $trans-MCl(PPh_3)_2$ unit.⁸ An X-ray structural analysis of a typical representative of this class of compounds (M = Pd; $R = R_2 =$ C_6H_4OMe-p ; $R_1 = Me$) has shown that the palladated α -diimino moiety has a virtually planar "trans" N=C-C=N configuration, almost perpendicular to the metal coordination plane:8a



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We have recently found a new method for the preparation of a related series of complexes, trans-[PdCl{C(2- $C_5H_4N = NR(PPh_3)_2$ (2- $C_5H_4N = 2$ -pyridyl; R = C_6H_4OMe-p , Me), containing a palladated pyridine-2carbaldimino group.⁹ For these compounds, however, the presence of two mutually trans PPh₃ ligands prevented a detailed ¹H NMR investigation in order to establish the preferred conformation in solution, because of the shielding effects of PPh₃ phenyl ring currents on the pyridyl proton resonances. As will be reported herein, these shieldings are much reduced or completely eliminated in the analogous derivatives trans-[PdCl{C(2-C₅H₄N)=NR}(L)₂] (L = PMe_2Ph or PEt_3), which can be prepared by the same synthetic route. Incidentally, the latter compounds are much more soluble in chlorinated solvents even at low temperatures and can be obtained in a more crystalline form, suitable for X-ray investigation.

Experimental Section

Materials and Apparatus. NMR spectra were obtained on a Varian FT 80A spectrometer in CDCl₃ of CD₂Cl₂ solution. Infrared spectra were recorded with a Perkin-Elmer 983 G instrument. Molecular weights were determined in 1,2-dichloroethane at 37 °C with a Knauer osmometer. Elemental analyses were carried out by the Microanalysis Laboratory of the Institute of Organic Chemistry, University of Padua, Italy.

The N-protonated complex cis- $[PdCl_2(2-C_5H_5N)(PPh_3)]$,¹⁰ the isocyanides,¹¹ and the pyridine-2-carbaldimines, C_5H_4N -2-CH= NR (R = Me, C_6H_4OMe-p),¹² were prepared by published methods. Isocyanides were stored in Schlenk tubes in the dark under nitrogen at -10 °C and were distilled or sublimed before use. All other chemicals and solvents were of analytical grade and were used without further purification.

Preparation of *trans*-[PdCl(2-C₅H₅N)(L)₂]Cl (L = PMe₂Ph, PEt₃). A diethyl ether suspension of *cis*-[PdCl₂(2-C₅H₅N)(PPh₃)₂] (2.08 g, 2 mmol in 150 mL of Et₂O) was treated with 4.1 mmol of phosphine (L) under nitrogen and stirred for 24 h at ambient temperature. The white product was filtered off, washed several times with Et₂O, and dried in vacuo (yield, based on the theoretical amount, 94–96%). These compounds were characterized by IR spectra in the solid [ν (NH) as a broad and strong absorption at ca. 2500 cm⁻¹, due to hydrogen bonding with the chloride ion; ν (PdP) and ν (PdCl) in the ranges 416–427 and 310–315 cm⁻¹, respectively] and by reaction with an excess of NaClO₄-H₂O, which yielded the known perchlorate derivatives *trans*-[PdCl(2-C₅H₅N)(L)₂]ClO₄.¹⁰

Preparation of trans-[PdCl|C(2-C₅H₄N)=NR](L)₂] (L = **PMe**₂**Ph**, **PEt**₃; **R** = $C_6H_4OMe \cdot p$, **Me**). The synthesis of these compounds was carried out by using the same procedure previously described for $L = PPh_{3.9}$ With the more basic PMe₂Ph and PEt₃ phosphines, however, the reaction proceeded at a lower rate and in some cases a gentle heating was applied. Furthermore, for the increased solubility of the products, different solvents were used for recrystallization. In a typical preparation, a CH_2Cl_2 solution of the isocyanide CNR (1 mmol in 5 mL of solvent) was added dropwise to a stirred CH₂Cl₂ solution of trans-[PdCl(2- $C_5H_5N(L)_2$]Cl (1 mmol in 20 mL of solvent). After the addition, the IR spectrum of the reaction mixture showed the presence of both the bis-cationic complex trans- $[Pd(2-C_5H_5N)(CNR)(L)_2]Cl_2$ and a considerable amount of unreacted isocyanide. The subsequent addition of NEt₃ (0.11 g, 1.1 mmol) yielded the deprotonated intermediate trans- $[Pd(2-C_5H_4N)(CNR)(L)_2]Cl$, which underwent migratory insertion of the isocyanide into the palladium-2-pyridyl bond to give the final product. When this step was completed, the solvent was evaporated to dryness and the

Table I. Crystal Data and Structure Determination Parameters

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formula	C ₂₉ H ₃₃ ON ₂ P ₂ ClPd
mol wt	629.4
space group	$P2_1/n$
crystal system	monoclinic
a/Å	16.520 (2)
b/Å	10.953 (1)
c/Å	16.544 (2)
β/deg	97.46 (2)
$\dot{U}/Å^3$	2968.2
Z	4
$D(calcd)/Mg m^{-3}$	1. 41
cryst size, mm	$0.32 \times 0.24 \times 0.30$
temp, K	295
F(000)	1288
radiatn (λ/Å)	Mo Kα (0.7107)
collected reflctns	$\pm h, \pm k, \pm l$
reflctns measd	5637
scan method	$\theta/2\theta$
scan speed/deg min ⁻¹	1.8
scan width/deg	1.2
bkgd/counts/s	10
$2\theta \min/\deg$	3
$2\theta \max/\deg$	50
$\sigma \lim \mathbf{I} > n\sigma(I) $	3
unique obsd refletns $ I > 3\sigma(I) $	3969
weighting scheme w	1
$R = (\sum F_{o} - F_{c} / \sum F_{o})$	0.029
$\mu(Mo K\alpha)/cm^{-1}$	7.60

