Nucleophilic and electrophilic platinum compounds for C-H bond activation

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Chapter 2, Part A

Synthesis of new ($\sigma^2$-N,N'-Diazadiene)(η²-alkene) platinum(0) compounds

2.1 Introduction

As has been shown by several groups, chelating bidentate nitrogen ligands are valid alternatives to phosphines and phosphites as stabilizing entities for the synthesis of zerovalent compounds containing a group 8, 9 or 10 metal atom\(^{[2-22]}\) and useful directing ligands in their reactivity.\(^{[23-42]}\) Nowadays, many examples of late transition metal complexes in low oxidation states containing bidentate nitrogen ligands, such as 1,10-phenanthroline, pyridine-carbaldimine (Pyca) derivatives, N,N'-disubstituted-1,4-diazabutadiene (R-DAB) and bis(arylimino)acenaphthene (Ar-BIAN) ligands, are known.

Pioneering work regarding the coordination chemistry of diaza(buta)dienes has been carried out notably by Vrieze and Van Koten, tom Dieck, Schurig, Frühauf, and quite a number of R-DAB-complexes of low-valent transition metals, often with CO as co-ligand, have been prepared (for a few examples, see Figure 2.1).\(^{[2-11]}\)

![Figure 2.1 Some examples of transition-metal diazadiene compounds](image)

An early publication by Cavell, Stufkens and Vrieze\(^{[12]}\) reports the isolation of mononuclear zerovalent Pd⁰(R-DAB)(η²-alkene) (A, Figure 2.2) for various R and electron-poor alkenes. In many cases, Pd⁰(R-DAB)(L) complexes derived from open-chain R-DAB exist as mononuclear species with the R-DAB acting as a bidentate chelating entity, notably

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when the ratio Pd:R-DAB:alkene is 1:1:1. Dinuclear compounds with a bridging R-DAB ligand are obtained in quite a number of cases as well,\(^{[12,3,12]}\) especially in the presence of more than one equivalent of alkene per palladium, and in some cases upon oxidative addition (e.g. of methallyl chloride to Pd\(^0\)(R-DAB)(\(\eta^2\)-alkene)). At a later stage, several other Pd\(^0\)(R-DAB)(\(\eta^2\)-olefin)\(^{[13-17]}\) and numerous divalent palladium and platinum compounds containing the R-DAB entity have been synthesized, e.g. Pt\(^{II}\)X\(_2\)(R-DAB)(\(\eta^2\)-olefin) and similar compounds.\(^{[23-31]}\)

![Figure 2.2](image)

**Figure 2.2** Generic structures of zerovalent Pd(diazadiene)(\(\eta^2\)-alkene) and Pd(Ar-BIAN)(\(\eta^2\)-alkene) compounds

The interest in our group in low-valent group 10 metal compounds containing chelating N-ligands, especially those containing the rigid Ar-BIAN ligand (B, Figure 2.2), stems largely from their excellent suitability as (pre)catalysts for a number of selective carbon-element coupling reactions,\(^{[38-42]}\) such as Suzuki/Negishi type C-C bond formation,\(^{[38,39]}\) three-component coupling reactions\(^{[39-41]}\) and stereoselective cis-hydrogenation of alkynes\(^{[42]}\) (Scheme 2.1).

![Scheme 2.1](image)

**Scheme 2.1** Stereoselective Pd(BIAN)-catalyzed cis-hydrogenation of alkynes to (Z)-alkenes.

For modeling purposes of some of these palladium-catalyzed reactions and for several platinum-catalyzed reactions, we needed a series of zerovalent platinum compounds similar to A, i.e. containing the simple diimine motif. The number of known zero-valent platinum compounds containing bidentate N-ligands is not very large, but a few Pt\(^0\)(NN)(alkene) compounds have been reported in the literature.\(^{[13,18-22]}\) Examples are Pt\(^0\)(R-phen)(\(\eta^2\)-olefin)}
alkene), \[19,21,22\] $\text{Pt}^0(\text{R-DAB})(\eta^4\text{-cod}),\] \[18\] and water-soluble analogues, $\text{Pt}^0(\text{R-DAB})(\text{alkene})$ complexes containing chiral substituents on the N-atoms, based on $\alpha$-D-Mannose, \[20\], although it is at least doubtful if these last complexes are really formed or stable during the conditions described. \[43\]

In this chapter we describe the efficient synthesis of new $\text{Pt}^0(\text{R-DAB})(\eta^2\text{-alkene})$ complexes, prepared from readily available $\text{Pt}^0$ precursors, various diazadiene (R-DAB) ligands and electron poor alkenes. The complexes obtained are relevant as an (alternative) entry into systems which are capable of performing carbon-element bond-forming (e.g., hydrosilation\[44\]), bond-breaking and bond-activation reactions (e.g., C-H activation\[45\]). For the latter application, cationic Pt(II) complexes are needed and these complexes can be synthesized via protonation of $\text{Pt}^0(\text{NN})(\text{alkene})$ complexes, or via oxidative addition of RX (R = alkyl, aryl; X = halide) to $\text{Pt}^0(\text{NN})(\text{alkene})$ complexes and successive addition of a silver salt (Scheme 2.2, see also Chapter 4).

