

## Intramolecular hydroamination of alkynes catalysed by late transition metals

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The cyclisation of 6-aminohept-1-yne to 2-methyl-1,2-dehydropiperidine in the presence of late transition metal catalysts was examined. The highest catalytic activity was observed for  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ , as well as with Group 12 metal salts. Slightly lower conversions were obtained with the rhodium(i) and palladium(ii) complexes  $[\text{Rh}(\text{COD})(\text{DiPAMP})]\text{BF}_4$  and  $[\text{Pd}(\text{Triphos})][\text{BF}_4]_2$ . Catalysis was also observed with complexes of all group 9 to 12 metals and  $[\text{Ru}_3(\text{CO})_{12}]$ . All catalytically active complexes contain a metal with a  $d^8$  or  $d^{10}$  electronic configuration. This observation allows preliminary conclusions about the mechanism to be made.

### Introduction

The direct addition of amine H–N bonds to alkenes and alkynes is an efficient method of carbon–nitrogen bond construction and provides a direct route to a variety of molecules containing an amine functionality. Although the corresponding addition of alcohol H–OR bonds to alkenes and alkynes has been known for a long time, additions of amines to alkenes and alkynes are rare.<sup>1–3</sup> Thermodynamic considerations indicate that the direct addition of amines to alkenes is approximately thermoneutral.<sup>4–6</sup> Although hydroamination of alkynes is thermodynamically more favourable, the reaction is hampered by a high activation barrier. Promoting the reaction by high temperatures is limited as the entropy is negative. Consequently, catalysis at relatively low temperatures is required.

Catalysts based on early transition metals, especially zirconium,<sup>7</sup> lanthanide metals<sup>8–10</sup> and actinide metals,<sup>11</sup> have recently been developed. Mechanistic investigations have shown that catalysis with early transition metals often involves activation of the amine by co-ordination to the metal.<sup>7–11</sup> The key step of the catalytic cycle is the insertion of the carbon–carbon double or triple bond into the M–N bond.

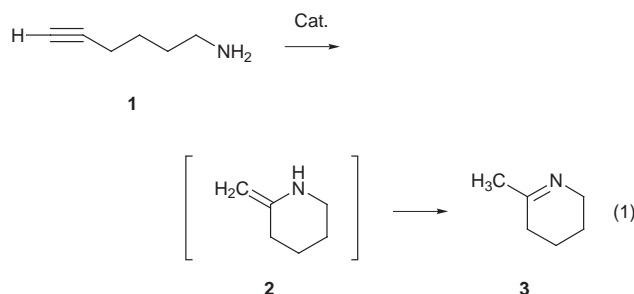
In contrast, examples for the direct addition of amines to alkenes and alkynes using late transition metal catalysts are rare. Tethered aminoalkynes have been cyclised using nickel,<sup>12</sup> palladium<sup>13,14</sup> and gold<sup>14</sup> complexes as catalysts. Moderate activity of the catalysts requires 3–5 mol% of the complexes (turnover number, TON = 13–22). Compared to an intramolecular reaction, the intermolecular addition of amines to alkynes is thermodynamically less favoured. Therefore stoichiometric use of transition metal complexes as promoters is generally required. The most established synthetic route is the aminomercuriation–demercuration sequence.<sup>15</sup> This method can be made catalytic by appropriate choice of the reaction conditions, although catalytic efficiency remains low (TON = 8–14).<sup>16</sup>

We now report that various complexes of Group 8 to 12 metals effectively catalyse the intramolecular addition of amines to alkynes.<sup>17,18</sup> Major factors affecting the catalytic activity of late transition metal complexes for the addition of amines to alkynes are discussed. Special focus is given to the oxidation state of the metal centre as mechanistic conclusions can be drawn from it.

