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Bonding and Fluxional Behaviour of N,N'-Di-*p*-tolylformamidino- and 1,3-Di-*p*-tolyltriazenido Complexes of Palladium(II) and Platinum(II)

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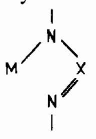
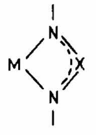
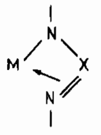
The fluxionality of $M(PPh_3)_2Cl(ArNXNAr)$ *and trans-*$Pt(PPh_3)_2H(ArNNNAr)$ *(M = palladium(II), platinum (II); Ar =* p-$CH_3C_6H_4$*; X = CH, N) is discussed on the basis of* ^1H *n.m.r., X-ray, and i.r. studies. The stereochemically non-rigid process is proposed as occurring via a pseudo penta-coordinated intermediate having both nitrogen atoms* σ *facing the metal through two electron lone pairs. A different mechanism via a* π*-bonding component in the M-(nitrogen ligand) bond is also discussed.*

Introduction

The properties of the isoelectronic 1,3-diaryltriazenido $(ArNNNAr)^-$ and N,N'-diarylformamidino-, acetamidino-, benzamidino- ligands (ArNCRNAr, R = H, CH_3, C_6H_5, respectively), herein indicated with the general formula $ArNXNAr^-$, have received much interest in view of their chemistry and mode of coordination[1–3]. Structures involving the above ligands in monodentate (I)[4], chelate (II)[1], and bridging (III)[4,5] derivatives have been proposed on the basis of spectroscopical data. Recent X-ray studies on mononuclear Co $(PhNNNPh)_3$·Toluene[6] and Pd(p-TolylNC(CH_3)N Tolyl-p)$_2$[7], and binuclear $[Ni(PhNNNPh)_2]_2$[8], $Cu_2(PhNNNPh)_2$[9], and [Pd(1-3-η-allyl)(p-TolylNNNTolyl-p)]$_2$[10] have confirmed the presence of chelate and bridging σ-bonded ligands, as in (IIa) and (III), respectively:


(I)


(IIa)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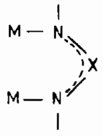
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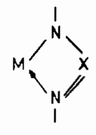
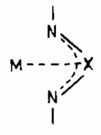

(IV)


(V)

(I) presents a σ-bonded ligand; (IIa) has a delocalized σ,σ'-attached group, while (IIb) has a localized σ,π-bonding; the σ,σ'-bridging moiety in (III) presents a delocalized π-electron system. In principle, structures (IV) and (V) are also possible. In (IV) the σ,σ'-chelating ligand presents a localized double bond; (V) has a delocalized pseudo π-allyl linkage. Structures (I)[11–13], or (IIb)[14] have been suggested on the basis of the fluxional behaviour of triazenido and formamidino complexes of the platinum metals, interpreted as occurring through a type (IIa) or (V) intermediate[11–14].

Here we describe the dynamic stereochemistry of complexes of the type $M(PPh_3)_2Cl(p$-$CH_3C_6H_4NXNC_6H_4CH_3$-$p)$ (M = Pd,Pt; X = N, CH) together with some X-ray results on triazenido complexes which present a type (I) arrangement.

Results and Discussion

Synthesis and General Properties

Previously it was reported that the zero oxidation state complexes $M(PPh_3)_4$ (M = Pd, Pt) react with 1,3-diaryltriazene yielding complexes of stoichiometry $M(PPh_3)_2(ArNNNAr)_2$[11]. Monotriazene complexes of the type *cis*-$Pt(PPh_3)_2Cl(ArNNNAr)$ were obtained from the triazene and *trans*-$Pt(PPh_3)_2(H)Cl$[11].

