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

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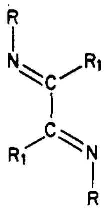
Reaction of *trans*-$[PdCl(2\text{-}C_5H_5N)(L)_2]Cl$ ($2\text{-}C_5H_5N$ = N-protonated 2-pyridyl; L = PMe_2Ph, PEt_3) with an equimolar amount of isocyanide, CNR (R = C_6H_4OMe-*p*, Me), followed by deprotonation with NEt_3, yields the imino(2-pyridyl)methyl complexes *trans*-$[PdCl\{C(2\text{-}C_5H_4N){=}NR\}(L)_2]$. These compounds have been characterized by usual spectroscopic techniques and by reaction with $ZnCl_2$, which gives 1:1 binuclear adducts containing the α-diimino group σ,σ′-N,N′ chelated to the zinc center. ^1H NMR spectra in CD_2Cl_2 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*-$[PdCl\{C(2\text{-}C_5H_4N){=}NC_6H_4OMe\text{-}p\}(PMe_2Ph)_2]$. 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, β = 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-diimino 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) = 2.323 (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-diimines 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]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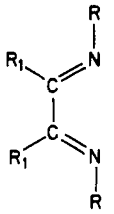
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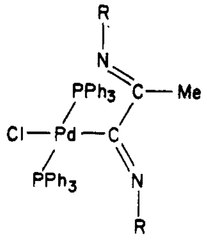
The "trans" conformation is the most stable one, according to quantum chemical calculations (which give a rotational barrier of 22–26 kJmol^{-1} for trans → cis conversion when R_1 = H)[5,6] and is the only one observed in the solid state for $RN{=}CH{-}CH{=}NR$ (R = c-C_6H_{11}).[7]

A similar conformational behavior is shown by the 1,2-bis(imino)alkyl group in the complexes *trans*-$[MCl\{C({=}NR)C(R_1){=}NR_2\}(PPh_3)_2]$ (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]


3, R=C_6H_4OMe-*p*

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[1] van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151.

[2] Kliegman, J. M.; Barnes, R. K. *Tetrahedron Lett.* **1969**, *24*, 1953.

[3] tom Dieck, H.; Renk, I. W. *Chem. Ber.* **1971**, *104*, 92.

[4] tom Dieck, H.; Franz, K. D. *Angew. Chem.* **1975**, *87*, 244.

[5] Reinhold, J.; Benedix, R.; Birner, P.; Hennig, H. *Inorg. Chim. Acta* **1979**, *33*, 209.

[6] Benedix, R.; Birner, P.; Birnstock, F.; Hennig, H.; Hofmann, H. J. *J. Mol. Struct.* **1979**, *51*, 99.

[7] Keijsper, J.; van der Poel, H.; Polm, L. H.; van Koten, G.; Vrieze, K.; Seignette, P. F. A. B.; Verenhorst, R.; Stam, C. *Polyhedron* **1983**, *2*, 1111.

[8] (a) Crociani, B.; Bandoli, G.; Clemente, D. A. *J. Organomet. Chem.* **1980**, *184*, 269 and references therein. (b) Crociani, B.; Mantovani, A.; Scrivanti, A. *J. Organomet. Chem.* **1982**, *233*, 387. (c) Mantovani, A.; Pelloso, M.; Bandoli, G.; Crociani, B. *J. Chem. Soc., Dalton Trans.* **1984**, 2223.

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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-2-carbaldimino group.[9] For these compounds, however, the presence of two mutually trans PPh_3 ligands prevented a detailed ^1H NMR investigation in order to establish the preferred conformation in solution, because of the shielding effects of PPh_3 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-C_5H_4N)=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 $CDCl_3$ of CD_2Cl_2 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-C_5H_5N)$(L)_2$]Cl (L = PMe_2Ph, PEt_3). A diethyl ether suspension of *cis*-[$PdCl_2$(2-C_5H_5N)$(PPh_3)_2$] (2.08 g, 2 mmol in 150 mL of Et_2O) 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 Et_2O, 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 $NaClO_4 \cdot H_2O$, which yielded the known perchlorate derivatives *trans*-[PdCl(2-C_5H_5N)$(L)_2$]ClO_4.[10]