\[
\text{Scheme 2.2 Synthesis of cationic Pt(II)-complexes starting from (NN)Pt(alkene)-complexes; an alternative entry into systems that are capable of performing C-H bond activation reactions.}
\]

### 2.2 Results and Discussion

#### 2.2.1 Synthesis

The R-DAB ligands 1a-e and similar diazadienes 1f-k (Figure 2.3) have been synthesized according to literature by condensation of glyoxal or 2,3-butadiene with the appropriate primary amine. \[46,47\]

\[
\begin{align*}
\text{Scheme 2.3 Preparation of N,N'-diazadiene}(\eta^2\text{-alkene})\text{platinum(0) compounds}
\end{align*}
\]

\[
\begin{align*}
\text{[Pt}^0(L)_n + \text{alkene} & \rightarrow \text{[Pt}^0(L)_{n-1}(\eta^2\text{-alkene}) + L} \\
\text{[Pt}^0(L)_{n-1}(\eta^2\text{-alkene}) + \text{R-DAB} & \rightarrow \text{[Pt}^0(\text{R-DAB})(\eta^2\text{-alkene}) + (n-1)L}
\end{align*}
\]
Synthesis of zerovalent platinum compounds of these R-DAB ligands was attempted starting from the readily available Pt\(^0\) precursors Pt(dba)\(_2\)\(^{[48]}\) and (Pt(dipdba))\(_2\)\(^{[49]}\) using dimethyl fumarate (dmfu, x), maleic anhydride (MA, y) or fumaronitrile (FN, z) as the alkene (Scheme 2.3). In all cases, first the alkene was allowed to react with the platinum reagent in dry diethyl ether for a given period of time and then the R-DAB was added in portions. Since the dba ligands are rather sluggishly substituted, the norbornene complex Pt(nbe)\(_3\) and the cyclooctadiene complex Pt(cod)\(_2\) were prepared.

\[
\text{R} \quad \text{R'} \quad \text{E}
\begin{align*}
1a & \quad H & \quad i-\text{Pr} & \quad 2ax & \quad \text{CO}_2\text{Me} \\
1b & \quad H & \quad n-\text{Bu} & \quad 2ay & \quad \text{C(O)OC(O)} \\
1c & \quad H & \quad t-\text{Bu} & \quad 2ax & \quad \text{CO}_2\text{Me} \\
1d & \quad H & \quad p-\text{Tol} & \quad 2by & \quad \text{CO}_2\text{Me} \\
1e & \quad H & \quad p-\text{anisyl} & \quad 2bz & \quad \text{CN} \\
1f & \quad \text{CH}_3 & \quad c-\text{Pr} & \quad 2cx & \quad \text{CO}_2\text{Me} \\
1g & \quad \text{CH}_3 & \quad n-\text{Bu} & \quad 2dx & \quad \text{CO}_2\text{Me} \\
1h & \quad \text{CH}_3 & \quad n-\text{Oct} & \quad 2ex & \quad \text{CO}_2\text{Me} \\
1i & \quad \text{CH}_3 & \quad \text{o-}\text{anisyl} & \quad 2fy & \quad \text{C(O)OC(O)} \\
1j & \quad \text{CH}_3 & \quad (m,m-\text{CF}_3)-\text{Ph} & \quad 2gy & \quad \text{CO}_2\text{Me} \\
1k & \quad \text{CH}_3 & \quad 4-\text{pentenyl} & \quad 2hy & \quad \text{CO}_2\text{Me}
\end{align*}
\]

Figure 2.3 Diazadienes and zerovalent Pt(diazadiene)(\(\eta^2\)-alkene) compounds studied.

Employing R-DAB ligands 1a – 1h resulted in the ready formation of the corresponding 1:1:1 complexes Pt\(^0\)(R-DAB)(\(\eta^2\)-alkene) 2ax – 2hy (Figure 2.3), albeit the ease of work-up and the yields varied drastically, as described below. When using Pt(dba)\(_2\) or Pt(dipdba)\(_2\) as Pt\(^0\) precursor, long reaction times were necessary for the substitution to go to completion for all complexes investigated, compounds 2dx, 2dz, 2jx, 2jz, 2kx and 2kz were obtained in very
Synthesis of new ($\sigma^2$-N,N'-Diazadiene)(1\^\text{2}-alkene) platinum(0) compounds

low yields or did not form at all. Also, because of the slow substitution of dba and dipdba with the R-DAB-ligand, much metallic platinum was formed in most cases. Furthermore, the similar solubility properties of dba and the target compounds posed difficulties in purification of the complexes. Upon repeated washing with ether/pentane, all of the dba could be removed, but altogether, the yields of the reactions employing these precursors were rather low. Column chromatography on alumina, eluting with toluene, gave a good separation and provided the pure complex 2ax in much higher yield (56%) as compared to washing the crude product with pentane (17%). Column chromatography also gave a reasonable to good yield for 2dx, but this method represents a rather tedious and time-consuming workup procedure.