The complexes here described were synthesized following the reaction

$$M(PPh_3)_2Cl_2 + LiArNXNAr \xrightarrow{THF} M(PPh_3)_2Cl(ArNXNAr) + LiCl$$

$$\left.\begin{array}{l} M = Pd,\ trans\ \text{isomer} \\ M = Pt,\ cis\ \text{isomer} \end{array}\right\}\ X = N, CH$$

and from *cis*-$Pt(PPh_3)_2Cl_2$ and the triazene in the presence of hydrazine leading to the hydride complex *trans*-$Pt(PPh_3)_2H(dtt)$.[12]

The X-ray diffraction studies here reported prove that the replacement of Cl^- by $ArNNNAr^-$ (above reaction) occurs with retention of geometry; it is interesting to note that the reaction between *trans*-$Pt(PPh_3)_2(H)Cl$ and triazene yields *cis*-$Pt(PPh_3)_2Cl(ArNNNAr)$ without retention of geometry[11].

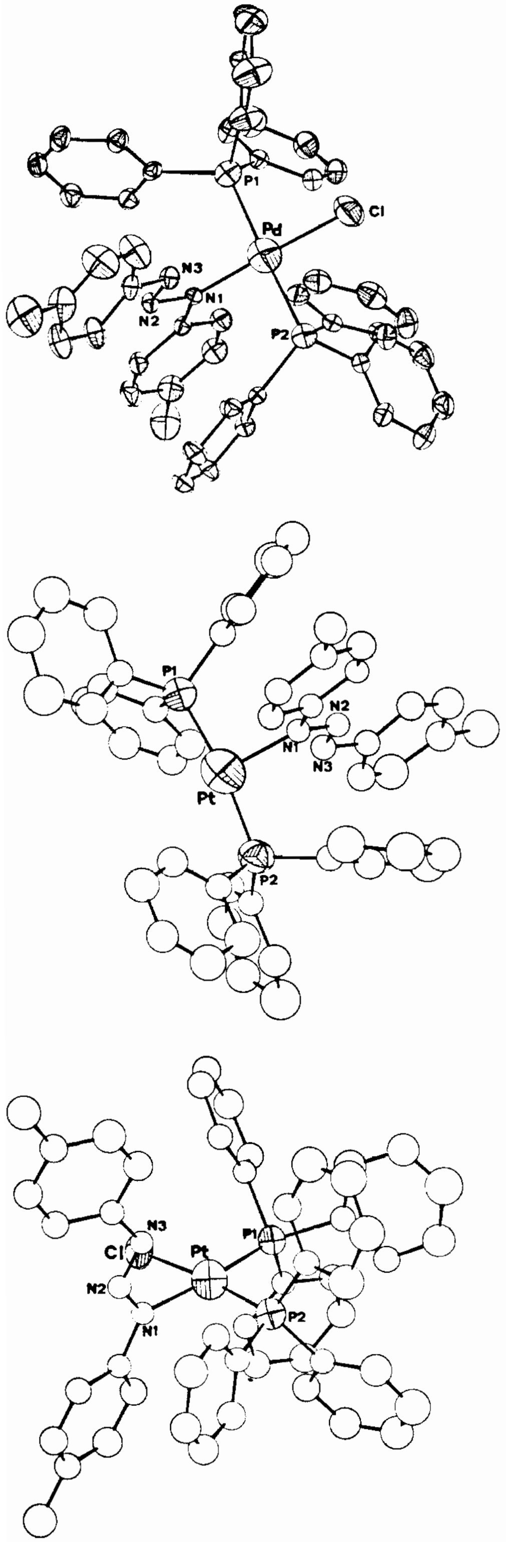


Figure 1. Prospective view of $Pd(PPh_3)_2Cl(dtt)$, $Pt(PPh_3)_2H(dtt)$, and $Pt(PPh_3)_2Cl(dtt)$; dtt = 1,3-di-*p*-tolyltriazenido.

The triazenido derivatives are more stable than the formamidino ones; however the hydride complex is stable only below –20° C. $Pd(PPh_3)_2Cl(ArNCHNAr)$ is the least stable[13] and we were able to detect its n.m.r. spectrum in $CDCl_3$ by dissolving it at low temperature.

