Complexes of Osazones with Palladium(II) and Platinum(II): Isomerization, Oxidation, and *ortho*-Metallation of the Co-ordinated Ligands[1]

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The preparation, properties, and reactions of a series of complexes of general formula $[MCl_2(L)]$ are described for the first time (M = Pt) or reinvestigated (M = Pd) [L = $Ph(H)N\cdot N{:}\overline{C\cdot[CH_2]_4\cdot C}{:}N\cdot N(H)Ph$ (L^1), $Ph(H)N\cdot N{:}C(Me)\cdot C(Me){:}N\cdot N(H)Ph$ (L^2), and $Ph(Me)N\cdot N{:}C(Me)\cdot C(Me){:}N\cdot N(Me)Ph$ (L^3)]. On treatment with base, complexes of L^1 and L^2 readily undergo hydrogen-chloride elimination to give species of formula $[\{MCl(L - H)\}_x]$ which contain a covalent M–N bond. These complexes in solution undergo further transformation with loss of a hydrogen molecule and formation of *ortho*-metallated diazoalkene derivatives, $[M(L - 3H)Cl]$. The complex $[PtCl_2(L^3)]$, on treatment with silica gel or refluxing in nitromethane, affords, as the palladium analogue, the cyclometallated species $[PtCl(L^3 - H)]$. The reactivities of the ligands with palladium and platinum are compared.

THE co-ordination of osazones to Pd^{II} and Pt^{II} has been subject of previous papers.[2-5] We reported [2,4] that the palladium complex $[PdCl_2L]$ [L = $Ph(Me)N\cdot N{:}C(Me)\cdot C(Me){:}N\cdot N(Me)Ph$] undergoes internal metallation to give the complex $[PdCl(L - H)]$ in which the phenyl ring

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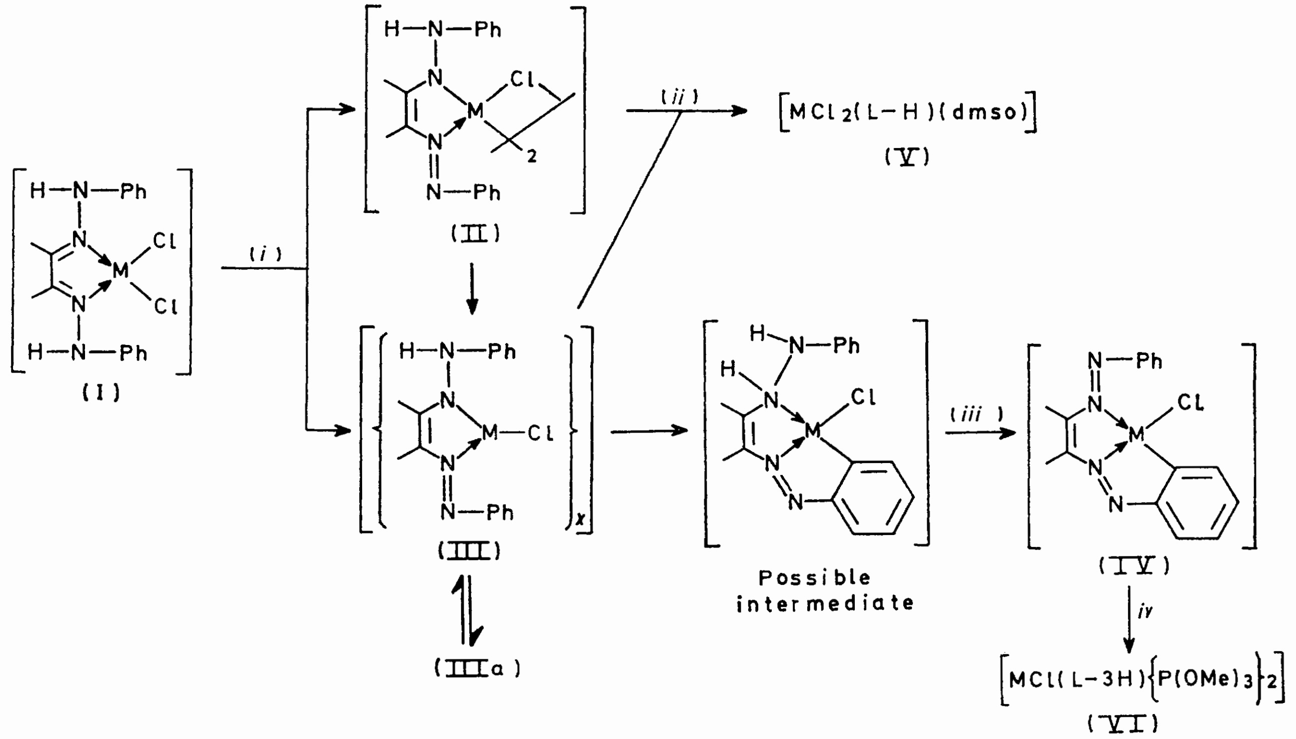
is σ bonded to palladium. On the other hand when L = Ph(H)N·N:C(Me)·C(Me):N·N(H)Ph or Ph(H)N·N:C·[CH$_2$]$_4$·C:N·N(H)Ph a complex of formula [PdCl(L − H)] can be obtained in which isomerization of the ligand with formation of a σ N–Pd bond occurs.[3] This complex is not stable in solution and gives rise to a series of transformations, investigated in the present work. We have also extended this investigation to platinum in order to make a comparison between the reactivity of the two metals.

