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AMIDES OF THE PLATINUM GROUP METALS

MICHAEL D. FRYZUK * and CRAIG D. MONTGOMERY

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. V6T 1Y6 (Canada)

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CONTENTS

A. INTRODUCTION

In a very thorough treatise [1] on the coordinative properties of the amide ligand with metalloids and metals, it was pointed out that while the amide donor has found widespread use with most of the elements, there were surprisingly few complexes of the later transition elements (groups 8, 9 and 10). This apparent anomaly spurred a number of research groups to investi-

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* Author to whom correspondence should be addressed.

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gate the coordination chemistry of this relatively simple ligand. In addition, it was also of interest to pursue late metal amide chemistry because of the possible connection to catalytic amination procedures [2]. As a result, many more amide derivatives of the later transition elements have since been prepared. The reactivity patterns of the amide linkage when coordinated to a late transition metal are beginning to emerge and they are distinctly different from those of the early metal complexes. This review attempts to give a comprehensive coverage of the literature up to the end of 1987 for amide derivatives of the second and third row elements of groups 8, 9 and 10, the so-called platinum group metals. In order to be complete, the relevant material from ref. 1 as well as pertinent examples apparently overlooked in that treatise are included here.

(i) Definition of an amide

Henceforth the term amide in this review will refer to a deprotonated primary or secondary amine: $^{-}$NHR or $^{-}$NRR′ where R, R′ = alkyl, aryl or silyl groups. This definition deliberately excludes deprotonated organic amides, $^{-}$NRCOR′, and the simple amido ligand $^{-}NH_2$. For each of these ligands, there are examples of complexes with the platinum metals, the latter serving primarily as a bridging ligand. Also excluded are porphyrin-type complexes wherein two of the four nitrogen donors can be considered formally as amide ligands, and dihalo and dicyano amides (e.g. $^{-}NCl_2$ and $^{-}N(CN)_2$).

(ii) Bonding

In valence bond terms, deprotonated amines have two lone pairs of electrons and thus are capable of three types of bonding modes as shown in Fig. 1. In **A**, the amido donor is bound to a single metal via a σ-bond leaving one electron pair localized on the nitrogen; such a structure requires that the nitrogen center be sp^3 hybridized and have a pyramidal geometry. Structure **B** invokes π-donation from the remaining lone pair of electrons to a suitable empty orbital on the metal or on the amide substituents (eg. SiR_3, Ph) [3]; in

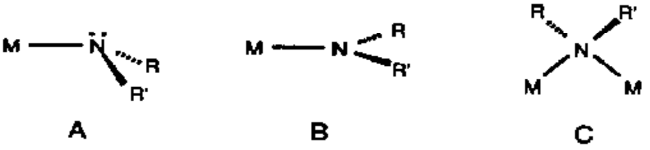


Fig. 1. Various possible forms of metal amides. In **A** the nitrogen is sp^3 hybridized; in **B** the nitrogen center is sp^2 hybridized either by donation of the electron pair to the metal or to the substituents on nitrogen; in **C** the bridging amide is sp^3 hybridized.

this case the nitrogen atom is now sp^2 hybridized and planar. In structure **C** in Fig. 1, both lone pairs are involved in σ-bonding to two separate metal centers; in this bridging mode, the amido ligand is sp^3 hybridized. Which bonding mode is found will depend on many factors, but it is well established that the bridging mode **C** will predominate if small substituents on the amide nitrogen are present.

(iii) β-Elimination

Because the amide unit $^-NR_2$ is isoelectronic with the alkyl ligand $^-CR_3$, β-elimination, a common decomposition pathway for transition metal alkyls [4], has also been found to be operative for metal amide derivatives (vide infra). As a result, the earliest stable platinum group amide derivatives contained no β-hydrogen atoms. For example, β-elimination-stable amide groups are $^-N(SiMe_3)_2$ and $^-NPh_2$. As will be discussed later, in certain systems, amide complexes containing β-hydrogen atoms are now known.

(iv) Synthetic procedures

The number of routes available for the incorporation of amide units onto a metal or metalloid are numerous [1]. However, for the platinum group metals, four main methods appear to have been utilized: (i) transmetallation with an alkali metal amide (lithium is common); (ii) deprotonation of a coordinated amine; (iii) elimination of HY (where Y is a basic ligand such as OH^- or an alkyl); (iv) hydride addition across an organic azide or related unsaturated nitrogen-containing substrate. General equations for these procedures are given below; specific examples are discussed for each metal. Other less common procedures are presented in the text where appropriate.

$$L_nM{-}X + LiNRR' \rightarrow L_nM{-}NRR' + LiX \tag{1}$$

$$L_nM(NHRR')^+ + B \rightarrow L_nM{-}NRR' + BH^+ \tag{2}$$

$$L_nM{-}Y + HNRR' \rightarrow L_nM{-}NRR' + HY \tag{3}$$

$$L_nM{-}H + RN_3 \rightarrow L_nM{-}NHR + N_2 \tag{4}$$

The most general procedure appears to be transmetallation, although care must be taken since reduction in lieu of metathesis is a common side reaction.

Deprotonation of cationic complexes containing ethylenediamine, alkylamines and arylamines to generate metal amide derivatives (eqn. (2)) has been rather extensively examined [5], but in many cases the characterization techniques are scant and ambiguous. However, we include this material

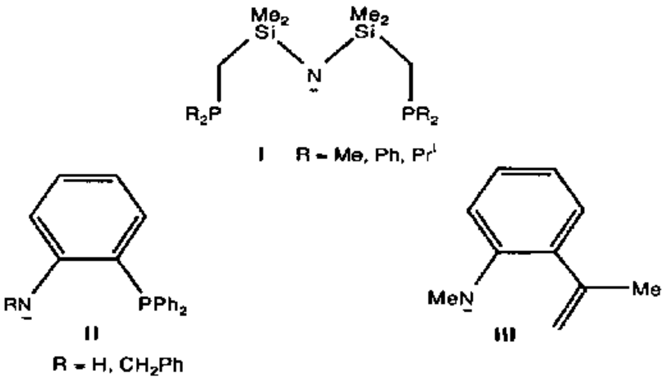


Fig. 2. Hybrid ligands that have been used to generate amides of the platinum group metals. See text and Table 1 for specific examples.

since it does represent some of the earliest work on the preparation of late metal amide complexes.

(v) Hybrid ligands

The recognition that few late metal amide complexes were known was partly responsible for the development of new multidentate, mixed-donor ligands [6] of the types shown in Fig. 2. All these ligands combine the amido donor with the "soft" phosphine ligand or other "soft" donors in a chelating array with either bidentate or tridentate chelating modes possible. The initial design of some of these ligand systems was based on the notion that the ubiquitous phosphine donor would help stabilize the amide linkage to a late transition metal.

B. SYNTHESIS

(i) Ruthenium and osmium

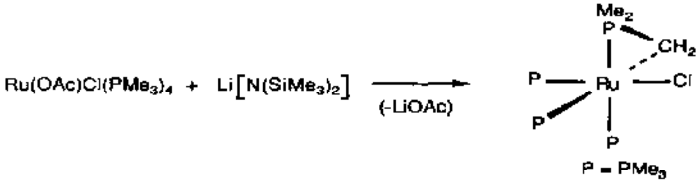
The first example of a ruthenium amide complex was $\mathrm{RuH(PPh_3)_2[N(SiMe_3)_2]}$ prepared [7] by transmetallation as shown in eqn. (5):

$$\mathrm{Ru(H)Cl(PPh_3)_3 + LiN(SiMe_3)_2 \xrightarrow[(-LiCl)]{} RuH(PPh_3)_2[N(SiMe_3)_2]} \tag{5}$$

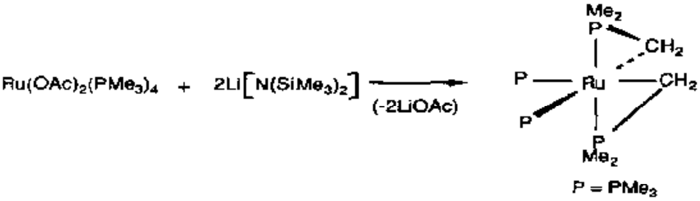
This complex is formally a $14e^-$ derivative and is reported to be one of the few examples of a four-coordinate d^6 complex. NMR studies have not provided definitive evidence as to the solution geometry of this complex since the phosphorus nuclei are magnetically equivalent (by $^{31}P\{^1H\}$ NMR spectroscopy) while there are two types of $\mathrm{SiMe_3}$ groups in the ^1H NMR spectrum at 30 °C. However, at 90 °C the $\mathrm{SiMe_3}$ groups coalesce on the ^1H

NMR time scale. These spectroscopic results indicate that the structure cannot be planar at Ru and there may be restricted rotation around the Ru–N bond. The low spin d^6 configuration and the diamagnetism are also not easily rationalized.

By contrast, when *cis*-[Ru(OAc)Cl$(PMe_3)_4$] or *cis*-[Ru$(OAc)_2(PMe_3)_4$] were reacted [8] with Li[N$(SiMe_3)_2$] in analogy to eqn. (5), no amides were formed. Rather, only metallacyclic complexes were isolated as shown in eqns. (6) and (7):



(6)



(7)

Presumably steric crowding precludes nucleophilic attack by the bulky disilylamido moiety at the metal center and deprotonation of the coordinated phosphine methyl-hydrogen atoms predominates.

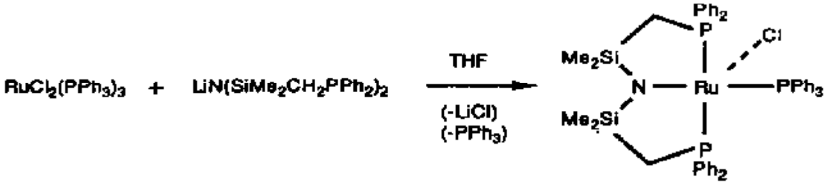
The reaction [9] of $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2OH$ with primary and secondary amines generates the corresponding amide complexes in equilibrium with the starting hydroxo complex (eqn. (8): R = H or Ph):

$$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2OH + HNRPh \rightleftarrows (\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(NRPh) + H_2O \qquad (8)$$

The measured equilibrium constants are 4.2 for R = H and 0.0046 for R = Ph. This work is significant since an attempt was made to compare bond strengths on a relative basis. For the late metals, it would appear that bond strengths are in the order alkyl > alkoxide > amide. The fact that metal–amide bonds are inherently weak might account for the sparsity of late metal amide derivatives. Both the amide derivatives $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(NRPh)$ could also be prepared by straightforward reaction of the corresponding chloride $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ with the appropriate lithium amide LiNRPh (R = H, Ph) in tetrahydrofuran (THF). Interestingly, the analogous reaction of $LiNHBu^t$ with $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ leads to the orthometallated product $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)(CH_2PMe_2)$, similar to that in eqns. (6) and (7) above.

A somewhat exotic procedure has been reported [10] for the preparation of $RuCl_2NO(PPh_3)_2(NEt_2)$. Treatment of $RuCl_3 \cdot xH_2O$ with *N*-nitrosodiethylamine in the presence of PPh_3 produced the above complex. The use of diaryl nitrosoamines led to straightforward nitrosylation without amide incorporation.

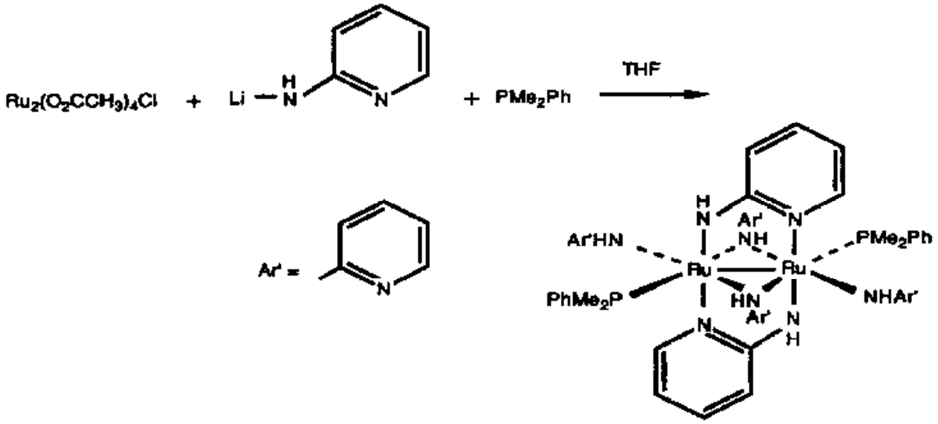
The incorporation of the amide donor into a chelating array that contains phosphine donors has allowed the preparation of amide derivatives of most of the late metals (vide infra). The reaction of $LiN(SiMe_2CH_2PPh_2)_2$ with $RuCl_2(PPh_3)_3$ generates [11] the five-coordinate complex $RuCl(PPh_3)[N(SiMe_2CH_2PR_2)_2]$ (eqn. (9)):



(9)

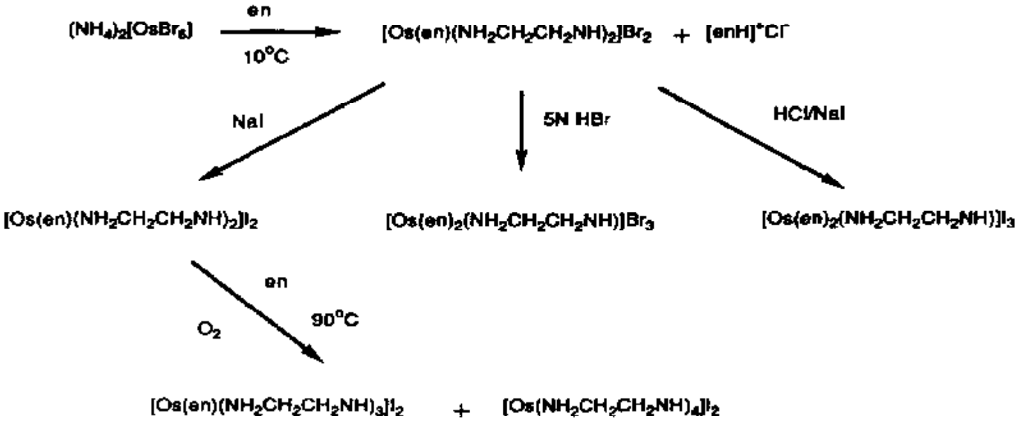
This complex is a useful starting material for the preparation of other amide complexes of ruthenium(II).

