voltammetry equipment and explanation and assistance on its use.

Registry No. $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2COFc$, 60349-55-5; $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2COFc$, 54804-00-1; $(\eta^5\text{-}C_5H_5)W(CO)_3COFc$, 52680-31-6; $(\eta^5\text{-}C_5H_5)Fe(CO)_2COFc$, 52462-21-2; $(\eta^5\text{-}C_5H_5)Mo(CO)_3Fc$, 60349-56-6; $(\eta^5\text{-}C_5H_5)Fe(CO)_2Fc$, 11067-36-0; $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2Fc$, 60349-57-7; $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2Fc$, 60349-58-8; $(CO)_5MnCH_2Fc$, 60349-59-9; $W(CO)_6$, 14040-11-0; chloroacetylferrocene, 51862-24-9; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 12154-95-9; $(\eta^5\text{-}C_5H_5)W(CO)_3^-Na^+$, 12107-36-7; chlorocarbonylferrocene, 1293-79-4; chloromethylferrocene, 12093-15-1; $(\eta^5\text{-}C_5H_5)W(CO)_3Fc$, 52472-04-5.

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Reactivity of Cyclopalladated Compounds. 4.[1] Crystal and Molecular Structures of Tetra-*n*-butylammonium Chlorobromo(*N*-(phenylamino)-α-methylbenzylidenimino-2-*C*,*N*)palladate(II) and *trans*-Chloro(*N*-(phenylamino)-α-methylbenzylidenimino-2-*C*,*N*)bis(triethylphosphine)palladium(II)

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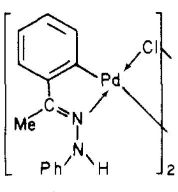
The crystal structures of $[(n\text{-Bu})_4N]^+[Pd(C\text{–}N)ClBr]^-$ and $[Pd(C\text{–}N)(PEt_3)_2Cl]$ where (C–N) is the ligand *N*-(phenylamino)-α-methylbenzylidenimino-2-*C*,*N*, have been determined by single-crystal diffraction methods. The first structure exhibits slight disorder: the halide trans to the carbon atom is 80% bromide and 20% chloride with the reverse proportions trans to the nitrogen atom. A proton of the $[(n\text{-Bu})_4N]^+$ cation belongs to the coordination sphere of the metal atom. The second structure shows that in this compound the direct coordination polyhedron of the palladium atom is not planar and that the ligand is distorted relative to the first structure. The relations between these distortions and the great reactivity of this compound are discussed.

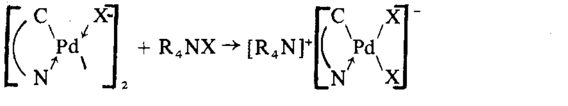
Introduction

The synthesis of metallocyclic compounds and study of their chemical properties have undergone considerable development over the last few years.[4] We are interested in the reactivities of cyclopalladated dimers of the type



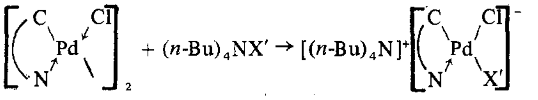
and of the monomers obtained by bridge-cleavage reactions on these dimers.[1,5–7]

According to reactions 1 and 2, addition of tetraalkylammonium halides to cyclopalladated dimers $[Pd(C\text{–}N)X]_2$ leads to two types of compounds.[6] Compounds of the second type are mixed anionic species which can also be synthesized by making use of the lability of pyridine,[8] according to reaction 3. The complexes obtained by reaction 3 are the same as those obtained by reaction 2.



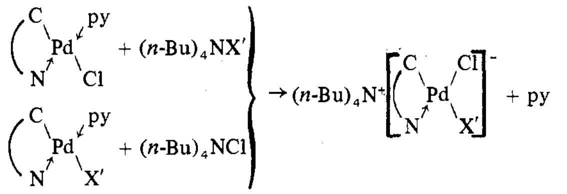
(1)

X = Cl, Br, I
R = Et, *n*-Bu



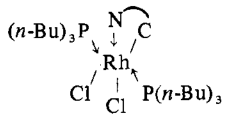
(2)

X′ = Br, I



(3)

Similar results have recently been reported for the compounds[9,10]



where (C–N) = 2-vinylpyridine or benzo[*h*]quinoline.

In these cases also, addition of lithium bromide or lithium iodide causes substitution of the chlorine trans to the carbon while the chlorine trans to the nitrogen cannot be displaced.

The existence of these anionic species was postulated by Parshall[11] as probable intermediates in the cyclometalation mechanism.

Addition of excess triethylphosphine to the dimer $[Pd(C–N)X]_2$ leads to $[Pd(C–N)(PEt_3)_2Cl]$ where nitrogen is no longer coordinated.[1] The substitution of the coordinated nitrogen by a phosphine is well-known in palladocyclic compounds. The x-ray structure of the azobenzene compound $[Pd(azo)(PEt_3)_2Cl]$ has been reported.[12]

Some information on the exchange process between nitrogen and phosphine may be obtained by comparing the crystal structures of $[Pd(C–N)ClBr]^-$, $[Pd(C–N)(PEt_3)_2Cl]$, and the azobenzene complex.

Experimental Section

The complexes were prepared by previously described methods.[1] Suitable single crystals were obtained by slow diffusion of pentane into a saturated solution in dichloromethane of $[(n\text{-Bu})_4N]^+[Pd(C–N)ClBr]^-$ and of $[Pd(C–N)(PEt_3)_2Cl]$, respectively.

Crystals of $[(n\text{-Bu})_4N]^+[Pd(C–N)ClBr]^-$ and $[Pd(C–N)(PEt_3)_2Cl]$ each belong to the monoclinic system. Precession photographs showed for $[(n\text{-Bu})_4N]^+[Pd(C–N)ClBr]^-$ systematic absence for $h0l$ reflections with l odd and $0k0$ reflections with k odd, indicating space group $P2_1/c$. For $[Pd(C–N)(PEt_3)_2Cl]$ possible space groups are $C2/c$ and Cc, the latter being eliminated by statistical tests on the intensity distributions.

The unit cell dimensions and their estimated standard deviations were obtained at room temperature (20 ± 2 °C) with Mo $K\alpha$ radiation (λ 0.709 26 Å) using the method outlined by Busing for a four-circle diffractometer.[13] The experimental densities were measured by flotation in a bromoform–carbon tetrachloride mixture. Final results are summarized: $[(n\text{-Bu})_4N]^+[Pd(C–N)ClBr]^+$, mol wt 673.5, a = 10.260 (2) Å, b = 15.984 (4) Å, c = 19.567 (5) Å, β = 96.48 (2)°, V = 3189 Å^3, d_{obsd} = 1.40 ± 0.02 g cm^{-3}, Z = 4, d_{calcd} = 1.38 g cm^{-3}, $P2_1/c$, μ = 19.6 cm^{-1}; $[Pd(C–N)(PEt_3)_2Cl]$, mol wt 587.4, a = 15.732 (4) Å, b = 18.746 (5) Å, c = 20.285 (5) Å, β = 106.29 (2)°, V = 5742 Å^3, d_{obsd} = 1.33 ± 0.02 g cm^{-3}, Z = 8, d_{calcd} = 1.35 g cm^{-3}, $C2/c$, μ = 8.5 cm^{-1}.

