Regiospecific Metallation in Palladium–Hydrazone Complexes

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The dimethylhydrazone of pinacolone, $Bu^tMeC{=}N^1N^2Me_2$, reacts with $[PdCl_2(NCR)_2]$ (R = Me or Ph) to give the complexes $[PdCl_2(Bu^tMeC{=}NNMe_2)_2]$ and $[\{PdCl_2(Bu^tMeC{=}NNMe_2)\}_2]$, in which the ligands co-ordinate preferentially through the aminic nitrogen, N^2. Both species, in solution, carbopalladate regiospecifically on the Me group to give $[\{Pd[CH_2C({=}NNMe_2)Bu^t]Cl\}_2]$. In contrast, $Bu^tMeC{=}N^1N^2MePh$ reacts with palladium to give only the 1 : 1 adduct $[\{PdCl_2(Bu^tMeC{=}NNMePh)\}_2]$ in which the ligand co-ordinates preferentially through the iminic nitrogen, N^1. This complex is fairly stable in benzene or dichloromethane solution where it slowly decomposes to give only a small amount of the methylpalladated complex $[\{Pd[CH_2C({=}NNMePh)Bu^t]Cl\}_2]$; however, in methanol solution and in the presence of a base, NaO_2CMe, it carbopalladates regiospecifically on the Bu^t group to give $[\{Pd[CH_2C(CH_3)_2C({=}NNMePh)Me]Cl\}_2]$. The reason for different regioselectivity and the relative rate of carbopalladation on the Me and Bu^t group (for N^2- and N^1-co-ordinated hydrazones respectively) are discussed.

The metallation of co-ordinated hydrazones has been the topic of quite a number of studies in the past few years.[1-4]

The most recent report on this subject described the carbopalladation of the dimethylhydrazone of pinacolone, $Bu^tMeC{=}NNMe_2$, and formation of $[\{Pd[CH_2C({=}NNMe_2)Bu^t]Cl\}_2]$ in which the ligand co-ordinates to the metal through the aminic nitrogen, N^2, and metallation occurs on the Me group of the ketiminyl residue.[5] This is in contrast to the generally preferred N^1 co-ordination of the hydrazone ligands which would have led to metallation on the Bu^t group.

Pursuing our current studies on the hydrazone complexes of palladium,[6-9] we gained some insight into the reaction studied by Shaw and co-workers[5] which clarifies the reason for its regiospecificity. The results of this investigation are reported in this paper.

Experimental

Starting Materials.—The ligands, $Bu^tMeC{=}NNMe_2$ (L^1) and $Bu^tMeC{=}NNMePh$ (L^2), were prepared by reaction of $Bu^tMeC{=}O$, with the appropriate hydrazine (H_2NNMe_2 or $H_2NNMePh$ respectively).[10] Their purity was checked by g.l.c., t.l.c., elemental analysis, and ^1H n.m.r. spectra. The complexes *trans*-$[PdCl_2(NCR)_2]$ (R = Me or Ph) were prepared from $PdCl_2$ and NCR according to the method of Kharasch *et al.*[11]

Complexes with L^1.—$[PdCl_2(L^1)_2]$. This complex was prepared by reaction of *trans*-$[PdCl_2(NCMe)_2]$ (0.44 g, 1.7 mmol) with twice the stoicheiometric amount of L^1 (0.48 g, 3.4 mmol) in benzene containing 10% v/v of hexane, at 0 °C. After stirring for 3 h the reaction mixture was filtered, concentrated to a small volume under vacuum, and treated with an excess of pentane to give a yellow solid. The crude product was purified by passing it through a chromatographic column of acetylated cellulose (acetyl content 40%) using benzene as eluant, yield *ca.* 55% {Found: C, 41.3; H, 7.3; Cl, 16.1; N, 12.1. $[PdCl_2(C_8H_{18}N_2)_2]$ requires C, 41.6; H, 7.9; Cl, 15.4; N, 12.1%}.

$[(PdCl_2L^1)_2]$. This complex was prepared by reaction of *trans*-$[PdCl_2(NCMe)_2]$ (0.44 g, 1.7 mmol) with the stoicheiometric amount of L^1 (0.24 g, 1.7 mmol) in benzene at 5 °C. After stirring for 3 h the solution was filtered, taken to dryness under vacuum, and the residue treated with pentane to give a brown solid, yield *ca.* 50% {Found: C, 30.3; H, 5.7; Cl, 22.2; N, 8.5. $[PdCl_2(C_8H_{18}N_2)]_2$ requires C, 30.1; H, 5.7; Cl, 22.2; N, 8.8%}.