The reaction [12] of the lithium salt of 2-aminopyridine, $LiNH(o\text{-}C_5H_4N)$, with $Ru_2(OAc)_4Cl$ in the presence of PMe_2Ph generates an unusual binuclear amido derivative in which the amido donor binds in a terminal mode and a bridging mode in the complex $Ru_2(o\text{-}NC_5H_4NH)_6(PMe_2Ph)_2$ (eqn. (10)):



(10)

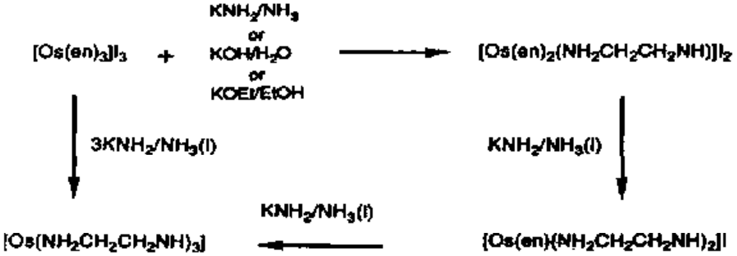
Mononuclear amides of osmium are rare. In the attempted preparation of $[Os(en)_3]Br_3$, a series of amides of osmium(IV), osmium(V) and osmium(VI) were isolated [13]. Thus the reaction of $[OsBr_6]^{2-}$ with neat ethylenediamine (en) generates the bis(amido) derivative, $[Os(en)(NH_2CH_2CH_2NH)_2]Br_2$, an osmium(IV) complex with two of the ethylenediamine ligands singly deprotonated at nitrogen. This complex dissolves in water without protona-



Scheme 1.

tion of the amide ligands; however, addition of 5N HBr does result in protonation and the formation of $[Os(en)_2(NH_2CH_2CH_2NH)]Br_3$, a monoamido derivative. Tris(amido) complexes of osmium(V) were prepared by oxidation of the above bis(amido) derivatives in the presence of ethylenediamine; a tetrakis(amido) complex of osmium(VI) was also reported (Scheme 1) [13]. The ease of formation of these amides was attributed to the high positive charge on the complex, which rendered the amino protons acidic and subject to deprotonation by the excess ethylenediamine. Later work [14] showed that osmium(III) amides could be accessed by deprotonation of $[Os(en)_3]I_3$ with alkoxides in alcohol or with KNH_2 in liquid ammonia (Scheme 2).

A number of polynuclear triosmium complexes with amido ligands in the bridging mode are known [15]. The synthetic procedure is somewhat general in that the reaction of the corresponding amine with $Os_3(CO)_{12}$ or a lightly stabilized analogue [16,17] usually generates bridging amidohydride complexes of the general formula $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-NRR}')$ by a formal oxidative addition. For R or R′ = aryl, other thermolysis products can be isolated involving N–H activation and orthometallation of the ring [18] or, for R or R′ = alkyl, CO attack [19]. Other procedures involve reaction [20] of the



Scheme 2.

anionic complex $[Os_3H(CO)_{11}]^-$ with Me_3SiN_3 to generate $Os_3(\mu\text{-}H)(\mu\text{-}NHSiMe_3)(CO)_{10}$ and reaction of H_2 with $Os_3(\mu\text{-}H)(\mu\text{-}N{=}CHCF_3)(CO)_{10}$ to produce [21] $Os_3(\mu\text{-}H)(\mu\text{-}NHCH_2CF_3)(CO)_{10}$.

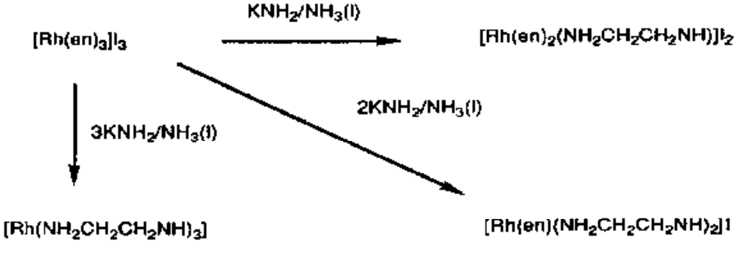
(ii) Rhodium and iridium

The first soluble well-characterized rhodium amide complex [7] was $Rh(PPh_3)_2[N(SiMe_3)_2]$, prepared by metathesis as shown in eqn. (11):

$$RhCl(PPh_3)_3 + LiN(SiMe_3)_2 \xrightarrow[\substack{(-LiCl)\\(-PPh_3)}]{THF} Rh(PPh_3)_2[N(SiMe_3)_2] \qquad (11)$$

The use of the bulky β-elimination-stable amide $^-[N(SiMe_3)_2]$ led to the isolation of this $14e^-$ complex. Although reported to be stable in the solid state, this complex is unstable in solution, decomposing with a half-life of 30 min at 25 °C. Although no structure has yet been published, it is likely to be trigonal planar in the solid state. As described in Section B(i), the analogous attempt [8] to generate a rhodium amide by the reaction of $LiN(SiMe_3)_2$ with the trimethylphosphine complex $[Rh(PMe_3)_4]OAc$ resulted once again in deprotonation of the PMe_3 ligand with $LiN(SiMe_3)_2$ to generate the binuclear complex $[(Me_3P)_2Rh]_2(\mu\text{-}CH_2PMe_2)_2$.

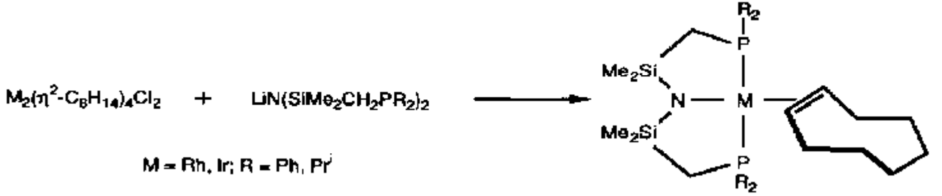
The first report [22] of authentic rhodium amides was in 1965. The successive deprotonation of the ethylenediamine *N*-hydrogen atoms of $[Rh(en)_3]I_3$ with KNH_2 in liquid ammonia generated a series of amides as shown in Scheme 3. Although these derivatives were characterized only by IR spectroscopy, X-ray powder diffraction and elemental analysis, there is little doubt as to their identity. All these amides are rather insoluble materials and very moisture sensitive; this undoubtedly prevented determination of the detailed geometry of these complexes. In the presence of excess KNH_2 in liquid ammonia, a curious paramagnetic rhodium(III) complex of apparent formula $K[Rh(NH_2CH_2CH_2NH)_2(NHCH_2CH_2NH)]$ was isolated [23]; the origin of the paramagnetism ($\mu_{eff} = 1.5 \pm 0.1$ BM) is still unknown. The same strategy of deprotonation with strong base gener-



Scheme 3.

ates amide derivatives from diethylenetriamine complexes of rhodium and iridium [24]. The deprotonation of $[Ir(en)_3]^{3+}$ has also been reported [25]; in this case, fewer isolable derivatives were obtained than with the analogous rhodium system (see Table 1).

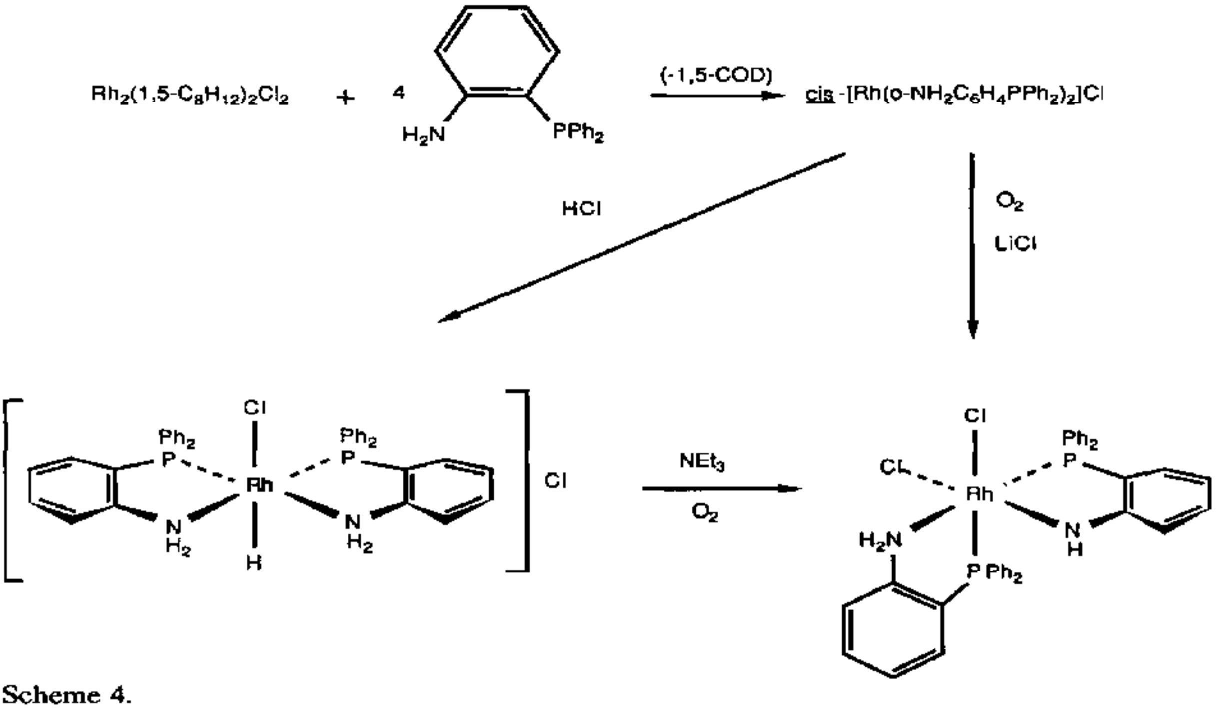
The tridentate anionic hybrid ligand $^-N(SiMe_2CH_2PR_2)_2$, where R = Ph or Pr^i, has proved quite versatile in the preparation of both rhodium and iridium amide derivatives [26]. The general procedure is shown in eqn. (12) whereby the lithium amide precursor is reacted with the corresponding cyclooctene chloride-bridged dimers:



(12)

In the case where M = Rh(I), other starting materials are possible. The rhodium(I) and iridium(I) amide complexes produced by this procedure are versatile starting materials not only for other M(I) derivatives by substitution of the relatively labile cyclooctene ligand, but also for M(III) complexes by oxidative addition [27]. A discussion of the further reactivity of these amide derivatives is the subject of a later section [28–30].

A bidentate modification of the above tridentate ligand has also been

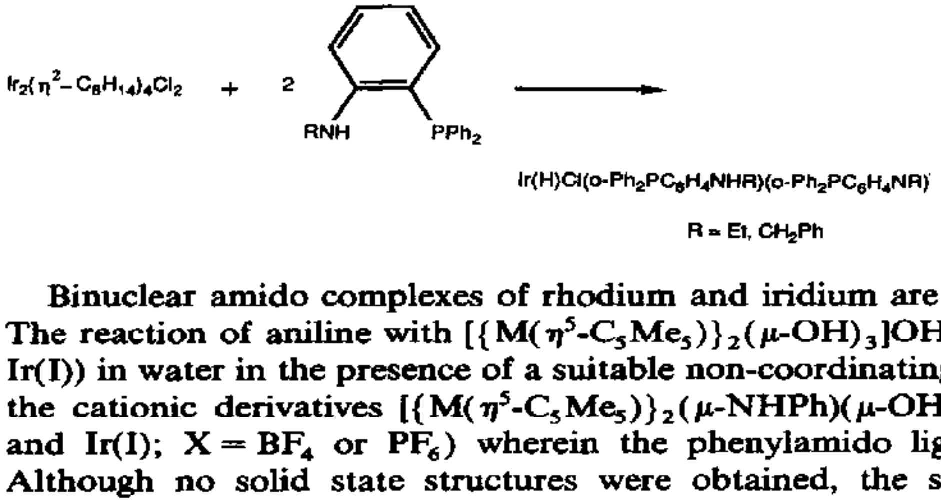


Scheme 4.

reported [30], and its coordination chemistry with rhodium(I) and iridium(I) briefly investigated. Reaction of $LiN(CH_2Ph)SiMe_2CH_2PPh_2$ with the 1,5-cyclooctadiene (COD) dimers of rhodium and iridium generates the corresponding square-planar complexes $M(COD)[N(CH_2Ph)SiMe_2CH_2PPh_2]$ (M = Rh and Ir).

The bidentate ligand *o*-(diphenylphosphino)phenylamine, *o*-$Ph_2P{-}C_6H_4{-}NH_2$, has been used [31] to prepare amino and amido complexes of rhodium. A serendipitous reaction with air generated an amido derivative, as summarized in Scheme 4. Thus the rhodium(III) bis(amine) hydride or the rhodium(I) bis(amine) derivative can be converted to the *cis* rhodium(III) monoamide amine complex, the crystal structure of which was obtained. The corresponding *trans* monoamido derivative was inferred as being present since addition of *p*-toluenesulfonic acid to the solution after filtration of the *cis* monoamide generated the *trans*-bis(amine) dichloride $[RhCl_2(o\text{-}Ph_2PC_6H_4NH_2)_2]OTs$.

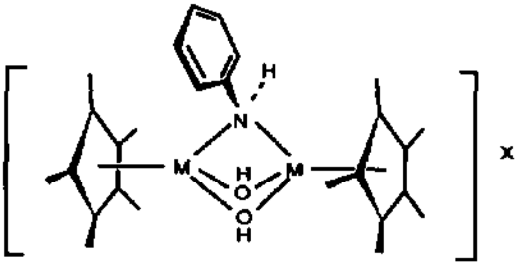
A modified version of the above ligand has been reported [32] to undergo oxidative addition of the N–H bond to generate an iridium(III) amido-hydride species as shown in eqn. (13):



(13)

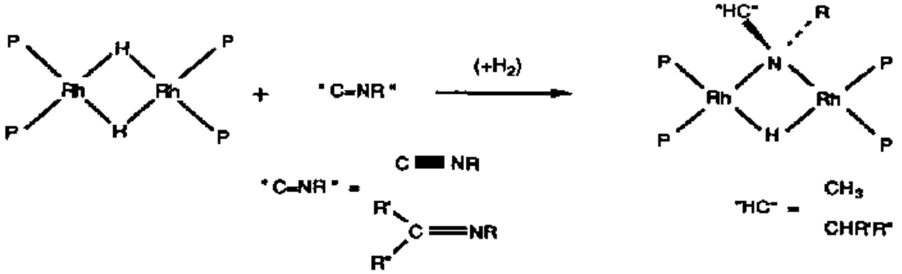
Binuclear amido complexes of rhodium and iridium are also known [33]. The reaction of aniline with $[\{M(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}OH)_3]OH$ (M = Rh(I) and Ir(I)) in water in the presence of a suitable non-coordinating anion generates the cationic derivatives $[\{M(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}NHPh)(\mu\text{-}OH)_2]X$ (M = Rh(I) and Ir(I); X = BF_4 or PF_6) wherein the phenylamido ligand is bridging. Although no solid state structures were obtained, the solution data are consistent with this formulation. Interesting, there appears to be NMR spectroscopic evidence for restricted rotation about the N–C bond of the amido unit. Molecular modelling supports the notion that the phenyl ring of the amido ligand does interact somewhat with the pentamethylcyclopentadienyl rings, and this interaction can be minimized by orienting the phenyl ring plane parallel with the planar C_5Me_5 ligands. Attempts to extend this to more basic amido units by the analogous reaction with benzylamine or propylamine only led to substitution and the formation of the cation $[M(\eta^5\text{-}C_5Me_5)(NH_2R)_3]^{2+}$.