### Results and discussion

The catalytic activity of various complexes for the direct

addition of amines to alkynes is compared for the cyclisation of 6-aminohept-1-yne **1**. The cyclisation of **1** with 1 mol% of the appropriate transition metal complex first generates 2-methylenepiperidine **2** with an exocyclic double bond. Subsequent 1,3-hydrogen shift converts the enamine into the more stable isomeric imine 2-methyl-1,2-dehydropiperidine **3** [eqn. (1)]. Close to quantitative conversions were observed for



the copper(i) compound  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  and Group 12 metal salts, like  $\text{Zn}(\text{O}_3\text{SCF}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  (see Table 1). Slightly less active are the rhodium(i) and palladium(ii) complexes  $[\text{Rh}(\text{COD})(\text{DiPAMP})]\text{BF}_4$ ,  $\text{DiPAMP} = 1,2$ -bis[*o*-methoxyphenyl](phenyl)phosphinoethane (80% conversion) and  $[\text{Pd}(\text{Triphos})][\text{BF}_4]_2$ ,  $\text{Triphos} = \text{bis}(\text{diphenylphosphinoethyl})\text{phenylphosphine}$  (83% conversion). A 44% conversion of **1** was observed when the silver(i) salt  $\text{AgBF}_4$  was employed at room temperature using  $\text{CH}_2\text{Cl}_2$  as solvent.

Catalysis with noble metal salts without co-ordinating ligands is hampered by their poor stability. During catalysis employing  $\text{AgBF}_4$  in  $\text{CH}_2\text{Cl}_2$ ,  $\text{AuCl}_3$  in  $\text{CH}_2\text{Cl}_2$ ,  $\text{AuCl}_3$  in  $\text{CH}_3\text{CN}$  or  $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$  in  $\text{CH}_3\text{CN}$  at reflux temperature the metal salts decomposed to varying degrees, although catalytic activity was still observed (51, 34, 57 and 83% conversion, respectively). In order to increase the stability of noble metal salts as catalysts, phosphines were added. Use of bidentate phosphines, however, leads to a dramatic drop in catalytic activity, e.g. with  $[\text{Pd}(\text{dppf})][\text{NO}_3]_2$  only 5% conversion of **1** was observed. In contrast, with  $\text{Triphos}$  as tridentate ligand the metal complexes were catalytically active, although under comparable conditions the complexes  $\text{M}^{n+}(\text{Triphos})(\text{X}^-)_n$ ,  $\text{M}^{n+} = \text{Ag}^+$ ,  $\text{Au}^{3+}$  or  $\text{Pd}^{2+}$ ,  $\text{X}^- = \text{BF}_4^-$ ,  $\text{Cl}^-$  or  $\text{PF}_6^-$ , respectively, were not as active as the corresponding salts of the naked metal. The good thermal stability of the complexes  $\text{M}^{n+}(\text{Triphos})(\text{X}^-)_n$  allowed the use of higher temperatures without catalyst decomposition, the best results being obtained using non-co-