Especially because of the long reaction times and purification problems required for reactions of diimines with Pt(dba)\textsubscript{2} (which in several cases led to very low or no isolated yields at all), we decided to apply Pt\textsuperscript{0} precursors containing more substitution-labile ligands, such as Pt(cod)\textsubscript{2} and Pt(nbe)\textsubscript{3}.\textsuperscript{[50]} Typically, Pt(cod)\textsubscript{2} was reacted with the appropriate alkene in diethyl ether whereupon Pt\textsuperscript{0}(cod)(1\^\text{2}-alkene) is formed within 10-20 minutes at 20 °C. This could be verified by isolation and characterization of Pt(cod)(dmfu).\textsuperscript{[51]} The subsequent reaction of this complex with diimines was fast and selective and readily resulted in Pt\textsuperscript{0}(R-DAB)(dmfu) compounds 2ax – 2hy. Similar reactions were carried out using maleic anhydride or fumaronitrile as alkene, for a few cases (see Table 2.1).

In all cases, evaporating the solvent and free cod, followed by one additional washing with pentane led to pure complexes. No column chromatography or repeated washing was necessary in these instances and the yields were generally good. The complexes 2ax – 2hy are dark-red to orange solids, which are stable in air for at least months.
Table 2.1 Yields of Pt(0)diazadiene(η^2-alkene) compounds synthesized from various precursors^a

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>R'</th>
<th>E</th>
<th>Precursor</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2ax</td>
<td>H</td>
<td>i-Pr</td>
<td>CO_2Me</td>
<td>Pt(dba)_2</td>
<td>56^b</td>
</tr>
<tr>
<td>2ax</td>
<td>H</td>
<td>i-Pr</td>
<td>CO_2Me</td>
<td>Pt(dipdba)_2</td>
<td>0</td>
</tr>
<tr>
<td>2ax</td>
<td>H</td>
<td>i-Pr</td>
<td>CO_2Me</td>
<td>Pt(nbe)_3</td>
<td>43</td>
</tr>
<tr>
<td>2ax</td>
<td>H</td>
<td>i-Pr</td>
<td>CO_2Me</td>
<td>Pt(cod)_2</td>
<td>77^c</td>
</tr>
<tr>
<td>2ay</td>
<td>H</td>
<td>i-Pr</td>
<td>C(O)OC(O)</td>
<td>Pt(cod)_2</td>
<td>80</td>
</tr>
<tr>
<td>2bx</td>
<td>H</td>
<td>n-Bu</td>
<td>CO_2Me</td>
<td>Pt(cod)_2</td>
<td>7</td>
</tr>
<tr>
<td>2cx</td>
<td>H</td>
<td>t-Bu</td>
<td>CO_2Me</td>
<td>Pt(cod)_2</td>
<td>67</td>
</tr>
<tr>
<td>2dx</td>
<td>H</td>
<td>p-Tol</td>
<td>CO_2Me</td>
<td>Pt(dba)_2</td>
<td>0</td>
</tr>
<tr>
<td>2dx</td>
<td>H</td>
<td>p-Tol</td>
<td>CO_2Me</td>
<td>Pt(nbe)_2</td>
<td>64</td>
</tr>
<tr>
<td>2dx</td>
<td>H</td>
<td>p-Tol</td>
<td>CO_2Me</td>
<td>Pt(cod)_2</td>
<td>49</td>
</tr>
<tr>
<td>2dz</td>
<td>H</td>
<td>p-Tol</td>
<td>C(O)OC(O)</td>
<td>Pt(dba)_2</td>
<td>6</td>
</tr>
<tr>
<td>2ex</td>
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<td>p-anisyl</td>
<td>CO_2Me</td>
<td>Pt(cod)_2</td>
<td>15</td>
</tr>
<tr>
<td>2fx</td>
<td>CH_3</td>
<td>c-Pr</td>
<td>CO_2Me</td>
<td>Pt(cod)_2</td>
<td>91</td>
</tr>
<tr>
<td>2gx</td>
<td>CH_3</td>
<td>n-Bu</td>
<td>CO_2Me</td>
<td>Pt(cod)_2</td>
<td>56</td>
</tr>
<tr>
<td>2hx</td>
<td>CH_3</td>
<td>n-Oct</td>
<td>CO_2Me</td>
<td>Pt(cod)_2</td>
<td>24</td>
</tr>
<tr>
<td>2hy</td>
<td>CH_3</td>
<td>n-Oct</td>
<td>C(O)OC(O)</td>
<td>Pt(cod)_2</td>
<td>19</td>
</tr>
</tbody>
</table>

^aAccording to Scheme 2.3. ^bPurified via column chromatography. ^cIsolated via Pt(cod)(dmfu).