Preparation of *trans*-[PdCl{C(2-C_5H_4N)=NR}$(L)_2$] (L = PMe_2Ph, PEt_3; R = C_6H_4OMe-*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 PMe_2Ph and PEt_3 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 CH_2Cl_2 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 NEt_3 (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 oily residue was stirred with 50 mL of water until a solid crude material was obtained. With *p*-$MeOC_6H_4NC$, the insertion step tood ca. 3 h for completion for L = PMe_2Ph and ca. 9 h for L = PEt_3, 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 = PMe_2Ph and in ca. 8 h for L = PEt_3. The PMe_2Ph derivatives were crystallized twice from a concentrated benzene solution by slow dilution with an Et_2O/*n*-hexane (1/1, v/v) mixture (R = C_6H_4OMe-*p*) or with *n*-hexane (R = Me). Both the PEt_3 derivatives were crystallized twice from a concentrated Et_2O solution by dropwise addition of *n*-hexane at -20 °C. The yields varied in the range 30–60%. The complex *trans*-[PdCl{C(2-C_5H_4N)=NC_6H_4OMe-*p*}$(PMe_2Ph)_2$] is a monomer in 1,2-dichloroethane: molecular weight, found 638, calculated 629.4.

Table I. Crystal Data and Structure Determination Parameters

formula	$C_{29}H_{33}ON_2P_2ClPd$
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)
U/Å^3	2968.2
Z	4
D(calcd)/Mg m^{-3}	1.41
cryst size, mm	0.32 × 0.24 × 0.30
temp, K	295
F(000)	1288
radiatn (λ/Å)	Mo Kα (0.7107)
collected reflctns	$\pm h,+k,+l$
reflctns measd	5637
scan method	$\theta/2\theta$
scan speed/deg min^{-1}	1.8
scan width/deg	1.2
bkgd/counts/s	10
2θ min/deg	3
2θ max/deg	50
σ limit $\|I > n\sigma(I)\|$	3
unique obsd reflctns $\|I > 3\sigma(I)\|$	3969
weighting scheme w	1
$R = (\sum \|\|F_o\| - \|F_c\|\| / \sum \|F_o\|)$	0.029
μ(Mo Kα)/cm^{-1}	7.60

Preparation of the Complexes [$ZnCl_2${C_5H_4N-2-C(R_1)=NR}] (R = C_6H_4OMe-*p*; R_1 = H, *trans*-$PdCl(PEt_3)_2$). 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*-$PdCl(PEt_3)_2$ 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-C_5H_4N)=NC_6H_4OMe-*p*}$(PMe_2Ph)_2$] (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 Kα 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 $9 \leq \theta \leq 18°$ 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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(9) Crociani, B.; Di Bianca, F.; Bertani, R.; Bisi Castellani, C. *Inorg. Chim. Acta* **1985**, *101*, 161.

(10) Crociani, B.; Di Bianca, F.; Giovenco, A.; Scrivanti, A. *J. Organomet. Chem.* **1983**, *251*, 393.

(11) (a) Appel, R.; Kleinstück, R.; Ziehn, K. D. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 132. (b) Casanova, J., Jr.; Schuster, R. E.; Werner, N. D. *J. Chem. Soc.* **1963**, 4280.

(12) Matsubayashi, G.; Okunaka, M.; Tanaka, T. *J. Organomet. Chem.* **1973**, *56*, 215.

(13) (a) Crociani, B.; Nicolini, M.; Richards, R. L. *J. Organomet. Chem.* **1976**, *104*, 259. (b) Crociani, B.; Nicolini, M.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1478.

Table II. Fractional Coordinates ($\times 10^4$) (hydrogens $\times 10^3$) with Esd's in Parentheses

	x	*y*	*z*		*x*	*y*	*z*
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)
C(7)	2503 (3)	10979 (4)	5529 (3)	H(7)	296 (2)	1139 (4)	549 (2)
C(9)	4360 (2)	7809 (3)	5354 (2)				
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(13)	4954 (3)	8643 (4)	5636 (4)	H(13)	477 (3)	930 (4)	585 (3)
P(1)	2653 (1)	7420 (1)	3576 (1)				
C(14)	1624 (4)	7249 (7)	3046 (4)	H(140)	122 (3)	778 (5)	327 (3)
				H(141)	160 (2)	755 (4)	252 (3)
				H(142)	146 (3)	647 (5)	306 (3)
C(15)	2883 (4)	9019 (5)	3423 (3)	H(150)	260 (2)	947 (4)	373 (2)
				H(151)	346 (3)	914 (4)	360 (3)
				H(152)	276 (2)	923 (4)	286 (3)
C(16)	3296 (2)	6655 (3)	2924 (1)				
C(17)	3785 (2)	5687 (3)	3244 (1)				
C(18)	4294 (2)	5092 (3)	2761 (1)				
C(19)	4315 (2)	5466 (3)	1958 (1)				
C(20)	3827 (2)	6434 (3)	1638 (1)				
C(21)	3317 (2)	7028 (3)	2121 (1)				
P(2)	2791 (1)	6024 (1)	6245 (1)				
C(22)	3389 (4)	6927 (6)	7028 (3)	H(220)	342 (2)	653 (4)	758 (3)
				H(221)	315 (3)	768 (4)	707 (3)
				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)
				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 Å^2 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 Å^2). 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.

