

Dynamic Behaviour of Carbon-metallated Palladium Hydrazone Complexes. Crystal Structures of $[\{\text{Pd}[\text{CH}_2\text{CMe}_2\text{C}(=\text{N}-\text{NMePh})\text{Me}]\text{Cl}\}_2]$ and $[\{\text{Pd}[\text{CH}_2\text{C}(=\text{N}-\text{NMePh})\text{Bu}^t]\text{Cl}\}_2]^\dagger$

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The carbon-palladated species $[\{\text{Pd}[\text{CH}_2\text{CMe}_2\text{C}(=\text{N}-\text{NMePh})\text{Me}]\text{Cl}\}_2]$ (**1a**) and $[\{\text{Pd}[\text{CH}_2\text{C}(=\text{N}-\text{NMePh})\text{Bu}^t]\text{Cl}\}_2]$ (**2**) have in the solid state a *trans* geometry and are planar; their crystal structures have been determined by X-ray methods. These species, as well as the bromo- and iodo-derivatives of (**1a**) and the complex $[\{\text{Pd}[\text{CH}_2\text{C}(=\text{N}-\text{NMe}_2)\text{Bu}^t]\text{Cl}\}_2]$, exhibit temperature-dependent n.m.r. spectra which have been interpreted on the basis of *cis-trans* isomerization of the complexes and of hindered rotation about the N-N single bond of the hydrazone. The latter process is also present in the mononuclear species obtained from (**1a**) by bridge-splitting reactions with triphenylphosphine, pyridine, and acetylacetonate. Crystals of (**1a**) are triclinic, space group $P\bar{1}$, $a = 10.642(8)$, $b = 11.793(9)$, $c = 6.269(6)$ Å, $\alpha = 98.05(6)$, $\beta = 97.46(6)$, $\gamma = 111.91(7)^\circ$, and $Z = 1$. Crystals of (**2**) are monoclinic, space group $P2_1/a$, $a = 24.059(12)$, $b = 10.035(8)$, $c = 6.018(5)$ Å, $\beta = 95.39(5)^\circ$, and $Z = 2$.

Organopalladium compounds are increasingly used in synthesis and catalysis and recent studies have increased the range of such compounds.¹⁻⁸

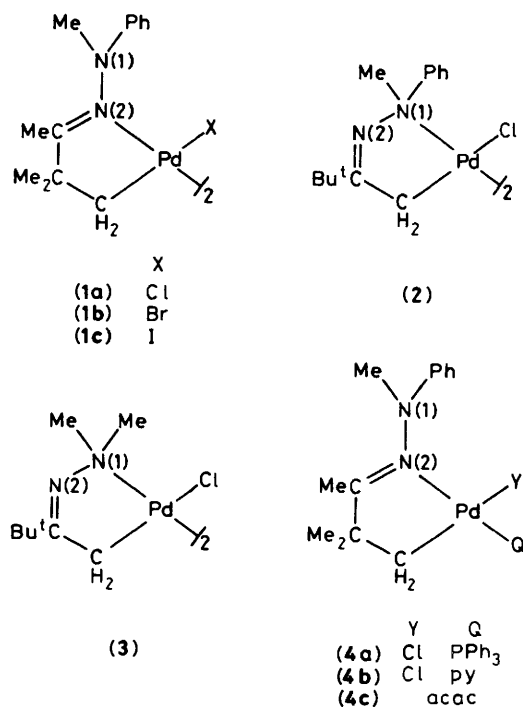
Regiospecific metallation of the aliphatic carbons was recently observed in the reaction of hydrazones of 3,3-dimethylbutan-2-one with palladium substrates which led to the isolation of $[\{\text{Pd}[\text{CH}_2\text{CMe}_2\text{C}(=\text{N}-\text{NMePh})\text{Me}]\text{Cl}\}_2]$ (**1a**), $[\{\text{Pd}[\text{CH}_2\text{C}(=\text{N}-\text{NMePh})\text{Bu}^t]\text{Cl}\}_2]$ (**2**), and $[\{\text{Pd}[\text{CH}_2\text{C}(=\text{N}-\text{NMe}_2)\text{Bu}^t]\text{Cl}\}_2]$ (**3**). These compounds exhibited temperature-dependent n.m.r. spectra which were indicative of the presence of different isomers and/or conformers in mutual interconversion.^{7,9} We therefore have undertaken an X-ray analysis of compounds (**1a**) and (**2**), which could be isolated in suitable crystalline form, in order to ascertain their structure in the solid, and a careful n.m.r. investigation which was extended to the bridged bromo- and iodo-derivatives and to the products of bridge splitting with triphenylphosphine, pyridine (py), and acetylacetonate (acac) in order to clarify their solution behaviour.

Results and Discussion

The structures of compounds (**1a**) and (**2**) are shown in Figures 1 and 2; selected bond distances and angles are given in Tables 1

[†] Bis[chloro(2,2,3-trimethyl-5-phenyl-4,5-diazahex-3-enyl- C^1N^4)-palladium(II)] and bis[chloro(2-t-butyl-4-phenyl-3,4-diazapent-2-enyl- C^1N^4)-palladium(II)].