The bridging amido unit can also be introduced by the reaction of



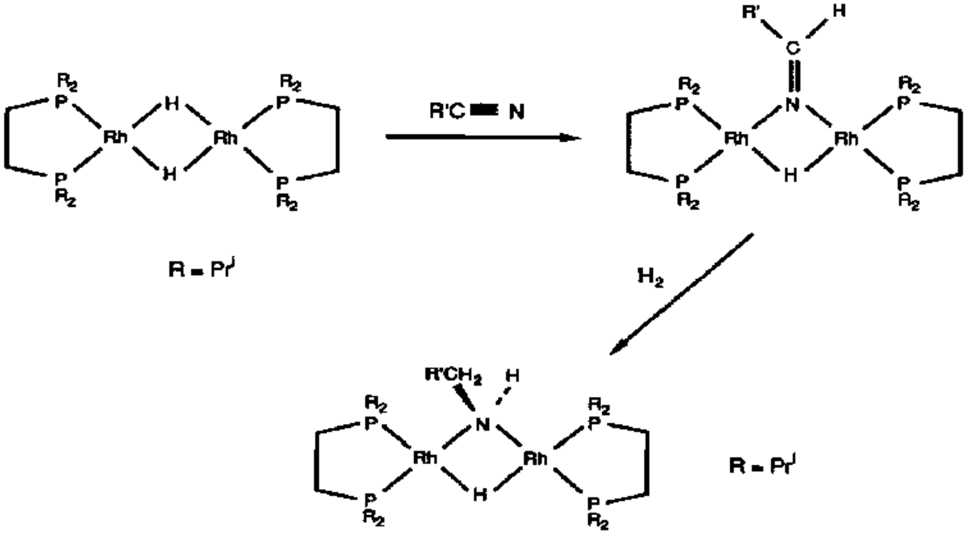
M = Rh, Ir

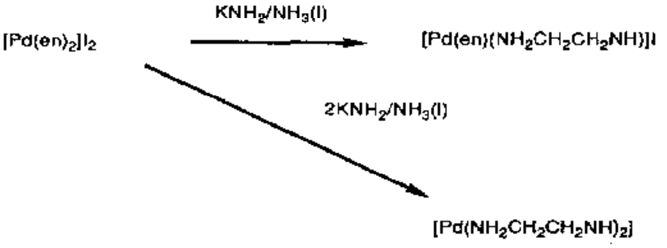
binuclear rhodium hydride complexes with unsaturated nitrogen-containing organic molecules such as imines and isonitriles. The general reaction is shown in eqn. (14):



(14)

In the case where $P = P(OPr^i)_3$, the insertion [34] of isonitriles, RNC, requires the presence of H_2 to complete the reduction to the amido oxidation level. For the electron-rich complexes where P_2 = 1,2-bis(diisopropylphosphino)ethane, the apparent insertion [35] of a variety of imines yields the bridging amido-hydride complexes directly. Nitriles are also reduced [36] by the electron-rich binuclear hydride complexes incorporating the above chelating phosphine; in this case, the intermediate complex with a bridging imino-hydride core can be isolated and converted to the amido hydride by further reaction with H_2.



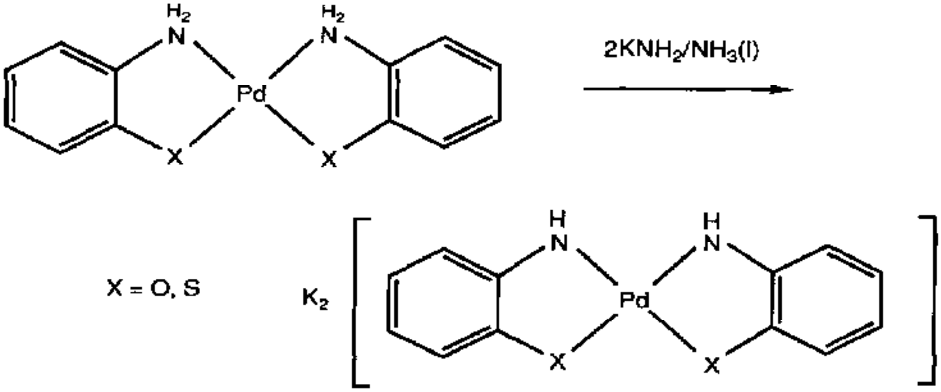


Scheme 5.

(iii) Palladium and platinum

Amides of palladium(II) date back to 1960 [37]. The now familiar reaction type involving deprotonation of ethylenediamine complexes with potassium amide in liquid ammonia also holds for [Pd(en)$_2$]I$_2$, generating monoamide and bis(amide) complexes as shown in Scheme 5. Interestingly, the monoamide derivative [Pd(en)(NH$_2$CH$_2$CH$_2$NH)]I was found to be stable for months in dry air but decomposed rapidly (8–10 h) in a dry helium atmosphere; this peculiar behaviour was ascribed to the reducing properties of the amide ligand which could be somewhat balanced by the presence of O$_2$. The bis(amide) derivative did not display this property.

The deprotonation [38] of coordinated amino groups was extended to *o*-aminophenolate and *o*-aminothiophenolate complexes of palladium to generate the corresponding anionic bis(amide) complexes K$_2$[Pd(*o*-XC$_6$H$_4$NH)$_2$] (X = O, S) as shown in eqn. (15):



(15)

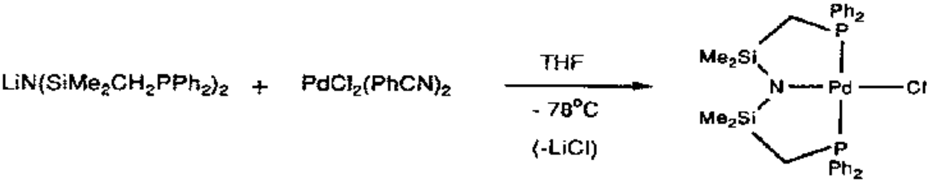
Similar deprotonation sequences obtain for the bis(aminoethanethiolate) derivative Pd(SCH$_2$CH$_2$NH$_2$)$_2$, although in this case the monoamide derivative was also isolated [39] (eqns. (16) and (17)):

$$\mathrm{Pd(SCH_2CH_2NH_2)_2 + KNH_2 \xrightarrow{NH_3(l)} K[Pd(SCH_2CH_2NH_2)(SCH_2CH_2NH)]} \qquad (16)$$

$$Pd(SCH_2CH_2NH_2)_2 + 2KNH_2 \xrightarrow{NH_3(l)} K_2[Pd(SCH_2CH_2NH)_2] \qquad (17)$$

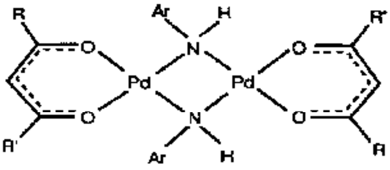
Not all amino ligands are deprotonated at nitrogen. In addition to other reactions, iminodinitrile complexes [40] are deprotonated at carbon using the above conditions.

The reaction [41] of the hybrid ligand $(Ph_2PCH_2SiMe_2)_2N^-$ with bis(benzonitrile)dichloropalladium(II) at low temperatures generates $PdCl[N(SiMe_2CH_2PPh_2)_2]$ (eqn. (18)), the first and only palladium amide so far to be structurally characterized by single-crystal X-ray diffraction [6(a)]. The Pd–N bond distance is 2.063(2) Å. In this metathesis reaction, it is critical to use low temperatures, otherwise reduction to palladium metal predominates.



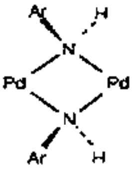
(18)

Binuclear amide complexes of palladium also exist [42]. The reaction of substituted aniline derivatives with bis(β-diketonate) complexes of palladium in refluxing benzene result in the formation of dimers of the general formula $Pd_2(\beta\text{-dik})_2(\mu\text{-NHAr})_2$; the structure is shown below:

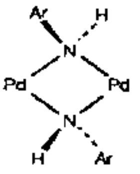


R = R' = CH_3, acac
R = CH_3, R' = CF_3, tfac
R = CH_3, R' = Ph, bzac
R = R' = CF_3, hfac

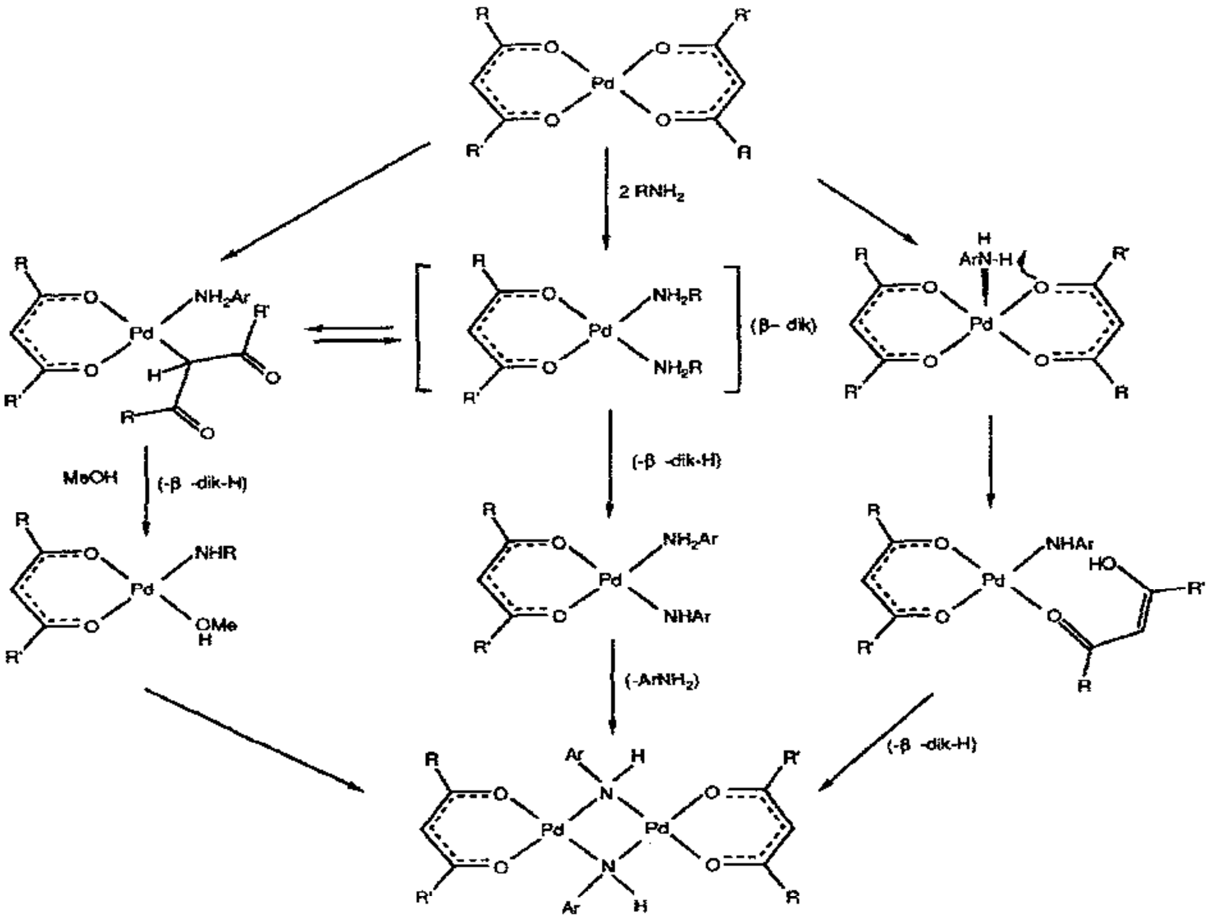
The bis(arylamido) core can exist in two isomeric forms: *syn* and *anti*. In solution, these forms can be detected but not assigned. Mechanical separation in the solid state is possible. The pure isomers are generated and no interconversion or change in the isomer ratio occurred with heating. Although it is clear that one of the β-diketonate ligands abstracts a proton from the relatively acidic aniline *N*-hydrogen atoms a number of possibilities exist as to intermediates and as to whether or not the proton abstraction



syn



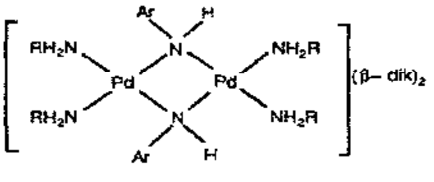
anti



Scheme 6.

is inner sphere or outer sphere. Stoichiometric reactions of aniline and its derivatives with Pd(hfac)$_2$ (hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) generate a variety of products depending on the ratio of reactants; thus the C-bound isomer was isolated and shown to convert spontaneously to the corresponding dimer in CH$_3$OH. The bis(amine) cation is also accessible by addition of two equivalents of RNH$_2$ to Pd(hfac)$_2$ and this material also might be involved in the production of the dimers. Possible routes are summarized in Scheme 6.

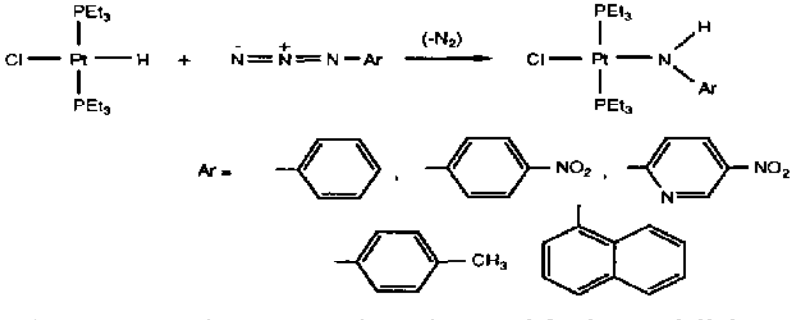
The dipalladium bis(anilido) core is rather stable. Addition of pyridine or primary amines RNH$_2$ (R = Ar, Me, Et, Pr) results [42] in the displacement of the remaining β-diketonate ligand and the formation of salts having the following structure:



R = Ar, Me, Et, Pr

Platinum amides are better known than the corresponding palladium derivatives. The deprotonation of cationic amine derivatives generates a wide variety of platinum(II) amide derivatives. Thus $[Pt(en)_2]I_2$ can be deprotonated [43,44] with KNH_2 in liquid ammonia to generate the cationic monoamide $[Pt(en)(NH_2CH_2CH_2NH)]I$, the neutral bis(amide) $Pt(NH_2CH_2CH_2NH)_2$, and the anionic tris(amide) $K[Pt(NH_2CH_2CH_2NH)(NHCH_2CH_2NH)]$ with the appropriate ratio of KNH_2 to $[Pt(en)_2]I_2$. Also reported was the reduction of these species with potassium metal in liquid ammonia to generate thermally labile platinum(I) and platinum(0) amides. The use [45] of 2,2′-bipyridyl (bipy) in the starting material $[Pt(bipy)(en)]I_2$ also produces the monoamide $[Pt(bipy)(NH_2CH_2CH_2NH)]I$ and the neutral bis(amide) $Pt(bipy)(NHCH_2CH_2NH)$ by reaction with the corresponding amounts of KNH_2 in liquid ammonia. Another deprotonation procedure utilizes concentrated NaOH or CsOH to precipitate amides; for example, $[PtCl(NH_3)(MeNH_2)_3(MeNH)]Cl_2$, $Pt(NO_2)_2Cl(en)(RNH)$ ($R = Et$, Pr), $M[PtCl_2(NO_2)_2(MeNH_2)(MeNH)]$ and $M[PtCl_3(NO_2)(NH_2CH_2CH_2NH)]$ ($M = Na$, Cs) have been reported [46–49].