**Table 1** Cyclisation of 6-aminohex-1-yne with Group 8 to 12 transition metal catalysts

Group	Metal	Catalyst <sup>a</sup>	Solvent	T/°C	Yield <sup>b</sup> (%)	Conversion <sup>c</sup> (%)
8	Ruthenium(0)	[Ru <sub>3</sub> (CO) <sub>12</sub> ]	CH <sub>2</sub> Cl <sub>2</sub>	40	21	18
9	Cobalt(-I)	K[Co(CO) <sub>3</sub> (PPh <sub>3</sub> )]	Toluene	111	66	2
9	Rhodium(I)	[Rh(COD)(DiPAMP)]BF <sub>4</sub>	Toluene	111	59	80
9	Iridium(I)	[Ir(COD)(PCy <sub>3</sub> )(py)]PF <sub>6</sub>	CH <sub>2</sub> Cl <sub>2</sub>	40	76	42
10	Nickel(0)	[Ni(PPh <sub>3</sub> ) <sub>4</sub> ]	THF	66	40	28
10	Palladium(II)	[Pd(CH <sub>3</sub> CN) <sub>4</sub> ][BF <sub>4</sub> ] <sub>2</sub> <sup>d</sup>	CH <sub>3</sub> CN	82	67	83
		[Pd(dppf)][NO <sub>3</sub> ] <sub>2</sub> ·CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	40	77	5
		[Pd(Triphos)][BF <sub>4</sub> ] <sub>2</sub> ·0.5CH <sub>3</sub> CN	Toluene	111	52	69
		[Pd(Triphos)][BF <sub>4</sub> ] <sub>2</sub> ·0.5CH <sub>3</sub> CN	Toluene	150 <sup>e</sup>	67	93
10	Platinum(II)	[PtH(PEt <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> NO <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	40	42	29
11	Copper(I)	[Cu(CH <sub>3</sub> CN) <sub>4</sub> ] <sub>2</sub> PF <sub>6</sub>	CH <sub>3</sub> CN	82	93	100
11	Silver(I)	AgBF <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	r.t.	56	44
		AgBF <sub>4</sub> <sup>d</sup>	CH <sub>2</sub> Cl <sub>2</sub>	40	69	51
		[Ag(Triphos)]BF <sub>4</sub>	Toluene	111	75	26
11	Gold(III)	AuCl <sub>3</sub> <sup>d</sup>	CH <sub>2</sub> Cl <sub>2</sub>	40	70	34
		AuCl <sub>3</sub> <sup>d</sup>	CH <sub>3</sub> CN	82	71	57
		AuCl <sub>3</sub> -Triphos	CH <sub>2</sub> Cl <sub>2</sub>	40	49	14
12	Zinc(II)	Zn(O <sub>2</sub> SCF <sub>3</sub> ) <sub>2</sub>	Toluene	111	85	100
12	Cadmium(II)	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	CH <sub>3</sub> CN	82	98	98
12	Mercury(II)	Hg(NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O	CH <sub>3</sub> CN	82	80	100

<sup>a</sup> Mol ratios 1 : catalyst = 100 : 1, time = 20 h. <sup>b</sup> Isolated yield of a mixture of 1·HCl and 3·HCl. <sup>c</sup> Determined by integration of the <sup>1</sup>H NMR spectra of the mixtures 1·HCl and 3·HCl. <sup>d</sup> Some decomposition of the catalysts was observed. <sup>e</sup> Using a pressure tube.

ordinating solvents. Thus, conversions of 26 and 93% were obtained with the noble metal complexes [Ag(Triphos)]BF<sub>4</sub> and [Pd(Triphos)][BF<sub>4</sub>]<sub>2</sub>, respectively.

In general, the cyclisation of compound **1** was achieved with complexes of all Group 9 to 12 metals and ruthenium. For a successful catalysis the valence state of the metal appears to be essential, since no conversion of **1** was observed when complexes in different oxidation states were employed. In contrast to the palladium(II) catalyst [Pd(Triphos)][BF<sub>4</sub>]<sub>2</sub>, no conversion was obtained with palladium(0) compounds like [Pd(P<sup>t</sup>Bu<sub>3</sub>)<sub>2</sub>], [Pd(dppf)<sub>2</sub>] and the palladium dimer [Pd<sub>2</sub>Br<sub>2</sub>(P<sup>t</sup>Bu<sub>3</sub>)<sub>4</sub>]. This is in accordance with the literature where a sharp increase in yield is reported for the cyclisation of a substituted 1-aminodec-3-yne with catalytic [Pd(PPh<sub>3</sub>)<sub>4</sub>] when the reaction mixture was left open to air.<sup>13</sup> Similarly, catalysis was observed with the rhodium(I) compound [Rh(COD)(DiPAMP)]BF<sub>4</sub> but not with the rhodium(III) complex [RhI<sub>2</sub>(COD)]Cl. Another example is the activity of the gold(III) catalyst AuCl<sub>3</sub>-Triphos (14% conversion), which is in contrast to that of the gold(I) complex [AuCl(PPh<sub>3</sub>)], for which no conversion was observed. There was also no reaction when the complex [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], [CoCp(CO)<sub>2</sub>] or [Ni(PPh<sub>3</sub>)<sub>2</sub>][NO<sub>3</sub>]<sub>2</sub> was employed, whereas a moderate catalytic activity was observed with the following ruthenium(0), cobalt(-I) and nickel(0) complexes: [Ru<sub>3</sub>(CO)<sub>12</sub>], K[Co(CO)<sub>3</sub>(PPh<sub>3</sub>)] and [Ni(PPh<sub>3</sub>)<sub>4</sub>] (18, 2 and 28% conversion).