Apparently, the exchange of cod is faster and is accompanied by less decomposition of the Pt^0 precursor compared to substitution of dba. Furthermore, we have evaluated Pt(nbe)_3 for the synthesis of the Pt^0(R-DAB)(η^2-alkene) complexes. The results for Pt(nbe)_3 were comparable to the results for Pt(cod)_2. Hence, Pt(cod)_2 and Pt(nbe)_3 are to be preferred as the starting materials. Since the former is obtained via the latter, application of Pt(nbe)_3 seems to be more economic. However, Pt(cod)_2 is the more stable of the two.^[50] Although the monodentate nbe ligands in the in situ prepared Pt(nbe)_2(dmfu)^^[44] should be more labile than the Pt(cod)(dmfu) analogue, this appears not to be the case. Rigid Ar-BIAN ligands are capable of displacing the nbe's,^[44] but using the less rigid R-DAB's this becomes less favorable, resulting in somewhat lower yields compared to the Pt(cod)_2 route.

2.2.2 Analysis

The compounds 2ax - 2hy have been analyzed by means of standard ^1H and ^13C NMR techniques, infrared, FAB-MS, and (in several cases) by elemental analysis. All compounds
showed the expected isotopic pattern in the mass spectra of their molecular ions for monomeric Pt\(^0\)(R-DAB)(\(\eta^2\)-alkene) complexes. The NMR data are in agreement with the proposed structures. A normal low-frequency shift of the CH\(_3\) imine, of the alkene protons and alkene carbon nuclei was observed. The usual high-frequency shifts of ca. 1.0 ppm (\(^1\)H NMR) and 2 ppm (\(^{13}\)C NMR) were observed for the imine protons and N=\(\text{C}\) carbon nuclei respectively. Coupling constants \(^nJ\(\text{Pt,}^1\text{H}\) and \(^nJ\(\text{Pt,}^{13}\text{C}\) are similar to values found in the literature for other Pt(N,N-chelate)(\(\eta^2\)-alkene) complexes.\(^{13,19-22}\) IR spectra showed a shift of the \(\nu(C=\text{N})\) stretch vibration at about 1630 cm\(^{-1}\) for the uncoordinated R-DAB ligand to values around 1550 cm\(^{-1}\) for the complexes, in agreement with the literature.\(^{46,52,53}\)

### 2.3 Conclusions

Novel, thermally stable Pt\(^0\)(R-DAB)(\(\eta^2\)-alkene) complexes have been synthesized in good yield from Pt(cod)\(_2\) or Pt(nbe)\(_3\) as Pt\(^0\) precursor, via stepwise substitution of the labile dienes by an electron-poor alkene, followed by the appropriate R-DAB ligand. In contrast, when using Pt(dbac)\(_2\) or Pt(dipdbac)\(_2\), the exchange of dbac and dipdbac for the alkenes and R-DAB-ligand is slow, much metallic platinum is formed and separation of the Pt(0)-complex from dbac or dipdbac is difficult, resulting in very low yields of the desired complexes.

The Pt\(^0\)(R-DAB)(\(\eta^2\)-alkene) complexes are dark-red to orange compounds and can, as solids, be safely handled and stored in air without decomposition. Normal coordination-induced shifts and coupling constants of Pt to the R-DAB ligand and alkene are observed in their NMR and IR spectra. The compounds obtained are members of a very useful category of starting materials for various endeavors in synthetic organoplatinum chemistry and catalysis. Not only may these be employed in oxidative additions of organic halides, to give models for related C-C bond forming Pd-catalysts, but also, by addition of appropriate acids, provide an alternative approach to systems suitable for activation of C-H bonds.\(^{45}\)

### 2.4 Experimental Section

#### 2.4.1 General

All reactions were carried out under nitrogen atmosphere in dry solvents. Acetone was distilled from CaSO\(_4\). Diethyl ether, THF and toluene were distilled from sodium metal and
dichloromethane was distilled from CaH₂. Chemicals were purchased from Acros Chimica, Aldrich and Fluka. The ¹H and ¹³C NMR spectra were recorded at appropriate frequencies on Varian Mercury 300 (¹H: 300.13 MHz, ¹³C: 75.47 MHz) and Inova 500 (¹H: 499.88 MHz, ¹³C: 125.70 MHz) spectrometers. ¹⁹⁵Pt NMR spectra were measured via a normal HMQC sequence at 298K on a Bruker DRX300 spectrometer (¹⁹⁵Pt 64.13 MHz). The IR spectra were recorded on a Perkin Elmer 283 spectrometer. Elemental analyses were carried out by Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

Compounds 1a-1f, 1k are known,[45-47] 1g-1j and 2a-2h (x, y, z) are new compounds. Synthesis and selected spectral data of these compounds are given below.