Supplementary data available (No. SUP 56160, 7 pp.): H-atom coordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii-xix. Structure factors are available from the editorial office.



and 2. Both complexes are centrosymmetric dimers with an asymmetric chlorine double bridge [(**1a**), Pd-Cl 2.334(5) and 2.490(4); (**2**), Pd-Cl 2.322(4) and 2.450(5) Å] and the co-ordinate nitrogen and carbon atoms of the hydrazone molecules mutually *trans* with respect to the di- μ -chloro-bridge. The

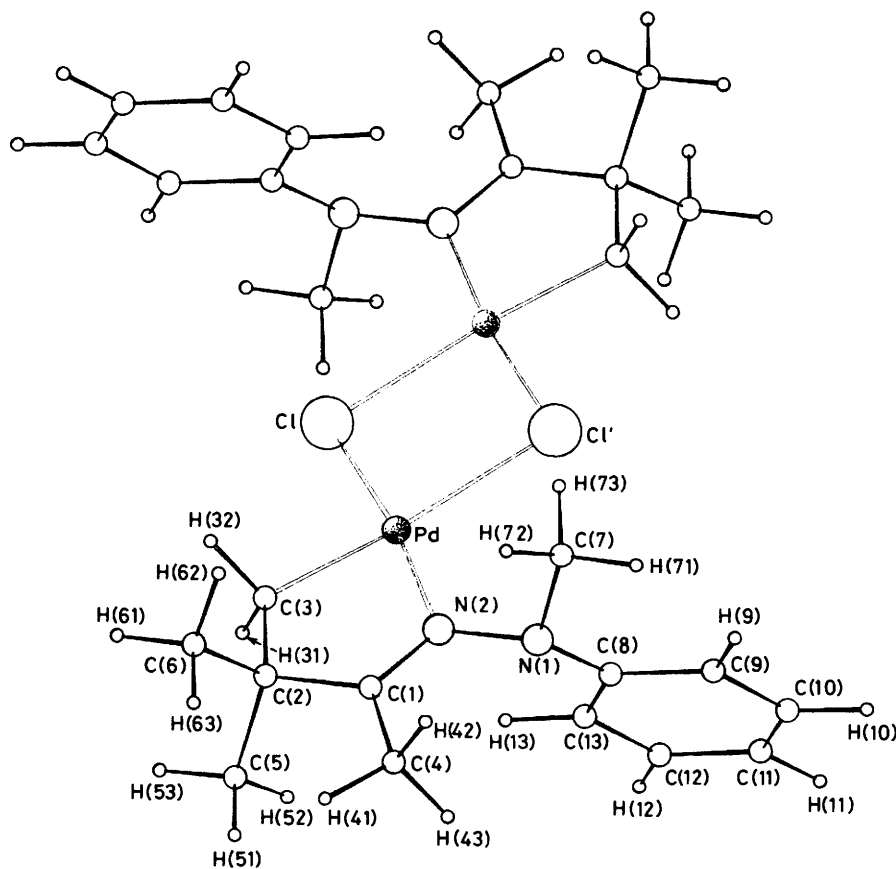


Figure 1. View of the complex $[\{\text{Pd}[\text{CH}_2\text{CMe}_2\text{C}(\text{=N-NMePh})\text{Me}]\text{Cl}\}_2]$ (**1a**) showing the atomic numbering scheme

Table 1. Selected bond distances (Å) and angles (°) in (**1a**)*

Pd-Cl	2.334(5)	N(2)-C(1)	1.31(1)
Pd-Cl'	2.490(4)	C(1)-C(4)	1.50(2)
Pd-N(2)	1.996(13)	C(1)-C(2)	1.51(2)
Pd-C(3)	1.985(12)	C(2)-C(3)	1.47(3)
N(1)-C(8)	1.41(2)	C(2)-C(5)	1.54(3)
N(1)-C(7)	1.47(2)	C(2)-C(6)	1.57(3)
N(1)-N(2)	1.44(2)	Pd...Pd'	3.511(4)
Cl-Pd-Cl'	86.6(2)	C(2)-C(1)-N(2)	114(1)
Cl-Pd-C(3)	92.2(5)	C(1)-N(2)-Pd	119(1)
C(3)-Pd-N(2)	80.7(7)	C(1)-N(2)-N(1)	114(1)
N(2)-Pd-Cl'	100.5(4)	N(1)-N(2)-Pd	127(1)
Pd-C(3)-C(2)	115(1)	N(2)-N(1)-C(7)	111(1)
C(1)-C(2)-C(3)	111(1)	N(2)-N(1)-C(8)	112(1)
C(2)-C(1)-C(4)	122(1)	C(7)-N(1)-C(8)	120(1)
C(4)-C(1)-N(2)	123(1)		

* Primed atoms are related to unprimed ones by the transformation $-x, -y, 2-z$.