A crystal of each complex was ground to a small sphere of diameter 0.200 mm for $[(n\text{-Bu})_4N]^+[Pd(C–N)ClBr]^-$ and 0.220 mm for $[Pd(C–N)(PEt_3)_2Cl]$, sealed in a Lindemann glass capillary, and mounted on a rotation-free goniometer head.[14] All quantitative data were obtained from a Picker four-circle diffractometer controlled by a PDP-8/I computer, using graphite-monochromated Mo $K\alpha$ radiation. The monochromator was set at a 2θ angle of 11.68°. The refined parameters listed above and the orientation matrix were obtained using standard Picker routines. Intensity data were collected using the θ–2θ scan technique with a scan rate of 2°/min and a scan ranges of 1.8° + tan θ for $[(n\text{-Bu})_4N]^+[Pd(C–N)ClBr]^-$ and 1.7° + tan θ for $[Pd(C–N)(PEt_3)_2Cl]$. Stationary background counts (20 s) were recorded at each end of the scan. Attenuation filters were used whenever the scan count exceeded 7000 counts/s. The intensities of three standard reflections were monitored throughout the data collections at intervals of 75 measurements; their intensities did not vary by more than 2% during the entire data collection periods.

A standard deviation was assigned to each measured intensity using the expression

$$\sigma(I) = \{C + (t_c/t_b)^2(B_1 + B_2) + (pI)^2\}^{1/2}$$

where C is the scan count, B_1 and B_2 are background counts, t_c and t_b are scan and background times, respectively, and p is an empirical coefficient of the net count I.[15] The factor p was given initial values of 0.05. A total of 6123 independent reflections were recorded in the range $2\theta < 50°$ for $[(n\text{-Bu})_4N]^+[Pd(C–N)ClBr]^-$; 3123 had $I > 3\sigma(I)$ and were retained. For $[Pd(C–N)(PEt_3)_2Cl]$, 5120 independent reflections were recorded in the range $2\theta < 60°$; 2444 had $I > 3\sigma(I)$ and were retained. No absorption corrections have been applied in view of the small crystal dimensions (μr = 0.19 and 0.09).

Three-dimensional Patterson maps readily yielded the positions of the heavy atoms. Fourier maps computed using these positions revealed the coordinates of all nonhydrogen atoms.

For all structure factor calculations, the atomic scattering factors used were those tabulated by Moore[16] using Pepinsky's modifications. The effects of anomalous dispersion were included for the Pd, Cl, Br, and P atoms; the values of $\Delta f\,'$ and $\Delta f\,''$ are those given in ref 17. Atomic coordinates and individual anisotropic thermal parameters for all nonhydrogen atoms and occupancy factors were refined by full-matrix least squares using the program SFLS-5.[18] In all least-squares computations, the function minimized was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The weight w was taken as $1/\sigma^2(F_o)$. A p value of 0.08 was used in the latter refinement cycles. Refinement converged to $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$ of 0.038 and 0.038 for $[(n\text{-Bu})_4N]^+[Pd(C–N)ClBr]^-$ and 0.034 and 0.039 for $[Pd(C–N)(PEt_3)_2Cl]$. The standard deviations of unit weight observations were 1.05 and 0.98, respectively.

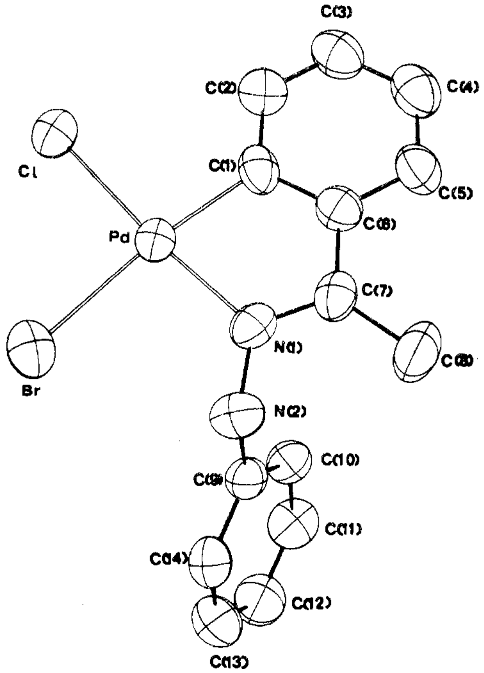


Figure 1. View and numbering scheme for the $[Pd(C–N)ClBr]^-$ ion.

At the end of the isotropic refinement for $[(n\text{-Bu})_4N]^+[Pd(C–N)ClBr]^-$, the temperature factors of the chlorine and bromine atoms were 0.6 and 7.5 e/Å^2, respectively. These values show that the chlorine and bromine sites are not fully occupied by these atoms. Refinement of occupancy yielded 80% of Cl and 20% of Br for the first site (with the sum constrained to be 100%). The reverse values were applied to the chlorine and bromine occupancy factors in the second site.

Fourier difference maps computed at the end of isotropic refinement revealed electron density concentrations close to the calculated positions for hydrogen atoms (C–H = 1 Å, C–C–H = 109.5°). These were introduced in all subsequent calculations with isotropic temperature factors derived from the expression $B_H = 1.6B_C - 2.0$[19] and their coordinates refined. The final difference Fourier maps show no maxima greater than 0.35 e Å^{-3}.

Tables I and II give the atomic coordinates and the anisotropic thermal parameters with their standard deviations for both compounds. Observed and calculated structure factors are listed in Tables III and IV, respectively (F_o and F_c times 10) (supplementary material).

Results and Discussion

1. $[(n\text{-Bu})_4]^+[Pd(C–N)ClBr]^-$. Selected bond distances and angles with their esd's are listed in Table V. The structure can be described as an arrangement of $[Pd(C–N)ClBr]^-$ and $[(n\text{-Bu})_4N]^+$ ions. Views of the Pd coordination polyhedra are shown in Figures 1 and 2.

The palladium atom is directly coordinated to five atoms: Cl, Br, C(1), N(1), and H1C27 forming a square prism. The Pd–C(1) and Pd–N(1) distances and the C(1)–Pd–N(1) angle are similar to those found in related compounds.[21–26]