### 2.4.2 Synthesis of R-DAB ligands

The syntheses were carried out in analogy to Kliegman *et al.*:⁴⁶,⁴⁷ 2 equivs. of the primary amine were stirred in MeOH at 0°C with 1 eq. of glyoxal (30 % in H₂O), or in dry MeOH at 20°C with 1 eq. of 2,3-butanedione. A catalytic amount of formic or p-toluenesulfonic acid was added for condensations with 2,3-butanedione. Upon completion of the reaction, solid R-DAB ligands were filtered off and washed. For liquid R-DAB ligands, the solvent was evaporated and the R-DAB distilled if necessary. Yields of new R-DAB ligands 1g; 98%, 1h; 57%, 1i; 41%, 1j; 64%. The NMR and some IR data of the R-DAB ligands 1a-1k, which have not yet been published, have been compiled below.

**3,6-Diaza-2,7-dimethyl-octa-3,5-diene (N,N'-diisopropyIDAB; 1a)**

IR (KBr, cm⁻¹): 1623 (C=N). ¹³C NMR (75.47 MHz, CDCl₃, δ (ppm)): 159.5 (HC=N), 61.1 (CH), 23.7 (CH₃).

**5,8-Diaza-dodeca-5,7-diene (N,N'-di-n-butylDAB; 1b)**

¹³C NMR (75.47 MHz, CDCl₃, δ (ppm)): 162.0 (HC=N), 61.3 (NCH₂), 32.7 (CH₂), 20.5 (CH₂), 13.9 (CH₃).

**3,6-Diaza-2,2,7,7-tetramethyl-octa-3,5-diene (N,N'-t-butylDAB; 1c)**

¹³C NMR (75.47 MHz, CDCl₃, δ (ppm)): 158.0 (HC=N), 58.3 (C(CH₃), 29.5 (CH₃).
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1,4-Di(4-methylphenyl)-1,4-diaza-1,3-butadiene (N,N'-di-p-tolyIDAB; 1d)

$^{13}$C NMR (75.47 MHz, CDCl$_3$, $\delta$ (ppm)): 159.3 (HC=N), 147.8 + 138.4 (ArCH), 130.3 + 121.6 (ArCH), 21.4 (CH$_3$).

1,4-Di(4-methoxyphenyl)-1,4-diaza-1,3-butadiene (N,N'-di-p-anisylDAB; 1e)

$^{13}$C NMR (75.47 MHz, CDCl$_3$, $\delta$ (ppm)): 160.0 (ArC-N), 157.8 (CH=N), 123.3 (ArCH), 114.88 (ArCH), 55.7 (OCH$_3$).

5,8-Diaza-6,7-dimethyl-dodeca-5,7-diene (N,N'-di-n-butylDAB-Me; 1g)

IR (KBr, cm$^{-1}$): 1636 cm$^{-1}$ (C=N). $^1$H NMR (300.13 MHz, CDCl$_3$, $\delta$ (ppm)): (t, $J_{HH} = 7.2$ Hz, 4H, NCH$_2$), 2.01 (s, 6H, N=C(CH$_3$)), 1.62 (quint, $J_{HH} = 6.6$ Hz, 4H, NCH$_2$CH$_2$), 1.37 (sext, $J_{HH} = 7$ Hz, 4H, CH$_2$CH$_2$). $^{13}$C NMR (75.47 MHz, CDCl$_3$, $\delta$ (ppm)): 167.8 (N=C(CH$_3$)), 52.2 (NCH$_2$), 33.1 (NCH$_2$CH$_2$), 20.8 (CH$_2$CH$_3$), 14.0 (CH$_2$CH$_3$), 12.5 ((CH$_3$)$_2$C=N).

9,12-Diaza-10,11-dimethyl-eicosa-9,11-diene (N,N'-di-n-octylDAB-Me; 1h)

IR (KBr, cm$^{-1}$): 1635 (C=N). $^1$H NMR (300.13 MHz, CDCl$_3$, $\delta$ (ppm)): 3.39 (t, $J_{HH} = 6.6$ Hz, 4H, NCH$_2$), 2.03 (s, 6H, N=C(CH$_3$)), 1.65 (m, 4H, 1.32, NCH$_2$CH$_2$), 1.32 (br m, 10H, CH$_3$(CH$_2$)$_3$), 0.86 (t, $J_{HH} = 7$ Hz, 6H, CH$_3$(CH$_2$)$_3$). $^{13}$C NMR (75.47 MHz, CDCl$_3$, $\delta$ (ppm)): 168.0 (N=C(CH$_3$)), 52.9 (NCH$_2$), 32.1 (NCH$_2$CH$_2$), 31.0 + 29.6 + 27.9 + 22.9 (CH$_2$), 14.3 (CH$_3$), 12.8 (CH$_3$C=N).

6,9-Diaza-7,8-dimethyl-tetradeca-1,6,8,13-tetraene (N,N'-di(4-pentenyl)DAB-Me; 1k)

$^1$H NMR (300.13 MHz, CDCl$_3$, $\delta$ (ppm)): 5.75 (m, 2H, CH=CH), 5.09 (m, 4H, CH$_2$=CH), 4.13 (m, 4H, NCH$_2$), 2.22 (s, 6H, N=C(CH$_3$)), 2.13 (m, 4H, =CHCH$_2$CH$_2$), 1.59 (m, 4H, =CHCH$_2$CH$_2$). $^{13}$C NMR (75.47 MHz, CDCl$_3$, $\delta$ (ppm)): 136.2 (CH=CH$_2$), 125.6 (N=C(CH$_3$)), 116.9 (CH=CH$_2$), 45.5 (NCH$_2$), 30.6 (=CHCH$_2$), 28.8 (NCH$_2$CH$_2$), 9.1(CH$_3$).