Structure and Bonding

The structures of $Pd(PPh_3)_2Cl(dtt)$, $Pt(PPh_3)_2H(dtt)$, and $Pt(PPh_3)_2Cl(dtt)$ (chloroform solvate; dtt = *p*-TolylNNNTolyl-*p*) have been determined by X-ray diffraction studies. We report here only essential results; detailed information will be given in a subsequent paper.

In all cases (see Fig. 1) the complexes exhibit basically square planar coordination with the PPh_3 ligands in *trans*, *trans*, and *cis* relation, respectively. The ligand is essentially bonded to the metal through a single nitrogen atom; the N–N–N linkage and the two adjacent carbon atoms are roughly coplanar together with the metal and are roughly orthogonal to the coordination plane. Thus, the N2–N3 π-electron system does not have the proper orientation to support the bonding with an olefinic type contribution as shown in (IIb). On the other hand, the conformation of the ligand about the N1–N2 bond brings the N3 atom close to the metal (see Table I), thus facilitating an interaction between the metal and the N3 lone pair. Such conformation (see Figure 2A) is present in all three cases, even in the *cis*-PtCl case where the conformational freedom of the ligand is greater. This seems

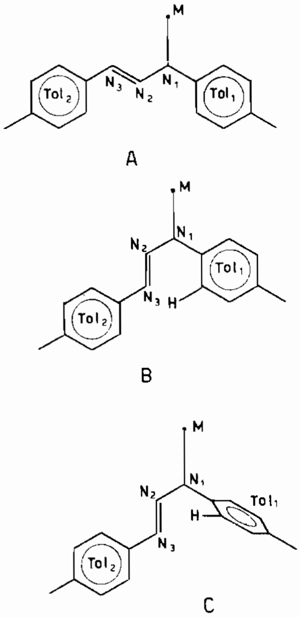


Figure 2. Some conformations of the dtt ligand around the M–N1 bond.

TABLE I. Relevant Bond Lengths (Å) and Angles (°) for the 1,3-Di-*p*-tolyltriazenido Complexes.
Average standard deviations are, for bond lengths: Pd–P (or Cl) 0.003, Pt–P (or Cl) 0.01, Pd–N 0.005, Pt–N 0.02; N–N (Pd case) 0.008, N–N (Pt case) 0.03; for angles: *ca.* 0.3° in Pd case and 0.8° in Pt case. The compounds of references 6 and 8–10 present a chelating type (IIa) and bridging type (III) arrangement, respectively, and are here reported for comparison.[a]

Compound	$PdCl(dtt)(PPh_3)_2$	$PtH(dtt)(PPh_3)_2$	$PtCl(dtt)(PPh_3)(CHCl_3$ solvate)	
M–P1	2.329	2.268	2.290	
M–P2	2.320	2.267	2.252	
M–Cl	2.333		2.354	
M–N1	2.033	2.090	2.114	
M–N3	2.836	2.908	3.008	
N1–N2	1.336	1.310	1.266	
N2–N3	1.286	1.264	1.257	
C–N1	1.368	1.386	1.434	
C–N3	1.415	1.438	1.419	
P1–M–P2	178.0	169.4	98.8	
N1–N2–N3	113.0	111.6	116.4	
C–N1–N2	116.1	114.5	117.1	
C–N3–N2	112.2	111.9	114.4	
Angular displacement of $M–N_1$ bond from CNNNC plane	8.0°	4.1°	2.6°	
	$Co(dpt)_3$[6]	$Ni_2(dpt)_4$[8]	$Cu_2(dpt)_4$[9]	$[Pd(Allyl)(dtt)]_2$[10]
N–N	1.31	1.32	1.30	1.30
N–C	1.39	1.43	1.44	1.42
N–N–N	105.0°	115.8°	116.0°	116.7°