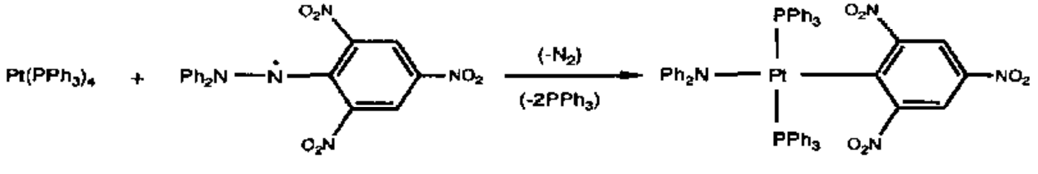
The reaction [50–52] of hydrido platinum(II) derivatives with a variety of aromatic azides appears to be a general procedure for the preparation of mononuclear arylamido complexes (eqn. (19)):



(19)

The mechanism may involve oxidative addition of the azide to generate a platinum(IV) derivative which extrudes N_2 and undergoes hydride migration to nitrogen. Other hydrides of ruthenium(II), iridium(III), cobalt(III) and cobalt(I) were also investigated [50], but monitoring these reactions by IR gave no evidence for species with N–H bands. Substitution of the PEt_3 ligands of platinum(II) by PPh_3 also provides the analogous amide using *p*-nitrophenylazide [53].

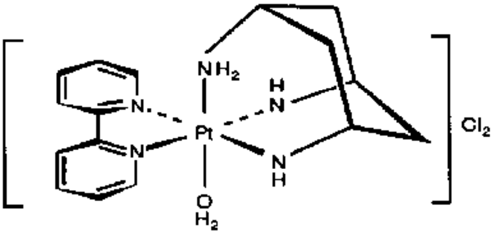
The reaction [54] of the organic radical 1,1-diphenyl-2-picrylhydrazyl (Ph_2NN-1,3,5-$(NO_2)_3C_6H_2$) with a platinum(0) complex generates a platinum(II) amide as shown in eqn. (20):



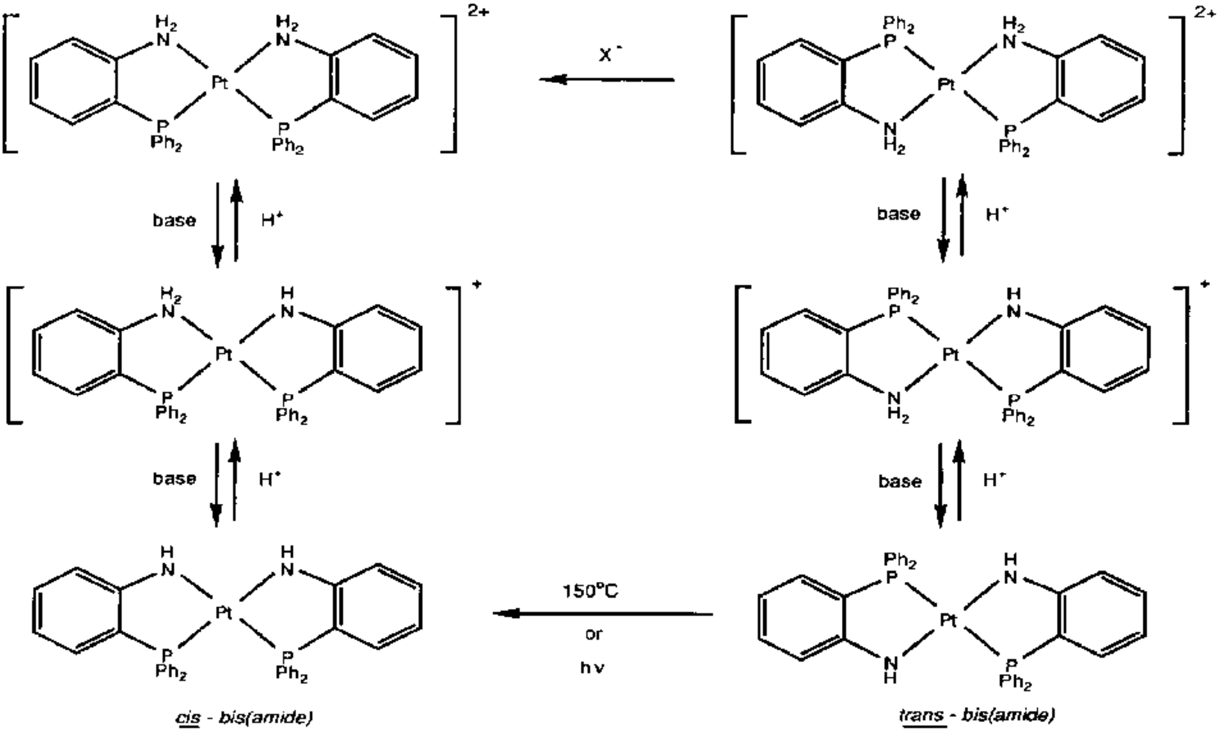
(20)

The generality of this procedure has not been reported.

A curious platinum(IV) complex containing a chelating bis(amide) was obtained [55] from the reaction of *cis,cis*-1,3,5-triaminocyclohexane with dichloro(bipy)platinum(II). The structure, shown below, was gleaned from a single-crystal X-ray structure determination and electron spectroscopy for chemical analysis (ESCA) studies as well as from NMR spectroscopy.



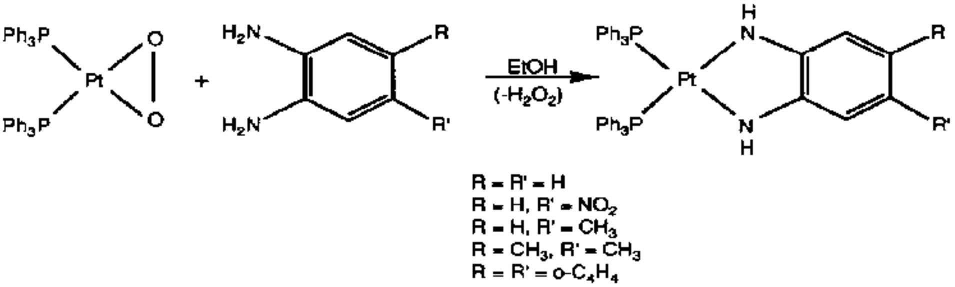
The use of the hybrid ligand o-$Ph_2PC_6H_4NH_2$ discussed above for rhodium(III) generates a series of interesting amide and amine derivatives of platinum(II). The reaction [6(b)] of the bis(amine) cation *cis*-$[Pt(o\text{-}Ph_2PC_6H_4NH_2)_2]^{2+}$ with bases generates the corresponding bis(amide) derivative *cis*-$Pt(o\text{-}Ph_2PC_6H_4NH)_2$; this compound is so stable that it can be sublimed at 300 ° C. Heating the bis(amine) chloride produced the mixed amido–ammonium salt $[Pt(o\text{-}Ph_2PC_6H_4NH_3)(o\text{-}Ph_2PC_6H_4NH)Cl]Cl$, iden-



Scheme 7.

tified on the basis of IR spectroscopy. The isomeric *trans* bis(amide) could be prepared and separated from the *cis* isomer and was shown to be thermodynamically unstable with respect to the *cis* bis(amide). Both of the isomeric bis(amide) complexes were characterized by single-crystal X-ray diffraction [56]. Both isomeric amides could be protonated by one equivalent of trifluoroacetic acid to generate the corresponding *cis* and *trans* monoamide derivatives [Pt(o-$Ph_2PC_6H_4NH_2$)(o-$Ph_2PC_6H_4NH$)]$OCOCF_3$. These reactions and syntheses are summarized in Scheme 7.

A series of bis(amido) complexes of platinum(II) was obtained [57] from the reaction of the peroxo complex $Pt(PPh_3)_2(\eta^2\text{-}O_2)$ with a series of substituted o-phenylenediamines, as shown in eqn. (21):



(21)

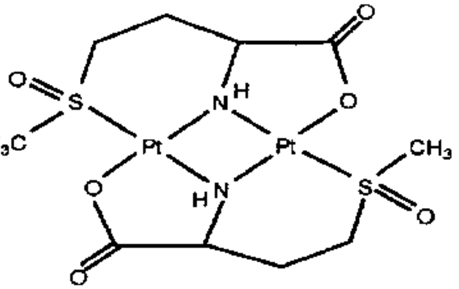
Although no ^1H NMR data were given for these complexes, it was noted that the derivatives with R or R′ = CH_3 did not show signals for the methyl groups on the aromatic nucleus even after the use of deuterated triphenylphosphine as a coligand. These complexes can also be considered in another canonical form, that of an o-benzoquinonediimine complex of platinum(0). However, on the basis of polarographic studies and on comparison with other systems, it was concluded that the platinum(II) bis(amido) formulation was the more accurate:

The reaction of other primary or secondary amines with the peroxo platinum complex did not generate amide derivatives.

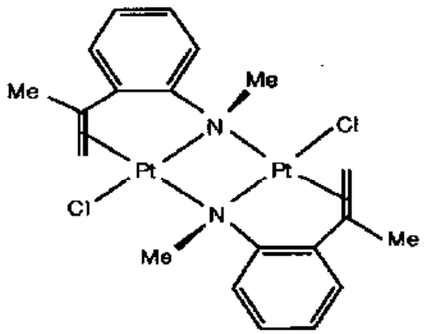
Amide complexes of platinum(II) can also be prepared by transmetallation. Thus the reaction [58] of $LiNPh_2$ with *cis*-$Pt(PEt_3)_2Cl_2$ generated the monoamide *cis*-$Pt(PEt_3)_2Cl(NPh_2)$ with retention of stereochemistry. A similar metathesis-type reaction with the lithium salt of the tridentate hybrid ligand $N(SiMe_2CH_2PPh_2)_2$ and Zeise's salt, $K[PtCl_3(\eta^2\text{-}C_2H_4)]$, produced [6(a)] $PtCl[N(SiMe_2CH_2PPh_2)_2]$, analogous to the palladium derivative (vide supra). The generality of the metathesis or transmetallation approach is clearly shown by the preparation [59] of a series of organoplatinum monoamides having the general formula $Pt(R_2PCH_2CH_2PR_2)R'[N(R'')R''']$ by reaction of the corresponding lithium amide $LiN(R'')R'''$ with $Pt(R_2PCH_2CH_2PR_2)R'Cl$. For example, LiNMePh and $LiNH(CH_2Ph)$ generate the respective amides; $LiNMe_2$ does generate the corresponding dimethylamide complex, but it was too thermally unstable to be isolated. The hydrido-phenylamido derivative, *trans*-$Pt(PEt_3)_2H(NHPh)$, has recently been reported [60] in the reaction of NaNHPh with *trans*-$Pt(PEt_3)_2H(NO_3)$.

The reaction of acidic amines with platinum hydroxides and alkoxides also produces the corresponding amides in an equilibrium reaction. For example, $Pt(Ph_2PCH{=}CHPPh_2)(CH_2CN)(OH)$ reacts [61] with methylaniline to generate $Pt(Ph_2PCH{=}CHPPh_2)(CH_2CN)(NMePh)$, and the analogous reaction [59] of $Pt(Ph_2PCH_2CH_2PPh_2)(CH_3)(OMe)$ generates $Pt(Ph_2PCH_2CH_2PPh_2)(CH_3)(NMePh)$.

Binuclear amide derivatives of platinum are also known. The addition of excess base to the methionine-*S*-oxide derivative, $PtCl_2[S,S\text{-}MeSOCH_2CH_2CH(CO_2H)NH_2]$, produced [62] a complex in which the methionine-*S*-oxide binds as a tridentate ligand but with the amide bridging the platinum(II) centers as shown below:



The crystal structure shows that the bridging amido groups are rather strained, being severely distorted from tetrahedral. A platinum(IV) dimer was prepared and characterized in solution only by deprotonation of a coordinated glycine ligand [63]. An octahedral coordination about both platinum(IV) centers with bridging amide donors was proposed on the basis of ^1H NMR studies. The hybrid ligand *o*-$(MeC{=}CH_2)C_6H_4NMeH$ coordinates to platinum(II) to generate an amine–olefin complex which, upon passage through a basic ion exchange resin, produced [6(c)] the μ-amido dimer represented below. The X-ray structure shows that the molecule is folded about the bis(amido) core.



C. REACTIVITY OF THE METAL–AMIDE BOND

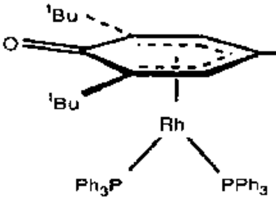
While the synthesis of late metal amide derivatives has reached a high level of understanding and sophistication, reactivity patterns for the late metal–amide bond have lagged behind and are only now just emerging. In this section, the known reactions of the amide complexes are discussed. Reactions of metal amide complexes which do not involve the metal–amide bond directly are not included, although some exceptions are noted. It should be mentioned that the presence of the amide donor in all probability does affect the overall reactivity of the complex; however, such effects are difficult to ascertain and would be speculative at this point. Since the emphasis in this area so far has been on the synthesis of amides, it is quite clear that more fundamental reactivity studies are required.

(i) Protonation reactions

Because a metal amide can be considered as a coordinated base, it can be protonated. However, the range of proton sources necessary varies considerably, depending mostly on the charge of the complex. Negatively charged derivatives [38,39] such as $K_2[Pd(o\text{-}XC_6H_4NH)_2]$ (X = O, S), $K[Pd(SCH_2CH_2NH_2)(SCH_2CH_2NH)]$ and $K_2[Pd(SCH_2CH_2NH)_2]$ are immediately protonated by H_2O, whereas positively charged species [13] such as $[Os(en)(NH_2CH_2CH_2NH)_2]I_2$ require concentrated acid (5N HBr) and can be recrystallized from water. As a general rule, the stability in water increases as the formal oxidation state of the central metal increases. This is exemplified by the platinum(II) bis(amide) complex $Pt(NH_2CH_2CH_2NH)_2$ which forms [43] strongly basic solutions in H_2O (i.e. $[Pt(en)_2]^{2+}$ and $2OH^-$) while the platinum(IV) bis(amide) $[Pt(bipy)(OH_2)(\mathit{cis,cis}\text{-}1,3,5\text{-}(C_6H_9)NH_2(NH)_2]Cl_2$ can be recrystallized [55] from H_2O. The two palladium amides that result from deprotonation [38] of $[Pd(en)_2]I_2$ with $KNH_2/NH_3(l)$ show contrasting behaviour in H_2O. While the bis(amide) $Pd(NH_2CH_2CH_2NH)_2$ instantaneously forms $[Pd(en)_2]^{2+}$ in aqueous solution, the monoamide derivative [Pd(en)($NH_2CH_2CH_2NH$)]I forms only weakly basic solutions in H_2O. In fact, the titration curve of the monoamide with aqueous HI resembles that of a strong acid–weak base titration. The behaviour of this palladium monoamide is anomalous not only in the palladium series but also for the corresponding platinum complexes [43,44].

Protonation with acids has generally served as a means of determining or confirming the number of amide donors in the complex, especially for those amide derivatives formed by reaction with successive amounts of KNH_2 in liquid ammonia. As mentioned above, titration with aqueous HI or with NH_4I in liquid ammonia is the method most utilized. The stoichiometric reaction [6(b)] of one equivalent of CF_3COOH with each of the *cis* and *trans* bis(amide) derivatives Pt(*o*-$Ph_2PC_6H_4NH)_2$ provides a stereoselective route to the corresponding monoamides, as outlined in Scheme 7.