2.4.3 Synthesis of [Pt$^0$(R-DAB)($\eta^2$-alkene)] compounds

The Pt$^0$ precursors employed were synthesized according to literature procedures; platinum dibenzylideneacetone (Pt(dba)$_2$),$^{[48]}$ platinum diisopropylidibenzylideneacetone (Pt(dipdba)$_2$),$^{[49]}$ platinum trisnorbornene (Pt(nbe)$_3$)$^{[50]}$, Pt(cod)Cl$_2$,$^{[50,54]}$ platinum
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biscyclooctadiene (Pt(cod)₂)[⁵⁰] and platinum cyclooctadiene dimethylfumarate (Pt(cod)(dmfu)).[⁵¹] The synthesis of [Pt° (R-DAB)(η^2-alkene)] compounds has been done via two routes depending on the Pt° precursor.

**Route A. Using Pt(dba)₂ or Pt(dipdba)₂**

An amount of 1.0 equiv. of Pt° precursor and 1.0-1.5 equiv. of the appropriate alkene (dmfu, MA or FN) were stirred in dry diethyl ether at 20 °C under N₂ for 10 minutes. An amount of 1 equiv. of the R-DAB ligand was then added in small portions to this solution. After stirring at 20 °C during 12-24 h, the reaction mixture was filtered over Celite, the solvent evaporated and the residue washed several times with pentane. The complex was then purified by column chromatography on Al₂O₃ ( deactivated with 7% H₂O, eluting with toluene).

**Route B. Using Pt(nbe)₂ or Pt(cod)₂**

The same procedure as above was followed up to and including the addition of R-DAB, but using 1.0 to 1.1 equiv. of the alkene. After a reaction time of 1-2 h, the solvent was evaporated *in vacuo* and the residue was washed once with a small amount of pentane and dried to yield the pure products.

**[(σ-N,σ'-N'-3,6-Diaza-2,7-dimethyl-octa-3,5-diene)(η^2-(E)-dimethylbut-2-ene-1,4-dioate)platinum(0)]**(2ax)

IR (KBr, cm⁻¹): 1547 cm⁻¹ (C=N). \(^1\)H NMR (300.13 MHz, CDCl₃, δ (ppm)): 8.90 (s, J_HH = 55.5 Hz, 2H, N=CH), 4.05 (m, 2H, CH(i-Pr)), 3.85 (s, J_HH = 86.4 Hz, 2H, HC=CH), 3.59 (s, 6H, OCH₃), 1.60 (d, J_HH = 6 Hz, 6H, (CH₃)₂CH), 1.38 (d, J_HH = 6.3 Hz, 6H, CH₃(i-Pr)). \(^1\)C NMR (75.47 MHz, CDCl₃, δ (ppm)): 177.7 (J_P=CO = 56 Hz, C=O), 160.3 (C=N), 64.7 (J_P=CO = 73 Hz, CH(CH₃)₂), 51.0 (OCH₃), 25.4 (J_P=CO = 399 Hz, C=C), 24.05 J_P=CO = 13.4 Hz, (CH₃)₂CH), 23.7 (CH₃(i-Pr)). FAB-MS: [MH]⁺ = 480.1. Anal. calculated for C₁₄H₂₄N₂O₄Pt (479.14): C 35.07, H 5.05, N 5.84; found: C 34.98, H 5.12, N 5.79.

**[(σ-N,σ'-N'-3,6-Diaza-2,7-dimethyl-octa-3,5-diene)(η^2-(Z)-but-2-ene-1,4-dicarboxylic acid anhydride)platinum(0)]**(2ay)

\(^1\)H NMR (300.13 MHz, CDCl₃, δ (ppm)): 8.86 (s, J_HH = 60.9 Hz, 2H, N=CH), 4.08 (m, 2H, CH(CH₃)₂), 3.76 (s, J_HH = 81 Hz, 2H, HC=CH), 1.56 (d, J_HH = 6.3 Hz, 6H, (CH₃)₂CH), 1.49
Synthesis of new ($\sigma^2$-$N,N'$-Diazadiene)(${\pi^2}$-alkene) platinum(0) compounds

(d, $J_{HH} = 6.3$ Hz, 6H, $(CH_3)_2CH$). $^{13}$C NMR (75.47 MHz, CDCl$_3$, $\delta$ (ppm)): 175.4 (C=O), 161.3 (C=N), 65.5 ((CH$_3$)$_2$CH), 24.8 ((CH$_3$)$_2$CH), 24.4 ($J_{PC} = 237$ Hz, C=C), 23.6 ((CH$_3$)$_2$CH).