oily residue was stirred with 50 mL of water until a solid crude material was obtained. With p-MeOC₆H₄NC, the insertion step tood ca. 3 h for completion for L = PMe₂Ph and ca. 9 h for L = PEt₃, both at 20 °C. With MeNC, a higher temperature of 40 °C was required: in these conditions, the reaction was completed in ca. 6 h for L = PMe₂Ph and in ca. 8 h for L = PEt₃. The PMe₂Ph derivatives were crystallized twice from a concentrated benzene solution by slow dilution with an Et₂O/*n*-hexane (1/1, v/v) mixture (R = C₆H₄OMe-*p*) or with *n*-hexane (R = Me). Both the PEt₃ derivatives were crystallized twice from a concentrated Et₂O solution by dropwise addition of *n*-hexane at -20 °C. The yields varied in the range 30–60%. The complex trans-[PdCl-{C(2-C₅H₄N)=NC₆H₄OMe-*p*)(PMe₂Ph)₂] is a monomer in 1,2dichloroethane: molecular weight, found 638, calculated 629.4.

Preparation of the Complexes $[ZnCl_2(C_5H_4N-2-C(R_1)=NR]]$ ($R = C_6H_4OMe-p$; $R_1 = H$, trans-PdCl(PEt₃)₂). These compounds were prepared in high yield (85-90%) in the same way as earlier reported for other α -diimino ligands.¹³ The adduct with $R = C_6H_4OMe-p$ and $R_1 = trans$ -PdCl(PEt₃)₂ is a monomer in 1,2-dichloroethane solution: molecular weight, found 740, calculated 725.7.

X-ray Measurements and Structure Determination. The crystal and refinement data for trans-[PdCl](C(2-C₅H₄N)= NC_6H_4OMe-p](PMe₂Ph)₂] (pale yellow transparent regular prisms) are summarized in Table I. A prismatic single crystal was lodged at the top of a glass fiber and centered on a four-circle Philips PW1100 diffractometer with graphite monochromated Mo K α radiation. The orientation matrix and preliminary unit cell dimensions were determined from 25 reflections found by mounting the crystal at random and varying each of the orientation angles χ and ϕ over a range of 120°, with $6 < \theta < 9°$. For the determination of precise lattice parameters 25 strong reflections with $9 \le \theta \le 18°$ were considered.

The intensities of three standard reflections, -1,1,7,1,-2,6, and 422, were monitored every 180 min. There was no significant fluctuation in intensities other than those expected from Poisson statistics.

The intensity data were corrected for Lorentz-polarization effects but not for absorption (ψ scans were with minor variations of intensities) and for extinction. The structure was solved by using three-dimensional Patterson and Fourier techniques and refined by full-matrix least squares, with anisotropic thermal

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Table II. Fractional Coordinates (×10⁴) (hydrogens ×10³) with Esd's in Parentheses

	x	у	z		<i>x</i>	У	<i>z</i>	
Pd	2756.1 (2)	6669.5 (2)	4898.6 (2)					
Cl	2043 (1)	4816 (1)	4414 (1)					
C(1)	3462 (2)	8100 (3)	5282 (2)					
N(1)	3304 (2)	9189 (3)	5476 (2)					
C(2)	2528 (2)	9721 (3)	5502 (2)					
C(3)	1798 (3)	9118 (4)	5543 (3)	H(3)	180 (2)	829 (4)	554 (2)	
C(4)	1097 (3)	9756 (5)	5627 (3)	H(4)	67 (2)	941 (4)	563 (3)	
C(5)	1093 (2)	11012 (4)	5659 (2)			(-/		
O(1)	359 (2)	11552 (3)	5748 (2)					
C(8)	348 (3)	12836 (5)	5829 (3)					
C(6)	1799 (3)	11620 (4)	5601 (3)	H(6)	179 (2)	1241 (4)	558 (2)	
$\mathbf{C}(7)$	2503 (3)	10979 (4)	5529 (3)	H(7)	296 (2)	1139 (4)	549 (2)	
C(9)	4360 (2)	7809 (3)	5354 (2)	(/)			ų 10 (1)	
N(2)	4574 (2)	6697 (3)	5150(2)					
C(10)	5376 (3)	6431 (4)	5211(3)	H(10)	551 (3)	566 (4)	505 (3)	
C(11)	5979 (3)	7214(4)	5475 (3)	H(11)	654 (2)	697 (3)	550 (2)	
C(12)	5765 (3)	8319 (5)	5700 (4)	H(12)	614 (3)	880 (4)	584 (3)	
C(12)	4954 (3)	8643 (4)	5636 (4)	H(13)	477 (3)	930 (4)	585 (3)	
P(1)	2653 (1)	7420 (1)	3576 (1)	11(10)	411 (0)	000 (4)	000 (0)	
C(14)	1624 (4)	7249 (7)	3046 (4)	H(140)	122 (3)	778 (5)	327 (3)	
0(14)	1024 (4)	1240 (1)	0040 (4)	H(141)	160 (2)	755 (4)	059 (3)	
				H(149)	100(2) 146(3)	647 (5)	202 (0)	
C(15)	2883 (4)	9019 (5)	3493 (3)	H(150)	260 (2)	047(0)	300 (3)	
0(10)	2000 (4)	3013 (0)	0420 (0)	H(150)	200 (2)	$\frac{347}{947}$ (4)	313 (2)	
				H(152)	276 (2)	029 (4)	300 (3) 286 (3)	
C(16)	3296 (2)	6655 (3)	2924 (1)	11(102)	210 (2)	920 (4)	200 (0)	
C(10)	3785 (2)	5687 (3)	3944(1)					
C(18)	A2QA (2)	5007 (3)	9761(1)					
C(10)	4234 (2)	5466 (3)	1059 (1)					
C(20)	4010 (2) 2807 (2)	6494 (9)	1629 (1)					
C(20)	3027(2)	7099 (2)	1000(1)					
D(21)	9701(2)	(020 (3) 6094 (1)	2121(1) 6945(1)					
$\Gamma(2)$	2791 (1)	6024(1)	0240 (1)	U(000)	040 (0)	050 (A)	FF0 (0)	
U(22)	3369 (4)	0927 (0)	7028 (3)	H(220)	342 (2) 015 (0)	603 (4) 700 (4)	758 (3)	
				H(221)	315 (3)	768 (4)	707 (3)	
0(00)	0000 (4)	(511 (0)	a	H(222)	396 (3)	701 (4)	692 (3)	
C(23)	3230 (4)	4511 (6)	6430 (4)	H(230)	316 (3)	424 (5)	698 (3)	
				H(231)	294 (3)	400 (5)	610 (3)	
G (a))				H(232)	386 (3)	449 (5)	640 (3)	
C(24)	1784 (2)	5914 (3)	6591 (1)					
C(25)	1073 (2)	5988 (3)	6038 (1)					
C(26)	312 (2)	5919 (3)	6315 (1)					
C(27)	262 (2)	5776 (3)	7145 (1)					
C(28)	974 (2)	5701 (3)	7698 (1)					
C(29)	1735 (2)	5770 (3)	7421 (1)					