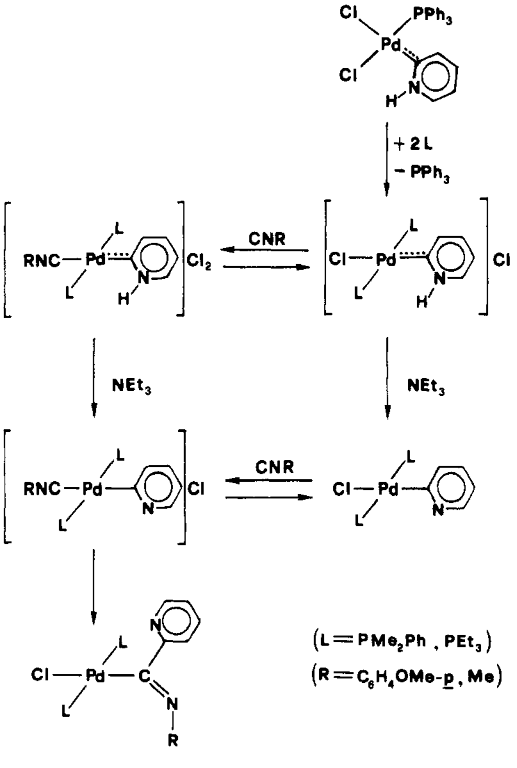
Fractional coordinates for non-hydrogen atoms ($\times 10^4$) and for hydrogens ($\times 10^3$) are in Table II. Listing of anisotropic thermal parameters, least-squares planes, and observed and calculated structure factors ($\times 10$) are provided as supplementary material.

The anomalous dispersion terms[14] 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

Scheme I



($L = PMe_2Ph$, PEt_3)
($R = C_6H_4OMe$-$\underline{p}$, Me)

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[14] *International Tables for X-Ray Crystallography*, 2nd ed.; Kynoch Press: Birmingham, England, 1974; Vol. 4, p 101.

[15] Sheldrick, G. M. SHELX 76; University of Cambridge, England, 1976.

Table III. Analytical Data and Characteristic IR Bands

		anal. data[a]				IR absorptns,[b] cm^{-1}		
R	R_1	C	H	N	Cl	ν(C=N)	ν(PdCl)	others
				C_5H_4N-2-C(R_1)=RN				
C_6H_4OMe-*p*	$PdCl(PMe_2Ph)_2$	55.1 (55.34)	5.3 (5.28)	4.4 (4.45)	5.7 (5.63)	1566 s (1565 s)[c]	275 ms	422 ms [ν(PdP)]
Me	$PdCl(PMe_2Ph)_2$	51.7 (51.41)	5.5 (5.44)	5.2 (5.21)	6.8 (6.60)	1609 s (1607 s)[c]	272 ms	424 ms [ν(PdP)]
C_6H_4OMe-*p*	$PdCl(PEt_3)_2$	50.6 (50.94)	7.0 (7.01)	4.6 (4.75)	6.2 (6.01)	1552 s (1552 s)[c]	287 m or 250 m	
Me	$PdCl(PEt_3)_2$	46.1 (45.89)	7.6 (7.50)	5.5 (5.63)	7.3 (7.13)	1596 s (1602 s)[c]	295 m or 270 m	
C_6H_4OMe-*p*	H					1628 s (1626 s)[c]		
Me	H					1650 s[d] (1651 s)[c]		
				[$ZnCl_2${C_5H_4N-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} [ν(ZnCl)]
C_6H_4OMe-*p*	H	44.6 (44.80)	3.4 (3.47)	8.0 (8.04)	20.2 (20.34)	1620 m		330 s 318 s} [ν(ZnCl)]