$[\{Pd[CH_2C({=}NNMe_2)Bu^t]Cl\}_2]$. This compound was first obtained by Shaw *et al.*[5] by reaction of $Na_2[PdCl_4]$, L^1, and NaO_2CMe in methanol at room temperature. We prepared the same compound, starting from the substitution products prepared above according to the following procedures. (*i*) A methanolic solution of either $[PdCl_2(L^1)_2]$ or $[(PdCl_2L^1)_2]$ was treated with twice the stoicheiometric amount of sodium acetate. After 1 d at room temperature a yellow precipitate separated out, this was collected by filtration of the mother-liquor, dried, and crystallized from dichloromethane–hexane. The yield referred to palladium was *ca.* 90% in both cases {Found: C, 33.8; H, 6.0; Cl, 12.6; N, 9.7. $[PdCl(C_8H_{17}N_2)]_2$ requires C, 33.9; H, 6.0; Cl, 12.5; N, 9.9%}. (*ii*) The same compound could be obtained directly from either $[PdCl_2(L^1)_2]$ or $[(PdCl_2L^1)_2]$ without the use of a base. In a typical experiment a solution of $[PdCl_2(L^1)_2]$ in benzene was left standing at room temperature for 2 d, a red solid separated out while the solution became orange-yellow. The precipitate, separated by filtration of the mother-liquor, was washed with benzene and shown to be the salt $[HL^1]_2[PdCl_4]$ [Found: C, 35.6; H, 7.1; Cl, 26.8; N, 10.4. $(C_8H_{19}N_2)_2(PdCl_4)$ requires C, 35.9; H, 7.2; Cl, 26.5; N, 10.5%]. The solution was evaporated to dryness under vacuum and the residue, crystallized from dichloromethane–hexane, afforded the desired complex, $[\{Pd[CH_2C({=}NNMe_2)Bu^t]Cl\}_2]$.

Complexes with L^2.—$[(PdCl_2L^2)_2]$. Only the 1 : 1 adduct,

Table. Proton chemical shifts [a] (δ/p.p.m., downfield from SiMe$_4$) of free and complexed hydrazones (R^{1}R^{2}C=NNR^{3}R^4)

	Isomer	R^1 = Bu^t	R^2 = Me	R^{3}R^4 = Me$_2$	R^4 = Ph
Bu^{t}MeC=NNMe$_2$		1.06	1.88	2.35	
Bu^{t}MeC=NNMe$_2$H$^+$		1.15	2.43	3.17 [b]	
[PdCl$_2$(Bu^{t}MeC=NNMe$_2$)$_2$]	(1c)	1.12	3.04	2.81	
	(1b)	1.13 1.90	2.90 2.28	2.85 [c] 2.92 [c]	
	(1c) [d]	1.08	2.89	2.74	
	(1b) [d]	1.12 1.80	2.76 1.86	2.82 [c] 2.92 [c]	
[{PdCl$_2$(Bu^{t}MeC=NNMe$_2$)}$_2$]	(2c)	1.1 [e]	3.3 [e]	2.8 [e]	
	(2b)	1.1 [e] 2.01	3.3 [e] 2.32	2.8 [e] 2.81 [f]	
[{Pd[CH$_2$C(=NNMe$_2$)Bu^t]Cl}$_2$]	(3a)	1.12	3.11 [g]	2.89	
Bu^{t}MeC=NNMePh		1.23	1.95	2.93	6.7—7.3
Bu^{t}MeC=NNMePhH$^+$ [h]		1.40	2.40	3.45	7.2—7.5
[{PdCl$_2$(Bu^{t}MeC=NNMePh)}$_2$]	(2a)	1.9—2.3 [i]		3.4—3.8 [i]	7.4—7.8
[{Pd[CH$_2$C(=NNMePh)Bu^t]Cl}$_2$]	(3a)	1.26	3.35 [g]	3.55	7.4—7.8
[{Pd[CH$_2$C(CH$_3$)$_2$C(=NNMePh)Me]Cl}$_2$]	(3b)	2.14 [g] 1.23 [j]	1.85	3.13	6.7—7.5

[a] All spectra were recorded in CD$_2$Cl$_2$ solution at 10 °C unless otherwise stated. [b] ^3J(HH) = 5 Hz. [c] The assignment of the NMe resonances to the two sets of signals is only tentative. [d] Spectrum recorded in C$_6$D$_6$ solution at 10 °C. [e] Broad resonance. [f] Tentative assignment. [g] PdCH$_2$. [h] Spectrum recorded in CDCl$_3$ solution at 34 °C. [i] Complex resonance band. [j] C(CH$_3$)$_2$.