EXPERIMENTAL

*Dichloro(cyclohexane-*1,2-*dione bisphenylhydrazone)platinum*(II), [PtCl$_2$(L^1)].—This complex was prepared by adding dropwise to a methanol solution of K[Pt(C$_2$H$_4$)Cl$_3$]·3OH$_2$ (1 mmol in a few cm^3 of solvent) the stoicheiometric amount of L^1 dissolved in the same solvent. Five-co-ordinate [Pt(C$_2$H$_4$)Cl$_2$(L^1)] partly precipitated at this stage,[5] but on leaving the mixture stirring for 1 d the ethylene was lost and a red precipitate of [PtCl$_2$(L^1)] in >80% yield was obtained. The solid was washed with small amounts of MeOH, then with diethyl ether, and dried.



Scheme (*i*), −HCl; (*ii*), dmso; (*iii*), −H$_2$; (*iv*), P(OMe)$_3$.

(*Butane-*2,3-*dione bismethylphenylhydrazone)dichloroplatinum*(II), [PtCl$_2$(L^3)], was prepared in a similar manner and crystallized as black crystals (yield >90%).

(*Butane-*2,3-*dione bisphenylhydrazone)dichloroplatinum*(II), [PtCl$_2$(L^2)].—Because of the very poor solubility of the ligand, this complex was prepared by stirring for several hours a suspension of the ligand in a methanol solution of [{Pt(C$_2$H$_4$)Cl$_2$}$_2$]. No five-co-ordinate intermediate could be isolated in this way. On filtering the reaction mixture reddish brown needles of [PtCl$_2$(L^2)] were isolated; these were washed with small portions of MeOH, then with diethyl ether, and dried (yield >80%).

The analogous palladium complexes were prepared as previously described.[2-4]

Reaction with NEt$_3$.—A suspension of [MCl$_2$(L)] (M = Pd^{II} or Pt^{II}; L = L^1 or L^2) in CH$_2$Cl$_2$ was treated while stirring with the stoicheiometric amount of NEt$_3$; after a few minutes the solvent was evaporated *in vacuo*. The residue was washed with water and dried *in vacuo*. The solid was then chromatographed over a column of Sephadex LH 20. We used columns of different size (height 50—90 cm, diameter 1.5—3 cm) depending on the relative R_F values of the compound to be eluted and the amount of raw material loaded which in any case could not be more than 0.2 g. Intermediate species (II) was always eluted before (III), and complex (IV) had an R_F value intermediate between these two (see Scheme).

Reaction with SiO$_2$.—The complex [PtCl$_2$(L^3)] (0.4 g) was stirred with silica gel (5 g) for 2 d in dichloromethane (100 cm^3). The solvent was then evaporated *in vacuo* and the solid loaded onto a silica-gel column. By eluting with CHCl$_3$, [PtCl(L^3 − H)] was first collected, followed by unchanged starting material.