Table 2. Selected bond distances (Å) and angles (°) in (**2**)*

Pd-Cl	2.322(4)	N(1)-N(2)	1.45(2)
Pd-Cl'	2.450(5)	N(2)-C(1)	1.28(2)
Pd-N(1)	2.063(12)	C(1)-C(2)	1.52(2)
Pd-C(2)	1.959(14)	C(1)-C(3)	1.52(2)
N(1)-C(8)	1.48(2)	Pd...Pd'	3.434(3)
N(1)-C(7)	1.50(2)		
Cl-Pd-Cl'	88.0(1)	C(1)-N(2)-N(1)	112.7(11)
Cl-Pd-C(2)	92.2(5)	N(2)-N(1)-Pd	112.6(8)
C(2)-Pd-N(1)	82.9(6)	N(2)-N(1)-C(7)	104.2(10)
N(1)-Pd-Cl'	96.9(4)	N(2)-N(1)-C(8)	105.9(10)
Pd-C(2)-C(1)	108.6(10)	C(7)-N(1)-Pd	109.7(9)
C(2)-C(1)-N(2)	123.0(13)	C(7)-N(1)-C(8)	113.6(11)
C(2)-C(1)-C(3)	119.8(13)	C(8)-N(1)-Pd	110.6(8)
C(3)-C(1)-N(2)	117.3(13)		

* Primed atoms are related to unprimed ones by the transformation $-x, 1-y, 1-z$.

molecules, as a whole, are nearly planar as indicated by the deviations of the metals, chloro-bridges, and atoms of the chelate ring systems from the mean plane passing through them [(**1a**): Pd, 0.03(1); Cl, 0.02(1); N(2), 0.06(1); C(1), -0.13(1); C(2), -0.21(1); C(3), -0.12(2) Å. (**2**): Pd, 0.01(1); Cl, 0.02(1); N(1), 0.04(1); N(2), 0.03(1); C(1), -0.07(1); C(2), -0.13(1) Å].

In this respect the molecules of (**1a**) and (**2**) greatly differ from the related $[\{\text{Pd}[\text{CH}_2\text{CMe}_2\text{C}(\text{=N-OH})\text{Me}]\text{Cl}\}_2]$ complex, already reported,⁷ which has a *cis* geometry and a

considerable folding of the Pd_2Cl_2 ring leading to a dihedral angle of 121.9° between the two PdCl_2 triangles and to a $\text{Pd}\cdots\text{Pd}$ distance of only 2.991(1) Å. In the compounds presently investigated the Pd_2Cl_2 rings are perfectly planar due to symmetry restrictions and the $\text{Pd}\cdots\text{Pd}$ distances are 3.511(4) and 3.434(3) Å in (**1a**) and (**2**) respectively.¹⁰

The square-planar co-ordination geometries of the palladium atoms in the two complexes differ significantly in the Pd-N bond distances [1.996(13) and 2.063(12) Å in (**1a**) and (**2**) respectively], reflecting the different hybridization of the

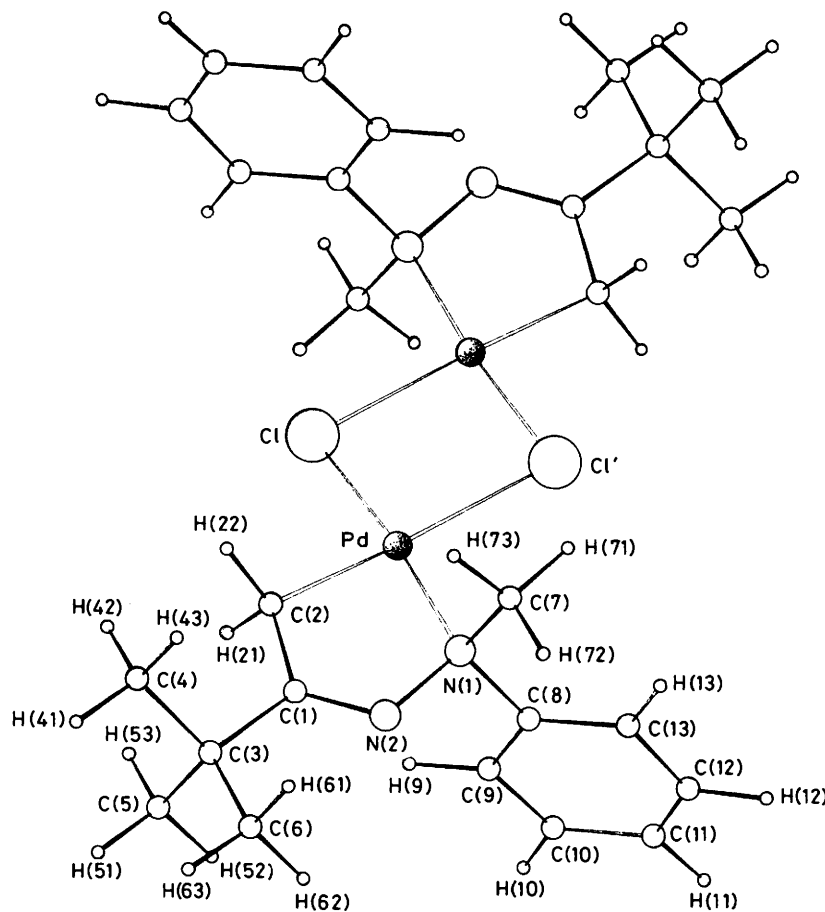


Figure 2. View of the complex $[\text{Pd}\{\overline{\text{CH}_2\text{C}(\text{=N-NMePh})\text{Bu}}\}\text{Cl}]_2$ (**2**) showing the atomic numbering scheme

nitrogen atoms [sp^2 in (**1a**) and sp^3 in (**2**)],¹¹ and, to a smaller extent, in the Pd–Cl' distances [2.490(4) and 2.450(5) Å in (**1a**) and (**2**) respectively], the longer bond being that of (**1a**) where a steric repulsion between the bulky NMePh group and Cl' is likely to occur.