As mentioned above, this structure could only be refined

Table I. Atomic Coordinates and Temperature Factors with Esd's for $[(n\text{-Bu})_4N]^+[Pd(C\text{-}N)ClBr]^-$ [a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	0.200 10 (5)	0.424 54 (2)	0.256 69 (2)	0.0408 (3)	0.0338 (2)	0.0455 (3)	−0.0017 (2)	0.0000 (2)	0.0041 (3)
Br	−0.013 0 (1)	0.453 75 (7)	0.306 80 (5)	0.0517 (6)	0.0588 (6)	0.0812 (7)	0.0018 (4)	0.0065 (6)	0.0075 (6)
Cl	0.090 4 (1)	0.383 98 (7)	0.146 73 (5)	0.0563 (6)	0.0627 (6)	0.0554 (7)	−0.0025 (4)	−0.0052 (5)	−0.0017 (4)
N(1)	0.308 1 (5)	0.457 5 (3)	0.345 3 (2)	0.057 (3)	0.048 (3)	0.044 (3)	−0.001 (2)	−0.002 (2)	0.004 (2)
N(2)	0.252 6 (5)	0.481 3 (3)	0.405 5 (2)	0.068 (4)	0.055 (3)	0.048 (3)	0.007 (3)	0.007 (3)	−0.001 (3)
C(1)	0.378 8 (6)	0.411 1 (4)	0.229 1 (3)	0.042 (4)	0.045 (4)	0.066 (4)	−0.007 (3)	0.004 (3)	0.010 (3)
C(2)	0.418 7 (7)	0.384 7 (4)	0.167 5 (4)	0.064 (5)	0.053 (4)	0.059 (5)	0.001 (3)	0.009 (4)	−0.002 (4)
C(3)	0.549 5 (8)	0.381 6 (4)	0.156 8 (4)	0.065 (5)	0.068 (5)	0.074 (5)	0.009 (4)	0.022 (4)	0.001 (4)
C(4)	0.648 1 (8)	0.405 2 (4)	0.208 1 (4)	0.058 (4)	0.063 (5)	0.086 (6)	0.001 (3)	0.014 (4)	0.018 (4)
C(5)	0.611 6 (6)	0.434 4 (4)	0.271 0 (4)	0.052 (5)	0.072 (5)	0.071 (5)	−0.011 (4)	0.011 (4)	0.010 (4)
C(6)	0.478 5 (6)	0.435 9 (4)	0.280 2 (3)	0.054 (4)	0.050 (4)	0.053 (4)	−0.001 (3)	0.010 (3)	0.003 (3)
C(7)	0.435 9 (6)	0.464 0 (4)	0.344 6 (3)	0.049 (4)	0.046 (4)	0.054 (4)	−0.005 (3)	−0.007 (3)	0.013 (3)
C(8)	0.523 5 (8)	0.498 2 (5)	0.404 4 (4)	0.069 (5)	0.086 (6)	0.066 (5)	−0.018 (5)	−0.019 (4)	0.001 (4)
C(9)	0.253 8 (6)	0.421 1 (4)	0.458 0 (3)	0.049 (4)	0.056 (4)	0.042 (3)	−0.015 (3)	0.004 (3)	−0.004 (3)
C(10)	0.334 6 (6)	0.352 1 (4)	0.463 7 (3)	0.057 (4)	0.046 (4)	0.050 (4)	−0.000 (3)	0.003 (3)	−0.005 (3)
C(11)	0.328 8 (8)	0.297 5 (4)	0.519 9 (4)	0.081 (6)	0.051 (5)	0.068 (5)	−0.007 (4)	0.004 (4)	0.007 (4)
C(12)	0.245 8 (8)	0.311 6 (5)	0.569 5 (4)	0.079 (6)	0.078 (6)	0.068 (6)	−0.015 (5)	0.010 (5)	0.016 (4)
C(13)	0.165 7 (8)	0.382 2 (6)	0.562 8 (4)	0.062 (5)	0.096 (7)	0.072 (6)	−0.018 (5)	0.019 (4)	−0.000 (5)
C(14)	0.171 3 (6)	0.437 3 (5)	0.508 7 (3)	0.046 (4)	0.071 (5)	0.061 (4)	−0.011 (3)	0.003 (3)	−0.003 (4)
N(3)	0.054 7 (5)	0.168 2 (3)	0.348 8 (2)	0.065 (3)	0.045 (3)	0.045 (3)	−0.010 (2)	0.014 (2)	0.000 (2)
C(15)	0.073 1 (6)	0.083 8 (3)	0.385 3 (3)	0.070 (4)	0.039 (3)	0.065 (4)	−0.008 (3)	0.015 (3)	0.009 (3)
C(16)	0.175 7 (7)	0.080 6 (4)	0.446 7 (3)	0.090 (5)	0.074 (5)	0.071 (5)	−0.014 (4)	−0.004 (4)	0.020 (4)
C(17)	0.196 8 (7)	−0.010 7 (5)	0.470 5 (4)	0.076 (5)	0.079 (5)	0.099 (6)	−0.006 (4)	−0.016 (4)	0.035 (5)
C(18)	0.309 0 (8)	−0.023 3 (5)	0.523 3 (5)	0.094 (6)	0.089 (6)	0.139 (8)	0.005 (5)	−0.009 (6)	0.010 (6)
C(19)	0.009 6 (6)	0.235 7 (4)	0.395 7 (3)	0.059 (4)	0.058 (4)	0.061 (4)	−0.006 (3)	0.016 (3)	−0.020 (3)
C(20)	−0.121 8 (6)	0.221 0 (4)	0.421 0 (3)	0.057 (4)	0.080 (5)	0.089 (5)	−0.004 (4)	0.025 (4)	−0.018 (4)
C(21)	−0.156 2 (8)	0.299 4 (5)	0.463 3 (4)	0.081 (6)	0.113 (7)	0.089 (6)	−0.002 (5)	0.040 (5)	−0.026 (5)
C(22)	−0.290 3 (8)	0.295 5 (6)	0.486 4 (5)	0.087 (6)	0.154 (9)	0.118 (8)	0.015 (6)	0.014 (6)	−0.000 (6)
C(23)	−0.046 3 (7)	0.151 9 (4)	0.286 5 (3)	0.068 (5)	0.045 (4)	0.057 (4)	−0.009 (3)	−0.005 (4)	0.000 (3)
C(24)	−0.082 2 (8)	0.229 1 (4)	0.242 8 (4)	0.094 (6)	0.057 (5)	0.068 (5)	−0.010 (4)	−0.010 (5)	0.001 (4)
C(25)	−0.166 5 (8)	0.205 1 (5)	0.175 9 (4)	0.083 (6)	0.079 (6)	0.062 (5)	−0.018 (5)	0.002 (4)	0.003 (4)
C(26)	−0.301 (1)	0.174 8 (5)	0.188 2 (5)	0.100 (7)	0.059 (5)	0.104 (8)	−0.015 (5)	−0.000 (6)	0.003 (5)
C(27)	0.183 9 (7)	0.199 0 (4)	0.326 9 (3)	0.065 (5)	0.044 (4)	0.065 (5)	−0.013 (3)	0.018 (4)	0.000 (3)
C(28)	0.247 1 (7)	0.142 8 (5)	0.278 0 (4)	0.073 (5)	0.072 (5)	0.063 (5)	−0.008 (4)	0.019 (4)	−0.013 (4)
C(29)	0.386 1 (8)	0.171 3 (5)	0.269 3 (4)	0.060 (5)	0.086 (6)	0.081 (6)	−0.004 (5)	0.026 (4)	−0.002 (5)
C(30)	0.481 1 (9)	0.154 (1)	0.333 3 (7)	0.070 (7)	0.18 (1)	0.121 (9)	0.006 (8)	0.001 (7)	−0.027 (8)