Chloro[2-(1′-*phenylazocyclohex-*1′-*en-*2′-*ylazo)phenyl-*C^{1}N$^{2'}$N$^{1'}$]*bis(trimethyl phosphite)platinum*(II), [PtCl(L^1 −3H){P(OMe)$_3$}$_2$].—A suspension of [PtCl(L^1 − 3H)] in benzene was treated with P(OMe)$_3$ in molar ratio 1 : 2; the solid dissolved immediately giving a violet solution which was then taken to dryness. The residue was dissolved in light petroleum, the solution filtered, and, by evaporating the solvent *in vacuo*, a violet, moisture-sensitive, complex of composition [PtCl(L^1 − 3H){P(OMe)$_3$}$_2$], (VI), was isolated. The complex [PtCl(L^2 − 3H){P(OMe)$_3$}$_2$] was prepared by treating [PtCl(L^2 − 3H)] with P(OMe)$_3$ in a similar way. After evaporation of the violet benzene solution the reddish-brown oil obtained was dissolved in a few cm^3 of diethyl ether and, on adding light petroleum, yellow crystals of $[PtCl(L^2 - 3H)\{P(OMe)_3\}_2]$ were precipitated. Although the crystals are stable to the air, they dissolve in organic solvents to give violet solutions which are sensitive towards traces of moisture.

$[PtCl(L^3 - H)(PPh_3)_2]$.—A suspension of $[PtCl(L^3 - H)]$ in benzene was treated with the stoicheiometric amount of triphenylphosphine (molar ratio 1 : 2). There was an instantaneous reaction and the starting compound dissolved to give a yellow solution. On adding light petroleum a yellow solid of composition $[PtCl(L^3 - H)(PPh_3)_2]$ was precipitated.

I.r. spectra in the range 4 000—300 cm^{-1} were recorded as KBr pellets with a Perkin-Elmer 456 spectrophotometer; spectra in the range 500—100 cm^{-1} were recorded as Nujol mulls or Polythene pellets with a Beckman I.R. 11 instrument. ^{1}H N.m.r. spectra were obtained with Varian NV 14 and Brucker 90 Mc spectrometers with $CDCl_3$, CCl_4, $(D_3C)_2SO$, and $PhNO_2$ as solvents and tetramethylsilane as internal standard.

RESULTS

The co-ordinating ability of osazones towards Pt^{II} is rather poor; in fact $[PtCl_2(NCPh)_2]$, which would appear to be a suitable starting material in preparation of the derivatives $[PtCl_2L]$ (L = osazone), did not react at room temperature with free osazones over a period of many days and on heating under reflux in benzene only extensive decomposition with formation of a negligible amount of the desired product occurred. However, these ligands reacted smoothly with Zeise's salt, $K[Pt(C_2H_4)Cl_3]$, or its dimer $[\{Pt(C_2H_4)Cl_2\}_2]$. The reaction proceeds in two stages: the first step is substitution of a chloride ion by the bidentate ligand and formation of a five-co-ordinate $[Pt(C_2H_4)Cl_2(L)]$ complex; in the second step the intermediate species loses ethylene giving the square-planar derivative $[PtCl_2(L)]$.[5] The co-ordinated ligand in the latter gives rise to different reactions depending on the type of osazone.

TABLE 1

Analytical (%)[a] and i.r. data (cm^{-1})