Bond distances in the hydrazone moieties are of normal length and are in accord with localized double and single bonds for C(1)–N(2) and N(1)–N(2) respectively.¹² Moreover, in compound (**1a**) the direction of the N(1) lone pair of electrons is almost orthogonal to that of the C(1)–N(2) π system, further excluding any possibility of charge delocalization.¹³

The n.m.r. data are given in Table 3. The mononuclear compounds obtained from (**1a**) by bridge splitting with triphenylphosphine, py, and acac, $[\text{Pd}\{\overline{\text{CH}_2\text{CMe}_2\text{C}(\text{=N-NMePh})\text{Me}}\}\text{Cl}(\text{PPh}_3)]$ (**4a**), $[\text{Pd}\{\overline{\text{CH}_2\text{CMe}_2\text{C}(\text{=N-NMePh})\text{Me}}\}\text{Cl}(\text{py})]$ (**4b**), and $[\text{Pd}\{\overline{\text{CH}_2\text{CMe}_2\text{C}(\text{=N-NMePh})\text{Me}}\}(\text{acac})]$ (**4c**), exhibit at 20 °C one sharp resonance for each type of proton; on lowering the temperature (–40 °C) the signal of CMe_2 splits into a doublet while that of metallated CH_2 splits into an AB quartet, all other resonances being left unchanged. The only plausible explanation for this behaviour is that a restricted rotation about the N(2)–N(1) bond leaves the Me and Ph groups of N(1) on opposite sides with respect to the coordination plane with consequent magnetic non-equivalence of groups emerging out of this plane.

The n.m.r. spectra of the bridged chloro-, bromo-, and iodo-derivatives [compounds (**1a**), (**1b**), and (**1c**) respectively] also show at 20 °C a single band for each type of proton. On lowering the temperature they exhibit two sets of signals, of

different intensities [*ca.* 1:2 ratio in (**1b**)], each of these having the same pattern shown by compounds (**4a**)–(**4c**), *i.e.* a doublet for CMe_2 and a multiplet for CH_2 (Figure 3). We can still assume that the splitting of the CMe_2 and CH_2 resonances in each set is caused by hindered rotation about the N–N bond which makes groups on opposite sides of the co-ordination plane inequivalent. On the other hand the presence of two sets of signals, instead of the one observed in compounds (**4a**)–(**4c**), must be connected with the dimeric nature of compounds (**1a**)–(**1c**); in fact restricted motion about the N–N bond should result in the formation of two conformers [(A) and (B) in Figure 4], each of these exhibiting one set of resonances. The NMe group gives, at low temperature, a single sharp resonance which is indicative of a very similar magnetic environment in the two conformers (splitting <0.01 p.p.m.); on increasing the temperature the n.m.r. signal becomes initially broader and then sharp again. A plausible explanation is that a *trans*–*cis* isomerization of the complex can also take place at higher temperatures. A careful inspection of the low-temperature spectra has revealed the net presence of a weak band [at δ 2.63, 2.77, and 2.90 for (**1a**), (**1b**), and (**1c**) respectively] which, on warming, coalesces with the main NMe resonance and could well belong to a *cis* isomer present in much smaller yield. Consistent with this interpretation, a mixture of (**1a**) and (**1c**) gives four NMe resonances, two consistent with the main NMe signal for (**1a**) and (**1c**) and two new ones attributable to the species with a mixed chloro-iodo-bridge. Spin-saturation transfer measurements clearly demonstrate exchange between the species.

The n.m.r. spectrum of compound (**2**) is characterized by

Table 3. Proton chemical shifts^a (δ /p.p.m., downfield from SiMe₄)

Compound	θ /°C	CH ₂	CMe ₂	C(Me,Bu ^t)	NMe	NPh		
						<i>ortho</i>	<i>meta</i>	<i>para</i>
(1a)	+20	2.03	1.21	1.84	3.06	6.62	7.24	6.86
	-40	{ 1.94br,m	1.08, 1.23 1.13, 1.18	1.80 1.82	2.99	6.60	7.33	6.85
(1b) ^b	+20	2.15	1.24	1.87	3.15	6.68	7.23	6.85
	-40	{ 2.08br 2.07, 2.17	1.09, 1.36 1.15, 1.27	1.88 1.89	3.13	6.64	7.24	6.88
(1c)	+20	2.04	1.23	1.87	3.12	6.65	7.21	6.84
	-40	{ 1.97 1.92, 2.02	1.11, 1.27 1.13, 1.25	1.87	3.07	6.61	7.22	6.85
(2)	+40	3.15		1.20	3.33		7.12—7.38	
	-40	{ 3.09 3.03, 3.15?		1.15 1.14	3.18, 3.34 3.25, 3.28		7.00—7.35	
(3)	+40	3.11		1.12	2.85			
	-40	{ 3.04 3.07		1.04	2.81 2.78			
(4a) ^c	+20	1.52	1.19	1.99	3.40	6.81	7.26	6.83
	-40	1.27, 1.78	1.15, 1.18	1.98	3.35	6.80	7.28	6.84
(4b) ^d	+20	2.12	1.34	1.95	3.29	6.73	7.24	6.81
	-40	2.05, 2.17	1.28, 1.32	1.94	3.23	6.67	7.22	6.78
(4c) ^e	+20	2.07	1.30	1.94	3.13	6.78	7.23	6.84
	-40	1.95, 2.03	1.25, 1.29	1.93	3.08	6.71	7.23	6.83