Considering the oxidation state of the catalytically active metal compounds, the following rules can be formulated (Scheme 1): (i) transition metals in the fourth period are catalytically

Group 8	Group 9	Group 10	Group 11	Group 12
	Co <sup>-I</sup>	Ni <sup>0</sup>	Cu <sup>I</sup>	Zn <sup>II</sup>
Ru <sup>0</sup>	Rh <sup>I</sup>	Pd <sup>II</sup>	Ag <sup>I</sup>	Cd <sup>II</sup>
	Ir <sup>I</sup>	Pt <sup>II</sup>	Au <sup>III</sup>	Hg <sup>II</sup>

**Scheme 1** Oxidation states of the catalytically active metals.

ically active if they have a d<sup>10</sup> electronic configuration (Co<sup>-I</sup>, Ni<sup>0</sup>, Cu<sup>I</sup>, Zn<sup>II</sup>); (ii) elements in the fifth period found to the right of palladium are active with a d<sup>10</sup> electronic configuration (Ag<sup>I</sup>, Cd<sup>II</sup>) whereas palladium and elements to the left are catalytically active if they have a d<sup>8</sup> electronic configuration (Ru<sup>0</sup>, Rh<sup>I</sup>, Pd<sup>II</sup>); (iii) elements in the sixth period are catalytically active only with a d<sup>8</sup> electronic configuration (Ir<sup>I</sup>, Pt<sup>II</sup>, Au<sup>III</sup>) except mercury, which is active with a d<sup>10</sup> electronic configuration (Hg<sup>II</sup>).

From these observations a number of mechanistic conclusions can be drawn. Common for all catalytically active complexes is that they are rather electron rich compounds. The metals with d<sup>10</sup> electronic configuration, especially Zn<sup>II</sup> and Cu<sup>I</sup>, can be described as typical Lewis acids. This suggests a mechanism where the transition metal activates the alkyne toward nucleophilic attack by the amine rather than one involving oxidative addition of the N-H bond to the metal. The metals with d<sup>8</sup> electronic configuration, especially Ir<sup>I</sup> and Pt<sup>II</sup>, can act either as Lewis acids or as Lewis bases. However, a mechanism based on the activation of the amine by oxidative addition of the amine to the metal centre requires a metal which can increase its oxidation state by two more units. Since it was demonstrated that for the redox pairs Pd<sup>0</sup>/Pd<sup>II</sup> and Au<sup>I</sup>/Au<sup>III</sup> only those complexes display catalytic activity which contain the metal in the higher oxidation state, a mechanistic cycle for the hydroamination of alkynes cannot involve an oxidative addition of the amine to the metal centre.

Support for this conclusion comes from the fact that for copper(I) and silver(I) only the increase of oxidation state by one unit is possible under normal conditions and no other oxidation state is available for zinc(II) during a catalytic cycle. Since, copper(I), zinc(II) and silver(I) salts have been shown to be good catalysts for the cyclisation of compound **1**, the reaction cannot involve a change of oxidation state at the metal centre. For the redox pairs Ru<sup>0</sup>/Ru<sup>II</sup>, Rh<sup>I</sup>/Rh<sup>III</sup> and Ni<sup>0</sup>/Ni<sup>II</sup> where catalytic activity was observed only for those complexes which contain the metal in the lower oxidation state, a mechanism *via* an oxidative addition to the metal centre cannot be excluded. However, the experimental results indicate that the same mechanism is valid for all metal complexes described here.

Most of the noble metal complexes mentioned have a square planar geometry. Typical examples for this geometry are [Rh(COD)(DiPAMP)]BF<sub>4</sub>, [Ir(COD)(PCy<sub>3</sub>)(py)]PF<sub>6</sub> and M<sup>n+</sup>-(Triphos)(X<sup>-</sup>)<sub>n</sub>. The high catalytic activity of the complexes with tridentate phosphines indicates that only one co-ordination site is required for catalysis. If no change of oxidation state occurs during catalysis the overall square planar co-ordination of the metal might be maintained throughout the catalytic cycle. However, a ligand exchange which proceeds *via* the co-ordination of a further ligand resulting in a five-co-ordinate transition state<sup>19</sup> cannot be excluded.