Compound	Colour	C	H	N	Cl	ν(N–H)	ν(C=N) or [ν(N=N) + ν(C=C)]	δ(C–H) Ring vibrations		ν(M–Cl)
L^1						3 356	1 600, 1 565	750, 740	700, 690	
$[PdCl_2(L^1)]$ (I)	Red	45.8 (46.0)	4.8 (4.3)	10.3 (11.9)	15.5 (15:1)	3 270, 3 220	1 590	750	690	345, 329
$[\{PdCl(L^1 - H)\}_x]$ (II)	Green	49.4 (49.9)	4.2 (4.4)	12.7 (12.9)	8.0 (8.2)	3 220	1 590	750	690	310—250[b]
$[\{PdCl(L^1 - H)\}_x]$ (III)	Purple	49.9 (49.9)	4.6 (4.4)	12.5 (12.9)	8.5 (8.2)	3 200br	1 600—1 560	745	690	305, 285, 260[b]
$[\{PdCl(L^1 - H)\}_x]$ (IIIa)	Dark red	49.2 (49.9)	4.3 (4.4)	12.6 (12.9)	8.9 (8.2)	3 200br				
							1 600—1 560	745, 735 710[c]	680spl	295w
$[PdCl(L^1 - 3H)]$ (IV)	Brown	49.7 (50.1)	3.7 (4.0)	12.6 (13.0)	8.8 (8.2)		1 585, 1 570	763spl	687	305
$[PdCl(L^1 - H)(dmso)]$ (V)	Red	46.7 (47.0)	4.9 (4.9)	11.0 (11.0)	6.9 (6.9)	3 220	1 600—1 560	755	690	*ca.* 290vw
$[PtCl_2(L^1)]$ (I)	Red	38.65 (38.7)	3.9 (3.6)	9.6 (10.0)	13.0 (12.7)	3 280spl	1 590	751, 745	690	349, 333
$[\{PtCl(L^1 - H)\}_x]$ (III)	Green	42.0 (41.4)	4.1 (3.7)	9.5 (10.7)	7.1 (6.8)	3 200	1 600, 1 575	745	690	320
$[PtCl(L^1 - 3H)]$ (IV)	Green	41.5 (41.6)	3.4 (3.3)	10.5 (10.8)	7.0 (6.8)		1 595, 1 580	770, 760 720[c]	687	323
$[PtCl(L^1 - 3H)\{P(OMe)_3\}_2]$ (VI)	Violet	38.5 (37.5)	4.7 (4.6)	7.0 (7.3)	4.0 (4.6)		1 590	*d*		*ca.* 285vw
L^2						5 340	1 590, 1 565	750	695	
$[PdCl_2(L^2)]$ (I)	Red	43.4 (43.3)	4.2 (4.0)	12.7 (12.6)	16.0 (15.9)	3 270, 3 230	1 590	750	690	340, 310
$[\{PdCl(L^2 - H)\}_x]$ (II)	Green	46.9 (47.1)	4.2 (4.1)	13.2 (13.7)	8.4 (8.6)	3 220br	1 590	750	690	297, 265[e]
$[PdCl(L^2 - 3H)]$ (IV)	Brown	47.4 (47.4)	3.9 (3.7)	13.5 (13.8)	8.8 (8.7)		1 585—1 565	760	710[c] 680	295w
$[PtCl_2(L^2)]$ (I)	Reddish brown	36.9 (36.1)	3.7 (3.4)	10.3 (10.5)	12.5 (13.3)	3 280, 3 240 (sh)	1 595	755	690	340, 330
$[PtCl(L^2 - 3H)]$ (IV)	Green	39.1 (38.9)	3.4 (3.1)	10.6 (11.3)	6.8 (7.2)		1 595—1 570	760	718[c], 682	320
$[PtCl(L^2 - 3H)\{P(OMe)_3\}_2]$ (VI)	Yellow	36.4 (35.6)	4.2 (4.5)	8.2 (75.)	4.3 (4.8)		1 590		*d*	*ca.* 285vw
L^3							1 597, 1 565 (sh)	747	689	
$[PtCl_2(L^3)]$ (I)	Green	38.7 (38.6)	4.0 (4.0)	10.0 (10.0)	12.6 (12.6)		1 595, 1 575	750	685	338, 328
$[PtCl(L^3 - H)]$ (VII)	Dark brown	41.4 (41.3)	4.1 (4.0)	10.4 (10.7)	7.4 (6.8)		1 595, 1 575 (sh)	765, 755	718[c] 690	300 (335[f])
$[PtCl(L^3 - H)(PPh_3)_2]$ (VIII)	Yellow	62.2 (61.9)	5.2 (5.2)	5.2 (4.9)	3.5 (3.4)		1 595, 1 570		*d*	*ca.* 280vw

[a] Calculated values are given in parentheses. [b] Assignment unreliable because of overlapping with ligand absorptions. [c] Characteristic of C–H out-of-plane deformation for *ortho*-disubstituted aromatic rings. [d] The phosphine absorptions overlapped with those of the metallated ligand. [e] Indicative of bridging chlorine in complexes (II). [f] Alternative assignment.