^a All spectra were recorded in CD₂Cl₂ solution on a Varian XL 200 instrument unless otherwise stated. ^b Solvent was CDCl₃. ^c Proton resonances of PPh₃ in the region 7.30—7.60 p.p.m. ^d Proton resonances of py are 8.60, 7.25, and 7.68 p.p.m. for *ortho*-, *meta*-, and *para*-hydrogens respectively. ^e Proton resonances of acac are at 1.44 and 1.70 for CMe and 4.97 p.p.m. for CH protons.

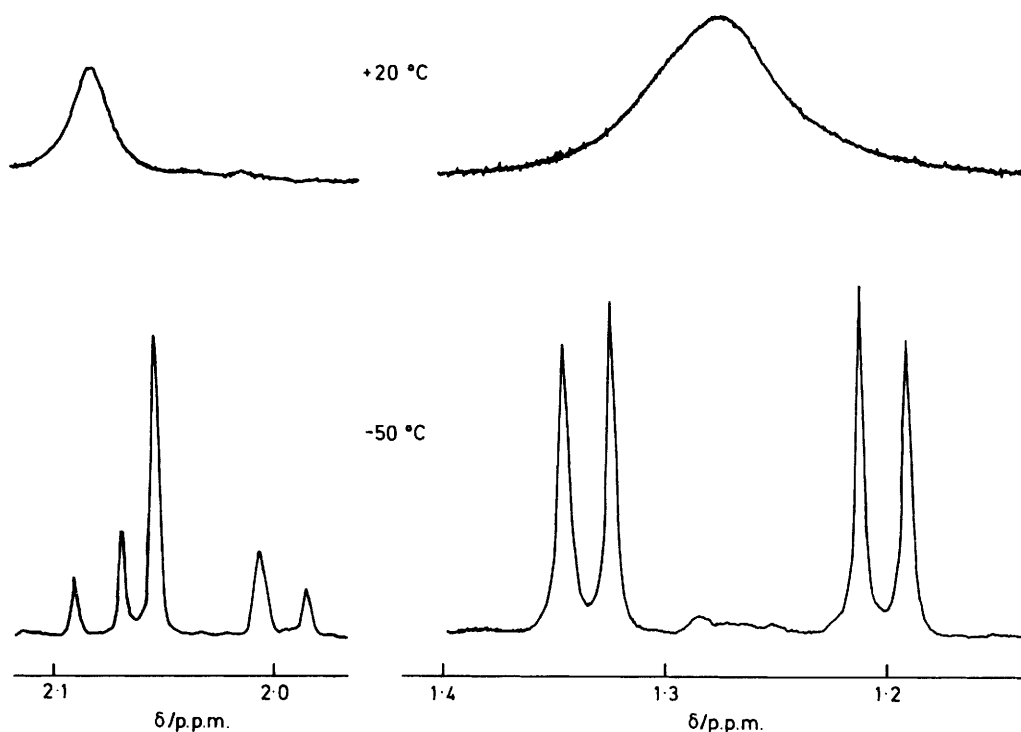


Figure 3. N.m.r. signals of CH₂ (left) and CMe₂ (right) in $[\{\text{Pd}[\text{CH}_2\text{CMe}_2\text{C}(\text{=N-NMePh})\text{Me}]\text{I}\}_2]$ (1c) as a function of temperature. Note that the CH₂ AB quartet is well resolved only in one of the two sets of signals. Solvent CDCl₃, Bruker WH 400 spectrometer

having at 40 °C a broad resonance for CH₂ and NMe groups and a sharp band for Bu^t. Lowering the temperature, the Bu^t resonance splits into two sharp signals of unequal intensities, the NMe resonance into four signals, two more intense than the

others, and the CH₂ band into a complex multiplet. The splitting of the NMe resonance into four signals requires the presence of four different molecular species; these could be the *cis* and *trans* isomers with each isomer present in two