[a] dtt = ditolyltriazenido, dpt = diphenyltriazenido.

not to be induced by packing forces nor influenced by the bulkiness of the PPh_3 ligands. Clearly the other possibility which preserves planarity (see Figure 2B) can be ruled out due to the unacceptable N3···H interaction; the conformation C with the $Tolyl_1$ group twisted would have the advantage of a greater M···N3 distance preserving the conjugation of the N2=N3 system with the adjacent $Tolyl_2$, and it should be preferred. Thus the observed conformation. A has two possible explanations: i) there is a (weak) bonding interaction between N3 and metal through donation of the lone pair on N3 to the metal; ii) the N1–N2 bond must have partial double bond character and this forces $Tolyl_1$ group to be coplanar with the N1–N2–N3 system and thus A is the only possible conformation. All this better supports the fluxional mechanism 1) than 2) (see later).

Infrared Spectra

The main stretching bands arising from the triazene skeleton vibrations appear at 1580–1600 cm^{-1} and at 1280–1310 cm^{-1}; other bands associated with this ligand appear at 1150 and 1220 cm^{-1}, as found in other complexes of Pd(II) and Pt(II)[11]. It was suggested that these latter bands are indicative of the ligand acting as monodentate and that chelate derivatives present only the other bands[11]. This is confirmed by the X-ray results here reported.

In the formamidino complexes the most characterizing i.r. absorption band occurs at *ca.* 1550 cm^{-1}, close to that of type (III) bridging compounds[5,13], where the π-electron system of the N$\overset{\text{---}}{=}$CH$\overset{\text{---}}{=}$N linkage is completely delocalized, and *ca.* 120 cm^{-1} lower than ν(C=N) in the neutral formamidine, indicating that there is a considerable π-delocalization also in the formamidino derivatives here reported. Other characterizing bands are present in these complexes. These results parallel those on related triazenido complexes and, since the two classes of compounds show a similar fluxional behaviour, we suggest a monodentate arrangement also for the formamidino complexes.

^1H N.m.r. Spectra

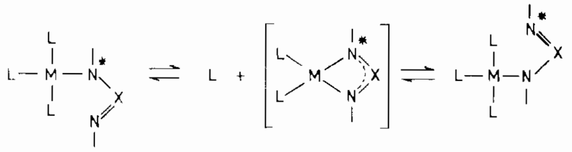
They are temperature dependent for all complexes here reported. The magnetic equivalence of the methyl group of the *p*-TolylNXNTolyl-*p* ligand observed at r.t. is reversibly lost at low temperature as two signals appear approximately of the same intensity, indicating the occurrence of a dynamic process. The hydride complex $Pt(PPh_3)_2H(dtt)$ shows three 1:2:1 triplets centered at *ca.* τ24 in the ratio 1:4:1 at any temperature with value of J_{P-H} and J_{Pt-H} (see Table I) character-

TABLE II. IR and ^{1}H NMR Data for $M(PPh_3)_2(p\text{-}CH_3C_6H_4NXNC_6H_4CH_3\text{-}p)Y$.

M	X	Y	IR (cm^{-1})[a] Nujol Mull	^{1}H NMR (CDCl$_3$)		
				τ_{CH_3}	Temp., °C	Collapse Temp., °C
trans-Pd	N	Cl	1605w, 1308vs, 1282s, 1202s, 1160m	7.76 7.65; 7.80	–20 –60	–42
cis-Pt	N	Cl	1602w, 1308vs, 1282s, 1202s, 1158m	7.69 7.63; 7.74	–30 –64	–48
trans-Pt	N	H[b]	1604w, 1306vs, 1282s, 1210s, 1156m	7.80 7.74; 7.84	–30[c] –65[e]	–58[d]
trans-Pd	(CH)	Cl	1608w, 1548vs (broad) 1322s, 1205s	7.79 7.70; 7.84	+10 –40	–4
cis-Pt	(CH)	Cl	1610w, 1560vs (broad) 1311s, 1201s	7.73 7.65; 7.76	+10 –40	–9

[a] Only main bands associated with the triazenido- or formamidido-linkages. [b] ν(Pt–H) = 2143 cm^{-1}. [c] $\tau_{Pt\text{–}H}$ = 24.13; $J_{Pt\text{–}H}$ = 891 Hz; $J_{P\text{–}H}$ = 14.1 Hz. [d] $\tau_{Pt\text{–}H}$ = 24.04. [e] $\tau_{Pt\text{–}H}$ = 24.00.