parameters for all non-hydrogen atoms. The two phenyl rings of the dimethylphenylphosphine ligands were treated as a rigid group with the hydrogen atoms at the calculated positions (C-H = 0.95 Å; C-C-C = 120°; C-C = 1.395 Å) with a unique isotropic thermal parameter of U = 0.08 Å² for hydrogens. The hydrogen atoms belonging to the *p*-methoxy group were also introduced at calculated positions and refined as a rigid group (U = 0.08 Å²). The remaining hydrogen atoms were introduced at the positions indicated by a ΔF synthesis calculated at the last stages of the refinement (R = 0.043) with individual isotropic temperature factors. The difference Fourier map obtained after refinement to convergence (R = 0.029) contained no peaks of chemical significance.

Fractional coordinates for non-hydrogen atoms $(\times 10^4)$ and for hydrogens $(\times 10^3)$ are in Table II. Listing of anisotropic thermal parameters, least-squares planes, and observed and calculated structure factors $(\times 10)$ are provided as supplementary material.

The anomalous dispersion terms¹⁴ for Pd and P were taken into account in the refinement. Atomic scattering factors are from ref 14. Data processing and computation were carried out by using the SHELX 76 program package.¹⁵

Results and Discussion

Preparation and Characterization of Complexes. The [imino(2-pyridyl)methyl]palladium(II) compounds are

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	anal. data ^a]	IR absorptns, ^b cm ⁻¹	
R	\mathbf{R}_1	C	Н	N	Cl	ν(C=N)	ν(PdCl)	others
$C_5H_4N-2-C(R_1)=RN$								
C_6H_4OMe-p Me C_6H_4OMe-p Me C_6H_4OMe-p Me	$\begin{array}{l} PdCl(PMe_2Ph)_2\\ PdCl(PMe_2Ph)_2\\ PdCl(PEt_3)_2\\ PdCl(PEt_3)_2\\ H\\ H\end{array}$	55.1 (55.34) 51.7 (51.41) 50.6 (50.94) 46.1 (45.89)	5.3 (5.28) 5.5 (5.44) 7.0 (7.01) 7.6 (7.50)	4.4 (4.45) 5.2 (5.21) 4.6 (4.75) 5.5 (5.63)	5.7 (5.63) 6.8 (6.60) 6.2 (6.01) 7.3 (7.13)	1566 s (1565 s) ^c 1609 s (1607 s) ^c 1552 s (1552 s) ^c 1596 s (1602 s) ^c 1628 s (1626 s) ^c 1650 s ^d (1651 s) ^c	275 ms 272 ms 287 m or 250 m 295 m or 270 m	422 ms [ν(PdP)] 424 ms [ν(PdP)]
$[\text{ZnCl}_{2}[C_{5}H_{4}N-2-C(R_{1})] = RN]$								
C_6H_4OMe-p	$PdCl(PEt_3)_2$	41.2 (41.38)	5.7 (5.69)	3.8 (3.86)	14.8 (14.65)	1526 m	no ^e	${}^{337 s}_{313 s}[\nu(ZnCl)]$
C_6H_4OMe -p	Н	44.6 (44.80)	3.4 (3.47)	8.0 (8.04)	20.2 (20.34)	1620 m		330 s 318 s [ν (ZnCl)]

^aCalculated values in parentheses. ^bNujol mulls. ^c1,2-Dichloroethane solution. ^dNeat liquid. e Not observed, masked by the intense ν (ZnCl) bands.

prepared by the synthetic route reported in Scheme I.