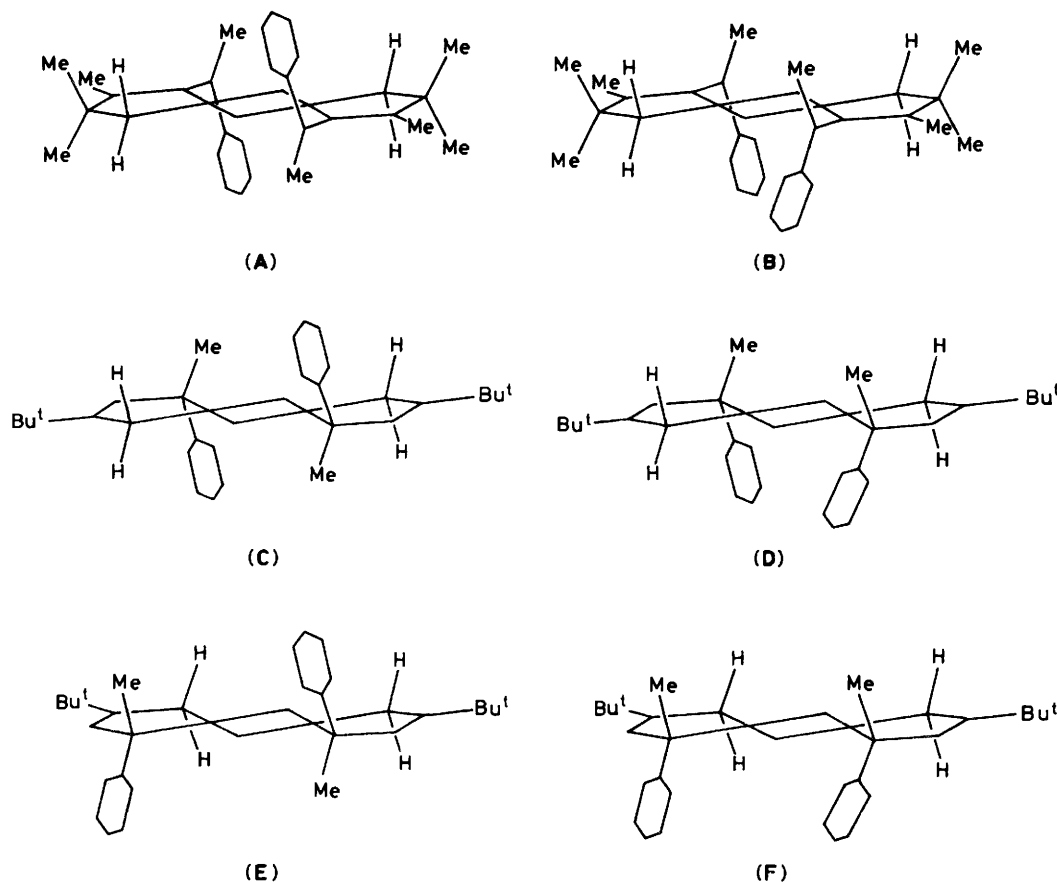


Figure 4. Different conformations (multiple bonds not indicated) of $\overline{\text{trans-}}[\{\text{Pd}[\text{CH}_2\text{CMe}_2\text{C}(=\text{N}-\text{NMePh})\text{Me}]\text{X}\}_2]$, (A) and (B), $\overline{\text{trans-}}[\{\text{Pd}[\text{CH}_2\text{C}(=\text{N}-\text{NMePh})\text{Bu}^t]\text{X}\}_2]$, (C) and (D), and $\overline{\text{cis-}}[\{\text{Pd}[\text{CH}_2\text{C}(=\text{N}-\text{NMePh})\text{Bu}^t]\text{X}\}_2]$, (E) and (F)

conformations differing in the mutual orientation of the NMe (and NPh) groups which can be either on the same or on opposite sides of the co-ordination plane [conformations (C), (D) and (E), (F) of Figure 4]. Probably the Bu^t resonance is more sensitive to geometrical isomerism and is split only into two signals of different intensities. In each species the two protons of CH_2 are inequivalent and should give rise to an AB spectrum; the superposition of these allows for the observed multiplet.

Compound (3) is the simplest of the examined cases since because both substituents at N(1) are equal, one possibility of isomerism is ruled out. The spectrum taken at 40°C shows only one resonance for each type of proton. Lowering the temperature, the CH_2 and NMe_2 protons give rise to two resonances of approximately equal intensity while the Bu^t group still gives a single band. This is in accord with the presence of two geometrical isomers, *cis* and *trans*, in comparable concentration. The splitting is only detectable for the CH_2 and NMe_2 groups which are bound to palladium and directly face the second half of the molecule. This interpretation is fully consistent with the observation that the monomeric species obtained from (3) by the bridge-splitting reaction with triphenylphosphine, pyridine, and acetylacetonate⁷ show a single resonance for each type of proton which is left unchanged at low temperature.

In conclusion, two dynamic processes, *cis-trans* isomerization of the complexes and restricted motion about the N-N bond of the hydrazone, can fully account for the solution behaviour of the compounds presently investigated.

The former process is favoured by the *trans* labilizing effect of

the metal-bonded alkyl group,¹⁴ the influence of which is also revealed by the X-ray structures indicating a Pd-Cl bond *trans* to carbon *ca.* 0.15 \AA longer than that *trans* to nitrogen.

The latter process, that is the hindered rotation about the N-N bond, has never been observed in simple co-ordination compounds of hydrazones. These are characterized by having the ligand N(2) atom bonded to the metal and with its plane perpendicular to that of co-ordination.^{10,12,13,15} This molecular arrangement keeps the N(1)MePh group in an uncrowded axial position and free to rotate about the N-N bond. On the other hand in these compounds the hydrazone molecule, as a whole, is hindered in its rotation about the Pd-N(2) co-ordination bond by the *cis* ligands.¹⁶

In the compounds presently investigated the hydrazone is bidentate to the metal and lies in the plane of co-ordination and so does the N(1)MePh group which, in near proximity to the *cis* ligand, is hindered in its rotation about the N-N bond. The steric origin of the restricted motion is also apparent from the crystallographic data showing the absolute absence of *p*-orbital overlap within the N-N bond. The X-ray data also show a further lengthening of the Pd-Cl' bond in compound (1a), as compared to compound (2), which could be ascribed to a steric repulsion between the chlorine atom and the substituents on N(1). It is also to be noted that restricted motion about the N-N bond is not observed in free hydrazones except in the case of extreme steric crowding as in *N*-ketiminyll-2,2,6,6-tetramethylpiperidines, $\overline{\text{CMe}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CMe}_2\text{N}-\text{N}=\text{CR}_2}$.¹⁷