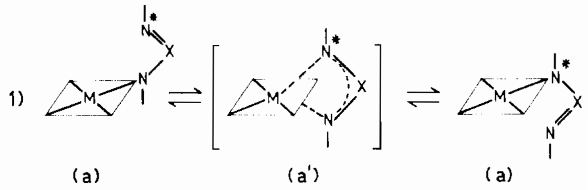
istic of a *trans* four-coordinated structure[15–17] as found in solid. It is likely that all the other complexes also present a four-coordinated structure with only one nitrogen atom bonded to the metal atom, as of type (I). Thus the variable temperature n.m.r. behaviour indicates the presence of a fluxional process which is responsible for the equivalence of the CH$_3$ groups at higher temperature, similarly to what found for $Pt(PPh_3)_2(p\text{-}CH_3C_6H_4NNNC_6H_4CH_3\text{-}p)_2$[18]. The collapse temperature (see Table I) is independent of the concentration and the mixture of corresponding complexes shows the same behaviour which is also independent of the presence of the related uncoordinated neutral ligand ArNHXNAr. These observations rule out the occurrence of an intermolecular process or of one involving dissociation of the ligand. However, the fact that $Pd(PPh_3)_2Cl(p$-TolylNCHNTolyl-$p)$ is rather unstable and in a benzene–ethanol medium the main decomposition products are *trans*-$Pd(PPh_3)_2Cl_2$ and $[Pd(ArNCHNAr)_2]_2 \cdot 1/2C_6H_6$ involving a ligand exchange reaction[13], might suggest a mechanism through a four-coordinated species of a σ,σ'-coordinating nitrogen linkage:



(the displaced L ligand might be Cl$^-$ or PPh$_3$ as well). Variable temperature ^{1}H n.m.r. experiments in the presence of uncoordinated PPh$_3$ or Cl$^-$ (this ion derived from a mixture of *trans*-$Pt(PPh_3)_2HCl$ and PPh$_3$ which is known to undergo the equilibrium[19].

$$trans\text{-}Pt(PPh_3)_2HCl + PPh_3 \rightleftharpoons [Pt(PPh_3)_3H]^+ + Cl^-$$

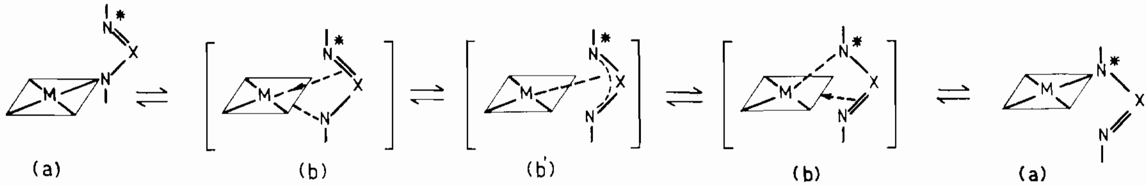
did not influence the fluxional behaviour of all the complexes here reported, so that the above mechanism can be ruled out. Thus the most likely intramolecular mechanisms responsible for the above n.m.r. behaviour are the following. Scheme 1) involves an intermediate in which the M–N (or –N*) bond is progressively broken as the other M–N* (or –N) bond is forming. The pseudo[20] five-coordinate intermediate (a^1) has a type (IIa) arrangement σ,σ'-facing the metal in a four-membered ring. Although this presents considerable steric strain and five coordination for Pd(II) and Pt(II) complexes is uncommon, (a′) seems likely as an intermediate since type (IIa) linkage has been established by X-ray diffraction studies on the closely related Co $(PhNNNPh)_3 \cdot$Toluene[6] and $Pd(p$-TolylNC(CH$_3$)N Tolyl-$p)_2$[7]. This has been suggested also for other fluxional triazenido complexes of the platinum metals[11, 12, 18].