TABLE 2

Proton chemical shifts (δ downfield from $SiMe_4$)

Compound	Solvent	Type of protons					
		NH	$C_6H_{5(4)}$	CH_2	C–CH_3	N–CH_3	O–CH_3
L^1	$CDCl_3$	*a*	7.5—6.6	2.5 (m), 1.7 (m)			
$[PdCl_2(L^1)]$ (I)	$CDCl_3$	8.5	7.5—6.2	2.5 (m), 1.7 (m)			
$[\{PdCl(L^1 - H)\}_x]$ (II)	$CDCl_3$	8.8	7.7—6.5	2.4 (m), 1.6 (m)			
$[PdCl(L^1 - 3H)]$ (IV)	$CDCl_3$		8.2—6.8	3.0 (m), 2.0 (m)			
$[PdCl(L^1 - H)(dmso)]$ (V)	$(D_3C)_2SO$	9.4	7.4—6.2	2.5 (m),[b] 1.7 (m)			
$[PtCl(L^1 - 3H)]$ (IV)	$CDCl_3$		8.0—6.7	3.1 (m), 2.0 (m)			
$[PtCl(L^1 - 3H)\{P(OMe)_3\}_2]$ (VI)	CCl_4		8.0—6.5	3.0 (m), 2.0 (m)			3.75 (d), 3.5 (d)[c]
$[\{PdCl(L^2 - H)\}_x]$ (II)	$CDCl_3$	8.7	7.5—6.5		2.02, 1.93		
$[PdCl(L^2 - 3H)]$ (IV)	$CDCl_3$		8.1—7.1		2.62, 2.45		
$[PtCl(L^2 - 3H)]$ (IV)	$CDCl_3$		8.0—6.5		2.66, 2.59		
$[PtCl_2(L^3)]$ (I)	$PhNO_2$		*d*		2.26	3.81	

[a] Obscured by the phenyl protons. [b] Affected by solvent impurities. [c] ^3J(P–H) 12 Hz. [d] Obscured by the solvent. m = multiplet and d = doublet.

Cyclohexane-1,2-*dione Bisphenylhydrazone*, L^1.—The reaction of $[PdCl_2(L^1)]$, (I), with triethylamine did not give the chlorine-bridged dimer $[\{PdCl(L^1 - H)\}_2]$ (II) as the only product but another species (red), (III), having the same composition as (II) (see Scheme) was formed in comparable yield. Over a period of 8—10 h at room temperature in CH_2Cl_2 solution, complex (II) was transformed almost quantitatively into (III) which underwent a further transformation to a brown species, (IV), which also analysed as (II) and (III).

The i.r. spectrum of (IV) showed the following features:

no absorption due to N-H stretchings; a new band at 710 cm^{-1} in the region of phenyl CH deformations characteristic of an *ortho*-disubstituted benzene ring;[6] and only one band due to Pd-Cl stretching. The ^{1}H n.m.r. spectrum in $CDCl_3$ showed, again, the absence of protons bound to nitrogen atoms and a downfield shift for the phenyl protons (see Table 2) consistent with the presence of an *ortho*-metallated ring.[7] Thus complex (IV) is formulated as [PdCl(L^1 − 3H)], the probable structure being shown in the Scheme, and it can be described as a 1,2-bisphenylazocyclohex-1-ene derivative. The intermediate species (II), already reported, had elemental analysis and i.r. and n.m.r. spectra consistent with the given formulation [{PdCl(L^1 − H)}$_2$]. Complex (III), when freshly prepared, dissolves readily in several organic solvents, but when its concentration becomes high and the medium has poor co-ordinating ability (CH_2Cl_2 or $CHCl_3$) in a few minutes another complex (IIIa) is precipitated. The elemental analyses of (IIIa) were similar to those of (III).