	x	y	z	B, Å^2		x	y	z	B, Å^2
HC2	0.359 (7)	0.369 (4)	0.123 (3)	0.07	H2C20	−0.112 (8)	0.166 (5)	0.455 (4)	0.11
HC3	0.590 (7)	0.354 (4)	0.109 (3)	0.08	H1C21	−0.11 (1)	0.281 (6)	0.506 (5)	0.12
HC4	0.741 (8)	0.402 (4)	0.201 (3)	0.08	H2C21	−0.168 (9)	0.353 (6)	0.426 (4)	0.12
HC5	0.686 (7)	0.450 (4)	0.314 (3)	0.07	H1C22	−0.32 (1)	0.237 (6)	0.484 (5)	0.13
H1C8	0.50 (1)	0.545 (7)	0.419 (5)	0.14	H2C22	−0.351 (9)	0.332 (6)	0.456 (5)	0.13
H2C8	0.61 (1)	0.514 (7)	0.387 (5)	0.14	H3C22	−0.29 (1)	0.316 (7)	0.535 (5)	0.13
H3C8	0.58 (1)	0.458 (6)	0.437 (5)	0.14	H1C23	−0.006 (7)	0.105 (4)	0.261 (3)	0.07
HN2	0.151 (7)	0.500 (4)	0.389 (3)	0.06	H2C23	−0.128 (7)	0.124 (4)	0.306 (3)	0.07
HC10	0.404 (6)	0.333 (4)	0.427 (3)	0.06	H1C24	−0.139 (8)	0.271 (5)	0.268 (4)	0.09
HC11	0.386 (8)	0.252 (5)	0.524 (4)	0.08	H2C24	0.007 (8)	0.247 (5)	0.231 (4)	0.09
HC12	0.236 (7)	0.266 (5)	0.611 (4)	0.09	H1C25	−0.174 (8)	0.259 (5)	0.145 (4)	0.10
HC13	0.112 (8)	0.387 (5)	0.608 (4)	0.10	H2C25	−0.129 (8)	0.154 (5)	0.154 (4)	0.10
HC14	0.116 (6)	0.493 (4)	0.505 (3)	0.06	H1C26	−0.351 (8)	0.160 (5)	0.143 (4)	0.09
H1C15	−0.015 (7)	0.070 (4)	0.396 (3)	0.07	H2C26	−0.327 (8)	0.222 (5)	0.226 (4)	0.09
H2C15	0.094 (7)	0.037 (4)	0.348 (3)	0.07	H3C26	−0.295 (8)	0.125 (5)	0.214 (4)	0.09
H1C16	0.267 (8)	0.090 (5)	0.432 (4)	0.09	H1C27	0.169 (6)	0.256 (4)	0.301 (3)	0.06
H2C16	0.146 (8)	0.115 (5)	0.485 (4)	0.09	H2C27	0.244 (7)	0.211 (4)	0.366 (3)	0.06
H1C17	0.116 (8)	−0.032 (5)	0.477 (4)	0.10	H1C28	0.248 (7)	0.084 (5)	0.292 (3)	0.08
H2C17	0.241 (8)	−0.050 (5)	0.435 (4)	0.10	H2C28	0.194 (7)	0.146 (5)	0.230 (4)	0.08
H1C18	0.381 (9)	0.021 (6)	0.508 (5)	0.13	H1C29	0.409 (8)	0.137 (5)	0.225 (4)	0.10
H2C18	0.32 (1)	−0.078 (6)	0.536 (5)	0.13	H2C29	0.377 (9)	0.226 (5)	0.258 (4)	0.10
H3C18	0.247 (9)	0.016 (6)	0.571 (4)	0.13	H1C30	0.571 (9)	0.145 (6)	0.320 (5)	0.13
H1C19	0.080 (7)	0.245 (4)	0.438 (3)	0.06	H2C30	0.45 (1)	0.103 (8)	0.357 (6)	0.13
H2C19	0.017 (7)	0.289 (4)	0.368 (3)	0.06	H3C30	0.482 (9)	0.203 (6)	0.365 (5)	0.13
H1C20	−0.194 (8)	0.209 (5)	0.378 (4)	0.11					

[a] Anisotropic temperature factors are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

by allowing 80% occupancy for bromine and 20% for chlorine in the positions trans to carbon C(1). Therefore, the Pd–Cl and Pd–Br distances of 2.402 (1) and 2.538 (1) Å are affected and differ from those found in related compounds (2.31[21,27] and 2.58 Å[28]).

As shown in Table VI, the five atoms Pd, Cl, Br, C(1), and N(1) are roughly planar. The Pd–H1C27 distance of 2.86 (7) Å is shorter than the sum of the van der Waals radii of Pd and H (3.1 Å) but corresponds only to a weak interaction between these atoms compared to that found by Cotton[29] and Maitlis[30] where the distances Mo–H and Pd–H are 2.2 and 2.3 Å, respectively.

The two phenyl rings are planar within experimental error and their geometry is normal (see Tables V and VI). The angle between the planes of the two rings is 107.1°.

The values in Table V show that the geometry of the $[(n\text{-Bu})_4N]^+$ ions is normal. The bromine atom is bonded to hydrogen HN (2) at a distance of 2.31 Å. Anions and cations