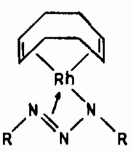
An alternative mechanism 2) involves a five-coordinate intermediate (b) of the chelating type (IIb) having a M–N (or –N*) σ bond supported by olefinic-type bonding through the X = N* (or X = N) double bond and eventually a ligand acting through a system of a pseudo π-allylic arrangement (b′). This is a similar to the π–σ process occurring in the closely related allylic systems[21].

Although X-ray structural evidence for type (IIb) arrangement has not yet been reported, this has been

2)



suggested to explain the fluxional behaviour of Rh $(C_8H_8)(p\text{-}FC_6H_4NNNC_6H_4F\text{-}p)$ as low temperature limiting formula to account for the electronic requirements of the metal atom, which would have a 14-electron configuration if the triazenido linkage acts as a σ-monodentate ligand, while a 16-electron configuration preferred by Rh(I) complexes is achieved by chelating the ligand[14].



The main difference between mechanism 1) and 2) is that the former involves an intermediate with σ-bonds only, while the intermediate in the latter is supported also by π-bonding. Even though it is not possible to discriminate between these two mechanisms, the former one seems the most likely since a nitrogen ligand competing between σ or π bonding possibilities usually prefers σ coordination, at variance with related carbon systems. Thus for example, $[Ni(PhNNNPh)_2]_2$[8] shows bridging σ,σ'-coordinating ligand of the type (III), and $Co(PhNNNPh)_3\cdot$Toluene[6] and $Pd(p\text{-}TolylNC(CH_3)N\ Tolyl\text{-}p)_2$[7] present σ,σ'-chelating systems of the type (IIa), while the related complexes $M(1\text{-}3\text{-}\eta\text{-}C_3H_5)_{2\,or\,3}$ (M = Pd,Ni[22] or Ir[23], Rh[24]) show π-allylic bonds. To this respect, particularly illustrative is the complex $[Pd(1\text{-}3\text{-}\eta\text{-}C_3H_5)(p\text{-}TolylNNNTolyl\text{-}p)]_2$[10] which presents π-allyl bonds and σ-bridging triazenido ligands. More significantly, the X-ray results here reported better support mechanism 1) which is essentially a displacement of the nitrogen ligand in a plane containing the metal and orthogonal to the coordination plane.

The above intramolecular non-rigidity may be compared to the bimolecular nucleophilic displacement reactions of square planar, lowspin d^8 systems[25]. The nitrogen atom N* (or N) is displaced by the N(or N*) one (see the proposed mechanisms), through a pseudo[20] five-coordinate species, similarly to the well established stereochemical mechanism of square planar substitutions[25]. Robinson *et al.* found that $Pd(PPh_3)_2(p\text{-}CH_3C_6H_4NNNC_6H_4CH_3\text{-}p)_2$ presents an activation energy for the fluxional process smaller than the platinum analog[18], in agreement with the observation that the Pd^{II} systems are more reactive than the Pt^{II}analogs[25]. However, it must be pointed out that the similarity between these fluxional processes and the bimolecular nucleophilic dislacement reactions[25] cannot be so close, since the steric strain due to the four-membered ring in the intermediate (a') (or (b)) must play an important role which is absent in the case of the nucleophilic displacement.

Qualitative considerations on the chemical shift separation of the CH_3 signals in the low temperature limiting spectra of the triazenido- and forammidino-complexes suggest that the latter ones are dynamically more rigid. Detailed kinetic studies are in progress in order to get some insight on the role of the above mentioned steric strain together with the effect of the ligand *trans* to the nitrogen atom.