[(PdCl$_2$L^2)$_2$], could be obtained by reaction of *trans*-[PdCl$_2$(NCR)$_2$] with L^2 even when a large excess of ligand was used. In a typical experiment *trans*-[PdCl$_2$(NCPh)$_2$] (0.58 g, 1.5 mmol) and L^2 (0.31 g, 1.5 mmol) were allowed to react in benzene at room temperature for 1.5 h. The resulting dark red solution was filtered to separate a small amount of brown precipitate, concentrated to small volume (3—4 cm^3) and passed through a chromatographic column of acetylated cellulose (acetyl content 40%) using hexane containing 30% v/v of ethyl acetate as eluant. The chromatographed solution was taken to dryness under vacuum and the solid residue crystallized from dichloromethane–hexane {Found: C, 41.3; H, 5.4; Cl, 18.9; N, 7.0. [PdCl$_2$(C$_{13}$H$_{20}$N$_2$)]$_2$ requires C, 40.9; H, 5.3; Cl, 18.6; N, 7.3%}.

[{Pd[CH$_2$C(=NNMePh)Bu^t]Cl}$_2$]. Performing the reaction between *trans*-[PdCl$_2$(NCR)$_2$] (R = Me or Ph) and L^2 as reported above but using a longer reaction time (3—4 d), in addition to [(PdCl$_2$L^2)$_2$], a small amount of the methyl-palladated compound was formed. (*i*) In a typical experiment a mixture of [PdCl$_2$(NCPh)$_2$] and L^2 (ratio 1 : 1) in benzene was left at room temperature under stirring for 7 d. The resulting solution was filtered, to separate a black decomposition product, concentrated to small volume, and passed through a chromatographic column of acetylated cellulose (acetyl content 40%) using hexane containing 30% v/v of ethyl acetate as eluant. Two distinct fractions were collected, these were taken to dryness and the solid residues crystallized from dichloromethane–hexane. The former fraction afforded yellow crystals of the metallated species {Found: C, 45.5; H, 5.5; Cl, 10.2; N, 8.2. [PdCl(C$_{13}$H$_{19}$N$_2$)]$_2$ requires C, 45.2; H, 5.5; Cl, 10.3; N, 8.1%}. The second fraction afforded the simple substitution product [(PdCl$_2$L^2)$_2$]. (*ii*) The same products were obtained when a mixture of *trans*-[PdCl$_2$(NCPh)$_2$] and L^2 (ratio 1 : 2) in dichloromethane was left at room temperature, under stirring, for 1 d. The resulting solution, filtered and concentrated to small volume afforded by treatment with excess diethyl ether, a brown precipitate of [(PdCl$_2$L^2)$_2$]. The mother-liquor, treated with an excess of pentane, afforded the metallated species.

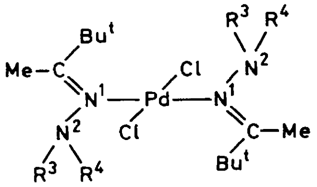
[{Pd[CH$_2$C(CH$_3$)$_2$C(=NNMePh)Me]Cl}$_2$]. (*i*) This species was obtained by performing the reaction between *trans*-[PdCl$_2$(NCPh)$_2$] and L^2 in the presence of a base (NaO$_2$CMe) (ratio 1 : 1 : 1.2) in methanol and leaving the mixture under stirring at room temperature for 1 d. The product, quite insoluble in methanol, was separated by filtration of the solution and crystallized from dichloromethane–hexane, yield *ca.* 50% {Found: C, 45.8; H, 5.2; Cl, 10.4; N, 8.3. [PdCl(C$_{13}$H$_{19}$N$_2$)]$_2$ requires C, 45.3; H, 5.5; Cl, 10.3; N, 8.1%}. (*ii*) The same product was obtained by treating the simple substitution product, [(PdCl$_2$L^2)$_2$], with sodium acetate (a slight excess) in methanol. (*iii*) The t-butylmetallated complex was also obtained by performing the reaction under the conditions reported by Shaw and co-workers.[5] A mixture of Na$_2$[PdCl$_4$], L^2, and NaO$_2$CMe (mol ratio 1 : 1 : 1.2) in methanol, left under stirring at room temperature for 1 d, afforded a brown precipitate which, when separated by filtration of the mother-liquor and crystallized from dichloromethane–hexane, gave the desired product.