[a] Calculated values in parentheses. [b] Nujol mulls. [c] 1,2-Dichloroethane solution. [d] Neat 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 NEt_3) yields both complexes *trans*-[Pd(2-C_5H_4N)(CNR)$(L)_2$]$^+$ and *trans*-[PdCl(2-C_5H_4N)$(L)_2$] [δ(^{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-C_5H_5N)-$(L)_2$]$^+$ [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 − π* 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 = PPh_3, 2230 cm^{-1}; PMe_2Ph, 2223 cm^{-1}, PEt_3, 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).

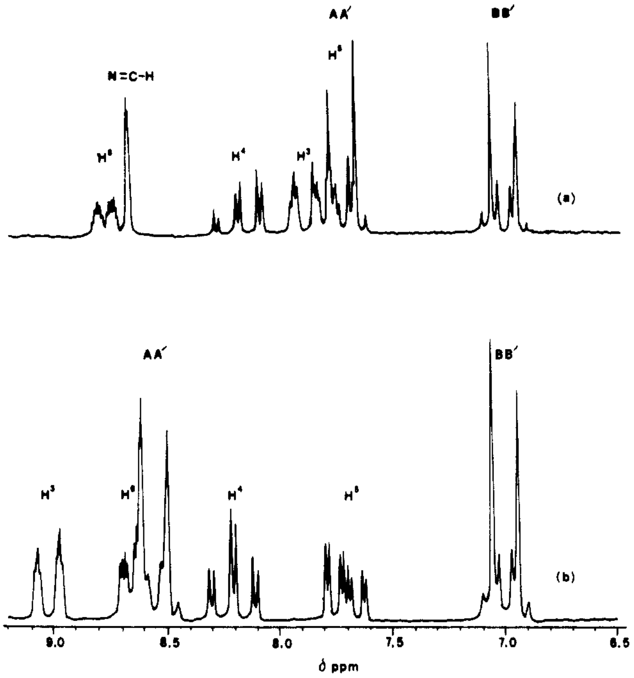
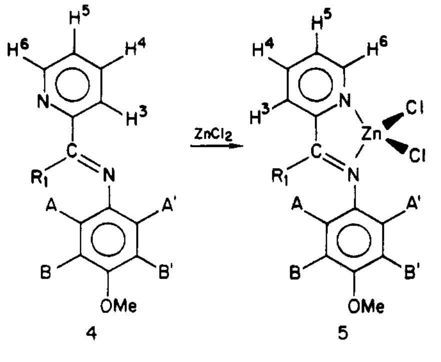


Figure 1. ^{1}H NMR spectra of [$ZnCl_2${C_5H_4N-2-C(R_1)=NC_6H_4OMe-*p*}]: (a) R_1 = H and (b) R_1 = *trans*-$PdCl(PEt_3)_2$ in CD_2Cl_2 at 30 °C in the range 6.5–9.2 ppm.

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 PPh_3 analogue[9] and of other [1,2-bis(imino)alkyl]palladium(II) derivatives,[8b,13] the reaction with $ZnCl_2$ yields 1:1 adducts, characterized by two strong ν(ZnCl) bands in the range 337–313 cm^{-1} (eq 1).



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(16) Isobe, K.; Kai, E.; Nakamura, Y.; Nishimoto, K.; Miwa, T.; Kawaguchi, S.; Kinoshita, K.; Nakatsu, K. *J. Am. Chem. Soc.* **1980**, *102*, 2475.