The formation of the cationic intermediates and the influence of the isocyanide substituent R on the reaction rate were previously studied for $L = PPh_3$.⁹ For substrates with $L = PMe_2Ph$ or PEt_3 , however, the IR and ${}^{31}p-{}^{1}H$ spectra taken at the various stages of the reaction show that in the first step (addition of CNR to trans-[PdCl(2- $C_5H_5N)(L)_2$ Cl in a molar ratio of 1:1) both the unreacted isocyanide and the starting complex are present in a substantial amount at equilibrium. Consequently, the second step (deprotonation with NEt₃) yields both complexes $trans-[Pd(2-C_5H_4N)(CNR)(L)_2]^+$ and $trans-[PdCl(2-C_5H_4N)(CNR)(L)_2]^+$ $C_5H_4N(L)_2$] [$\delta(^{31}P)$ singlet at 15.9 and 12.7 ppm, respectively, for $L = PEt_3$ from the parent N-protonated species. In the third step (migratory insertion), the final products are obtained essentially from interaction of chloride ions with trans- $[Pd(2-C_5H_4N)(CNR)(L)_2]^+$.⁹ The latter intermediate is also formed in the equilibrium reaction of trans- $[PdCl(2-C_5H_4N)(L)_2]$ with the free isocyanide still present in the system, as is shown by independent experiments in which trans- $[PdCl(2-C_5H_4N)(L)_2]$ is first prepared from deprotonation of trans-[PdCl(2-C₅H₅N)- $(L)_2^{+10}$ and then allowed to react with an equimolar amount of CNR.

For a given isocyanide, the rate of migratory insertion depends on the phosphine ligand and decreases in the order $PPh_3 > PMe_2Ph > PEt_3$. Such a trend suggests that the electronic properties of L play a much greater role than the steric ones, in the sense that they can affect the charge density on the central metal of the cationic intermediate trans- $[Pd(2-C_5H_4N)(CNR)(L)_2]^+$, and hence influence the attack by the chloride ions and the extent of $d - \pi^*$ back donation toward CNR and the migrating 2-pyridyl ligand.¹⁶ For trans- $[Pd(2-C_5H_4N)(CNMe)(L)_2]^+$, the isocyanide CN stretching frequency actually decreases with increasing electron-donating ability of L^{17} (L = PPh₃, 2230 cm⁻¹; PMe₂Ph, 2223 cm⁻¹, PEt₃, 2214 cm⁻¹), indicating a progressively reduced electrophilic character of the recipient isocyanide carbon, in line with the observed reactivity order.

The complexes trans-[PdCl{C(2- C_5H_4N)=NR}(L)₂] are nonconducting monomers in 1,2-dichloroethane and are characterized by a strong ν (C=N) absorption in the range 1552-1609 cm⁻¹, both in the solid and in solution (Table III).



Figure 1. ¹H NMR spectra of $[ZnCl_2[C_5H_4N-2-C(R_1)] = NC_6H_4OMe-p]$: (a) $R_1 = H$ and (b) $R_1 = trans-PdCl(PEt_3)_2$ in CD_2Cl_2 at 30 °C in the range 6.5–9.2 ppm.

If compared with the C=N stretching frequency of the related pyridine-2-carbaldimines, C_5H_4N -2-CH=NR, a shift to lower energy of ca. 50 cm⁻¹ for R = Me and of ca. 70 cm⁻¹ for R = C_6H_4OMe -*p* is observed, which suggests a significant electron donation from palladium to the imino(2-pyridyl)methyl group. As in the case of the PPh₃ analogue⁹ and of other [1,2-bis(imino)alkyl]palladium(II) derivatives,^{8b,13} the reaction with ZnCl₂ yields 1:1 adducts, characterized by two strong ν (ZnCl) bands in the range 337-313 cm⁻¹ (eq 1).



(1)

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8.8 (s) 8.4 (s) 11.3 (8) 14.5 (s) 11.4 (s) ^{a 1}H chemical shifts from Me₄Si in CDCl₃ solution at 30 °C (δ , ±0.01 ppm, J, ±0.1 Hz); multiplicity and coupling constants in parentheses; s = singlet, d = doublet, t = triplet, q = quartet 31Pd 8.71 (d, ⁵J_{HH} 0.62)ⁱ N-C-H 8.39 (dq) 8.63 (d) R₁ protons 1.00 (quint, J = 7.5) (quint, J = 7.6)0.93 (quint, J = 7.2) $(t, J_{PH} = 6.4)^{/}$ $_{PH} = 7.2)^{1}$ = 6.9 (t, J_{PH} Me, (f, J $\boldsymbol{\widehat{\Xi}}$.46 99 22 5 5 3.57 (d, ⁴J_{HH} = 1.7)⁶ NMe 3.70 (s) ۲ 3.46 R protons OMe 3.78 (s) 3.83 (s) ۲ 3.86 (s) and ³¹P(¹H) NMR Data^a 3.87 7.00 6.76 [ZnCl₂[C₆H₄N-2-C(R₁)=NR]] 6.95 7.04 6.9 BB C₆H₄N-2-C(R₁)=NR = 9.1) = 9.5) = 8.8) $(m, J_{AB} = 9.3)$ $(m, J_{AB} = 8.8)$ (m, J_{AB} (m, J_{AB} : 7.76 (m, *J*_{AB} AA″ 7.33 7.92 8.20 8.69 H **Table IV.** 8.49 (m) 8.58 (m) 8.50 (m) 8.69 (m) 8.64 (m) 8.75 (m) 8.81 (m) 8.46 (m) β 7.11 (m) 7.35 (m) E 7.74 (m) 7.18 (m) 7.30 (m) εĤ 8. protons 7.52 (m) 7.79 (m, $^{5}J_{\rm HH} = 0.65)^{g}$ 7.74 (m, ${}^{5}J_{\rm HH} = 0.63)$ 2-pyridyl H 7.62 (m) 8.23 (m) ₫ 8.22 7.69 (m) 8.19 (m) 7.91 (m) <u>e</u> 7.96 (m) 9.07 (m) H3 7.93 PdCl(PMe₂Ph)₂ PdCl(PMe₂Ph)₂ PdCl (PEt₃)₂ PdCI (PEt₃)₂ PdCl(PEt₃)₂ ų Н Ψ Ξ C₆H₄OMe-*p*^h C_aH₄OMe-p C_aH_AOMe-p C_aH₄OMe-p C_nH_nOMe-p R Me Me Me