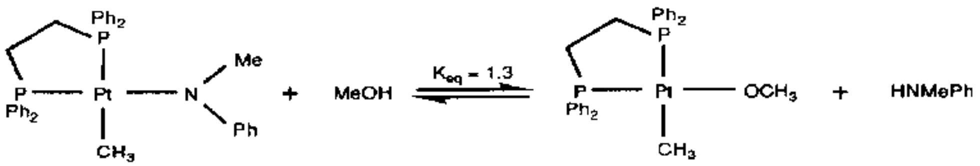
Proton abstraction with a metal amide is also useful for the introduction of other ligands. The reaction [64] of 2,6-di-*tert*-butyl-4-methylphenol with $Rh(PPh_3)_2[N(SiMe_3)_2]$ generated the cyclohexadienylone derivative $Rh(PPh_3)_2(\eta^5\text{-}OAr)$ (ArO = 2,6-Bu^t_2-4-MeC_6H_2O) by expulsion of $NH(SiMe_3)_2$:



The platinum(II) amide derivative $Pt(Ph_2PCH_2CH_2PPh_2)(CH_3)(NMePh)$ is reported [59] to react with weak carbon acids such as acetone, acetonitrile and phenylacetylene to give the corresponding hydrocarbylplatinum complexes $Pt(Ph_2PCH_2CH_2PPh_2)(CH_3)R$ ($R = CH_2COCH_3$, CH_2CN and CCPh) and methylaniline.

Not all protonation reactions are irreversible. Reversible equilibria are set up in the reaction [9] of H_2O with $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(NPh_2)$ (eqn. (22)) and in the reaction of CH_3OH with $Pt(Ph_2PCH_2CH_2PPh_2)(CH_3)(NMePh)$ (eqn. (23)):

$$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(NPh_2) + H_2O \overset{K_{eq} = 217}{\rightleftharpoons} (\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2OH + HNPh_2 \tag{22}$$

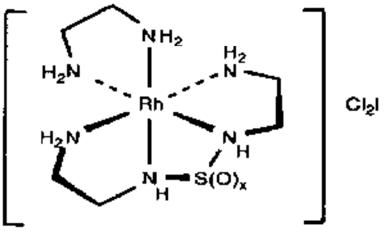


(23)

The fact that these equilibria are nearly thermoneutral has enabled the relative bond strengths of Ru–ligand and Pt–ligand bonds to be estimated. Thus the Ru–O bond in $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(OH)$ is about 35 kcal mol^{-1} stronger than the Ru–N bond in $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(NPh_2)$; similarly, the Pt–O bond in $Pt(Ph_2PCH_2CH_2PPh_2)(CH_3)(OMe)$ is calculated to be 17 kcal mol^{-1} stronger than the Pt–N bond in $Pt(Ph_2PCH_2CH_2PPh_2)(CH_3)(NMePh)$.

(ii) Metal amides as nucleophiles

Related to the protonation reactions discussed above are the reactions of late metal amides with electrophiles and Lewis acids. Methyl iodide reacts [65] with the tris(amide)rhodium(III) complex $Rh(NH_2CH_2CH_2NH)_3$ to give tris(*N*-methylethylenediamine)rhodium(III) iodide $[Rh(enMe)_3]I_3$. Comparison of this product with the material obtained by reaction of authentic *N*-methylethylenediamine with aqueous rhodium(III) shows that the two are isomers. The geometries have been assigned, on the basis of IR spectroscopy, as *facial* for the independently prepared $[Rh(enMe)_3]I_3$ and *meridional* for the product obtained by methylation of the tris(amide). The reactions of the bis(amide) $[Rh(en)(NH_2CH_2CH_2NH)_2]I$ have also been examined [65]. With excess CH_3I or CH_3Br, the corresponding dimethylated complexes $[Rh(en)(NH_2CH_2CH_2NHMe)_2]IX_2$ ($X = I$ or Br) are produced. With BF_3, a complex formulated as $[Rh(en)(NH_2CH_2CH_2NH\text{–}BF_3)_2]I$ was isolated; it was suggested that the amide donor acts as a bridge between the rhodium center and the boron. This bis(amide) also reacts with SO_2Cl_2 and $SOCl_2$ to give 1:1 adducts of the general formula $[Rh(en)\{NH_2CH_2CH_2NH)_2SO_x\}]ICl_2$ (where $x = 2$ or 1) having the structure shown below, wherein the SO_x moiety bridges the two nitrogen centers.

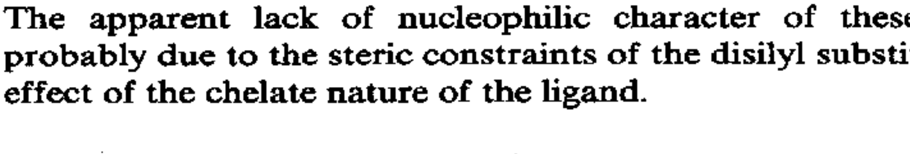


Methylation of certain palladium amides is also known. Thus the reaction [38] of excess CH_3I with $K_2[Pd(o\text{-}XC_6H_4NH)_2]$ ($X = O$, S), obtained as shown above in eqn. (15), is reported to give a product with both *N*- and *S*-methylation, $PdI_2(o\text{-}MeXC_6H_4NHMe)$. In contrast, the analogous reaction of the related mono and bis(β-amidoethanethiolato) derivatives $K[Pd(SCH_2CH_2NH_2)(SCH_2CH_2NH)]$ and $K_2[Pd(SCH_2CH_2NH)_2)]$ (eqns. (16) and (17) above) with excess methyl iodide generates [39] a product with only *S*-methylation, $PdI_2(MeSCH_2CH_2NH_2)$. This is somewhat counter-intuitive, since in the latter two cases the amido moiety should be more nucleophilic with the alkyl substituent than with the aryl substituent.

Platinum amides were alkylated with CH_3I, although the ancillary ligands appear to be important. Reaction of both the monoamide $[Pt(bipy)(NH_2CH_2CH_2NH)]I$ and the bis(amide) $Pt(bipy)(NHCH_2CH_2NH)$ with CH_3I generates [45] the corresponding monomethylated and dimethylated derivatives, $[Pt(bipy)(NH_2CH_2CH_2NHMe)]I_2$ and $[Pt(bipy)(MeNHCH_2CH_2NHMe)]I_2$ respectively. These methylation reactions are reported [44] to fail for the related bis(amide) $Pt(en)(NHCH_2CH_2NH)$, even though the only difference is the replacement of bipy with en.

The monoamido complex $Pt(Ph_2PCH_2CH_2PPh_2)(CH_3)(NMePh)$ reacts [60] with both acetyl chloride and CD_3I at the amide nitrogen with cleavage of the Pt–amide bond; with CH_3COCl, *N*-methyl-*N*-phenylacetamide ($CH_3CONMePh$) and $Pt(Ph_2PCH_2CH_2PPh_2)(CH_3)Cl$ are obtained, and with CD_3I, $PhNMe(CD_3)$ and $Pt(Ph_2PCH_2CH_2PPh_2)(CH_3)I$ are the products.

The reaction [26] of excess methyl halide with the rhodium(I) and iridium(I) derivatives having the amido donor as part of a chelate array, $M(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PR_2)_2]$, does not result in methylation at nitrogen, rather oxidative addition is observed at the metal center (eqn. (24)):



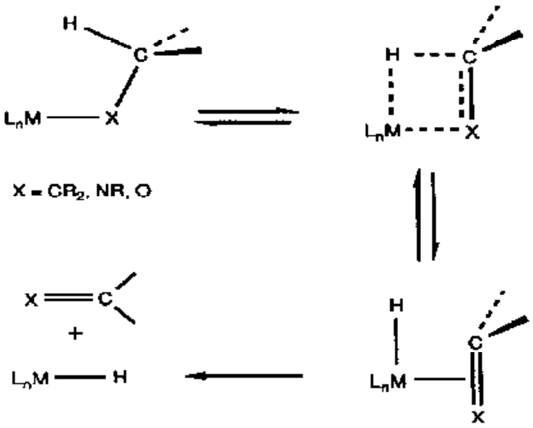
(24)

The apparent lack of nucleophilic character of these amido donors is probably due to the steric constraints of the disilyl substituents and is not an effect of the chelate nature of the ligand.

(iii) β-Elimination of metal amides

Because the amide ligand $^-NR_2$ is isoelectronic with an alkyl $^-CR_3$, it is not surprising that similar decomposition pathways are potentially accessible, in particular β-elimination (Scheme 8). In the case of an amide in Scheme 8 ($X = NR$), β-elimination would generate a π-coordinated imine which, because such a bonding mode is relatively unknown [35], would be eliminated.

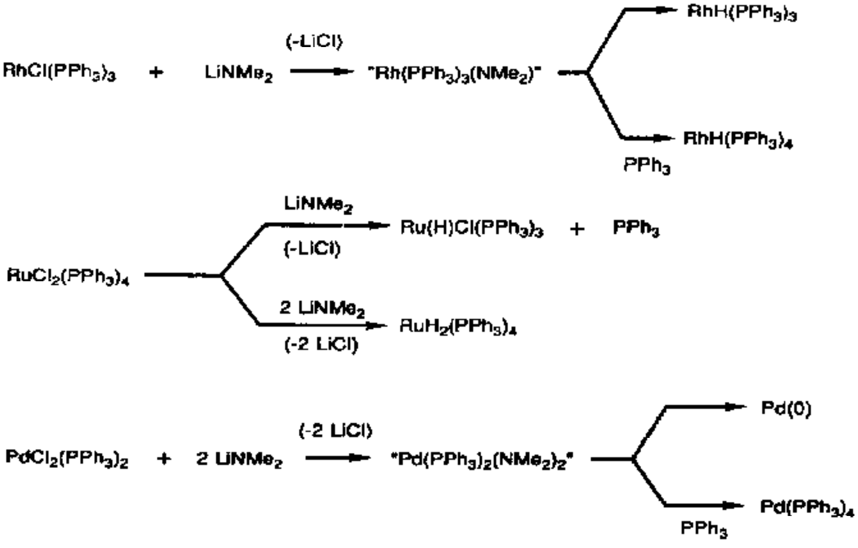
A definitive study [66], albeit in communication form, established the viability of this decomposition pathway and, furthermore, showed that this



Scheme 8.

process was a useful preparative reaction for the synthesis of late metal hydrides. The reaction of lithium dimethylamide, $LiNMe_2$, was examined with a number of late metal complexes containing metathesizable chloride ligands. In all cases, β-elimination occurred to generate metal hydrides or their decomposition products; this work is summarized in Scheme 9. The identity of the eliminated imine was established by the use of lithium isopropylamide, $LiNH(CHMe_2)$, which generates acetone imine, $HN{=}CMe_2$, and ultimately acetone upon hydrolysis.

The use of lithium trideuteriodimethylamide, $LiN(CD_3)Me$, in the reaction with $RhCl(PPh_3)_3$ generated both $RhH(PPh_3)_3$ and $RhD(PPh_3)_3$ in the ratio 6 : 1; thus the deuterium isotope effect, k_H/k_D, is 6 ± 1, indicating that C–H bond breaking is rate determining.



Scheme 9.

Circumvention of this decomposition pathway is possible by the use of β-elimination-stable amide ligands [7,58] such as bis(trimethylsilyl)amido, $N(SiMe_3)_2^-$, or diphenylamido, NPh_2^-. For example, the successful preparation of both $Rh(PPh_3)_2[N(SiMe_3)_2]$ and *cis*-$Pt(PEt_3)_2Cl(NPh_2)$ support the contention that β-elimination of metal amides is viable.

The synthesis of stable platinum alkyl complexes with β-hydrogen atoms has been achieved by the use of an ancillary chelating phosphine ligand; thus the complex $Pt(CH_2CH_3)_2(Ph_2PCH_2CH_2PPh_2)$ is stable [70] to 120°C in solution. As seen above, the same strategy obtains for platinum amides since complexes of the type $Pt(R_2PCH_2CH_2PR_2)R'[N(R'')R''']$ are isolable [59] as long as $R'' = R''' \neq CH_3$. The incorporation of an amide donor with β-hydrogen atoms as part of a chelate ligand, as found [30] in $^-N(CH_2Ph)(SiMe_2CH_2PPh_2)$, for example, also provides β-elimination-stable complexes. Of course, the deprotonated ethylenediamine-type of amide derivative (see Table 1) is another variation of this.

(iv) Migratory insertion reactions of metal amides

(a) Carbonylation

The recent report [60] that carbon monoxide preferentially inserts into the Pt–amide bond of $Pt(Ph_2PCH_2CH_2PPh_2)(CH_3)[NH(CH_2Ph)]$ to generate $Pt(Ph_2PCH_2CH_2PPh_2)(CH_3)[CONH(CH_2Ph)]$ over the Pt–C bond is quite important as a model for the catalytic formation of ureas by metal complexes from amines and CO. With these platinum(II) derivatives, the CO insertion seems to be general, although the de-insertion does prevent some derivatives from being isolated.

However, migratory insertion of CO may not be a common reaction of late metal amide complexes. The aforementioned platinum derivatives are the only examples reported so far, and with other amides, this reaction fails or is superceded by another reaction path. For example, $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(NPh_2)$ reacts [9] with CO by displacement of PMe_3 to give the carbonyl complex $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)CO(NPh_2)$ with no evidence for insertion. With the complex *trans*-$Pt(PEt_3)_2H(NHPh)$, addition of CO results [60] in the formation of the platinum(0) derivative $Pt(PEt_3)_2(CO)_2$ and free aniline. Calculations for the insertion of CO into the metal–amide bond suggest [9] that it is only mildly exothermic ($\Delta H° = -7.1$ kcal mol^{-1}).

In those complexes where the amide donor resides as part of a chelate array, again carbonylation reactions lead [26] to the formation of carbonyl complexes with no evidence for insertion into the metal–amide bond. Thus the complexes $M(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PR_2)_2]$ ($M = Rh, Ir$; $R = Ph, Pr^i$; C_8H_{14} = cyclooctene) react with CO to generate the carbonyl derivatives

$M(CO)[N(SiMe_2CH_2PR_2)_2]$ by substitution of the relatively labile cyclooctene ligand. The coordinatively unsaturated rhodium(III) and iridium(III) methyl-iodide derivatives $M(CH_3)I[N(SiMe_2CH_2PR_2)_2]$ ($R = Ph$, Pr^i) also add CO stereoselectively to generate the carbonyl adducts $M(CH_3)I(CO)[N(SiMe_2CH_2PR_2)_2]$. The CO addition to the iridium dihydride $IrH_2[N(SiMe_2CH_2PPh_2)_2]$ is also selective to form *mer,cis*-$IrH_2(CO)[N(SiMe_2CH_2PPh_2)_2]$. With the palladium(II) methyl complex $PdMe[N(SiMe_2CH_2PPh_2)_2]$, insertion occurs [68] to generate the acetyl derivative $Pd(COMe)[N(SiMe_2CH_2PPh_2)_2]$ with the amide bond still intact. In these systems, it can be argued that the chelate ligand so constrains the amide donor that migratory insertion is disfavored.

Formation of the bridging amido–hydride unit in triosmium carbonyl clusters by reaction of amines with the so-called "lightly-stabilized" derivatives $Os_3(CO)_{10}L_2$ ($L = CH_3CN$, η^2-cyclooctene; $L_2 = \eta^4$-cyclohexadiene) probably proceeds [15] by oxidative addition. However, direct reaction of amines with $Os_3(CO)_{12}$ results in attack at CO to generate η^2-carbamoyl derivatives. Thus for the reaction of benzylamine [19] with $Os_3(CO)_{12}$, the first product isolated is $Os_3(CO)_{10}(\mu\text{-}H)(\eta^2\text{-}PhCH_2NHCO)$ which decarbonylates at 150 °C to give $Os_3(CO)_{10}(\mu\text{-}H)[NH(CH_2Ph)]$; the reverse reaction, carbonylation, does not proceed at any temperature and pressure. Interestingly, dibenzylurea can be produced catalytically by reaction of $PhCH_2NH_2$ with CO (45 atm) at 150 °C in the presence of a catalytic amount of $Os_3(CO)_{12}$; the turnover is 26 over a period of 6 h.