(17) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

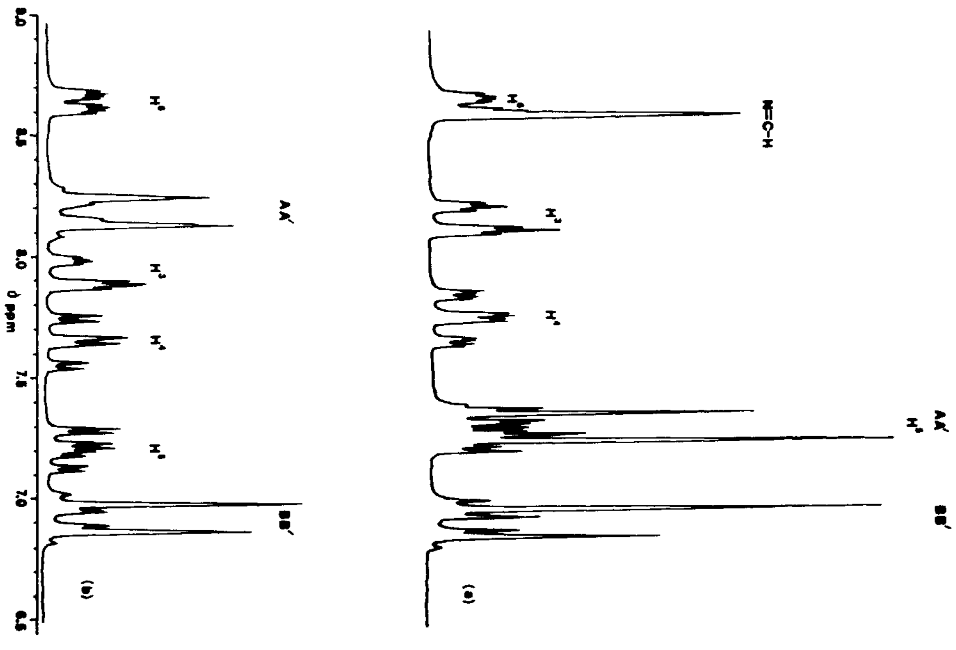

Figure 2. ^1H NMR spectra of C_5H_4N-2-$C(R_1)$=NC_6H_4OMe-*p*: (a) R_1 = H and (b) R_1 = *trans*-$PdCl(PEt_3)_2$ in CD_2Cl_2 at 30 °C in the range 6.5–9.0 ppm.

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 ν(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*-$PdCl(PEt_3)_2$ (1526 cm^{-1}) gives further evidence of an increased d – π* 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 ^{31}P singlet, and of 1:3:1 triplets or 1:4:6:4:1 quintets for the phosphine methyl signals of PMe_2Ph or PEt_3 derivatives, indicate that all complexes [PdCl{C(2-C_5H_4N)=NR}$(L)_2$] have a trans L–Pd–L arrangement which is retained in the corresponding $ZnCl_2$ adducts.

Configuration in Solution. As can be seen in Table IV, the equivalence of the two ^{31}P phosphine nuclei and the occurrence of two distinct P–Me triplets (1:1 integration ratio) for *trans*-[PdCl{C(2-C_5H_4N)=NR}$(PMe_2Ph)_2$] 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

Table IV. ^1H and $^{31}P\{^1H\}$ NMR Data[a]

		2-pyridyl protons[b]				R protons				R₁ protons		
R	R₁	H³	H⁴	H⁵	H⁶	AA′[c]	BB′[c]	OMe[c]	NMe	$Me_{phosphine}$	N=C—H	^{31}P[d]
						C_5H_4N-2-$C(R_1)$=NR						
C_6H_4OMe-*p*	$PdCl(PMe_2Ph)_2$	*e*	*e*	*e*	8.49 (m)	7.92 (m, J_{AB} = 9.5)	6.76	3.78 (s)		1.51 (t) 1.46 (t, J_{PH} = 6.9)[f]		–8.8 (s)
Me	$PdCl(PMe_2Ph)_2$	*e*	*e*	*e*	8.46 (m)				3.46 (s)	1.66 (t, J_{PH} = 7.2)[f] 1.50 (t, J_{PH} = 6.4)[f]		–8.4 (s)
C_6H_4OMe-*p*	PdCl $(PEt_3)_2$	7.91 (m)	7.62 (m)	7.18 (m)	8.58 (m)	8.20 (m, J_{AB} = 8.8)	6.90			0.93 (quint, *J* = 7.2)		11.3 (s)
Me	PdCl $(PEt_3)_2$	7.69 (m)	7.52 (m)	7.11 (m)	8.50 (m)				3.70 (s)	1.00 (quint, *J* = 7.5)		14.5 (s)
C_6H_4OMe-*p*	H	8.19 (m)	7.79 (m, $^5J_{HH}$ = 0.65)[g]	7.35 (m)	8.69 (m)	7.33 (*m*, J_{AB} = 9.1)	6.95	3.83 (s)			8.63 (d)	
Me	H	7.96 (m)	7.74 (m, $^5J_{HH}$ = 0.63)[g]	7.30 (m)	8.64 (m)				3.57 (d, $^4J_{HH}$ = 1.7)[g]		8.39 (dq)	
						[$ZnCl_2${C_5H_4N-2-$C(R_1)$=NR}]						
C_6H_4OMe-*p*	$PdCl(PEt_3)_2$	9.07 (m)	8.23 (m)	7.74 (m)	8.75 (m)	8.69 (m, J_{AB} = 8.8)	7.00	3.86 (s)		1.01 (quint, *J* = 7.6)		11.4 (s)
C_6H_4OMe-*p*[h]	H[h]	7.93 (m)	8.22 (m)	7.80 (m)	8.81 (m)	7.76 (m, J_{AB} = 9.3)	7.04	3.87 (s)			8.71 (d, $^5J_{HH}$ = 0.62)[i]	