Apparatus.—Infrared spectra in the range 4 000—250 cm^{-1} were recorded as KBr pellets on a Perkin-Elmer 457 spectrophotometer. Proton n.m.r. spectra were obtained with a Varian EM 390 spectrometer. Separations by liquid chromatography were performed on a Waters model ALC/GPC-202 chromatograph equipped with U6-K universal injector, model M6000 solvent-delivery system, and model 440 differential u.v. detector (254 and 405 nm).

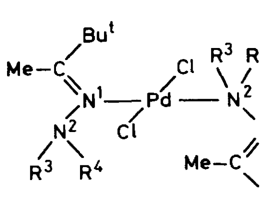
Results and Discussion

In order to understand the reason for the regioselectivity observed in the carbopalladation reaction of the dimethylhydrazone of pinacolone, we investigated the nature of the simple substitution products. The hydrazones of aliphatic ketones, R^{1}R^{2}C=N^{1}N^{2}R^{3}R^4 (L) (R^{1}R^2 = Me$_2$, Et$_2$, Bu^{n}Me, or Pr^{i}Me *etc.*; R^{3}R^4 = Me$_2$ or MePh), react with *trans*-[PdCl$_2$(NCPh)$_2$] to give two types of complexes: *trans*-[PdCl$_2$(L)$_2$] and *trans*-[(PdCl$_2$L)$_2$], depending upon the metal to ligand ratio. In both types of complexes the hydrazones co-ordinate exclusively through the iminic nitrogen, N^1, in spite of the fact that this type of co-ordination is very sterically demanding and leads to hindered rotation about the Pd–N^1 bond.[6–9,12] In this context it is to be noted that the free ligands are synthesized as the geometrical isomer with the bulkier substituent of the ketiminyl residue (Bu^t in the case of pinacolone) *cis* to the lone pair of electrons of N^1.[13]

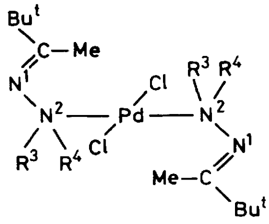
By reaction of *trans*-$[PdCl_2(NCMe)_2]$ with twice the stoicheiometric amount of $Bu^tMeC{=}NNMe_2$ (L^1) in benzene at 5 °C the expected 2 : 1 adduct $[PdCl_2(L^1)_2]$ was obtained. The n.m.r. spectrum of a freshly prepared solution of this compound exhibited one set of signals (see Table) with resonances of CBu^t, CMe, and NMe shifted to lower field, with respect to those of the free ligand, by 0.06, 1.16, and 0.46 p.p.m. respectively. The large deshielding effect suffered by the CMe group clearly indicates that this radical is *cis* to the metal[7] and therefore the ligand is N^2-co-ordinated to the metal [structure (1c)]. The n.m.r. spectrum changed with time and, in addition to the original set of signals, two new sets of resonances of increasing intensity appeared. It was possible to show by high pressure liquid chromatography experiments * that both of the new sets of signals belonged to the same compound which, presumably, has the same stoicheiometry, but where the ligands are unsymmetrically bonded to the metal [structure (1b)]. In fact, while one set of resonances exhibited downfield shifts comparable to those of the initial compound (0.07, 1.02, and 0.5—0.6 p.p.m. for the CBu^t, CMe, and NMe groups respectively), the second set of resonances exhibited a much bigger downfield shift for the CBu^t group (0.84 p.p.m.) than for the CMe group (0.40 p.p.m.) therefore indicating that the former radical is now *cis* to palladium and the ligand is N^1-co-ordinated.