(b) Other insertion reactions

The reaction [60] of carbon dioxide with *trans*-$Pt(PEt_3)_2H(NHPh)$ results in overall insertion to give *trans*-$Pt(PEt_3)_2H(OCONHPh)$; this reaction is in accord with early metal amide complexes and their reaction with CO_2 to generate carbamato derivatives. In contrast, there is no reaction [53] between carbon disulfide and *trans*-$Pt(PPh_3)_2Cl(NH\text{-}p\text{-}NO_2C_6H_4)$.

Certain olefins, namely electron-deficient ones, are known [69] to insert into metal–amide bonds, particularly for the early transition metals and metalloids. For the late transition metals, the only report to date is the insertion [60] of acrylonitrile into the Pt–amide bond of *trans*-$Pt(PEt_3)_2H(NHPh)$ to generate the complex *trans*-$Pt(PEt_3)_2H(CH(CN)CH_2NHPh)$. The regioselectivity is the same as in a Michael addition, that is, the nucleophilic amide adds to the β-carbon of the activated olefin. The thermodynamics of olefin insertion into a metal–amide bond have also been calculated [9] to be exothermic ($\Delta H^0 = -19.2$ kcal mol^{-1}).

(v) Hydrogenolysis of metal amides

The hydrogenolysis of a metal–amide bond to generate a metal hydride can be anticipated to follow one of the pathways shown in Scheme 10. The

TABLE 1

Amide complexes of the platinum group metals [a]

Complex	Characterization [b]	Synthesis [c]	Ref.
$RuH(PPh_3)_2[N(SiMe_3)_2]$	IR, NMR	$RuHCl(PPh_3)_3 + LiN(SiMe_3)_2$	7
$Ru(\eta^5\text{-}C_5Me_5)(PMe_3)_2(NPhR)$ R = Ph, H	NMR, IR	$Ru(\eta^5\text{-}C_5Me_5)(PMe_3)_2Cl + LiNPhR$ R = Ph, H	9
$Ru(NO)Cl_2(PPh_3)_2(NEt_2)$	IR	$RuCl_3 \cdot xH_2O + Et_2NNO + PPh_3$	10
$RuCl(PPh_3)[N(SiMe_2CH_2PPh_2)_2]$	NMR, IR	$RuCl_2(PPh_3)_3 + LiN(SiMe_2CH_2PPh_2)_2$	11
$Ru_2(PMe_2Ph)_2(o\text{-}NC_5H_4NH)_6$ [d]	X-ray	$Ru_2(OAc)_4Cl + LiNH\text{-}o\text{-}NC_5H_4 + PMe_2Ph$	12
$[Os(en)(NH_2CH_2CH_2NH)_2]X_2$ X = Br, I	IR, MAGSC, COND	$[OsBr_6]^{2-}$ + excess en (+NaI for X = I) X = Br, I	13, 14
$[Os(en)_2(NH_2CH_2CH_2NH)]X_3$ X = Br, I	MAGSC, IR	$[Os(en)(NH_2CH_2CH_2NH)_2]Br_2 + HBr$ (HCl + NaI for X = I).	13, 14
$[Os(en)(NH_2CH_2CH_2NH)_3]I_2$	MAGSC, COND	$[Os(en)(NH_2CH_2CH_2NH)_2]I_2 + en + O_2$	13
$[Os(NH_2CH_2CH_2NH)_4]I_2$	MAGSC, COND	$[Os(en)(NH_2CH_2CH_2NH)_2]I_2 + en + O_2$	13
$[Os(en)_2(NH_2CH_2CH_2NH)]I_2$	MAGSC, IR	$[Os(en)_3]I_3 + KNH_2/NH_3(l)$	14
$[Os(en)(NH_2CH_2CH_2NH)_2]I$	IR	$[Os(en)_3]I_3 + 2KNH_2/NH_3(l)$	14
$[Os(NH_2CH_2CH_2NH)_3]$ [e]	IR	$[Os(en)_3]I_3 + 3KNH_2/NH_3(l)$	14
$Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}NPh_2)$ [d]		$Os_3(CO)_{10}(NCCH_3)_2 + HNPh_2$	16
$Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}NHR)$ [d] R = Bu, Ph	NMR, IR	$Os_3(CO)_{10}(\eta^4\text{-}C_6H_8) + H_2NR$ R = Bu, Ph	17
$Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}NHR)$ R = CH_2Ph, Ph, $p\text{-}C_6H_4F$, $p\text{-}C_6H_4Me$	NMR, IR	$Os_3(CO)_{12} + H_2NR$ R = CH_2Ph, Ph, $p\text{-}C_6H_4F$, $p\text{-}C_6H_4Me$	18, 19
$Os_3(CO)_{10}(\mu\text{-}H)[\mu\text{-}NH(CH_2Ph)]$	NMR, IR	$Os_3(CO)_{10}(\eta^2\text{-}C_8H_{14})_2 + H_2NCH_2Ph$	19
$Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}NHSiMe_3)$	NMR, IR, X-ray	$[Os_3H(CO)_{11}]^- + Me_3SiN_3$	20
$Os_3(CO)_{10}(\mu\text{-}H)[\mu\text{-}NH(CH_2CF_3)]$	NMR, IR, X-ray	$Os_3(CO)_{10}(\mu\text{-}H)[\mu\text{-}N{=}CH(CF_3)] + H_2$	21
$Rh(PPh_3)_2[N(SiMe_3)_2]$	NMR, IR	$RhCl(PPh_3)_3 + LiN(SiMe_3)_2$	7
$[Rh(en)_2(NH_2CH_2CH_2NH)]I_2$	IR, POWDIFF	$[Rh(en)_3]I_3 + KNH_2/NH_3(l)$	22
$[Rh(en)(NH_2CH_2CH_2NH)_2]I$	IR, POWDIFF	$[Rh(en)_3]I_3 + 2KNH_2/NH_3(l)$	22
$Rh(NH_2CH_2CH_2NH)_3$	IR, POWDIFF	$[Rh(en)_3]I_3 + 3KNH_2/NH_3(l)$	22
$K[Rh(NHCH_2CH_2NH)\text{-}(NH_2CH_2CH_2NH)_2]$	IR, POWDIFF MAGSC	$[Rh(en)_3]I_3 + 5KNH_2/NH_3(l)$	23

$[Rh(NH_2CH_2CH_2NHCH_2CH_2NH)_2]I$	IR, POWDIFF	$[Rh(dien)_2]I_3 + 2KNH_2/NH_3(l)$	24
$[Rh(NH_2CH_2CH_2NHCH_2CH_2NH)$-$NH(CH_2CH_2NH)_2]$	IR, POWDIFF	$[Rh(dien)_2]I_3 + 3.5KNH_2/NH_3(l)$	24
$Rh(\eta^2$-$C_8H_{14})[N(SiMe_2CH_2PR_2)_2]$ $R = Ph, Pr^i$	NMR	$Rh_2(\eta^2$-$C_8H_{14})_4Cl_2 + 2LiN(SiMe_2CH_2PR_2)_2$ $R = Ph, Pr^i$	26
$Rh(L)[N(SiMe_2CH_2PPh_2)_2]$ $L = CO, \eta^2$-C_2H_4, PMe_3, PPh_3	NMR, IR	$Rh(\eta^2$-$C_8H_{14})[N(SiMe_2CH_2PPh_2)_2] + L$ $L = CO, \eta^2$-C_2H_4, PMe_3, PPh_3	26
$Rh(CH_3)X[N(SiMe_2CH_2PR_2)_2]$ $R = Ph, X = Br, I; R = Pr^i, X = I$	NMR	$Rh(\eta^2$-$C_8H_{14})[N(SiMe_2CH_2PR_2)_2] + CH_3X$ $R = Ph, X = Br, I; R = Pr^i, X = I$	26
$Rh(CH_3)I(CO)[N(SiMe_2CH_2PR_2)_2]$ [d] $R = Ph, Pr^i$	NMR, IR	$Rh(CH_3)I[N(SiMe_2CH_2PR_2)_2] + CO$ $R = Ph, Pr^i$	26
$Rh(\eta^4$-$1,5$-$C_8H_{12})[N(CH_2Ph)$-$SiMe_2CH_2Ph_2]$	NMR	$Rh_2(\eta^4$-$1,5$-$C_8H_{12})_2Cl_2$ $+ 2LiN(CH_2Ph)SiMe_2CH_2PPh_2]$	30
$Rh(CH_2Ph)X[N(SiMe_2CH_2PPh_2)_2]$ $X = Cl, Br, I$	NMR	$Rh(\eta^2$-$C_8H_{14})[N(SiMe_2CH_2PPh_2)_2] + PhCH_2X$ $X = Cl, Br, I$	29
cis-$RhCl_2(o$-$Ph_2PC_6H_4NH_2)$-$(o$-$Ph_2PC_6H_4NH)$	NMR, X-ray	*cis*-$[Rh(o$-$Ph_2PC_6H_4NH_2)_2]Cl + O_2$	31
$[Rh_2(\eta^5$-$C_5Me_5)_2(\mu$-$OH)_2(\mu$-$NHPh)]X$ $X = PF_6, BF_4$	NMR, IR	$[Rh_2(\eta^5$-$C_5Me_5)_2(\mu$-$OH)_3]OH + NH_2Ph$ $(+ KPF_6$ or $NaBF_4)$	33
$Rh_2\{P(OPr^i)_3\}_2(\mu$-$H)[\mu$-$N(CH_3)R]$ $R = CH_2Ph, p$-C_6H_4Cl	NMR, IR, X-ray	$Rh_2\{P(OPr^i)_3\}_2(\mu$-$H)_2 + H_2 + RNC$ $R = CH_2Ph, p$-C_6H_4Cl	34
$Rh_2(Pr^i_2PCH_2CH_2PPr^i)_2(\mu$-$H)$-$[\mu$-$N(CH_2Ph)Ph]$	NMR, IR	$Rh_2(Pr^i_2PCH_2CH_2PPr^i)_2(\mu$-$H)_2 + PhC{=}NPh$	35
$[Ir(en)(NH_2CH_2CH_2NH)_2]I$	POWDIFF	$[Ir(en)_3]I_3 + 2KNH_2/NH_3(l)$	25
$K_2[Ir(NH_2CH_2CH_2NH)$-$(NHCH_2CH_2NH)_2]$	POWDIFF	$[Ir(en)_3]I_3 + > 5KNH_2/NH_3(l)$	25
$[Ir(NH_2CH_2CH_2NHCH_2CH_2NH)$-$NH(CH_2CH_2NH)_2]$ [e]		$[Ir(dien)_2]I_3 + 3.5KNH_2/NH_3(l)$	24
$Ir(\eta^2$-$C_8H_{14})[N(SiMe_2CH_2PR_2)_2]$ $R = Ph, Pr^i$	NMR	$Ir_2(\eta^2$-$C_8H_{14})_4Cl_2 + 2LiN(SiMe_2CH_2PR_2)_2$ $R = Ph, Pr^i$	26
$Ir(L)[N(SiMe_2CH_2PPh_2)_2]$ $L = CO, \eta^2$-C_2H_4, PMe_3, PPh_3	NMR, IR	$Ir(\eta^2$-$C_8H_{14})[N(SiMe_2CH_2PPh_2)_2] + L$ $L = CO, \eta^2$-C_2H_4, PMe_3, PPh_3	26

TABLE 1 (continued)

Complex	Characterization [b]	Synthesis [c]	Ref.
$Ir(CH_3)X[N(SiMe_2CH_2PR_2)_2]$ $R = Ph, X = Br, I; R = Pr^i, X = I$	NMR	$Ir(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PR_2)_2] + CH_3X$ $R = Ph, X = Br, I; R = Pr^i, X = I$	26
$Ir(CH_3)I(CO)[N(SiMe_2CH_2PR_2)_2]$ [f] $R = Ph, Pr^i$	NMR, IR	$Ir(CH_3)I[N(SiMe_2CH_2PR_2)_2] + CO$ $R = Ph, Pr^i$	26
$Ir(\eta^4\text{-}1,5\text{-}C_8H_{12})[N(CH_2Ph)\text{-}$ $SiMe_2CH_2Ph_2]$	NMR	$Ir_2(\eta^4\text{-}1,5\text{-}C_8H_{12})_2Cl_2$ $+ 2LiN(CH_2Ph)SiMe_2CH_2PR_2$	30
$Ir(Ar)X[N(SiMe_2CH_2PPh_2)_2]$ $Ar = m\text{-}C_6H_4Me : p\text{-}C_6H_4Me\ 1:4;$ $X = Cl, Br, I$	NMR	$Ir(CH_3)X[N(SiMe_2CH_2PPh_2)_2] + C_6H_5Me$ $X = Cl, Br, I$	29
$IrH_2[N(SiMe_2CH_2PPh_2)_2]$	NMR, IR	$Ir(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PPh_2)_2] + H_2$ (then vacuum)	27
mer,cis-$IrH_2(L)[N(SiMe_2CH_2PPh_2)_2]$ $L = PMe_3, CO$	NMR, IR	$IrH_2[N(SiMe_2CH_2PPh_2)_2] + L$ $L = PMe_3, CO$	27
mer,trans-$IrH_2(CO)[N(SiMe_2CH_2PPh_2)_2]$	NMR, IR	$Ir(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PPh_2)_2] + (HCHO)_n$	27
fac-$IrH_2(PMe_3)[N(SiMe_2CH_2PPh_2)_2]$	NMR, IR, X-ray	$Ir(PMe_3)[N(SiMe_2CH_2PPh_2)_2] + H_2$	27
$Ir(CH_3)R[N(SiMe_2CH_2PPh_2)_2]$ $R = CH_3, CH_2CMe_3, CH_2SiMe_3,$ CH_2Ph	NMR, X-ray	$Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2] + RLi$ $R = CH_3, CH_2CMe_3, CH_2SiMe_3, CH_2Ph$	29
$Ir{=}CH_2[N(SiMe_2CH_2PPh_2)_2]$	NMR, X-ray	$Ir(CH_3)CH_2CMe_3[N(SiMe_2CH_2PPh_2)_2] + h\nu$	28
$Ir(H)Cl(o\text{-}Ph_2PC_6H_4NHR)\text{-}$ $(o\text{-}Ph_2PC_6H_4NR)\ R = CH_2Ph, Et$	NMR, IR	$Ir_2(\eta^2\text{-}C_8H_{14})_4Cl_2 + 4\,o\text{-}Ph_2PC_6H_4NHR$ $R = CH_2Ph, Et$	32
$[Ir_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}OH)_2(\mu\text{-}NHPh)]PF_6$	NMR, IR	$[Ir_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}OH)_3]OH + N_2HPh + KPF_6$	33
$[Pd(en)(NH_2CH_2CH_2NH)]I$	POWDIFF	$[Pd(en)_2]I_2 + KNH_2/NH_3(l)$	37
$Pd(NH_2CH_2CH_2NH)_2$	POWDIFF	$[Pd(en)_2]I_2 + 2KNH_2/NH_3(l)$	37
$K_2[Pd(o\text{-}OC_6H_4NH)_2]$	POWDIFF, IR	$Pd(o\text{-}OC_6H_4NH_2)_2 + 2KNH_2/NH_3(l)$	38
$K_2[Pd(o\text{-}SC_6H_4NH)_2]$	POWDIFF, IR	$Pd(o\text{-}SC_6H_4NH_2)_2 + 2KNH_2/NH_3(l)$	38
$K[Pd(SCH_2CH_2NH_2)(SCH_2CH_2NH)]$	POWDIFF, IR	$Pd(SCH_2CH_2NH_2)_2 + KNH_2/NH_3(l)$	39
$K_2[Pd(SCH_2CH_2NH)_2]$	POWDIFF, IR	$Pd(SCH_2CH_2NH_2)_2 + 2KNH_2/NH_3(l)$	39
$PdCl[N(SiMe_2CH_2PPh_2)_2]$	NMR, X-ray	$PdCl_2(PhCN)_2 + LiN(SiMe_2CH_2PPh_2)_2$	6(a)
$Pd(CH_3)[N(SiMe_2CH_2PPh_2)_2]$	NMR	$PdCl[N(SiMe_2CH_2PPh_2)_2] + MeMgCl$	6(a)