[a] ^1H chemical shifts from Me_4Si in $CDCl_3$ 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, quint = quintet, m = multiplet; satisfactory integration values were obtained. [b] Second-order spectra in which each proton appears as a multiplet of characteristic pattern (see Figures 1 and 2). [c] Resonances of the C_6H_4OMe-*p* group; the ortho AA′ and meta BB′ protons give rise to a symmetrical AA′BB′ system. [d] ^{31}P chemical shifts (δ, ±0.1 ppm) from external 85% H_3PO_4, downfield shifts being taken as positive. [e] Masked by the phenyl proton resonances of PMe_2Ph ligand in the range 7.6–7.0 ppm. [f] $J_{PH} = |^2J_{PH} + {}^4J_{P'H}|$. [g] Coupling with N=C—H proton. [h] In a saturated CD_2Cl_2 solution. [i] Coupling with H⁶ proton.

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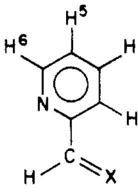
(18) Sandrini, P. L.; Mantovani, A.; Crociani, B.; Uguagliati, P. *Inorg. Chim. Acta* **1981**, *51*, 71 and references therein.

(19) Crociani, B.; Bertani, R.; Boschi, T.; Bandoli, G. *J. Chem. Soc., Dalton Trans.* **1982**, 1715.

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-carbaldehyde[20] and related derivatives, such as the corresponding oxime[21] 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 aldehyde[22] and oxime[21] 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 ^5J between the X = C–H proton and the H^4 pyridyl proton,[20a,21] band-shape analysis of low-temperature ^{13}C NMR spectra,[20b] and the low-field shift of the H^3 resonance in the trans conformer 6, due to magnetic anisotropy of the C=X bond.[12]



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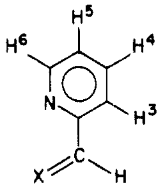

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X=O, NOH, NR

For the [imino(2-pyridyl)methyl]palladium(II) complexes, a further magnetic anisotropy term is introduced by the d^8 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 $[ZnCl_2\{C_5H_4N\text{-}2\text{-}C(R_1){=}NC_6H_4OMe\text{-}p\}]$ when the imino proton (R_1 = H) is replaced by the *trans*-$PdCl(PEt_3)_2$ 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 H^3 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*-$PdCl(PEt_3)_2$ 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_6H_4OMe-*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 R_1 (only small upfield shifts are observed in the palladated derivative, the largest of which (ca. 0.25 ppm) occurs for the H^3 proton). Since the pyridine-2-carbaldimine (R_1 = H) is essentially in an *E*-trans form,[12,24] 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.

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)
		Pd–P(mean)	2.327 (2)

Bond Angles

C(1)–Pd–Cl	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)
P(1)–Pd–C(1)	89.4 (1)	P(2)–Pd–C(1)	89.6 (1)

(b) [(*p*-Methoxyphenyl)imino](2-pyridyl)methyl Ligand

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(13)–C(9)	1.377 (6)
C(5)–C(6)	1.357 (6)		

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)		

(c) Dimethylphenylphosphine Ligand

Bond Distances

P(1)–C(14)	1.818 (7)	P(2)–C(22)	1.817 (6)
P(1)–C(15)	1.817 (6)	P(2)–C(23)	1.819 (7)
P(1)–C(16)	1.814 (4)	P(2)–C(24)	1.832 (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)

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*-$PdCl(PH_3)_2$) in a planar *E*-trans form show only a slight increase in electron density on the pyridyl system

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(20) (a) Dancura, W.; Schaefer, T.; Rowbotham, J. B.; Wood, D. J. *Can. J. Chem.* **1974**, *52*, 3986. (b) Drakenberg, T. *J. Chem. Soc., Perkin Trans. 2* **1976**, 147.