Table II. Atomic Coordinates and Temperature Factors with Esd's for [Pd(C-N)(PEt$_3$)$_2$Cl][a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	0.212 01 (3)	0.033 60 (1)	0.130 58 (1)	0.0350 (4)	0.0343 (1)	0.0247 (1)	−0.0021 (2)	0.0062 (1)	0.0008 (1)
Cl	0.190 2 (1)	0.094 08 (7)	0.022 23 (5)	0.068 (1)	0.0518 (8)	0.0329 (5)	0.0047 (8)	0.0116 (7)	0.0089 (5)
P(1)	0.265 0 (1)	−0.064 76 (7)	0.085 91 (7)	0.046 (2)	0.0457 (7)	0.0339 (7)	0.0021 (8)	0.0106 (8)	0.0014 (5)
C1P1	0.205 5 (6)	−0.088 7 (3)	−0.002 6 (2)	0.063 (9)	0.050 (3)	0.037 (2)	0.008 (4)	0.015 (3)	−0.003 (2)
C2P1	0.112 3 (7)	−0.116 9 (4)	−0.009 6 (3)	0.05 (1)	0.094 (6)	0.049 (3)	−0.014 (5)	0.007 (4)	−0.018 (3)
C3P1	0.281 4 (6)	−0.148 4 (3)	0.133 0 (3)	0.06 (1)	0.050 (3)	0.061 (3)	0.024 (4)	0.036 (4)	0.013 (2)
C4P1	0.317 6 (7)	−0.211 2 (4)	0.097 2 (4)	0.12 (1)	0.067 (4)	0.069 (5)	0.038 (5)	0.041 (5)	0.016 (3)
C5P1	0.372 9 (5)	−0.040 9 (4)	0.077 8 (3)	0.048 (8)	0.078 (4)	0.055 (3)	−0.008 (4)	0.026 (4)	−0.003 (3)
C6P1	0.445 8 (6)	−0.029 0 (6)	0.147 5 (5)	0.03 (1)	0.124 (8)	0.104 (6)	0.001 (7)	0.009 (5)	−0.013 (5)
P(2)	0.196 3 (1)	0.143 33 (7)	0.180 21 (7)	0.045 (1)	0.0407 (7)	0.0379 (7)	−0.0057 (8)	0.0105 (8)	−0.0043 (5)
C1P2	0.208 6 (5)	0.150 2 (3)	0.272 6 (2)	0.048 (7)	0.062 (4)	0.037 (2)	−0.013 (4)	0.020 (3)	−0.011 (2)
C2P2	0.133 2 (6)	0.115 1 (4)	0.295 1 (3)	0.07 (1)	0.067 (4)	0.061 (4)	−0.007 (4)	0.039 (5)	−0.011 (3)
C3P2	0.283 0 (6)	0.203 9 (3)	0.168 8 (3)	0.052 (9)	0.053 (3)	0.066 (4)	−0.018 (4)	0.025 (4)	−0.007 (3)
C4P2	0.375 (1)	0.176 8 (6)	0.198 2 (7)	0.04 (1)	0.10 (1)	0.093 (6)	−0.014 (8)	0.013 (5)	0.008 (6)
C5P2	0.093 0 (5)	0.190 1 (3)	0.140 5 (3)	0.041 (7)	0.055 (3)	0.061 (3)	0.012 (3)	0.006 (4)	−0.002 (3)
C6P2	0.084 0 (7)	0.266 4 (4)	0.167 3 (4)	0.07 (1)	0.071 (5)	0.106 (6)	0.025 (5)	0.028 (6)	−0.007 (4)
C(1)	0.220 0 (4)	−0.019 8 (2)	0.217 9 (2)	0.034 (6)	0.041 (3)	0.033 (2)	0.002 (3)	0.006 (2)	0.000 (2)
C(2)	0.292 5 (5)	−0.013 1 (3)	0.275 6 (2)	0.046 (7)	0.054 (3)	0.040 (2)	0.003 (3)	0.009 (3)	−0.000 (2)
C(3)	0.295 7 (5)	−0.046 4 (3)	0.337 4 (2)	0.047 (7)	0.062 (4)	0.039 (2)	0.009 (4)	0.001 (3)	0.005 (2)
C(4)	0.227 0 (5)	−0.089 2 (3)	0.342 3 (2)	0.059 (7)	0.057 (3)	0.037 (2)	0.002 (4)	0.008 (3)	0.008 (2)
C(5)	0.154 9 (5)	−0.100 3 (2)	0.285 3 (2)	0.045 (7)	0.050 (3)	0.042 (2)	0.003 (3)	0.019 (3)	0.003 (2)
C(6)	0.150 9 (4)	−0.066 3 (2)	0.222 9 (2)	0.039 (6)	0.036 (2)	0.032 (2)	0.005 (3)	0.009 (2)	−0.003 (2)
C(7)	0.072 2 (4)	−0.082 7 (2)	0.164 3 (2)	0.037 (6)	0.040 (3)	0.039 (2)	−0.010 (3)	0.013 (2)	−0.001 (2)
C(8)	0.010 1 (6)	−0.024 8 (3)	0.130 1 (3)	0.061 (7)	0.037 (3)	0.061 (3)	−0.003 (3)	−0.002 (4)	−0.000 (2)
N(1)	0.062 2 (3)	−0.150 3 (2)	0.150 8 (2)	0.048 (5)	0.049 (2)	0.043 (2)	−0.009 (2)	0.004 (2)	−0.005 (2)
N(2)	−0.011 7 (4)	−0.172 5 (2)	0.101 3 (2)	0.050 (5)	0.042 (2)	0.058 (3)	−0.002 (2)	−0.000 (2)	−0.006 (2)
C(9)	−0.010 7 (5)	−0.243 2 (2)	0.077 5 (2)	0.051 (7)	0.038 (3)	0.044 (3)	−0.002 (3)	0.014 (3)	0.004 (2)
C(10)	−0.087 7 (5)	−0.269 5 (3)	0.032 6 (2)	0.046 (7)	0.055 (3)	0.044 (3)	−0.011 (3)	0.005 (3)	0.003 (2)
C(11)	−0.087 5 (6)	−0.338 1 (4)	0.008 9 (3)	0.070 (9)	0.071 (4)	0.063 (4)	−0.027 (5)	0.012 (4)	−0.014 (3)
C(12)	−0.015 7 (6)	−0.382 2 (3)	0.028 0 (3)	0.085 (9)	0.047 (3)	0.073 (4)	−0.006 (4)	0.034 (4)	−0.013 (3)
C(13)	0.062 2 (5)	−0.355 9 (3)	0.073 6 (3)	0.062 (8)	0.046 (3)	0.074 (4)	0.001 (3)	0.011 (4)	−0.001 (3)
C(14)	0.064 4 (5)	−0.285 5 (3)	0.098 9 (3)	0.045 (7)	0.048 (3)	0.060 (3)	−0.005 (3)	0.008 (3)	−0.008 (2)

	x	y	z	B, Å^2		x	y	z	B, Å^2
H1C1P1	0.199 (4)	−0.045 (3)	−0.030 (3)	0.04	H1C4P2	0.425 (6)	0.218 (4)	0.193 (4)	0.09
H2C1P1	0.243 (4)	−0.129 (3)	−0.017 (3)	0.04	H2C4P2	0.383 (5)	0.165 (4)	0.253 (4)	0.09
H1C2P1	0.084 (5)	−0.131 (3)	−0.053 (3)	0.07	H3C4P2	0.38 (1)	0.137 (6)	0.186 (7)	0.09
H2C2P1	0.074 (6)	−0.083 (4)	0.006 (3)	0.07	H1C5P2	0.084 (5)	0.188 (3)	0.087 (3)	0.07
H3C2P1	0.111 (5)	−0.174 (3)	0.016 (3)	0.07	H2C5P2	0.037 (5)	0.155 (4)	0.145 (3)	0.07
H1C3P1	0.225 (6)	−0.165 (3)	0.148 (3)	0.06	H1C6P2	0.020 (7)	0.287 (4)	0.141 (4)	0.11
H2C3P1	0.331 (6)	−0.169 (5)	0.134 (4)	0.06	H2C6P2	0.146 (7)	0.293 (4)	0.166 (4)	0.11
H1C4P1	0.350 (7)	−0.194 (5)	0.075 (5)	0.10	H3C6P2	0.083 (6)	0.270 (4)	0.218 (4)	0.11
H2C4P1	0.265 (6)	−0.229 (4)	0.050 (4)	0.10	HC2	0.344 (5)	0.018 (3)	0.272 (3)	0.05
H3C4P1	0.341 (6)	−0.249 (4)	0.135 (4)	0.10	HC3	0.357 (5)	−0.037 (3)	0.373 (3)	0.06
H1C5P1	0.397 (5)	−0.084 (3)	0.051 (3)	0.06	HC4	0.232 (4)	−0.109 (3)	0.387 (3)	0.05
H2C5P1	0.367 (5)	0.006 (3)	0.046 (3)	0.06	HC5	0.099 (5)	−0.131 (3)	0.289 (3)	0.05
H1C6P1	0.501 (8)	−0.017 (5)	0.139 (5)	0.12	H1C8	−0.037 (5)	−0.040 (3)	0.097 (3)	0.05
H2C6P1	0.448 (6)	−0.077 (4)	0.178 (4)	0.12	H2C8	0.026 (5)	−0.010 (3)	0.095 (3)	0.05
H3C6P1	0.411 (7)	0.008 (5)	0.166 (5)	0.12	H3C8	0.013 (4)	0.019 (3)	0.152 (3)	0.05
H1C1P2	0.269 (5)	0.123 (3)	0.299 (3)	0.05	HN2	−0.056 (4)	−0.140 (3)	0.072 (3)	0.06
H2C1P2	0.227 (4)	0.209 (3)	0.284 (3)	0.05	HC10	−0.143 (4)	−0.235 (3)	0.016 (3)	0.05
H1C2P2	0.127 (5)	0.059 (3)	0.284 (3)	0.06	HC11	−0.143 (5)	−0.358 (3)	−0.016 (3)	0.08
H2C2P2	0.080 (6)	0.138 (4)	0.283 (3)	0.06	HC12	−0.016 (4)	−0.437 (3)	0.014 (3)	0.07
H3C2P2	0.156 (4)	0.115 (3)	0.352 (3)	0.06	HC13	0.122 (5)	−0.391 (3)	0.097 (3)	0.07
H1C3P2	0.272 (4)	0.212 (3)	0.114 (3)	0.06	HC14	0.121 (5)	−0.267 (3)	0.128 (3)	0.05
H2C3P2	0.272 (5)	0.257 (3)	0.195 (3)	0.06					

[a] Anisotropic temperature factors are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

are held together by the Pd–H1C27 bond already described. Table VII gives selected packing distances (less than 3.20 Å) which are essentially hydrogen bonds.