A final point which deserves comment is the presence in solution, at low temperature, of only one isomer (probably the

trans) for compounds (1a)–(1c) and of both the *cis* and *trans* isomers in comparable concentrations for compounds (2) and (3). The greater conformational stability of the *trans* over the *cis* isomer in (1) could have a steric origin. We have already seen how in compound (1a) the bulky NMePh group creates considerable steric strain on the *cis* chlorine atom with the consequence of a longer Pd–Cl' distance and of restricted motion about the N–N bond. In the *cis* isomer an analogous effect upon Cl' would be produced from the other side of the molecule with the consequence of a still greater destabilization.

Experimental

Commercial reagent-grade chemicals were used without further purification. The complexes (1a), (2), and (3) were prepared as previously described.^{7,9}

[{Pd[CH₂CMe₂C(=N–NMePh)Me]Br}₂] (1b).—A large excess (0.150 g, 1.73 mmol) of lithium bromide was added to a solution of the chloride (1a) (0.200 g, 0.29 mmol) in acetone (50 cm³). The yellow solution was stirred at room temperature for 1 d, the solvent was removed under reduced pressure and the residue was extracted with dichloromethane (30 cm³). Evaporation of the extract under reduced pressure gave a solid from which the required product was obtained as dark yellow crystals on crystallization from dichloromethane–hexane. Yield 85% (Found: C, 39.6; H, 5.30; Br, 21.3; N, 7.00. [Pd{CH₂CMe₂C(=N–NMePh)Me}Br]₂ requires C, 40.05; H, 4.90; Br, 20.5; N, 7.20%).

[{Pd[CH₂CMe₂C(=N–NMePh)Me]I}₂] (1c).—A solution of the chloride (1a) (0.200 g, 0.29 mmol) in acetone (50 cm³) was treated with a large excess (0.230 g, 1.72 mmol) of lithium iodide. The solution was stirred at room temperature for 1 d, the solvent was evaporated under reduced pressure and the residue was extracted with dichloromethane (30 cm³). The extract was passed through a column of Celite and concentrated to small volume. The addition of hexane afforded orange crystals of the desired product in 65% yield (Found: C, 35.8; H, 4.75; I, 28.75; N, 6.25. [Pd{CH₂CMe₂C(=N–NMePh)Me}I]₂ requires C, 35.75; H, 4.40; I, 29.05; N, 6.40%).

[Pd{CH₂CMe₂C(=N–NMePh)Me}Cl(PPh₃)] (4a).—Triphenylphosphine (0.083 g, 0.32 mmol) was added to a suspension of the dimer (1a) (0.100 g, 0.15 mmol) in benzene (35 cm³). After few minutes all the solid dissolved giving a pale yellow solution which was left stirring for *ca.* 1 h. The solvent was evaporated and the solid residue crystallized from dichloromethane–hexane affording white crystals of the desired product in 90% yield (Found: C, 55.4; H, 5.35; Cl, 15.8; N, 3.90. [Pd{CH₂CMe₂C(=N–NMePh)Me}Cl(PPh₃)]·CH₂Cl₂ requires C, 55.5; H, 5.25; Cl, 15.35; N, 4.05%).

[Pd{CH₂CMe₂C(=N–NMePh)Me}Cl(py)] (4b).—Pyridine (0.050 g, 0.63 mmol) was added to a solution of the dimer (1a) (0.200 g, 0.29 mmol) in chloroform (8 cm³). The solution was stirred for 1 d, the solvent was evaporated under reduced pressure and the white residue crystallized from dichloromethane–diethyl ether–hexane. Yield 75% (Found: C, 49.0; H, 5.80; Cl, 8.05; N, 9.55. [Pd{CH₂CMe₂C(=N–NMePh)Me}Cl(py)]·H₂O requires C, 48.9; H, 5.90; Cl, 8.00; N, 9.50%).

[Pd{CH₂CMe₂C(=N–NMePh)Me}(acac)] (4c).—A mixture of the bridged complex (1a) (0.233 g, 0.34 mmol), acetylacetonate (0.076 g, 0.76 mmol), and sodium hydroxide (0.030 g, 0.75 mmol) in methanol (5 cm³) was stirred at room temperature for 1 d.