downfield shifts being taken as positive. * Masked by the phenyl proton resonances of PMe₃Ph ligand in the range 7.6–7.0 ppm. fJ_{PH} + 4J_{PH} + * Coupling with N=C--H proton. * In

a saturated CD₂Cl₃ solution. ⁱCoupling with H⁶ proton

Figure 2. ¹H NMR spectra of C_5H_4N -2-C(R_1)=NC₆H₄OMe-*p*: (a) $R_1 = H$ and (b) $R_1 = trans$ -PdCl(PEt₃)₂ in CD₂Cl₂ at 30 °C in the range 6.5-9.0 ppm.

In these binuclear complexes, the α -diimino moiety is σ, σ' -N,N'-chelated to the zinc center, as shown by the downfield shift of most of the α -diimino proton resonances upon coordination (Table IV and Figures 1 and 2).¹⁸

The large $\nu(C=N)$ change in the adducts $[ZnCl_2 + \{C_5H_4N-2-C(R_1)=NC_6H_4OMe_p\}]$ on going from $R_1 = H$ (1620 cm⁻¹) to $R_1 = trans$ -PdCl(PEt₃)₂ (1526 cm⁻¹) gives further evidence of an increased $d - \pi^*$ back donation in the Pd—C=N group, when the imino nitrogen is σ ,N bonded to a second metal center.¹⁹ Spectroscopic data, such as the occurrence of only one Pd–P stretching frequency, of only one ³¹P singlet, and of 1:3:1 triplets or 1:4:6:4:1 quintets for the phosphine methyl signals of PMe₂Ph or PEt₃ derivatives, indicate that all complexes [PdCl{C(2-C₅H₄N)=NR}(L)₂] have a trans L-Pd-L arrangement which is retained in the corresponding ZnCl₂ adducts.

Configuration in Solution. As can be seen in Table IV, the equivalence of the two ³¹P phosphine nuclei and the occurrence of two distinct P-Me triplets (1:1 integration ratio) for *trans*-[PdCl{C(2-C₅H₄N)=NR}(PMe₂Ph)₂] is indicative of a molecular structure in which the asymmetric α -diimino ligand lies in a plane (or in a time-averaged plane) perpendicular to the metal coordination plane, with hindered rotation around the Pd-C_{imino} bond. In this geometry, the two methyl groups on the same phosphine have different magnetic environments because

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there is no plane of symmetry through the $PdCl(C_{imino})P_2$ atoms.

As far as the conformation of the palladated pyridine-2-carbaldimino group is concerned, various NMR studies on pyridine-2-carbaldehyde²⁰ and related derivatives, such as the corresponding oxime²¹ and imines,¹² have shown that these compounds are present in solution as two conformational isomers (6 and 7), the trans conformer 6 being largely predominant. For X = NOH and NR, only the



E configuration at the C=N double bond was observed. The E-trans form is the most stable one, according to MO calculations for the aldehyde²² and oxime²¹ and is the only one found in the solid for the imine $C_5H_4N-2-CH=NPh$.²³ The assignment of the conformation in solution is based on the stereospecific long-range coupling constant ${}^{5}J$ between the X = C-H proton and the H⁴ pyridyl proton,^{20a,21} band-shape analysis of low-temperature ¹³C NMR spectra,^{20b} and the low-field shift of the H³ resonance in the trans conformer 6, due to magnetic anisotropy of the C=X bond.12

For the [imino(2-pyridyl)methyl]palladium(II) complexes, a further magnetic anisotropy term is introduced by the d⁸ metal center, which may cause large low-field shifts to resonances of protons located at close proximity above or below the metal coordination plane. This effect is nicely illustrated by the downfield shifts of ca. 0.8 ppm for the C_6H_4OMe -p ortho protons AA' and of ca. 1.1 ppm for the pyridyl ³H proton of the complexes [ZnCl₂- $\{C_5H_4N-2-C(R_1)=NC_6H_4OMe-p\}$ when the imino proton $(R_1 = H)$ is replaced by the trans-PdCl(PEt₃)₂ group (Figure 1). In these adducts, the α -diimino moiety is forced to assume an *E*-cis conformation by the σ , σ' -N, N' chelation, and, for the binuclear complex, this brings the AA' and H³ protons very close to the Pd center (structure 5 of eq 1).

In Figure 2 are reported the ¹H NMR spectra of the uncoordinated compounds $C_5H_4N-2-C(R_1)=NC_6H_4OMe-p$ in the range of pyridyl and phenyl proton resonances. Also in this case the replacement of the imino proton by the trans-PdCl(PEt₃)₂ group brings about a large deshielding (ca. 0.9 ppm) for the AA' ortho protons, which can be rationalized in terms of an E configuration for the $C_{6}H_{4}OMe$ -p substituent at the imino nitrogen atom, by using the same arguments as above. In contrast, the pyridyl proton resonances appear to be little influenced by the nature of \mathbf{R}_1 (only small upfield shifts are observed in the palladated derivative, the largest of which (ca. 0.25 ppm) occurs for the H³ proton). Since the pyridine-2carbaldimine ($R_1 = H$) is essentially in an *E*-trans form,^{12,24}