The infrared frequencies of the ν(Pd–X) vibrations are characteristic of a chlorine trans to nitrogen: ν(Pd–Cl) 349 cm^{-1} for X′ = Br and 347 cm^{-1} for X′ = I, whereas the ν(Pd–X′) are characteristic of a bromine or an iodine trans to carbon (ν(Pd–Br) 178 cm^{-1}, ν(Pd–I) 162 cm^{-1})[6]. These results do not show any mixed occupancy trans to carbon as found in the crystal structure.

This structure shows that substitution may partly occur trans to nitrogen; the trans effect of the σ-bonded carbon is not strong enough to prevent this partial substitution. Once the anionic cyclopalladated species is formed, no further substitution occurs by the excess bromine present in the solution.

2. [Pd(C–N)(PEt$_3$)$_2$Cl]. This structure is molecular as is shown in Figure 3. (For the PEt$_3$, only the P atoms are drawn.) Selected bond distances and angles with their esd's are given in Table VIII.

As in the structure of [n-Bu$_4$N]$^+$[Pd(C–N)ClBr]$^-$, the palladium atom is coordinated to five atoms Cl, P(1), P(2), C(1), and H2C8, but the five atoms Pd, Cl, P(1), P(2), and C(1) are not coplanar as shown in Table IX; the deviations from a mean plane are significant. The H2C8 hydrogen atom is near the "normal" of mean plane 1 of Table IX through the palladium atom. By contrast with the previous structure, no other atom of the (C–N) ligand is coordinated to the Pd atom, the Pd–N(1) distance being greater than 4 Å and the C(1)–C(6) phenyl ring making an angle of 104.3° with plane 1 of Table IX. The two phenyl rings have normal geometry

Table V. Selected Interatomic Distances (Å) and Bond Angles (deg) with Esd's for $[(n\text{-Bu})_4N]^+[Pd(C\text{–}N)ClBr]^-$

Pd–Cl	2.402 (1)	Cl–Pd–Br	93.37 (0.04)
Pd–Br	2.538 (1)	Cl–Pd–N(1)	174.71 (0.15)
Pd–N(1)	2.020 (5)	Br–Pd–C(1)	171.66 (0.17)
Pd–C(1)	1.981 (6)	Cl–Pd–C(1)	91.65 (0.15)
Pd–H1C27	2.86 (7)	Br–Pd–N(1)	91.90 (0.12)
C(1)–C(2)	1.383 (9)	C(1)–Pd–N(1)	80.07 (0.23)
C(2)–C(3)	1.383 (9)	H1C27–Pd–C(1)	96 (2)
C(3)–C(4)	1.39 (3)	H1C27–Pd–N(1)	93 (2)
C(4)–C(5)	1.40 (1)	H1C27–Pd–Cl	87 (2)
C(5)–C(6)	1.39 (1)	H1C27–Pd–Br	85 (2)
C(6)–C(1)	1.404 (9)	C(1)–C(6)–C(7)	116.06 (0.59)
C(6)–C(7)	1.452 (9)	C(5)–C(6)–C(7)	126.76 (0.63)
C(7)–C(8)	1.49 (1)	C(6)–C(7)–C(8)	125.37 (0.67)
C(7)–N(1)	1.317 (9)	C(6)–C(7)–N(1)	112.49 (0.57)
N(1)–N(2)	1.415 (8)	C(8)–C(7)–N(1)	122.13 (0.66)
N(2)–C(9)	1.407 (8)	C(7)–N(1)–N(2)	118.81 (0.57)
C(9)–C(10)	1.377 (9)	N(1)–N(2)–C(9)	116.92 (0.54)
C(10)–C(11)	1.40 (1)	N(2)–C(9)–C(10)	124.21 (0.60)
C(11)–C(12)	1.38 (1)	C(14)–C(9)–N(2)	115.81 (0.59)
C(12)–C(13)	1.39 (1)		
C(13)–C(14)	1.38 (1)		
C(14)–C(9)	1.39 (1)		

Mean Distances

$$[(n\text{-Bu})_4N]^+\begin{cases} N\text{–}C = 1.525\ (4) \\ C\text{–}C = 1.518\ (13) \end{cases}$$

Mean Angles

$$[(n\text{-Bu})_4N]^+\begin{cases} C\text{–}N\text{–}C = 105.44\ (0.25) \\ N\text{–}C\text{–}C = 115.41\ (0.25) \\ C\text{–}C\text{–}C = 111.53\ (0.30) \end{cases}$$

Table VI. Least-Squares Planes and Deviations Therefrom for $[(n\text{-Bu})_4N]^+[Pd(C\text{–}N)ClBr]^-$

Plane	Atom	Dev, Å	Plane	Atom	Dev, Å	Plane	Atom	Dev, Å
1	Pd	−0.0011 (5)	2	C(1)	−0.004 (6)	3	C(9)	0.011 (6)
	Br	0.001 (1)		C(2)	0.006 (7)		C(10)	−0.005 (7)
	Cl	0.000 (1)		C(3)	0.002 (7)		C(11)	−0.002 (8)
	N(1)	0.013 (5)		C(4)	−0.011 (7)		C(12)	−0.002 (9)
	C(1)	0.074 (6)		C(5)	0.009 (7)		C(13)	0.009 (8)
				C(6)	−0.001 (6)		C(14)	−0.014 (7)

Interplanar Angle: Plane 2–Plane 3 = 107.1°

Distances (Å) of Other Atoms from the Planes

Plane 1: N(2), −0.033 (5); HN(2), 0.30 (3); C(8), 0.393 (9); C(7), 0.193 (6); C(6), 0.193 (6)
Plane 2: Pd, 0.0496 (5); Br, 0.196 (1); Cl, 0.209 (1); N(1), −0.079 (5); N(2), −0.117 (5)
Plane 3: N(2), −0.022 (5); N(1), 0.335 (5)

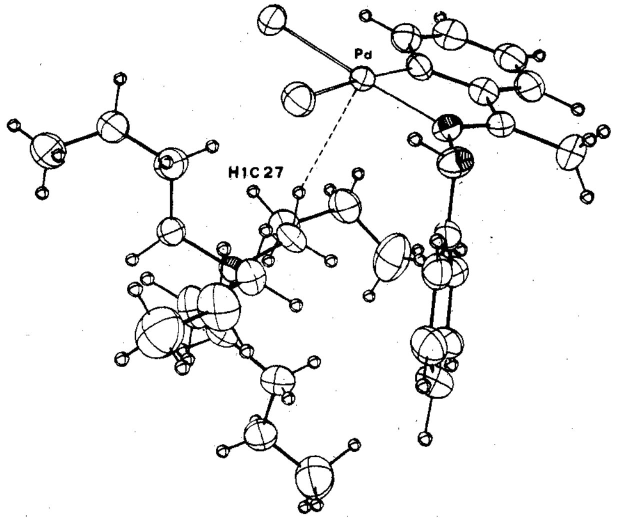


Figure 2. View of the complete coordination polyhedra of Pd in $[(n\text{-Bu})_4N]^+[Pd(C\text{–}N)ClBr]^-$.