$Pd(\eta^1\text{-}C_3H_5)[N(SiMe_2CH_2PPh_2)_2]$	NMR	$PdCl[N(SiMe_2CH_2PPh_2)_2] + H_2C{=}CHCH_2MgCl$	6(a)
$Pd(COCH_3)[N(SiMe_2CH_2PPh_2)_2]$	NMR, IR	$Pd(CH_3)[N(SiMe_2CH_2PPh_2)_2] + CO$	6(a)
$Pd_2(\beta\text{-dik})_2(\mu\text{-NHAr})_2$ [g]	NMR, IR	$Pd(\beta\text{-dik})_2 + H_2NAr$	43
β-dik [h] = acac, tfac, bzac, hfac			
Ar = Ph, 2-Me-C_6H_4, 4-Me-C_6H_4,			
2,5-Me_2-C_6H_3, 2-Me-C_6H_4,			
2,6-Me_2-C_6H_3, 3,5-Me_2-C_6H_3,			
2,4,6-Me_3-C_6H_2, 3-CF_3-C_6H_4,			
2-NO_2-C_6H_4, 4-NO_2-C_6H_4			
$[(PdL_2)_2(\mu\text{-NHAr})](\beta\text{-dik})_2$	NMR, IR	$Pd_2(\beta\text{-dik})_2(\mu\text{-NHAr})_2 + > 4L$	42
L = py, Ar = Ph, 2-Me-C_6H_4			
Ar = 2-Me-C_6H_4, L = 2-Me-$C_6H_4NH_2$,			
3,5-Me_2-$C_6H_3NH_2$, $MeNH_2$, $PrNH_2$			
Ar = 3,5-Me_2-C_6H_3,			
L = 3,5-Me_2-$C_6H_3NH_2$			
Ar = 4-Me-C_6H_4, L = 4-Me-$C_6H_4NH_2$			
Ar = Ph, L = $PrNH_2$			
$[Pt(en)(NH_2CH_2CH_2NH)]I$	POWDIFF	$[Pt(en)_2]I_2 + KNH_2/NH_3(l)$	43
$Pt(NH_2CH_2CH_2NH)_2$	POWDIFF	$[Pt(en)_2]I_2 + 2KNH_2/NH_3(l)$	43
$K[Pt(NH_2CH_2CH_2NH)$- $(NHCH_2CH_2NH)]$	POWDIFF	$Pt(NH_2CH_2CH_2NH)_2 + KNH_2/NH_3(l)$	44
$[Pt(bipy)(NH_2CH_2CH_2NH)]I$	POWDIFF	$[Pt(bipy)(en)]I_2 + KNH_2/NH_3(l)$	45
$Pt(bipy)(NHCH_2CH_2NH)$	POWDIFF	$[Pt(bipy)(en)]I_2 + 2KNH_2/NH_3(l)$	46
$[Pt(NH_3)Cl(MeNH_2)_3(MeNH)]Cl_2$		$[Pt(NH_3)Cl(MeNH_2)_4]Cl_3 + NaOH$	46
$Pt(NO_2)_2Cl(en)(RNH)$		$[PtCl_2(en)NO_2(RNH_2)]Cl + 2KNO_2 + NaOH$	47
R = Et, Pr			
$M[PtCl_2(NO_2)_2(MeNH_2)(MeNH)]$		*cis*-$PtCl_2(NO_2)_2(MeNH_2)_2 + MOH$	48, 49
M = Na, Cs		M = Na, Cs	
$M[PtCl_3(NO_2)(NH_2CH_2CH_2NH)]$		$PtCl_3(NO_2)(en) + MOH$	48, 49
M = Na, Cs		M = Na, Cs	
$Pt(PEt_3)_2Cl(NHAr)$	IR	$Pt(PEt_3)_2Cl(H) + ArN_3$	50
Ar = Ph, *p*-NO_2-C_6H_4		Ar = Ph, *p*-NO_2-C_6H_4	
$Pt(PPh_3)_2[2,4,6\text{-}C_6H_2(NO_2)_3](NPh_2)$		$Pt(PPh_3)_4 + Ph_2NN(2,4,6\text{-}C_6H_2(NO_2)_3)$	54

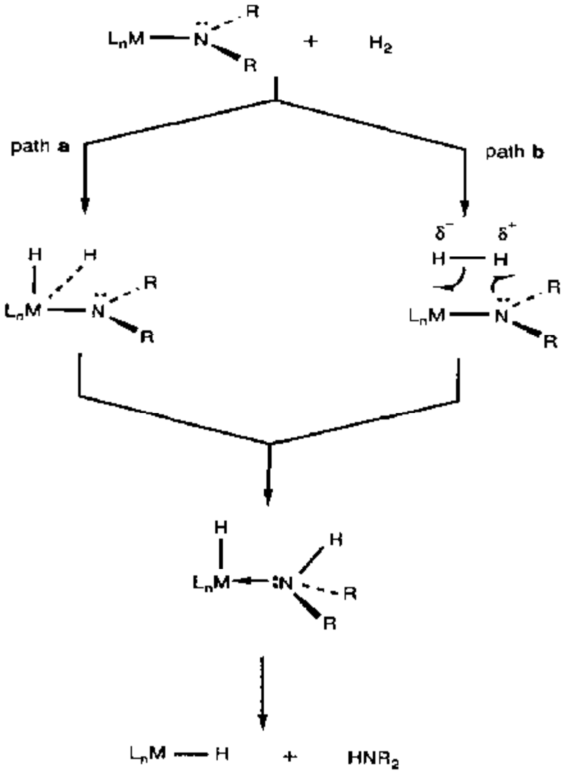
TABLE 1 (continued)

Complex	Characterization [b]	Synthesis [c]	Ref.
$Pt(PEt_3)_2Cl(NHAr)$	IR	$Pt(PEt_3)_2Cl(H) + ArN_3$	51
Ar = $5\text{-}NO_2\text{-}3\text{-}C_5H_3N$		Ar = $5\text{-}NO_2\text{-}3\text{-}C_5H_3N$	
$Pt(PPh_3)_2Cl(NHAr)$	NMR, IR	*trans*-$Pt(PPh_3)_2Cl(H) + ArN_3$	53
Ar = *p*-$NO_2\text{-}C_6H_4$		*p*-$NO_2\text{-}C_6H_4$	
$Pt(PEt_3)_2Cl(NHAr)$		*trans*-$Pt(PEt_3)_2Cl(H) + ArN_3$	52
Ar = 4-Me-C_6H_4, 1-naphthyl		Ar = 4-Me-C_6H_4, 1-naphthyl	
$[Pt(bipy)(OH_2)($*cis,cis*-1,3,5-$(C_6H_9)\text{-}NH_2(NH)_2]Cl_2$	NMR, X-ray, ESCA	$PtCl_2(bipy)$ + *cis,cis*-1,3,5-$(NH_2)_3C_6H_9$	55
cis-$Pt(o\text{-}Ph_2PC_6H_4NH)_2$	NMR, IR, X-ray	*cis*-$[Pt(o\text{-}Ph_2PC_6H_4NH_2)_2]Cl_2$ + base	6(b), 56
trans-$Pt(o\text{-}Ph_2PC_6H_4NH)_2$	NMR, IR, X-ray	$o\text{-}Ph_2PC_6H_4NH_2 + K_2[PtCl_4] + NEt_3$	6(b), 56
cis-$[Pt(o\text{-}Ph_2PC_6H_4NH_3)\text{-}(o\text{-}Ph_2PC_6H_4NH)]Cl$	IR	*cis*-$[Pt(o\text{-}Ph_2PC_6H_4NH_2)_2]Cl_2$ + heat	6(b)
cis-$[Pt(o\text{-}Ph_2PC_6H_4NH_2)\text{-}(o\text{-}Ph_2PC_6H_4NH)]OCOCF_3$	NMR, IR	*cis*-$Pt(o\text{-}Ph_2PC_6H_4NH)_2 + CF_3CO_2H$	6(b)
trans-$[Pt(o\text{-}Ph_2PC_6H_4NH_2)(o\text{-}Ph_2PC_6H_4NH)]OCOCF_3$	NMR, IR	*trans*-$Pt(o\text{-}Ph_2PC_6H_4NH)_2 + CF_3CO_2H$	6(b)
$Pt(PPh_3)_2[o\text{-}NH(Ar)NH]$	IR	$Pt(PPh_3)(\eta^2\text{-}O_2) + o\text{-}H_2N(Ar)NH_2$	57
Ar = substituted *o*-phenylene	(see eqn. (21) in text)		
cis-$Pt(PEt_3)_2Cl(NPh_2)$	NMR, X-ray	*cis*-$Pt(PEt_3)_2Cl_2 + LiNPh_2$	58
$PtCl[N(SiMe_2CH_2PPh_2)_2]$	NMR, IR	$K[PtCl_3(\eta^2\text{-}C_2H_4)] + LiN(SiMe_2CH_2PPh_2)_2$	6(a)
$Pt(R_2CH_2CH_2PR_2)R'(NMePh)$	NMR, X-ray	$Pt(R_2CH_2CH_2PR_2)R'(Cl) + LiNMePh$	59
R = Ph, R′ = Me, Ph, CH_2Ph		R = Ph, R′ = Me, Ph, CH_2Ph	
R = Me, R′ = Me		R = Me, R′ = Me	
$Pt(Ph_2CH_2CH_2PPh_2)Me[NH(CH_2Ph)]$	NMR	$Pt(Ph_2CH_2CH_2PPh_2)Me(Cl) + LiNH(CH_2Ph)$	59
trans-$Pt(PEt_3)_2H(NHPh)$ [d]	NMR	*trans*-$Pt(PEt_3)_2H(NO_3) + NaNHPh$	60
$Pt(Ph_2PCH{=}CHPPh_2)CH_2CN)\text{-}(NMePh)$ [i]	NMR, IR	$Pt(Ph_2PCH{=}CHPPh_2)(CH_2CN)(OH) + HNMePh$	61

$Pt_2[\mu\text{-}(S,S)\text{-}MeSOCH_2CH_2CH(CO_2)NH]_2$	X-ray	$PtCl_2[(S,S)\text{-}MeSOCH_2CH_2CH(CO_2H)NH_2]$ + excess base	62
$Na_2[Pt_2Me_4(OH)_2(\mu\text{-}O_2CCH_2NH)_2]$ [d]	NMR	$[PtMe_2Br(gly)]_2$ + 5M NaOH (to pH 12.5)	63
$Pt_2Cl_2[\mu\text{-}o\text{-}(\eta^2\text{-}MeC{=}CH_2)C_6H_4NMe]_2$	NMR, X-ray	$PtCl_2[\mu\text{-}o\text{-}(\eta^2\text{-}MeC{=}CH_2)C_6H_4NHMe]$ + basic ion exchange resin	6(c)

---

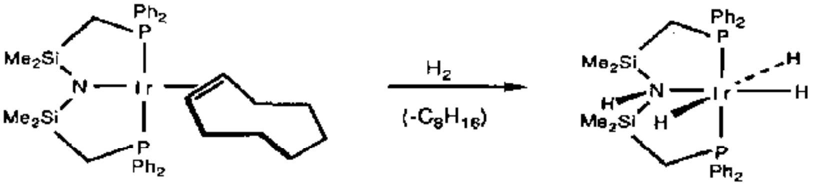
[a] The amide ligand is listed last in the molecular formula; only those complexes for which reasonable analytical and spectroscopic data are available are included. Where possible, general formulae are used to conserve space. [b] Ir = infra-red spectra; NMR = nuclear magnetic resonance spectra (no particular nucleus or experiment is implied); X-ray = single-crystal X-ray diffraction; POWDIFF = powder X-ray diffraction; COND = solution conductivity; MAGSC = magnetic susceptibility. [c] Only reagents are given; solvents, reaction temperatures and times are omitted. In those cases where more than one synthesis is given, the one with the highest reported yield is given. [d] No elemental analyses reported. [e] Only metal analysis reported. [f] Two isomeric forms for R = Ph were prepared by different, rational routes. [g] Not all combinations of Ar and β-dik were reported; however, for hfac [h], all the indicated substituted anilines were prepared. [h] β-dik = β-diketonate, i.e. acac = 2,4-pentanedionate; tfac = 1,1,1-trifluoro-2,4-pentanedionate; bzac = 1-phenyl-1,3-butanedionate; hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate. [i] Isolated as a 70 : 30 mixture with starting material.



Scheme 10.

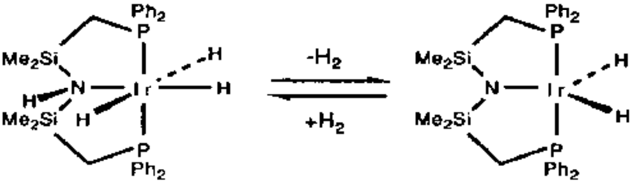
difference lies in how the dihydrogen is activated [70]: either wholly by the metal via oxidative addition (path **a**), followed by reductive transfer, or assisted by the amide ligand in a heterolytic cleavage process (path **b**). The penultimate product, the amine hydride, can then eliminate the amine to generate the metal hydride derivative.