Table V. Distances (Å) and Principal Angles (deg) with Esd's in Parentheses

(a) Palladium Environment									
Bond Distances									
Pd-Cl	2.430 (2)	Pd-P(1)	2.323 (2)						
Pd-C(1)	2.006(4)	Pd-P(2)	2.331(2)						
14 0(1)	2.000 (1)	Pd-P(mean)	2.001 (2)						
Pd-P(mean) = 2.327 (2)									
	Bond	Angles	155 0 (0)						
	173.5 (3)	P(1) - Pd - P(2)	175.8 (2)						
P(1)-Pd-Cl	90.7 (1)	P(2)-Pd-Cl	90.7 (1)						
$\mathbf{P}(1) - \mathbf{Pd} - \mathbf{C}(1)$	89.4 (1)	P(2)-Pd-C(1)	89.6 (1)						
(b) [(p-Me	thoxypheny)imino](2-pyridyl)m	ethyl						
	Li	gand							
	Bond	Distances							
C(1) - N(1)	1.271 (5)	C(6) - C(7)	1.377 (7)						
C(1) - C(9)	1.507 (5)	C(7) - C(2)	1.379 (6)						
N(1)-C(2)	1.414 (5)	C(9) - N(2)	1.324 (5)						
C(2) - C(3)	1.384 (6)	N(2)-C(10)	1.348 (6)						
C(3) - C(4)	1.375 (7)	C(10) - C(11)	1.344 (7)						
C(4) - C(5)	1.377(7)	C(11) - C(12)	1.328(7)						
C(5) = O(1)	1.374 (5)	C(12)-C(13)	1.377(7)						
O(1) - C(8)	1 413 (6)	C(12) - C(9)	1.377 (6)						
C(5) - C(6)	1.357 (6)	0(10) 0(0)	1.511 (0)						
	1.001 (0)								
	Bond	Angles							
Pd-C(1)-N(1)	133.1 (5)	C(5) - O(1) - C(8)	117.4 (6)						
Pd-C(1)-C(9)	112.7(4)	C(5)-C(6)-C(7)	120.0 (6)						
N(1)-C(1)-C(9)	114.3 (5)	C(6)-C(7)-C(2)	122.8 (6)						
C(1)-N(1)-C(2)	127.7 (5)	C(1)-C(9)-N(2)	117.8 (5)						
N(1)-C(2)-C(3)	127.2 (5)	C(1)-C(9)-C(13)	122.5 (5)						
N(1)-C(2)-C(7)	116.3 (6)	N(2)-C(9)-C(13)	119.6 (6)						
C(3)-C(2)-C(7)	116.4 (6)	C(9)-N(2)-C(10)	118.2 (5)						
C(2)-C(3)-C(4)	120.9 (6)	N(2)-C(10)-C(11)	124.5 (6)						
C(3)-C(4)-C(5)	121.3 (6)	C(10)-C(11)-C(12)	117.4 (7)						
C(4)-C(5)-O(1)	116.3 (6)	C(11) - C(12) - C(13)	120.4 (6)						
C(4) - C(5) - C(6)	118.6 (6)	C(12)-C(13)-C(9)	119.9 (6)						
O(1)-C(5)-C(6)	125.1 (6)	-(, -(, -(-,	(0)						
(c) D	(c) Dimethylphenylphosphine Ligand								
(c) =									
P(1) = C(14)	1 818 (7)	P(9)_C(99)	1 817 (6)						
D(1) = O(14)	1.010(1) 1.917(6)	P(0) = C(22)	1,017 (0)						
P(1) = O(10) D(1) = O(16)	1.017(0) 1.914(4)	P(2) = O(23) P(0) = O(04)	1.019 (1)						
$\Gamma(1) = O(10)$	1.014 (4)	F(2) = C(24)	1.032 (4)						
Bond Angles									
Pd-P(1)-C(14)	111.6 (3)	Pd-P(2)-C(22)	117.4 (3)						
Pd-P(1)-C(15)	118.8 (2)	Pd-P(2)-C(23)	113.4 (2)						
Pd-P(1)-C(16)	114.8 (2)	Pd-P(2)-C(24)	114.1 (2)						
C(14)-P(1)-C(15)) 103.4 (4)	C(22)-P(2)-C(23)	102.0 (4)						
C(14)-P(1)-C(16) 104.4 (3)	C(22)-P(2)-C(24)	104.2 (2)						
C(15)-P(1)-C(16) 102.3 (3)	C(23)-P(2)-C(24)	104.2 (3)						
P(1)-C(16)-C(17) 118.7 (2)	P(2)-C(24)-C(25)	120.8 (2)						
P(1)-C(16)-C(21	121.3(4)	P(2) - C(24) - C(29)	119.1 (4)						

this result implies that the same conformation is predominant also for $R_1 = trans-PdCl(PEt_3)_2$, even though the conformer ratio cannot be estimated quantitatively.