(21) Dancura, W.; Wasylishen, R. E.; Delikatny, J.; Graham, M. R. *Can. J. Chem.* **1979**, *57*, 2135.

(22) John, I. G.; Ritchie, G. L. D.; Radom, L. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1601.

(23) Wiebcke, M.; Mootz, D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 2008.

(24) The predominance of the *E*-trans conformation for C_5H_4N-2-CH=NC_6H_4OMe-*p* is further supported by the value of 0.65 ± 0.02 Hz measured in a high-resoltuion spectrum for the coupling constant ^5J between the N=C—H and the H^4 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 ± 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]

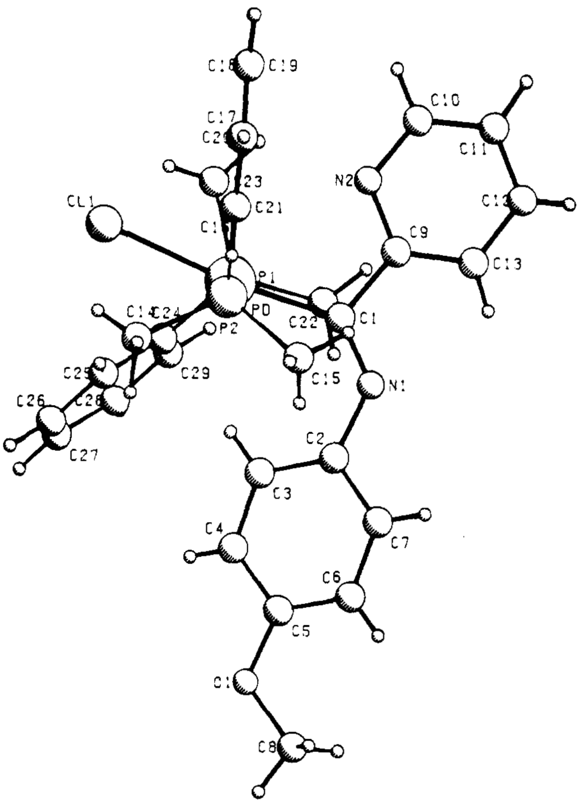

Figure 3. Molecular geometry of *trans*-[PdCl{C(2-C_5H_4N)=NC_6H_4OMe-*p*}($PMe_2Ph)_2$] viewed parallel to the N1)–C(1)–C(9) plane (Pluto drawing).

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-$(PEt_3)_2$ (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-C_5H_4N)=NC_6H_4OMe-*p*}-$(PMe_2Ph)_2$] is composed of four discrete molecules in a monoclinic centrosymmetric cell. Figure 3 is a Pluto drawing[26] 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 PMe_2Ph ligands, to a chlorine atom, and to the imino carbon atom of the [(*p*-methoxyphenyl)imino](2-pyridyl)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 PMe_2Ph 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 Pd–Cl distances of chloride ligands trans to a Pd–C(sp^2) σ bond.[8a] This lengthening suggests that the imino(2-pyridyl)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(sp^2) σ bonds.[8a]

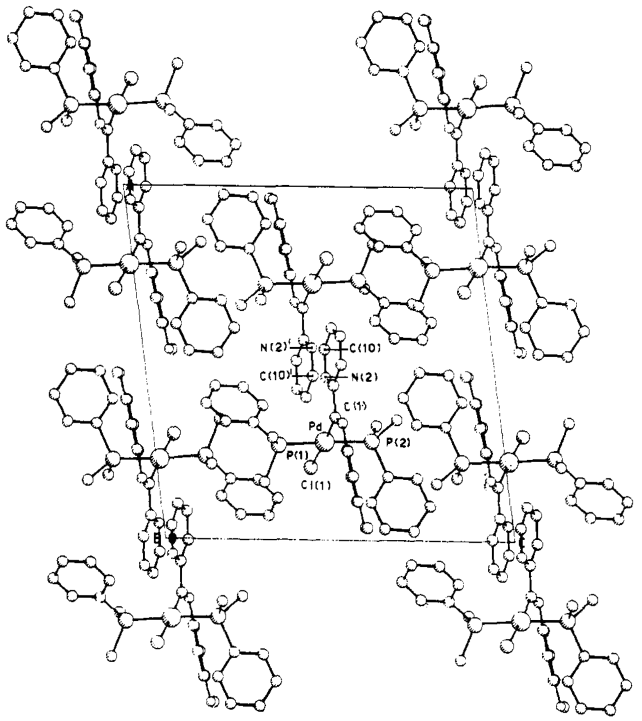

Figure 4. Crystal packing of *trans*-[PdCl{C(2-C_5H_4N)=NC_6H_4OMe-*p*}$(PMe_2Ph)_2$] viewed down the *b* axis (Pluto drawing).