The first reported [27] activation of dihydrogen by a transition metal amide complex involved the reaction of an iridium(I) amide as shown in eqn. (25):



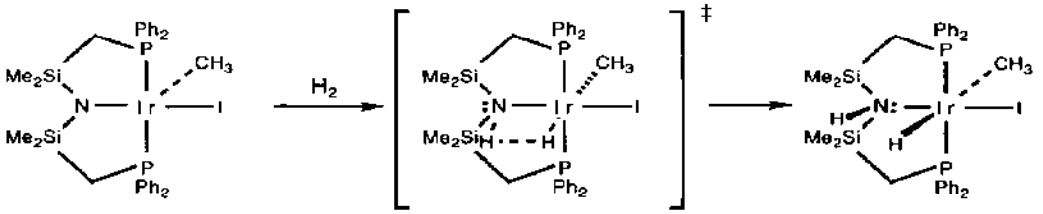
(25)

Because the resulting amine function is part of the chelate array, it cannot be eliminated. The amine trihydride product is stable only under H_2; under N_2 or vacuum, it reversibly eliminates H_2 to generate the amide dihydride $IrH_2[N(SiMe_2CH_2PPh_2)_2]$ (eqn. (26)):



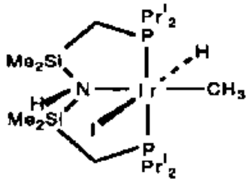
(26)

In an effort to distinguish between the two mechanistic pathways presented in Scheme 10, the hydrogenation of the iridium(III) methyl halides $Ir(CH_3)X[N(SiMe_2CH_2PR_2)_2]$ ($X = I$, Br; $R = Ph$, Pr^i) was studied [71]. These systems were thought to be ideally suited for heterolytic activation (path **b**) since the metal is in a high oxidation state and the dihydrogen molecule can interact with both the lone pair on the amide nitrogen and the metal at the open site *trans* to the apical methyl group; this is shown in eqn. (27):



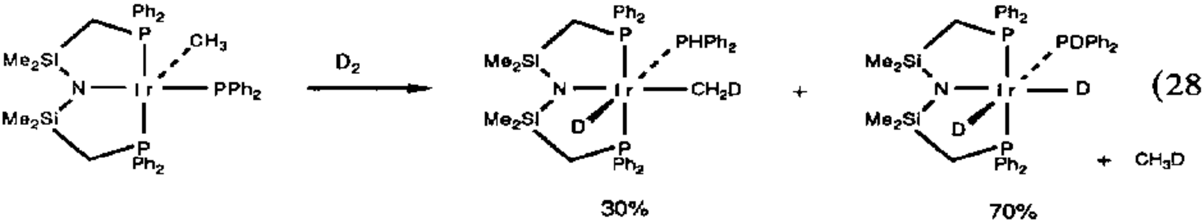
(27)

Therefore observation of the indicated stereochemistry, hydride *trans* to methyl and amine *trans* to the halide, would strongly support activation of dihydrogen heterolytically. However, this stereochemical argument can only be used if the reaction is proceeding under kinetic control. It was found that the stereochemistry of the product was in fact quite different from that in eqn. (27); hydride was *trans* to halide and methyl *trans* to amine (see below):



This stereochemistry was shown to be controlled by the formation of an intramolecular hydrogen bond between the N–H of the coordinated amine and the halide. Thus, because the reaction of the iridium(III) amide with H_2 proceeds under thermodynamic control, no information on the intermediate steps was available.

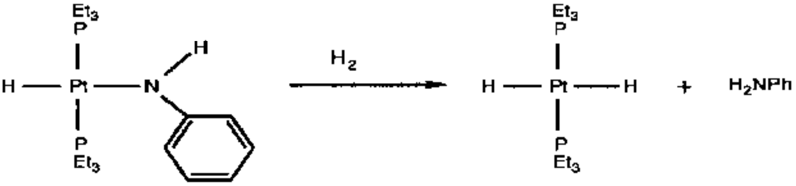
Not all iridium(I) and iridium(III) complexes with the amide donor as part of a chelate array activate dihydrogen as shown above. Simple oxidative addition is observed [27] with $Ir(PMe_3)[N(SiMe_2CH_2PPh_2)_2]$ to generate *fac,cis*-$IrH_2(PMe_3)[N(SiMe_2CH_2PPh_2)_2]$. In addition, a more complex process results [72] with other basic ligands present, as shown for the reaction of deuterium with the iridium(III) phosphide derivative in eqn. (28):



(28)

There are only two other reports of mononuclear late metal amide complexes undergoing reaction with dihydrogen and both result in loss of the amide donor: $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(NPh_2)$ reacts [9] with H_2 to generate an equilibrium mixture of a ruthenium(II) hydride and a ruthenium(IV) trihydride (eqn. (29)), and *trans*-$Pt(PEt_3)_2H(NHPh)$ gives [63] $Pt(PEt_3)_2H_2$ (eqn. (30)):

$$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(NPh_2) \xrightarrow[\substack{4\text{ atm}\\(-HNPh_2)}]{H_2} \begin{matrix}(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2H\\+\\(\eta^5\text{-}C_5Me_5)Ru(PMe_3)H_3\end{matrix} \qquad (29)$$



(30)

No information on the mechanisms of these reactions was given. The rhodium binuclear amide derivatives shown above in eqn. (14) undergo slow hydrogenolysis to generate amine and binuclear hydrides; here again, no information about the mechanism is available [34–36].

Hydrogenolysis of amides of the later transition metals should be a general reaction just on thermodynamic grounds. To break the H–H bond in H_2 requires 103 kcal mol^{-1} of which approximately 92 kcal mol^{-1} is returned by formation of the N–H bond of the amine [73]. Thus the metal–hydride bond must be stronger than the metal–amide bond by only 11 kcal mol^{-1}, and estimates suggest [9] that this difference is much higher. Of course, kinetic factors may also be involved.

For the amides of the early transition metals, just the opposite should obtain since the strength of the metal–amide bond increases [74] as one goes to the left of the transition series. Indeed, the hydridic character of early transition metal hydride complexes, often compared with the hydrides of boron and aluminum, suggests that amines should react with the early metal hydrides to generate amides by elimination of H_2, as found in boron and aluminum chemistry, and in fact they do [75].

TABLE 2

Summary of crystallographic data for platinum metal amides

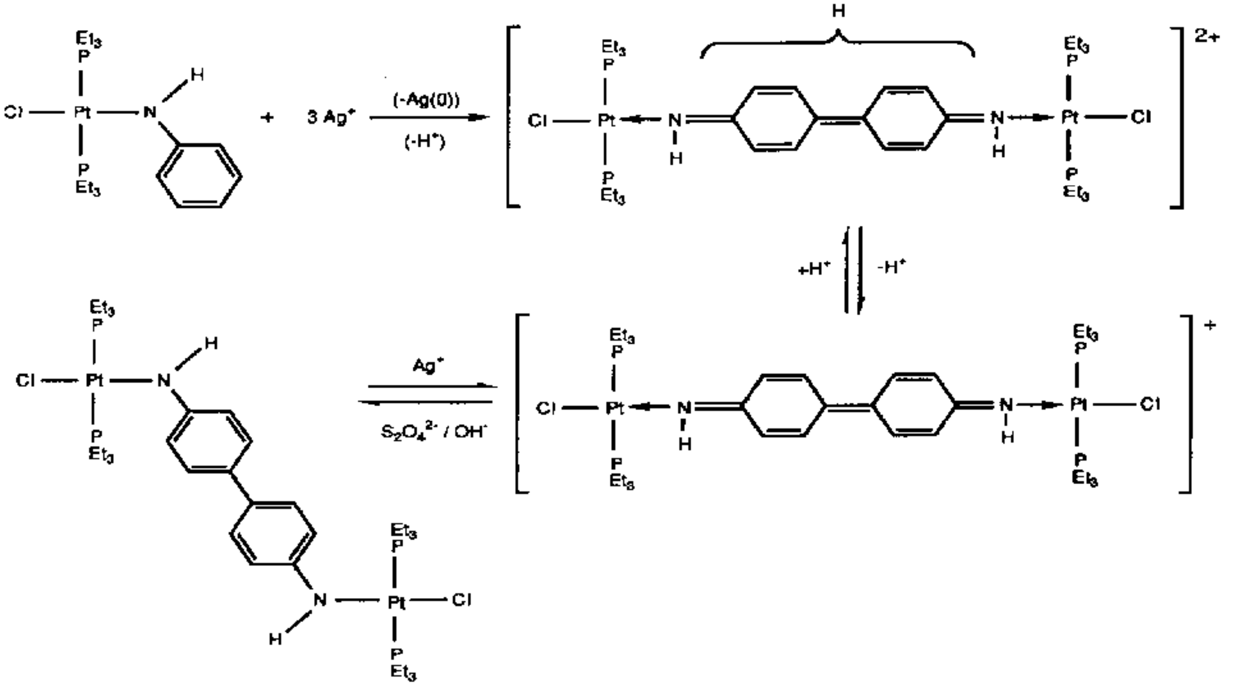
Complex	M–N bond distance (Å)	Geometry about N (sum of angles about N)	Ref.
Ru$_2$(PMe$_2$Ph)$_2$(*o*-NC$_5$H$_4$NH)$_6$	2.073(11)	Not reported	12
	2.054(9)		
	2.085(9) (bridging N)	Distorted tetrahedron	
	2.104(9) (bridging N)	Distorted tetrahedron	
Os$_3$(CO)$_{10}$(μ-H)(μ-NHSiMe$_3$)	2.104(14) 2.129(15)	Distorted tetrahedron	20
Os$_3$(CO)$_{10}$(μ-H)[μ-NH(CH$_2$CF$_3$)]	2.166(14) 2.150(15)	Distorted tetrahedron	21
cis-RhCl$_2$(*o*-Ph$_2$PC$_6$H$_4$NH$_2$)-(*o*-Ph$_2$PC$_6$H$_4$NH)	2.018(5)	Planar	31
[Rh{N(SiMe$_3$)$_2$}(PPh$_3$)$_2$]	2.010(5)	Planar	76
Ir(CH$_3$)I[N(SiMe$_2$CH$_2$PPh$_2$)$_2$]	2.079(5)	Planar (359.9(9)°)	26
fac-IrH$_2$(PMe$_3$)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$]	2.211(8)	Planar (361.8(13)°)	27
Ir=CH$_2$[N(SiMe$_2$CH$_2$PPh$_2$)$_2$]	2.080(5)	Planar	28(a)
Ir(CH$_3$)(CH$_2$CMe$_3$)[N(SiMe$_2$CH$_2$-PPh$_2$)$_2$]	2.109(7)	Planar	28(b)
PdCl[N(SiMe$_2$CH$_2$PPh$_2$)$_2$]	2.063(2)	Planar (360.00(30)°)	6(a)
[Pt(bipy)(OH$_2$){*cis,cis*-1,3,5(C$_6$H$_9$)-NH$_2$(NH)$_2$}]Cl$_2$	2.013(8) 2.044(8)	Not reported	55
trans-Pt(*o*-Ph$_2$PC$_6$H$_4$NH)$_2$	2.02(1)	Not reported	56
cis-Pt(*o*-Ph$_2$PC$_6$H$_4$NH)$_2$	2.04(1)	Not reported	56
cis-Pt(PEt$_3$)$_2$Cl(NPh$_2$)	2.09(2)	Planar	58
Pt(DPPE)Me(NMePh)	Not reported	Not reported	59
Pt$_2$[μ-(*S,S*)-MeSOCH$_2$CH$_2$-(CO$_2$)NH]$_2$	2.040(7) 2.046(7) 2.038(6) 2.040(7)	Distorted tetrahedron	62
Pt$_2$Cl$_2$[μ-*o*-(η^2-MeC=CH$_2$)-C$_6$H$_4$NMe]$_2$	2.07(2) 2.10(2)	Distorted tetrahedron	6(c)
[Pt(COD)Cl{N(SiMe$_3$)$_2$}]	2.049(6)	Planar (356.0(10)°)	76

hydrides to generate amides by elimination of H$_2$, as found in boron and aluminum chemistry, and in fact they do [75].

(vi) Other reactions

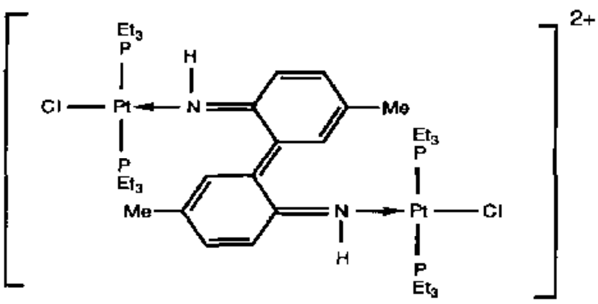
The thermolysis of certain triosmium amido–hydride derivatives derived from primary amines is reported to involve α-hydrogen activation to produce a triply bridging imido ligand. Thus thermolysis [18,20] of $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-NHAr})$ (Ar = Ph, $p\text{-}C_6H_4F$, $p\text{-}C_6H_4Me$) leads to $Os_3(CO)_9(\mu\text{-H})_2(\mu_3\text{-NAr})$ as the thermodynamic product. Also isolable in the case of Ar = Ph and $p\text{-}C_6H_4F$ is a kinetically stable isomer wherein orthometallation of the aromatic ring has occurred to give $Os_3(CO)_{10}(\mu\text{-H})_2(\mu\text{-NHC}_6H_3X)$ (X = H and F). A similar type of conversion has been reported [21] for the trifluoroethylideneimido osmium cluster $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-N=CHCF}_3)$ upon reaction with H_2 at 140 °C to give the mixture of products: $Os_3(CO)_{10}(\mu\text{-H})[\mu\text{-NH(CH}_2CF_3)]$, $Os_3(CO)_9(\mu\text{-H})_2(\mu_3\text{-NCH}_2CF_3)$ and $Os_3(CO)_8(\mu\text{-H})_3H(\mu_3\text{-NCH}_2CF_3)$. The latter two derivatives contain the triply bridging imido unit.

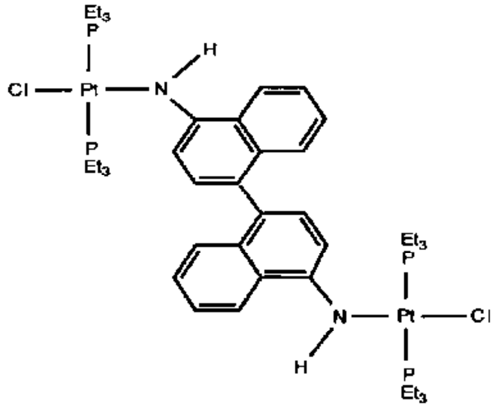
The reaction of the platinum(II) phenylamido complex *trans*-$Pt(PEt_3)_2Cl(NHPh)$ with silver(I) generates [52] a weakly paramagnetic, deep red complex and deposits a silver mirror. The isolated product does not involve direct reaction of the platinum–amide bond, but rather oxidative dimerization via aryl coupling at the *para* position; reaction of base with the deep red oxidation product gave a monocation with a bridging *para*-ben-



Scheme 11.

zidine moiety, the crystal structure of which was obtained. Further reaction with base and sodium dithionite produced the neutral complex having the *p,p′*-biphenyldiamido unit bridging two platinum(II) centers; this latter neutral product could be reoxidized with Ag^+ to give the monocation. These reactions are summarized in Scheme 11. When the *para* position was blocked, oxidative dimerization occurred at the *ortho* position. A similar reaction sequence obtains for the 1-naphthylamido complex *trans*-$Pt(PEt_3)_2Cl(NH\text{-}1\text{-}Np)$ but no intermediate cationic species could be isolated; only the neutral dimer containing the bridging 4,4′-diamido-1,1′-binaphthyl unit was isolated:





The mechanism of this oxidative dimerization is not known, but aryl radical cations have been implicated.

D. SUMMARY

By restricting the scope of this work to the heavier members of groups 8, 9 and 10, the so-called platinum group metals, and furthermore, defining the amide as being derived from a primary or secondary amine, we have been able to provide a fairly comprehensive summary of this area to the end of 1987. In the monograph entitled "*Metal and Metalloid Amides*", an obviously more daring and all-encompassing labor, the keen observation of the lack of late metal amides provided the basis for this review article. Indeed, there now exist well over 150 amides in this class, and hopefully that will suffice to put to rest the phrase "amides of the later metals are rare".

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