(1a)



(1b)



(1c)

It is to be noted that neither the initial compound, type (1c), nor species type (1b) showed the presence of rotational isomers which were observed in all complexes of hydrazones having structure of type (1a).[8,9] The explanation is that in complexes of type (1a) there is the possibility of having two isomers differing in the mutual orientation of the two ligands [symmetric in one case (*syn* isomer) and antisymmetric in the other (*anti* isomer)] because, being both N^1-co-ordinated to the metal, they are not free to rotate about the Pd–N^1 bonds. This is not possible in the complexes having structure type (1b) or (1c) where at least one ligand, being N^2-co-ordinated to the metal and hence less sterically demanding, is free to rotate about the Pd–N^2 axis.

The species having structure (1b) reached a maximum concentration corresponding to *ca.* 50% of the total substrate after *ca.* 5 h at 10 °C. For a longer reaction time the metallation reaction took place according to the stoicheiometry of equation (i) and the n.m.r. spectrum showed, in addition

$$3[PdCl_2(L^1)_2] \longrightarrow [\{PdCl(L^1 - H)\}_2] + [PdCl_4]^{2-} + 2[HL^1]^+ + 2L^1 \quad \text{(i)}$$

to the previous resonances, those of the cyclopalladated complex $[\{\overline{Pd[CH_2C(=NNMe_2)Bu^t]}Cl\}_2]$ and of partially protonated ligand. It is to be noted that the equilibrium between the symmetrically bonded (1c) and unsymmetrically bonded $[PdCl_2(L^1)_2]$ complexes (1b) was maintained until the metallation reaction was complete.

An experiment was performed in which *trans*-$[PdCl_2(NCPh)_2]$ and L^1 (mol ratio 1 : 2) were mixed in deuteriodichloromethane at 10 °C and the n.m.r. spectrum recorded immediately. In this case, also, the first species to be formed was (1c), which then isomerized partially to (1b), and for a longer reaction time gave rise to the formation of cyclopalladated species. This experiment showed conclusively that L^1 co-ordinates first through the aminic nitrogen, N^2, and subsequently part of it isomerizes to the N^1-bonded species. Moreover, only the hydrazone co-ordinated through the aminic nitrogen could undergo the metallation reaction which occurred exclusively on the CMe group.

By reaction of *trans*-$[PdCl_2(NCMe)_2]$ with the stoicheiometric amount of L^1, in benzene at 5 °C, the expected 1 : 1 adduct $[(PdCl_2L^1)_2]$ was obtained. The n.m.r. spectrum showed three unresolved resonances centred at δ 1.10, 3.30, and 2.78 p.p.m. of relative intensity 3 : 1 : 2. The downfield shifts, with respect to those of the free ligand, were 0.04, 1.42, and 0.43 p.p.m. for CBu^t, CMe, and NMe protons respectively and were indicative of N^2 co-ordination of the ligands [structure (2c)]. In addition to the above resonances a further set of signals, of weaker intensity, at δ 2.01, 2.32, and 2.81 p.p.m. were observed which could be assigned to a N^1-bonded hydrazone (downfield shifts, with respect to the free ligand, were 0.95, 0.44, and 0.46 p.p.m. for CBu^t, CMe, and NMe protons respectively). Performing the reaction between *trans*-$[PdCl_2(NCMe)_2]$ and L^1 (ratio 1 : 1) directly in the n.m.r. sample tube and monitoring the spectrum immediately we observed that the set of signals belonging to the N^1-bonded ligand was initially weaker and increased with time reaching a maximum value corresponding to *ca.* 20% of the total. Therefore in the dimeric 1 : 1 species $[(PdCl_2L^1)_2]$ also, the ligand co-ordinates initially through the aminic nitrogen, N^2, giving rise to structure (2c) and subsequently part of it isomerizes giving rise to structure (2b). It is to be noted that, owing to the dimeric nature of this adduct which brings the two hydrazones much farther apart than in the monomeric 2 : 1 adduct, the resonances of the N^2-bonded hydrazones in both complexes (2c) and (2b) overlap and this could be one reason for the broadening of the corresponding signals. Another additional cause could be the presence of geometrical isomers such as *cis*- and *trans*-$[(PdCl_2L^1)_2]$.