Table VII. Selected Packing Distances (Å) for $[(n\text{-Bu})_4N]^+[Pd(C\text{–}N)ClBr]^-$

Br–H1C23	III[a]	2.77 (7)	C(8)–H1C26	III	3.21 (8)
Cl–H3C18	II	2.80 (10)	C(9)–H3C8	IV	3.17 (10)
Cl–HC12	II	2.95 (8)	C(10)–H1C8	IV	3.16 (10)
Cl–H2C15	III	3.10 (7)	C(13)–H2C8	IV	2.95 (10)
Cl–H1C15	III	3.15 (7)	C(14)–H2C8	IV	2.99 (10)
N(1)–H3C26	III	2.91 (9)	C(14)–H3C8	IV	3.13 (10)
N(2)–H2C25	III	3.19 (8)	C(14)–H3C8	IV	3.13 (7)
C(2)–H3C18	II	2.91 (9)	C(17)–H2C20	IV	3.06 (9)
C(2)–HC12	II	3.17 (8)	C(18)–H2C20	IV	3.11 (9)
C(3)–H2C17	III	3.15 (9)	C(18)–HC2	II	3.15 (7)
C(4)–H1C27	III	3.04 (8)	C(25)–H3C22	II	3.15 (7)
C(5)–H1C28	III	3.10 (8)	C(26)–H3C32	II	3.02 (10)
C(7)–H3C26	III	3.11 (8)			

[a] The Roman numerals give the number of the equivalent positions as in ref 32.

within experimental error and their planes are at an angle of 74.8°.

Table X gives the intermolecular distances less than 3.20 Å. The molecules in the unit cell are linked together by hydrogen bonds.

The other important difference between the two structures is that in the latter, the ligand appears to have rotated about the C(6)–C(7) bond so that the N(1) atom is no longer near the palladium atom, thus allowing hydrogen H2C8 to interact with the metal atom.

The complex decomposes at 60 °C with the loss of one of its phosphine ligands.[1] The following reaction takes place in dichloromethane, in the presence of the dimer

$$2[Pd(C\text{–}N)(PEt_3)_2Cl] + [Pd(C\text{–}N)Cl]_2 \rightarrow 4[Pd(C\text{–}N)(PEt_3)Cl]$$

Similar behavior has recently been observed for $[Pt(C\text{–}N)(P\text{–}Ph_2Me)_2Cl]$ ((C–N) = 2-(phenylazo)phenyl)[31] in which there is ^1H NMR evidence of phosphine lability. The recoordination of nitrogen was explained by an intramolecular nucleophilic substitution mechanism.

Table VIII. Selected Interatomic Distances (Å) and Bond Angles (deg) with Esd's for $[Pd(C\text{-}N)(PEt_3)_2Cl]$

Pd–Cl	2.411 (1)	Cl–Pd–P(1)	89.57 (0.07)
Pd–P(1)	2.311 (1)	P(1)–Pd–P(2)	165.01 (0.09)
Pd–P(2)	2.334 (1)	Cl–Pd–C(1)	175.31 (0.19)
Pd–C(1)	2.008 (5)	P(1)–Pd–C(1)	90.44 (0.15)
Pd–H2C8	2.92 (8)	Cl–Pd–P(2)	88.48 (0.07)
C(1)–C(2)	1.391 (7)	C(1)–Pd–P(2)	92.71 (0.15)
C(2)–C(3)	1.389 (8)	H2C8–Pd–C(1)	83 (2)
C(3)–C(4)	1.37 (1)	H2C8–Pd–P(1)	97 (2)
C(4)–C(5)	1.389 (8)	H2C8–Pd–P(2)	83 (2)
C(5)–C(6)	1.402 (7)	H2C8–Pd–Cl	92 (2)
C(6)–C(1)	1.419 (9)	C(1)–C(6)–C(7)	123.46 (0.56)
C(6)–C(7)	1.488 (7)	C(5)–C(6)–C(7)	116.39 (0.57)
C(7)–C(8)	1.495 (8)	C(6)–C(7)–C(8)	120.71 (0.61)
C(7)–N(1)	1.298 (6)	C(6)–C(7)–N(1)	113.25 (0.54)
N(1)–N(2)	1.370 (6)	C(8)–C(7)–N(1)	125.89 (0.63)
N(2)–C(9)	1.413 (7)	C(7)–N(1)–N(2)	118.60 (0.55)
C(9)–C(10)	1.386 (9)	N(1)–N(2)–C(9)	116.50 (0.55)
C(10)–C(11)	1.373 (9)	N(2)–C(9)–C(10)	117.79 (0.61)
C(11)–C(12)	1.36 (1)	C(14)–C(9)–N(2)	121.32 (0.63)
C(12)–C(13)	1.40 (1)		
C(13)–C(14)	1.413 (8)		
C(14)–C(9)	1.38 (1)		

Mean Angles

$$\mathrm{PEt_3}\left\{\begin{array}{l}\mathrm{P\text{–}C\text{–}C} = 114.61\ (0.25)\\ \mathrm{C\text{–}P\text{–}C} = 103.89\ (0.20)\end{array}\right.$$

Mean Distances

$$\mathrm{PEt_3}\left\{\begin{array}{l}\mathrm{P\text{–}C} = 1.825\ (4)\\ \mathrm{C\text{–}C} = 1.539\ (2)\end{array}\right.$$

Table IX. Least-Squares Planes and Deviations Therefrom for $[Pd(C\text{-}N)(PEt_3)_2Cl]$

Plane	Atom	Dev, Å	Plane	Atom	Dev, Å	Plane	Atom	Dev, Å
1	Pd	0.0367 (6)	2	C(1)	−0.021 (5)	3	C(9)	0.004 (6)
	Cl	0.021 (2)		C(2)	0.019 (6)		C(10)	−0.003 (6)
	P(1)	−0.283 (2)		C(3)	0.001 (7)		C(11)	0.002 (8)
	P(2)	−0.244 (2)		C(4)	−0.016 (7)		C(12)	−0.001 (8)
	C(1)	0.212 (7)		C(5)	0.005 (6)		C(13)	0.002 (7)
				C(6)	0.011 (5)		C(14)	0.003 (7)

Interplanar Angles: Plane 1-Plane 2 = 104.3°; Plane 2-Plane 3 = 74.8°

Distances (Å) of Other Atoms from the Planes

Plane 1: C(8), 3.281 (9); N(1), 3.132 (5); C(7), 2.663 (6); C(4), 0.493 (8)
Plane 2: Pd, −0.1201 (5); Cl, −0.262 (1); C(7), 0.066 (5); C(8), −1.032 (7); N(1), 1.086 (5); N(2), 1.189 (5)
Plane 3: C(6), −0.156 (5); C(7), 0.131 (5); C(8), 0.578 (7); N(1), −0.127 (4); N(2), 0.000 (5)

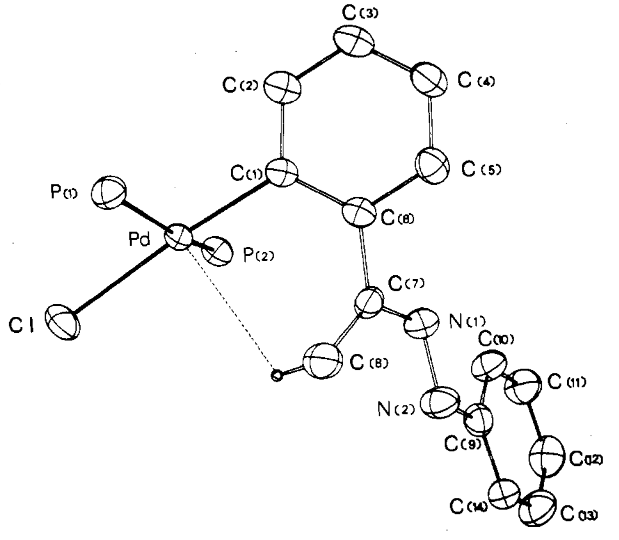


Figure 3. The $[Pd(C\text{-}N)(PEt_3)_2Cl]$ molecule (PEt_3 groups are shown only by the P atoms).