All the intermediate species, (II), (III), and (IIIa), reacted with dimethyl sulphoxide (dmso) to give the same complex [PdCl(L^1 − H)(dmso)], (V), indicating that they have the same basic structure with the co-ordination sphere of the metal ion saturated by chlorine atoms [complex (II)] or ligand molecules [probably complexes (III) and (IIIa)] acting as bridges between different metal ions. Moreover complex (V), which is stable in the solid state, can exist in solution only if some dmso is added, otherwise (III) is obtained.

In the reaction of the complex [$PtCl_2(L^1)$] with NEt_3 complex (II) could not be detected, and from column chromatography of the reaction mixture only two dark green products, identified from the i.r. spectra respectively as analogues of (III) and (IV), could be isolated. The *ortho*-metallation process occurs in this case at a much higher rate and the transformation (III) ⟶ (IV) was complete within 1 h at room temperature in CH_2Cl_2 solution. On reaction of (IV) with $P(OMe)_3$ the N-Pt bonds are cleaved and the complex [PtCl(L^1 − 3H){$P(OMe)_3$}$_2$], (VI), was obtained.

Butane-2,3-*dione Bisphenylhydrazone*, L^2.—The reaction of the palladium complex [$PdCl_2(L^2)$] with NEt_3 was completely analogous to that observed in the case of osazone L^1. However, in comparison with the previous system, we observed[1] an increased rate for the transformation (III) ⟶ (IV), which prevented the isolation of complex (III) since the transformation was complete in the elution time. In the platinum case it was impossible to detect any intermediate species and the reaction with NEt_3 led directly to complex (IV). The absence of nitrogen protons and the presence of an *ortho*-metallated ring in complexes (IV) was clearly indicated by the i.r. and ^{1}H n.m.r. spectra, and thus they can be described as a 2,3-bisphenylazobut-2-ene derivatives. Also, in this case, reaction of (IV) with phosphite gave the complex [PtCl(L^2 − 3H){$P(OMe)_3$}$_2$], (VI).

Butane-2,3-*dione Bisphenylmethylhydrazone*, L^3. [$PtCl_2(L^3)$] was not affected by treatment with NEt_3 and could be recovered unchanged after being heated under reflux for several hours in the pure amine. However, treatment with silica gel in dichloromethane afforded, as in the case of palladium,[2,4] the *ortho*-metallated species [PtCl(L^3 − H)], (VII), from which, on treatment with PPh_3, [PtCl(L^3 − H)(PPh_3)$_2$] was isolated. We also observed that the *ortho*-metallation process was promoted (although in low yield) by boiling (I) in $MeNO_2$ for several hours.

DISCUSSION

Substitution of an aryl group of part of a *N*-donor ligand has been studied extensively with palladium and platinum[8-12] and it has been found that this reaction has some general features: (*i*) the reaction proceeds more slowly for platinum than for palladium;[8,13] (*ii*) generally (but not always[8,10]) the presence of a base is required; (*iii*) unidentate ligands are internally metallated by platinum or palladium much more readily than bidentate ones, and the difference is probably due to the rigidity of the chelate ring which restricts approach of the *ortho*-carbon of the phenyl group towards the metal;[11] and (*iv*) in the case of Pd^{II} and Pt^{II} the *ortho*-metallation reaction has been described as electrophilic substitution at the phenyl ring and compared to mercuration reactions. (In the case of low-valent electron-rich transition-metal complexes, on the contrary, it is suggested that the nucleophilicity of the metal atom promotes its insertion into the sterically favoured *ortho*-carbon–hydrogen bond.[12]) The internal metallation observed for the osazone ligands does not seem to conform strictly to all the above observations.

The bidentate osazones have corresponding unidentate species in the hydrazone series. The reaction of benzophenone phenylhydrazone with Pd^{II} has already been investigated and it readily gives an *ortho*-metallated species. The reaction of cyclohexanone phenylhydrazone has also been investigated and, since in this case *ortho*-metallation does not occur, it was concluded that in the former case the metal–carbon σ bond was formed with an aromatic ring of the benzophenone residue.[9] Analogous results were obtained in the condensation reaction between the NH_2 group of a disubstituted hydrazine ($H_2N{\cdot}NR^1R^2$) co-ordinated to Pd^{II} and a carbonyl function R^3R^4CO.[14] It was found that the type of complex obtained depends only on the nature of groups R^3 and R^4 and not R^1 or R^2 and that only an *ortho*-carbon atom of the aromatic ring of the ketone was susceptible to electrophilic attack by Pd^{II} with formation of a five-membered ring containing two conjugated double bonds.