The dimeric 1 : 1 adduct (as with the monomeric 2 : 1 complex) in solution undergoes a metallation reaction according to the stoicheiometry of equation (ii), giving

$$2[(PdCl_2L^1)_2] \longrightarrow [\{PdCl(L^1 - H)\}_2] + [Pd_2Cl_6]^{2-} + 2[HL^1]^+ \quad \text{(ii)}$$

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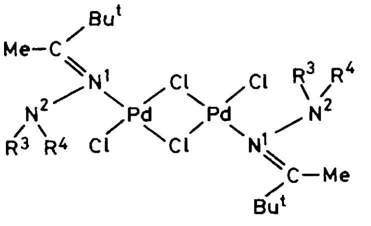
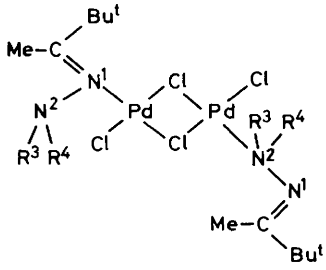
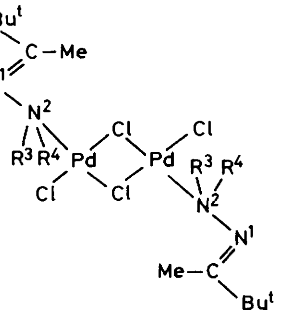
* Column, LiChrosorb DIOL 10 μm, 25 × 0.45 cm internal diameter; mobile phase, n-hexane–dichloromethane (90 : 10 v/v); flow rate 1.5 cm^3 min^{-1}; at room temperature.



(2a)



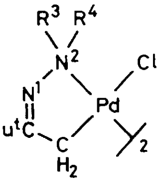
(2b)



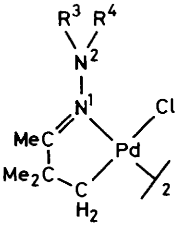
(2c)

rise to the formation of the cyclopalladated complex $[\{\overline{\mathrm{Pd}[\mathrm{CH_2C({=}NNMe_2)Bu^t}]}\mathrm{Cl}\}_2]$. Therefore in this case also only the N^2-bonded hydrazone is capable of undergoing a metallation reaction on the CMe group.

The metallation reaction which occurs spontaneously in both the 2 : 1 and 1 : 1 adducts can be accelerated by the addition of a base (NaO_2CMe); it can also be performed by direct mixing of $Na_2[PdCl_4]$, L^1, and NaO_2CMe in methanol as described by Shaw and co-workers.[5] In all cases the cyclopalladation occurs on the CMe group giving rise to structure (3a).



(3a)



(3b)

There is another report in the literature in which, because of steric interaction between the ligand substituents and the six-co-ordinate metal core, the hydrazones have adopted the N^2 co-ordination, *i.e.* in $[\mathrm{Ru(Me_2C{=}N^1N^2H_2)_2\{P(OMe)_3\}_4}][\mathrm{BPh_4}]_2$.[14] In the present case, however, the complexes are four-co-ordinate and the shift from N^1 to N^2 co-ordination must be caused exclusively by the steric hindrance of the Bu^t group; in fact it is sufficient to substitute the Bu^t group with the slightly smaller Pr^i radical to revert back to N^1 co-ordination. To investigate how strong this effect is, it would be necessary to reduce the basicity, and hence the co-ordination ability, of N^2 and see how this affects the co-ordination mode of the hydrazone; we therefore decided to investigate the reactivity of the methylphenylhydrazone of pinacolone, Bu^t-MeC=NNMePh (L^2), towards palladium.

Performing the reaction between *trans*-$[PdCl_2(NCPh)_2]$ and L^2, even in the presence of a very large excess of the ligand, we were unable to isolate the 2 : 1 adduct but, instead, we always obtained the dimeric 1 : 1 complex $[(PdCl_2L^2)_2]$.

The n.m.r. spectrum of this compound was characterized by resonances in the ranges δ 1.9—2.3 and 3.4—3.8 of relative intensity 4 : 1. Since no bands were observed at δ lower than 1.9 p.p.m., it was clear that the resonances of the Bu^t protons had been shifted to lower field (with respect to those of the free ligand) by no less than 0.7 p.p.m. This result is indicative of a *cis* position of the Bu^t group with respect to palladium and hence of a N^1 co-ordination of the hydrazone; as a consequence, the CMe group, *trans* to palladium, should not suffer its deshielding effect and resonate at a field not far from that of the free ligand. Therefore we can confidently assign the resonances in the range δ 1.9—2.3 to the CBu^t and CMe protons and those in the range δ 3.4—3.8 to the NMe protons. The reason why we observed several resonances, instead of one or two lines, for each type of equivalent protons, can be ascribed to different causes: (*i*) the presence of rotational isomers which were always observed in bis-hydrazone complexes, even dimers, having both ligands N^1-co-ordinated to the metal; (*ii*) the presence of geometrical isomers such as *cis*- and *trans*-$[(PdCl_2L^2)_2]$.