Table 4. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for the non-hydrogen atoms of (1a)

Atom	X/a	Y/b	Z/c
Pd	583(1)	1 392(1)	11 974(2)
Cl	1 557(4)	544(4)	9 393(6)
N(1)	–1 380(11)	1 906(11)	14 812(18)
N(2)	–27(11)	2 301(10)	14 276(19)
C(1)	895(15)	3 298(13)	15 643(23)
C(2)	2 330(14)	3 712(13)	15 122(25)
C(3)	2 362(14)	2 839(15)	13 229(38)
C(8)	–2 382(14)	1 908(12)	13 099(23)
C(9)	–3 794(15)	1 340(15)	13 296(28)
C(10)	–4 805(16)	1 404(17)	11 735(34)
C(11)	–4 450(19)	2 001(17)	9 988(31)
C(12)	–3 076(18)	2 561(16)	9 779(28)
C(13)	–2 038(15)	2 518(13)	11 398(23)
C(4)	556(17)	4 011(16)	17 492(28)
C(5)	2 732(25)	5 012(23)	14 561(39)
C(6)	3 332(27)	3 736(24)	17 222(44)
C(7)	–1 675(16)	829(15)	15 882(26)

Table 5. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for the non-hydrogen atoms of (2)

Atom	X/a	Y/b	Z/c
Pd	554(1)	5 358(1)	6 917(2)
Cl	333(2)	3 605(4)	4 473(7)
N(1)	822(5)	6 850(12)	9 121(19)
N(2)	1 356(5)	6 551(13)	10 345(20)
C(1)	1 539(6)	5 395(17)	9 895(21)
C(2)	1 232(6)	4 464(16)	8 218(26)
C(3)	2 088(6)	4 961(15)	11 129(26)
C(4)	1 998(8)	3 612(17)	12 245(29)
C(5)	2 506(7)	4 831(21)	9 469(27)
C(6)	2 296(8)	5 968(18)	12 951(28)
C(7)	426(6)	6 974(16)	10 901(24)
C(8)	904(6)	8 113(13)	7 911(24)
C(9)	1 258(7)	8 074(16)	6 278(25)
C(10)	1 315(7)	9 219(18)	4 989(28)
C(11)	1 024(8)	10 350(22)	5 385(34)
C(12)	703(10)	10 347(21)	7 002(44)
C(13)	613(9)	9 229(13)	8 350(36)

The solution, concentrated to half volume and cooled to 0 °C, afforded colourless cubic crystals of the desired product in 50% yield (Found: C, 51.95, H, 6.65; N, 6.60. [Pd{CH₂CMe₂C(=N–NMePh)Me}(acac)] requires C, 52.9; H, 6.40; N, 6.85%).

Crystal Structure Determinations of (1a) and (2).—The intensity data were collected on a Siemens AED diffractometer using the $\theta/2\theta$ scan technique and nickel-filtered Cu- K_α radiation for (1a), niobium-filtered Mo- K_α radiation for (2). For (1a) 2 367 independent reflections ($3 \leq \theta \leq 65^\circ$, $\pm h$, $\pm k$, l) were measured, 2 550 ($3 \leq \theta \leq 25^\circ$, $\pm h$, k , l) for (2); of these 1 461 for (1a) and 1 107 for (2) were considered observed having $I \geq 2\sigma(I)$. The usual Lorentz and polarization reduction, but no correction for absorption, because of the very low absorbance of the samples, were applied.

Crystal data for (1a). C₂₆H₃₈Cl₂N₄Pd₂, $M = 690.32$, triclinic, $a = 10.642(8)$, $b = 11.793(9)$, $c = 6.269(6)$ Å, $\alpha = 98.05(6)$, $\beta = 97.46(6)$, $\gamma = 111.91(7)^\circ$, $U = 708(1)$ Å³ (by least-squares refinement of the θ values of 20 reflections accurately measured, $\bar{\lambda} = 1.54178$ Å), space group $P\bar{1}$, $Z = 1$, $D_c = 1.618$ g cm^{–3}. A pale yellow crystal of approximate dimensions $0.03 \times 0.06 \times 0.20$ mm was used for data collection, $\mu(\text{Cu-}K_\alpha) = 124.44$ cm^{–1}.

Crystal data for (2). $C_{26}H_{38}Cl_2N_4Pd_2$, $M = 690.32$, monoclinic, $a = 24.059(12)$, $b = 10.035(8)$, $c = 6.018(5)$ Å, $\beta = 95.39(5)^\circ$, $U = 1447(2)$ Å³ (by least-squares refinement of the θ values of 16 reflections accurately measured, $\bar{\lambda} = 0.71069$ Å), space group $P2_1/a$, $Z = 2$, $D_c = 1.585$ g cm⁻³. A yellow prismatic crystal of approximate dimensions $0.10 \times 0.13 \times 0.28$ mm was used in the analysis, $\mu(Mo-K\alpha) = 14.34$ cm⁻¹.

Structure analyses and refinements. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares methods using the SHELX system of computer programs.¹⁸ Atomic scattering factors were corrected for anomalous dispersion of Pd and Cl.¹⁹ Anisotropic thermal parameters of all atoms except hydrogens [and also C(4)—C(7) in compound (1a)] were used in the last cycles of refinements. Hydrogen atoms of both (1a) and (2) were placed in their geometrically calculated positions but not refined; unit weights gave satisfactory agreement analyses. Final R and R' values were 0.054 and 0.066 for (1a) and 0.044 and 0.049 for (2). Final atomic co-ordinates of non-hydrogen atoms are given in Tables 4 and 5 for (1a) and (2) respectively.

Spectroscopy.—Infrared spectra in the range 4000—400 cm⁻¹ were recorded as KBr pellets on a FT-IR 5DX Nicolet instrument, spectra in the range 400—200 cm⁻¹ as Polythene pellets on a Perkin-Elmer 683 instrument. Proton n.m.r. spectra were obtained with Varian XL 200 and Bruker WH 400 spectrometers.

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