Table X. Selected Packing Distances (Å) for $[Pd(C\text{-}N)(PEt_3)_2Cl]$

Cl–HN2	II[a]	2.56 (6)	C(3)–H1C6P1	III	3.15 (10)
Cl–HC10	II	2.79 (9)	C(4)–H2C3P2	VII	2.98 (7)
Cl–HC4	IV	3.01 (7)	C(4)–H2C6P2	VII	3.00 (10)
Cl–HC11	V	3.07 (9)	C(4)–HC11	VIII	3.19 (7)
Cl–H1C8	II	3.07 (6)	C(5)–H2C3P2	VII	2.90 (7)
C1P1–H3C2P2	IV	2.88 (7)	N(1)–HC5	III	3.13 (8)
C2P1–H3C2P2	IV	3.08 (8)	N(2)–HC5	III	3.03 (7)
C2P1–H2C5P2	II	3.15 (6)	N(2)–H1C4P2	V	3.11 (9)
C3P1–H2C1P2	VII	3.18 (6)	C(9)–H1C4P2	V	2.88 (9)
C4P1–H1C6P2	V	3.06 (11)	C(10)–H1C5P2	II	2.88 (7)
C4P1–H2C1P2	VII	3.07 (7)	C(10)–H1C3P2	V	3.12 (8)
C4P1–H2C4P1	VI	3.11 (8)	C(11)–H2C5P1	V	3.15 (7)
C5P1–HC12	V	3.13 (7)	C(12)–H1C5P1	VI	2.85 (8)
C1P2–H3C4P1	VII	2.91 (9)	C(12)–H2C5P1	V	2.88 (7)
C2P2–H3C4P1	VII	2.88 (8)	C(13)–H1C5P1	VI	3.00 (7)
C5P2–H1C2P1	II	3.05 (7)	C(13)–H1C1P2	VII	3.16 (6)
C(3)–H2C6P2	VII	3.14 (9)	C(14)–H2C4P2	VII	3.02 (6)

[a] The Roman numerals give the number of the equivalent positions as in ref 32.

A comparison of the crystal structure of $[Pd(C\text{-}N)(PEt_3)_2Cl]$ with that of the analogous azobenzene complex which shows no such reactivity and with that of $[(n\text{-}Bu)_4N]^+[Pd(C\text{-}N)ClBr]^-$ gives an explanation of the reactivity of $[Pd(C\text{-}N)(PEt_3)_2Cl]$.

(1) In $[Pd(C\text{-}N)(PEt_3)_2Cl]$ the atoms directly coordinated to the palladium atom are not coplanar, as opposed to the azobenzene compound and the anionic species.

(2) The angle between the phenyl ring C(1)···C(6) and the best plane through Pd, P(1), P(2), Cl, and C(1) is 104.3° in $[Pd(C\text{-}N)(PEt_3)_2Cl]$, whereas it is 91.5° in the azobenzene compound and nearly 0° for the corresponding plane in the $[Pd(C\text{-}N)ClBr]$ anions.

(3) The ortho-metalated azobenzene has a "trans" planar structure, while our ligand is quite distorted in the complex, the C(8) and N(1) atoms being at 1.03 and 1.09 Å (respectively) from the C(1)···C(6) plane. The ligand thus has an unstable conformation in this complex, which is due to the

interaction of the C(8) methyl group with palladium and to the subsequent blocked rotation around the C(6)–C(7) axis. [Pd(C–N)$(PEt_3)_2$Cl] is thus in an intermediate state, which precedes nitrogen recoordination. The first stage of this intramolecular nucleophilic substitution reaction probably involves distortion of the palladim coordination plane and simultaneous rotations of the ortho-metalated phenyl ring about the Pd–C(1) bond and of the C(7)–N(1) bond about the C(6)–C(7) axis.

Registry No. [$(n\text{-}Bu)_4N$][Pd(C–N)ClBr], 53488-34-9; [Pd(C–N)$(PEt_3)_2$Cl], 56550-92-6.

Supplementary Material Available: Tables III and IV listing structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Rhodium and Iridium Complexes of Biimidazole. 1. Mononuclear and Dinuclear Species

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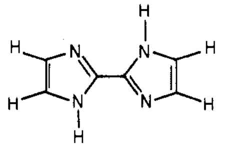
Complexes of univalent rhodium and iridium with the monoanion and dianion of 2,2′-biimidazole (H_2BiIm) have been investigated. In this paper we describe the syntheses and characterizations of M(COD)(HBiIm), $M(CO)_2$(HBiIm), and $M_2(COD)_2$(BiIm) (where M = Rh(I), Ir(I), COD = 1,5-cyclooctadiene, HBiIm = 2,2′-biimidazole monoanion, and BiIm = 2,2′-biimidazole dianion). The complexes of HBiIm are monomeric square-bonded species in which HBiIm is bidentate. These compounds show little tendency to add ligands and form saturated valency (18-electron) compounds, although HCl will add oxidatively. The addition of triphenylphosphine to $Rh(CO)_2$HBiIm displaces CO to give $Rh(CO)P(C_6H_5)_3$(HBiIm). The quadridentate planar bridging between two metals by BiIm was confirmed by a three-dimensional, single-crystal x-ray diffraction study on $Rh_2(COD)_2$(BiIm), done by counter methods. The yellow complex of $Rh_2C_{22}H_{28}N_4$ was found to crystallize in the monoclinic space group $P2_1/c$ with $a = 9.842$ (2) Å, $b = 14.590$ (3) Å, $c = 13.929$ (3) Å, $\beta = 90.45$ (2)°, and $Z = 4$ molecules/cell. The structure was refined by full-matrix methods to final $R = 0.032$ and $R_w = 0.038$ for 2531 nonzero reflections. The Rh(BiIm)Rh moiety is planar with an average Rh–N distance of 2.134 (5) Å. The Rh–Rh nonbonded distance across the bridge is 5.455 (3) Å. The COD groups assume their normal tub conformation and complex as diolefins, normal to the rhodium square coordination planes. The average bonded distance from the rhodium to the midpoint of the double bonds is 2.003 (6) Å. This is the first time the very weak proton acid H_2BiIm has been found complexed as the dianion.

Introduction

The molecule 2,2′-biimidazole, **1**, has unique properties as a coordinating ligand. As a bidentate chelate it can complex as the neutral molecule, H_2BiIm, the monoanion HBiIm, **2**, or the dianion, BiIm, **3**. In the case of the dianion, quadridentate chelation between pairs of metal ions is feasible. Not all of these possibilities have been experimentally realized, and in general biimidazole has not been heavily investigated.

Reactions of H_2BiIm with Ag(I),[1] Hg(II),[1] Pt(II),[1,2] and Pt(IV)[1,2] were reported early but were often incompletely characterized. More recently, complexes with Cu(II),[3] Ni(II),[3,4] Co(II),[3] Fe(II),[3] and Mo(I)[5] have been prepared and are generally well characterized. The crystal structure of the nickel complex, $Ni(H_2BiIm)_2(H_2O)_2(NO_3)_2$, **4**, has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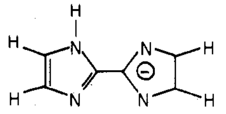
1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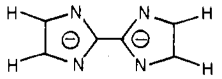
2


BiIm
3

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