Therefore the presence of a phenyl group on N^2 has lowered the basicity, and hence the co-ordination ability of this atom, to such an extent that N^1 has become the preferred co-ordination site of L^2 in spite of the serious steric interaction which is built up between the Bu^t group and the metal core. Moreover, only the 1 : 1 adduct is obtained in this case probably because of the dimeric nature of this complex which allows the two hydrazones to be farther apart one from the other and the *cis* chlorines to be slightly bent outwards from the organic ligands.[12]

The complex $[(PdCl_2L^2)_2]$ in solution (either benzene or dichloromethane) slowly decomposes to give a black solid, which is insoluble in most common solvents and has not been identified, and leaving in solution, in addition to the original substrate, a small amount of the cyclopalladated species $[\{\overline{\mathrm{Pd}[\mathrm{CH_2C({=}NNMePh)Bu^t}]}\mathrm{Cl}\}_2]$ in which the hydrazone is co-ordinated through N^2 and metallation has occurred on the CMe group [structure (3a)].

The metallation reaction occurs much more readily in methanol in the presence of a base (NaO_2CMe). Under these circumstances, however, a change in regioselectivity is observed and the new cyclopalladated complex which is formed, $[\{\overline{\mathrm{Pd}[\mathrm{CH_2C(CH_3)_2C({=}NNMePh)Me}]}\mathrm{Cl}\}_2]$, has the hydrazone N^1-co-ordinated to the metal and metallation has occurred on the Bu^t group [structure (3b)]. The same product is obtained if the reaction is carried out under the conditions of Shaw and co-workers[5] (*i.e.* from $[PdCl_4]$, L^2, and NaO_2CMe in methanol). The structures of the two stereoisomers (3a) and (3b), which were initially assigned on the basis of n.m.r. data in solution (see Table), have been confirmed by preliminary *X*-ray data.

The peculiar behaviour of $[(PdCl_2L^2)_2]$ which gives different cyclopalladated species under different experimental conditions can be tentatively explained on the basis that the metallation on the CMe group, for a N^2-co-ordinated hydrazone, occurs much more readily than that on the Bu^t group, for a N^1-co-ordinated ligand. Therefore although the $[(PdCl_2L^2)_2]$ complex has the hydrazone ligands N^1-co-ordinated to the metal, we cannot exclude that an undetectable part of it is N^2-bonded to palladium and that, in a very inert solvent such as benzene or dichloromethane and in the absence of a base, this is capable of undergoing metallation reaction. In contrast, in a different solvent such as methanol and in the presence of a base, the bulk of the ligand, N^1-co-ordinated to palladium, undergoes metallation reaction on the Bu^t group. This hypothesis is supported by the observation that in the complexes with L^1, although both types of co-ordination were present (through N^1 and N^2), only the N^2-bonded hydrazone gave cyclopalladation on the Me group. Also in accord with this hypothesis, the downfield shifts of the Me and Bu^t groups (of N^2- and N^1-co-ordinated hydrazones respectively) were bigger for the former than for the latter group.

In conclusion we can confirm that the hydrazones co-ordinate to palladium preferentially through the iminic nitrogen (N^1) and that only in extreme cases [*i.e.* when N^1 is shielded by a very bulky group such as Bu^t and the aminic nitrogen (N^2) is activated by two methyl substituents] can co-ordination occur through N^2. Moreover, the different regiospecific metallation observed in normal conditions for L^1 and L^2 originates from a different co-ordination mode, the former co-ordinates preferentially through N^2 and metallates on the Me group, the second co-ordinates preferentially through N^1 and metallates on the Bu^t group. We can recall at this point that the metallation on Bu^t observed in the reaction of the oxime of pinacolone ($Bu^tMeC{=}NOH$) with palladium and investigated by Shaw and co-workers [5] stems from the N co-ordination of this ligand which brings the Bu^t group *cis* to the metal. Finally, it appears that metallation on the Me group of a N^2-bonded hydrazone occurs more readily than that on the Bu^t group of a N^1-bonded ligand.

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