A cyclopalladation involving the phenyl ring of the hydrazine residues of the osazone has been reported[2,4] for the complex [$PdCl_2(L^3)$]; a completely analogous reaction is given by the analogue [$PtCl_2(L^3)$]. In the case of the bidentate osazone L^3, *ortho*-substitution is not

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promoted by a proton acceptor such as triethylamine and the reaction conditions required are more drastic than those used in the case of unidentate hydrazones. It is noteworthy that, whereas in the case of hydrazones (as it was for azobenzene) formation of the metal–carbon σ bond leads to formation of a five-membered ring containing two conjugated double bonds, this extra stabilization does not exist in the cyclometallated complexes obtained with osazone L^3.

Complexes of type (I) with osazones L^1 and L^2 behave in a completely different way. They react readily with NEt_3 at room temperature to commence a series of reactions which concludes with formation of an *ortho*-metallated species but, in the meanwhile, oxidation of the osazone to bisphenylazoalkene also occurs. The first step of the reaction is HCl elimination promoted by the amine; the abstracted proton, however, is an amine one and the obtained complexes (II), (III), and (IIIa) are *N*-metallated derivatives of a phenylazo(phenylhydrazo)-alkene moiety. Although the complete structure of (III) and (IIIa) is not clear, we have been able to ascertain that all the intermediate species [(II), (III), and (IIIa)] have the same basic structure. It is known that osazone can isomerize to azo(hydrazo)alkene as shown below;[15] therefore this first step can be considered as a ligand isomerization accompanied by HCl elimination and formation of a metal–nitrogen σ bond (see Scheme).

$$\begin{matrix}\mathrm{RC{:}N{\cdot}N(H)Ph}\\ \mathrm{RC{:}N{\cdot}N(H)Ph}\end{matrix} \longleftrightarrow \begin{matrix}\mathrm{RC{\cdot}N{:}NPh}\\ \mathrm{RC{\cdot}N(H){\cdot}N(H)Ph}\end{matrix}$$

Complex (III) undergoes spontaneous internal metallation and the reaction is accompanied by formal oxidation of the hydrazo-function to an azo-group. The presence of a phenylazo-group in (III) could explain why such a complex gives *ortho*-metallation very readily whereas in the case of osazone L^3 *ortho*-metallation is much more difficult. It should be noted, however, that the presence of a nitrogen–metal σ bond and the dimeric or polymeric structure of (III) could not be without effect. The proton abstracted from the phenyl ring in the metallation reaction is not neutralized by elimination of a chloride ion co-ordinated to the metal atom in a way that the overall reaction results in net HCl elimination; on the contrary, another hydrogen atom is lost by the organic moiety and the total reaction results in loss of a hydrogen molecule. Since in some cases [16] hydrazo-compounds (by simple exposure to the air) can be readily oxidized to azo-compounds, we suggest that the proton from the phenyl ring is transferred to the nitrogen atom as shown in the Scheme (' possible intermediate ') and by H_2 elimination from this intermediate complex (IV) is obtained. Another possible intermediate is a metal hydride formed by insertion of the metal atom in a carbon–hydrogen bond and in this case the reaction could be described as oxidative addition followed by reductive elimination. Although the latter hypothesis does not seem to be probable, it is in accord with the observation that, in contrast to what has usually been found, in the present case the platinum complex reacts faster than the palladium. It is recognized that the tendency of Pt^{II} complexes to undergo oxidative addition is intermediate between that of Pd^{II} and Rh^{I} and Ir^{I},[17] and stable hydride intermediates have been isolated in *ortho*-metallation reactions of Ir^{I} complexes.[6]

The easy internal metallation observed with the osazones L^1 and L^2 to give complex (IV) led us to attempt further metallation to obtain a quadridentate species; however, until now, all our efforts have been unsuccessful in accord with the findings of other workers.[11]

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