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 (α = 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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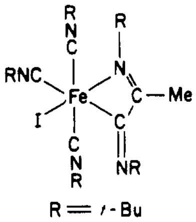
[25] Granozzi, G., personal communication.

[26] Motherwell, W. D. S.; Clegg, W. Pluto 78, A program for plotting molecular and crystal structure; University of Cambridge, England, 1978.

[27] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960.

[28] Bruke-Laing, M.; Laing, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 3216.

and C(2) deviate significantly from the idealized sp^2 value of 120°: Pd–C(1)–N(1) = 133.1 (5)°, Pd–C(1)–C(9) = 112.7 (4)°, N(1)–C(1)–C(9) = 114.3 (5)°, C(1)–N(1)–C(2) = 127.7 (5)°, and N(1)–C(2)–C(3) = 127.2 (5)°. 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) Å, 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) = 2.68 Å) and of a weak bonding interaction with the N(2) 2-pyridyl atom. A four-membered metallacycle with a C,N-chelated 1,2-bis(imino)propyl ligand was proposed for the iron(II) complex:[29]



The structure of *trans*-[PdCl{C(2-C_5H_4N)=NC_6H_4OMe-*p*}$(PMe_2Ph)_2$] accounts also for some features of its ^1H NMR spectrum. Thus, the downfield shift of the C_6H_4OMe-*p* ortho protons clearly results from their close proximity to the d^8 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 PMe_2Ph ligands, even though some contribution of electronic factors, such as a certain degree of $d - \pi^*$ 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$(PEt_3)_2$), 101652-38-4; 5 (R_1 = H), 101652-39-5; *trans*-[PdCl(2-C_5H_5N)$(PMe_2Ph)_2$]Cl, 101652-34-0; *trans*-[PdCl(2-C_5H_5N)$(PEt_3)_2$]Cl, 101652-35-1; *cis*-[$PdCl_2$(2-C_5H_5N)(PPh_3)], 88227-30-9; *p*-$MeOC_6H_4NC$, 10349-38-9; MeNC, 593-75-9; *trans*-[PdCl{C(2-C_5H_4N)=NC_6H_4OMe-*p*}$(PMe_2Ph)_2$], 101670-83-1; *trans*-[PdCl{C(2-C_5H_4N)=NMe}$(PMe_2Ph)_2$], 101670-84-2; *trans*-[PdCl{C(2-C_5H_4N)=NC_6H_4OMe-*p*}$(PEt_3)_2$], 101652-36-2; *trans*-[PdCl{C(2-C_5H_4N)=NMe}$(PEt_3)_2$], 101652-37-3; C_5H_4N-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.

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[29] Bassett, J. M.; Green, M.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1980, 1779.

Reaction of $[P(C_6H_5)_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CHCH_2)]$ 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, $[P(C_6H_5)_4][Fe_3Rh_2(CO)_{10}(\mu\text{-}CO)_3(\mu_4\text{-}\eta^3\text{-}CH_3C=C=CH_2)]$

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$[P(C_6H_5)_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CHCH_2)]$ reacts with $[RhCl(CO)_2]_2$ in the presence of $TlBF_4$ at room temperature to give a 17% yield of $[P(C_6H_5)_4][Fe_3Rh_2(CO)_{10}(\mu\text{-}CO)_3(\mu\text{-}\eta^3\text{-}CH_3C=C=CH_2)]$ (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, β = 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 $RhFe_3$ 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 publication[1] we have shown that the mixed iron–rhodium cluster $HFe_3Rh(CO)_{11}[\mu_4\text{-}\eta^2\text{-}C=CH(C_6H_5)]$, synthesized by the reaction of the $[HFe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C=CHC_6H_5)]^-$ 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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[1] Attali, S.; Mathieu, R. *J. Organomet. Chem.* 1985, *291*, 205–211.

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