In a structure of type 4 (eq 1), the pyridyl protons (and, in particular, the H^3 proton) are far away from the d^8 palladium center for $R_1 = trans-PdCl(PEt_3)_2$, and their chemical shifts are not expected to be much different from those of the analogous (E)-trans-pyridine-2-carbaldimine. Preliminary MO calculations on $C_5H_4N-2-C(R_1)$ =NH (R_1 = H, trans-PdCl(PH₃)₂) in a planar E-trans form show only a slight increase in electron density on the pyridyl system

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⁽²⁴⁾ The predominance of the *E*-trans conformation for C₅H₄N-2-CH=NC₆H₄OMe-*p* is further supported by the value of 0.65 ± 0.02 Hz measured in a high-resolution spectrum for the coupling constant 5J between the N=C-H and the H⁴ protons and by the disappearance of this coupling constant when the compound assumes an E-cis configuration in its $ZnCl_2$ adduct. For the oxime C_5H_4N-2 -CH=NOH, a ⁵J value of 0.62 ± 0.02 Hz was reported, from which a fractional population of 0.86 \pm 0.14 for the *E*-trans conformer was estimated, by assuming ⁵J values of 0.72 Hz and zero for the E-trans and E-cis conformations, respectively.²¹



Figure 3. Molecular geometry of trans-[PdCl $(C(2-C_5H_4N)=$ $NC_6H_4OMe_{-p}(PMe_2Ph)_2$ viewed parallel to the N1)-C(1)-C(9) plane (Pluto drawing).

of the palladated compound, which would account for the observed small shieldings of pyridyl protons in $C_5H_4N-2-C(R_1)$ =NR on going from $R_1 = H$ to $R_1 = trans$ -PdCl-(PEt₃)₂ (see Table IV).²⁵

On the other hand, the rate of interconversion and the population of conformers are not appreciably affected by varying the temperature from 30 to -80 °C, as no relevant line broadening or chemical shift change is detected in the ¹H NMR spectra of both compounds $C_5H_4N-2-C(R_1)=$ NC_6H_4OMe-p in CD_2Cl_2 .

Crystal and Molecular Structure. The crystal structure of trans-[PdCl{C(2-C₅H₄N)=NC₆H₄OMe-p}-(PMe₂Ph)₂] is composed of four discrete molecules in a monoclinic centrosymmetric cell. Figure 3 is a Pluto drawing²⁶ of the molecule showing the molecular geometry and the atom numbering scheme used. Bond lengths and angles are listed in Table V.

The palladium atom is four-coordinated to two trans PMe₂Ph ligands, to a chlorine atom, and to the imino carbon atom of the [(p-methoxyphenyl)imino](2pyridyl)methyl group, in an essentially square-planar geometry. Some deviations from planarity toward a tetrahedral arrangement are observed, which are lower than those found in the 1,2-bis(imino)propyl complex 3,8ª probably because of the less steric requirements of PMe₂Ph relative to PPh_3^{17} (cf. the P(1)-Pd-P(2) angle of 175.8° vs. the 166.1° value in 3. The Pd-P bond lengths (2.323 (2) and 2.331(2) Å) are in agreement with those observed in 3 and with the literature data.8ª The Pd-Cl bond of 2.430 (2) Å is somewhat longer than that expected from the sum of covalent radii (2.30 Å)²⁷ and falls within the range of



Crystal packing of trans-[PdCl{C(2-C5H4N)= Figure 4. $NC_6H_4OMe_p$ (PMe₂Ph)₂ viewed down the b axis (Pluto drawing).

Pd–Cl distances of chloride ligands trans to a $Pd-C(sp^2)$ σ bond.^{8a} This lengthening suggests that the imino(2pyridyl)methyl group has a high trans influence, comparable with that of related 1,2-bis(imino)alkyl ligands, in line with the low value of the ν (PdCl) vibration (275 cm⁻¹). Also the Pd–C(1) bond distance (2.006 (4) Å) compares well with the reported values for Pd-C(sp²) σ bonds.^{8a}

As shown in Figure 3, the α -diimino moiety assumes only a trans N(1) = C(1) - C(9) N(2) configuration with an E (anti) $C_6H_4OMe_p$ N substituent, which corresponds to the predominant conformation of this ligand in solution. A remarkable feature of the structure is the close planarity of the N(1)C(1)C(9)N(2) fragment, the deviations from the best weighted mean plane (in which the C(2) atom of C_6H_4OMe -p group is also included) ranging from -0.015(4) to 0.018 (4) Å. The α -diimino unit is perpendicular to the palladium coordination plane (dihedral angle of 86.4 (2)° and coplanar to the 2-pyridyl ring (dihedral angle of 1.9 (2)°), whereas the phenyl ring of the C_6H_4OMe-p substituent is tilted out by 19.5 (2)°. The E-trans configuration of the imino(2-pyridyl)methyl ligand is similar to that of the pyridine-2-carbaldimine C_5H_4N -2-CH=NPh, for which an X-ray single-crystal analysis had revealed the presence of two independent molecules, both with a planar C(py)-C=N-C(Ph) skeleton, but with different dihedral angles for the phenyl (α) and pyridyl (β) rings ($\alpha = 17.9$ (7) and β -17.9 (7)° in one molecule; α = 8.9 (8) and β = -8.9 (8)° in the second one).²³ No comparison of bond distances and angles is, however, possible due to the orientational disorder of the molecules in the crystal of $C_5H_4N-2-CH=NPh$. In our case, the C(1)-N(1) bond distance of 1.271 (5) Å is very close to the $C(sp^2) = N(sp^2)$ double bond (1.27 Å), whereas the C(1)-C(9) distance of 1.507 (5) Å is longer than the accepted value of 1.48 Å for a $C(sp^2)-C(sp^2)$ single bond.²⁸ This result seems to rule out any π conjugation between the C=N imino group and the 2-pyridyl system. The bond angles about C(1), N(1),