($\sigma$-$N$,$\sigma$-$N'$-5,8-Diazadodeca-5,7-diene)($\eta^2$-E-dimethylbut-2-ene-1,4-dioate)platinum(0) (2bx)
$^1$H NMR (300.13 MHz, CDCl$_3$, $\delta$ (ppm)): 8.74 (s, $J_{PH} = 58.5$ Hz, 2H, N=CH), 4.05 (m, 4H, NCH$_2$), 3.88 (s, $J_{PH} = 87$ Hz, 2H, HC=CH), 3.61 (s, 6H, OCH$_3$), 2.03 (m, 4H, NCH$_2$CH$_2$), 1.38 (s, 4H, CH$_2$CH$_3$), 0.97 (t, 6H, CH$_2$CH$_3$).

($\sigma$-$N$,$\sigma$-$N'$-3,6-Diazaocta-2,2,7,7-tetramethyl-octa-3,5-diene)($\eta^2$-E-dimethylbut-2-ene-1,4-dioate)platinum(0) (2cx)
$^1$H NMR (300.13 MHz, CDCl$_3$, $\delta$ (ppm)): 8.92 (s, $J_{PH} = 53$ Hz, 2H, N=CH), 3.79 (s, $J_{PH} = 73.2$ Hz, 2H, HC=CH), 3.58 (s, 6H, OCH$_3$), 1.57 (s, 18H, C(CH$_3$)$_3$). $^{13}$C NMR (75.47 MHz, CDCl$_3$, $\delta$ (ppm)): 177.9 (C=O), 159.2 (C=N), 65.3 (C(CH$_3$)$_3$), 50.9 (OCH$_3$), 30.0 (C(CH$_3$)$_3$), 25.7 ($J_{PC} = 413$ Hz, C=C).

($\sigma$-$N$,$\sigma$-$N'$-1,4-Di(4-methylphenyl)-1,4-diaza-1,3-butadiene)($\eta^2$-E-dimethylbut-2-ene-1,4-dioate)platinum(0) (2dx)
$^1$H NMR (300.13 MHz, CDCl$_3$, $\delta$ (ppm)): 9.22 (s, $J_{PH} = 52$ Hz, 2H, N=CH), 7.62 (d, $J_{HH} = 8.7$ Hz, 4H, ArH), 7.05 (d, $J_{HH} = 8.1$ Hz, 4H, ArH), 4.01 (s, $J_{PH} = 84$ Hz, 2H, HC=CH), 3.52 (s, 6H, OCH$_3$), 2.36 (s, 6H, CH$_3$C$_6$H$_4$). FAB-MS: [MH]$^+$ = 576.1.

($\sigma$-$N$,$\sigma$-$N'$-1,4-Di(4-methylphenyl)-1,4-diaza-1,3-butadiene)($\eta^2$-E)-1,2-dicyanoethene)platinum(0) (2dz)
$^1$H NMR (300.13 MHz, CDCl$_3$, $\delta$ (ppm)): 9.16 (s, $J_{PH} = 48$ Hz, 2H, N=CH), 7.72 (d, $J_{HH} = 8.1$ Hz, 4H, ArH), 7.23 (d, $J_{HH} = 9.9$ Hz, 4H, ArH), 3.01 (s, $J_{PH} = 89.4$ Hz, 2H, HC=CH), 2.35 (s, 6H, CH$_3$C$_6$H$_4$).
Chapter 2, Part A

($\sigma$-$N,\sigma$-$N'$-$1,4$-Di(4-methoxyphenyl)-1,4-diaza-1,3-butadiene)($\eta^2$-(E)-dimethylbut-2-ene-1,4-dioate)platinum(0) (2ex)

$^1$H NMR (300.13 MHz, CDCl$_3$, $\delta$ (ppm)): 9.12 (s, $J_{PH} = 52.2$ Hz, 2H, N=CH), 7.72 (d, $J_{HH} = 9$ Hz, 4H, ArH), 6.73 (d, $J_{HH} = 9.3$ Hz, 4H, ArH), 3.97 (s, $J_{PH} = 85.2$ Hz, 2H, HC=CH), 3.83 (s, 6H, COOCH$_3$), 3.54 (s, 6H, OCH$_3$).

($\sigma$-$N,\sigma$-$N'$-$1,4$-Dicyclopropyl)-1,4-diaza-2,3-dimethyl-1,3-butadiene)($\eta^2$-(E)-dimethylbut-2-ene-1,4-dioate)platinum(0) (2fx)

$^1$H NMR (300.13 MHz, CDCl$_3$, $\delta$ (ppm)): 4.17 (s, $J_{PH} = 81.3$ Hz, 2H, HC=CH), 3.60 (s, 6H, OCH$_3$), 2.45 (m, 2H, c-PrH), 2.09 (m, 2H, c-PrH), 1.66 (m, 4H, c-PrH), 0.98 (s, 6H, N=C(CH$_3$)).