Experimental

Solvents were dried and purged with nitrogen before use. I.r. and ^1H n.m.r. spectra were recorded on a Perkin–Elmer 457 and on a 90 MHz Bruker HFX-10 instrument, respectively. Melting points were taken in air on a Kofler Hot Stage. N,N'-di-*p*-tolylformamidine[26], 1,3-di-*p*-tolyltriazene[27], *cis*-$Pt(PPh_3)_2Cl_2$[28] and *trans*-$Pd(PPh_3)_2Cl_2$ were prepared following literature methods.

$Pt(PPh_3)_2Cl(p\text{-}TolylNCHNTolyl\text{-}p)$

This was prepared from *cis*-$Pt(PPh_3)_2Cl_2$ and LiAr NCHNAr in THF, as previously reported for the Pd analog[13], m.p. 223–4° C. *Anal.* Calcd for $C_{51}H_{45}ClN_2P_2Pt$: C, 62.61; H, 4.64; Cl, 3.62; N, 2.86; mol.wt. 978.36. Found: C, 62.34; H, 4.87; Cl, 3.88; N, 2.74.

Trans-$Pt(PPh_3)_2H(p\text{-}TolylNNNTolyl\text{-}p)$

This was prepared by dissolving *cis*-$Pt(PPh_3)_2Cl_2$ in ethanol with hydrazine hydrate and then adding the triazene in excess, as already described[12].

Trans-$Pd(PPh_3)_2Cl(p\text{-}TolylNNNTolyl\text{-}p)$

A solution of n-butyllithium in hexane (0.25 ml. *ca.* 2.5*M*, 0.6mmol) was added to a THF solution of 1,3-di-*p*-tolyltriazene (20 ml, 0.6 mmol) at r.t. under nitrogen. Then, *trans*-$Pd(PPh_3)_2Cl_2$ (0.5 mmol) was added as a solid, which dissolved in a few minutes while heating to b.p., yielding a deep red solution, whose volume was reduced to *ca.* 5 ml by a vigorous nitrogen flux which cooled the system in about 10 minutes. Addition of EtOH afforded the red complex, which was crystallized from $CHCl_3/EtOH$, m.p. 203–4 °C dec. *Anal.* Calcd for $C_{50}H_{44}ClN_3P_2Pd$: C, 67.42; H, 4.98; Cl, 3.98; N, 4.72; mol.wt. 890.67. Found: C, 67.60; H, 5.02; Cl, 4.07; N, 4.84.

Similarly prepared was the platinum analog from *cis*-$Pt(PPh_3)_2Cl_2$; m.p. 235–6 °C dec. *Anal.* Calcd for $C_{50}H_{44}ClN_3P_2Pt$: C, 61.32; H, 4.53; Cl, 3.62; N, 4.29; mol.wt. 979.36. Found: C, 61.11; H, 4.66; Cl, 3.81; N, 4.35. Slow crystallization from $CHCl_3/EtOH$ yielded the chloroform solvate. *Anal.* For 1 mol of $CHCl_3$ solvate, calcd: Cl, 12.91; found: Cl, 11.87.

Suitable crystals for X-ray diffraction studies for the trazenido-chloride or –hydride derivatives were obtained from $CHCl_3/EtOH$ and $C_6H_6/EtOH$, respectively. $Pt(PPh_3)_2Cl(ArNCHNAr)$ was crystallized from $CHCl_3$/n-hexane. Similar attempts to crystallize the palladium analog led to decomposition; however, the compound was obtained with an acceptable degree of purity directly from the reaction mixture.

X-ray Data

X-ray diffraction experiments were performed on a single crystal Philips PW-1100 diffractometer. Crystal structure analysis is based on complete sets of three-dimensional integrated intensity with a resolution of *ca.* 0.90 Å.

Acknowledgments

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