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and C(2) deviate significantly from the idealized sp² value of 120°: $Pd-C(1)-N(1) = 133.1 (5)^{\circ}$, Pd-C(1)-C(9) = 112.7(4)°, N(1)–C(1)–C(9) = 114.3 (5)°, $\dot{C}(1)$ –N(1)–C(2) = 127.7 $(5)^{\circ}$, and N(1)-C(2)-C(3) = 127.2 (5)^{\circ}. The ligand appears therefore to be bent in such a way as to shorten the Pd...N(2) intramolecular distance (2.977 (4) Å) and to increase the Pd…C(3) separation (3.357 (6) Å). The coplanarity of the 2-pyridyl ring with the C(2)-N(1)-C(1)-C-(9)-N(2) system and the distorted angles at C(1), N(1), and C(2) do not result from the crystal packing shown in Figure 4. No significant intermolecular contacts are observed: the shorter ones are between the two centrosymmetrically related 2-pyridyl rings with C(10)...N(2)' and C(10)...C(10)' of 3.481 (6) and 3.411 (7) A, respectively, which would increase by a further rotation of the rings around the C(1)-C(9) bond. Although some intramolecular steric requirements may be important, the above structural features are probably the result of a repulsion between the Pd center and the closely lying H(3) atom (Pd···H(3) = 2.68A) and of a weak bonding interaction with the N(2) 2pyridyl atom. A four-membered metallacycle with a C,Nchelated 1,2-bis(imino)propyl ligand was proposed for the iron(II) complex:²⁹



The structure of trans-[PdCl{C(2-C₅H₄N)= NC₆H₄OMe-*p*}(PMe₂Ph)₂] accounts also for some features of its ¹H NMR spectrum. Thus, the downfield shift of the C₆H₄OMe-*p* ortho protons clearly results from their close proximity to the d⁸ metal center. On the other hand, the restricted rotation of the α -diimino moiety around the Pd-C(1) bond is mainly due to sterical hindrance with adjacent PMe₂Ph ligands, even though some contribution of electronic factors, such as a certain degree of d – π * back donation in the Pd-C(1) bond and a weak Pd…N(2) interaction, cannot be ruled out.

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Registry No. 4 ($R_1 = H$), 42910-70-3; 5 ($R_1 = trans$ -PdCl-(PEt₃)₂), 101652-38-4; 5 ($R_1 = H$), 101652-39-5; trans-[PdCl(2- C_5H_5N)(PMe₂Ph)₂]Cl, 101652-34-0; trans-[PdCl(2- C_5H_5N)(PEt₃)₂]Cl, 101652-35-1; cis-[PdCl₂(2- C_5H_5N)(PPh₃)], 88227-30-9; p-MeOC₆H₄NC, 10349-38-9; MeNC, 593-75-9; trans-[PdCl₄C(2- C_5H_4N)=NC₆H₄OMe-p}(PMe₂Ph)₂], 101670-83-1; trans-[PdCl₄C(2- C_5H_4N)=NC₆H₄OMe-p}(PMe₂Ph)₂], 101670-84-2; trans-[PdCl₄C(2- C_5H_4N)=NC₆H₄OMe-p}(PEt₃)₂], 101652-36-2; trans-[PdCl₄C(2- C_5H_4N)=NMe}(PEt₃)₂], 101652-37-3; C₅H₄N-2-CH=NMe, 40468-83-5.

Supplementary Material Available: Listings of anisotropic thermal parameters, least-squares planes, and observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

Reaction of $[P(C_6H_5)_4][Fe_2(CO)_6(\mu-CO)(\mu-CHCH_2)]$ with $[RhCl(CO)_2]_2$. Synthesis of a Triiron–Dirhodium Cluster Anion Containing a $CH_3C=C=CH_2$ Triiron–Dirhodium Ligand with an Unusual μ_4 - η^3 Mode of Bonding, $[P(C_6H_5)_4][Fe_3Rh_2(CO)_{10}(\mu-CO)_3(\mu_4-\eta^3-CH_3C=C=CH_2)]$

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 $[P(C_6H_5)_4][Fe_2(CO)_6(\mu-CO)(\mu-CHCH_2)]$ reacts with $[RhCl(CO)_2]_2$ in the presence of TlBF₄ at room temperature to give a 17% yield of $[P(C_6H_5)_4][Fe_3Rh_2(CO)_{10}(\mu-CO)_3(\mu-\eta^3-CH_3C=C=CH_2)]$ (1) whose structure has been determined by X-ray diffraction. 1 is monoclinic of space group $P2_1/n$ with a = 10.076(2) Å, b = 30.326 (4) Å, c = 13.824 (3) Å, $\beta = 104.16$ (2)°, and Z = 4. The structure has been solved and refined to R and R_w values of 0.038 and 0.044, respectively, using 4018 reflections. The anionic part of 1 consists of a square-based pyramid of metals, with a rhodium atom at the top of the pyramid. The 3-methyl-3-allenyl ligand results from the coupling of an ethylidyne and vinylidene ligand derived from the initial vinyl ligands. The allenyl ligand shows an unusual μ_4 - η^3 mode of bonding to the RhFe₃ unit. Under hydrogen pressure (10 atm) and at 60 °C, 1 slowly transforms 1-octene into 25% octane and 75% mixture of 2- and 3-octene.

In a recent publication¹ we have shown that the mixed iron-rhodium cluster HFe₃Rh(CO)₁₁[μ_4 - η^2 -C—CH(C₆H₅)], synthesized by the reaction of the [HFe₃(CO)₉(μ_3 - η^2 -C— CHC₆H₅)]⁻ anion with [RhCl(CO)₂]₂, was catalytic precursor for the isomerization of alkenes under hydrogen pressure. The cluster was destroyed during the catalysis, but the results suggest that the active species was a mixed rhodium-iron system. At the end of the reaction the only isolable compound was $H_3Fe_3(CO)_9(\mu_3\text{-}CCH_2C_6H_5)$, but this cluster was not an active catalyst for isomerization of alkenes under the same conditions. All these observations

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