$^{13}$C NMR (75.47 MHz, CDCl$_3$, $\delta$ (ppm)): 176.9 (C=O), 169.6 (C=N), 50.3 (OCH$_3$), 38.7 (c-PrC), 25.1 (C=C), 17.5 (N=C(CH$_3$)), 12.6 (CH$_2$-c-Pr) 10.8 (CH$_2$-c-Pr). FAB-MS: [MH]$^+$ = 504.1 Anal. calculated for C$_{18}$H$_{24}$N$_2$O$_4$Pt: (503.45); C 38.17, H 4.88, N 5.56; found: C 38.52, H 4.75, N 5.64.

($\sigma$-$N,\sigma$-$N'$-$5,8$-Diaza-6,7-dimethyl-dodeca-5,7-diene)($\eta^2$-(E)-dimethylbut-2-ene-1,4-dioate)platinum(0) (2gx)

IR (KBr, cm$^{-1}$): 1558 (C=N). $^1$H NMR (300.13 MHz, CDCl$_3$, $\delta$ (ppm)): 4.07 (m, 4H, NCH$_2$), 3.66 (s, $J_{PH} = 87$ Hz, 2H, HC=CH), 3.57 (s, 6H, OCH$_3$), 1.88 (m, 4H, NCH$_2$CH$_2$), 1.88 (s, 6H, N=C(CH$_3$)), 1.44 (m, 4H, CH$_3$CH$_2$), 0.98 (t, $J_{HH} = 6.9$ Hz, 6H, CH$_3$CH$_2$).

$^{13}$C NMR (75.47 MHz, CDCl$_3$, $\delta$ (ppm)): 177.6 (C=O), 170.0 (C=N), 59.0 (NCH$_2$), 51.1 (OCH$_3$), 32.6 (NCH$_2$CH$_2$), 25.7 (N=C(CH$_3$)), 20.7 (CH$_3$CH$_2$), 17.6 (C=C), 14.2 (CH$_3$CH$_2$). FAB-MS: [MH]$^+$ = 536.2. Anal. calculated for C$_{18}$H$_{32}$N$_2$O$_4$Pt (535.6): C 40.37, H 6.02, N 5.23; found: C 40.29, H 5.97, N 5.14.

($\sigma$-$N,\sigma$-$N'$-$9,12$-Diaza-10,11-dimethyl-eicosa-9,11-diene)($\eta^2$-(E)-dimethylbut-2-ene-1,4-dioate)platinum(0) (2hx)

IR (KBr, cm$^{-1}$): 1558 (C=N). $^1$H NMR (300.13 MHz, CDCl$_3$, $\delta$ (ppm)): 4.06 (m, 4H, NCH$_2$), 3.67 (s, $J_{PH} = 88.2$ Hz, 2H, HC=CH), 3.58 (s, 6H, OCH$_3$), 1.95 (m, 4H, NCH$_2$CH$_2$), 1.94 (s, 6H, N=C(CH$_3$)), 1.31 (br m, 20H, CH$_3$(CH$_2$)$_3$), 0.85 (t, 6H, CH$_3$(CH$_2$)$_3$). $^{13}$C NMR (75.47 MHz, CDCl$_3$, $\delta$ (ppm)): 177.6 (C=O), 170.0 (C=N), 59.3 ($J_{PC} = 70.7$ Hz NCH$_2$), 51.1
Synthesis of new (σ-N,N'-Diazadiene)(π2-alkene) platinum(0) compounds

(OCH₃), 32.0 (NCH₂CH₂), 30.6 + 29.6 + 27.6 + 22.9 (CH₃(CH₂)₅), 25.7 ($J_{PC} = 370$ Hz, C=C), 17.6 (N=C(CH₃)), 14.3 (CH₃(CH₂)₅). FAB-MS: [MH]⁺ = 648.3.

(σ-N,σ'-N'-9,12-Diaza-10,11-dimethyl-eicsosa-9,11-diene)(ζ2-(Z)-but-2-ene-1,4-dicarboxylic acid anhydride)platinum(0) (2hy)

$^1$H NMR (300.13 MHz, CDCl₃, δ (ppm)): 4.05 (br m, 4H, NCH₂), 3.53 (s, $J_{PH} = 78$ Hz, 2H, HC=CH), 2.06 (s, 6H, N=C(CH₃)), 1.94 (br m, 4H, CH₃(CH₂)₅), 1.21 (br m, 20H, CH₃(CH₂)₅), 0.84 (t, 6H, CH₃(CH₂)₅). $^{13}$C NMR (75.47 MHz, CDCl₃, δ (ppm)): 175.5 (C=O), 171.6 (C=N), 59.4 (NCH₂), 31.99 (NCH₂CH₂), 30.6 + 29.5 + 27.4 + 22.9 (CH₃(CH₂)₅), 25.1 (C=C), 22.9, 17.9 (N=C(CH₃)), 14.3 (CH₃(CH₂)₅). FAB-MS: [MH]⁺ = 602.3.

2.5 References


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