With the aim of obtaining further insights into the mechanism, the triply deuteriated substrate DC≡C(CH<sub>2</sub>)<sub>4</sub>ND<sub>2</sub> was cyclised with various catalysts. The product was isolated

together with the remaining starting material as the hydrochlorides and  $^1\text{H}$  and  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectra taken of the mixture. For each catalyst the spectra were identical except for the relative intensities of the signals assigned to the deuteriated starting material  $\text{d}^3\text{-1}\cdot\text{HCl}$  and product  $\text{d}^3\text{-3}\cdot\text{HCl}$ . Closer inspection of the  $^{13}\text{C}\{-^1\text{H}\}$  NMR signals of  $\text{3}\cdot\text{HCl}$  reveals that in three positions they are split due to C–D coupling. A quintet at  $\delta$  24.4 is assigned to the methyl group attached to C2 with the approximate substitution  $\text{CHD}_2$ , a triplet at  $\delta$  31.7 to the methylene group at C3 with the substitution  $\text{CHD}$  (Scheme 2). A

Distribution of deuterium in the product:

Position	Experiment		Calculated	
Methyl group	1.4H	1.6D	1.6H	1.4D
Methylene group (C3)	1.0H	1.0D	1.0H	1.0D

**Scheme 2** Cyclisation of  $\text{DC}\equiv\text{C}(\text{CH}_2)_4\text{ND}_2$  with various catalysts.

further triplet at  $\delta$  17.8 is assigned to the methylene group at C4, the signal being split by coupling with the deuterium atoms at C3. The assignment is confirmed by the smaller coupling constant  $^2J(^{13}\text{C}, ^2\text{D}) = 10$  Hz for the signal at  $\delta$  17.8 in comparison to  $^1J(^{13}\text{C}, ^2\text{D}) = 20$  Hz for the multiplets at  $\delta$  31.7 and 24.4.

Integration of the  $^1\text{H}$  NMR spectrum of the deuteriated product  $\text{d}^3\text{-3}\cdot\text{HCl}$  gives 1.4 proton for the methyl group and 1.0 proton for the methylene group at C3 (Scheme 2). From this 1.6 deuterium atoms are calculated for the methyl group and 1.0 deuterium atom for the methylene group. The same ratio of protons to deuterium is observed for all catalysts employed including  $[\text{Ir}(\text{COD})(\text{PCy}_3)(\text{py})]\text{PF}_6$ ,  $[\text{Ni}(\text{PPh}_3)_4]$ ,  $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$  and  $\text{AgBF}_4$ . Within the statistical error these numbers agree with a random distribution of the three deuterium atoms over the methyl group and the methylene group at C3 which is calculated as in eqn. (2) and (3) with  $n =$  number

$$\text{Methyl group } n \times \frac{n(\text{D})}{n(\text{H} + \text{D})} \times a = 3 \times \frac{3}{5} \times 0.8 = 1.4\text{D} \quad (2)$$

$$\text{Methylene group } n \times \frac{n(\text{D})}{n(\text{H} + \text{D})} \times a = 2 \times \frac{3}{5} \times 0.8 = 1.0\text{D} \quad (3)$$

of positions in each group,  $n(\text{D}) =$  total number of deuterium atoms involved,  $n(\text{H} + \text{D}) =$  sum of protons and deuterium atoms involved. For a starting material with the three acidic protons completely exchanged by deuterium ( $a = 1.0$ ) a ratio H:D of 0.8:1.2 and 1.2:1.8 is calculated for the methylene and the methyl group, respectively, whereas for the partially deuteriated starting material used ( $a = 0.8$ ) a ratio H:D of 1.6:1.4 and 1.0:1.0 is calculated.

From the experimental results described and their discussion a mechanism can be proposed. It will be described using the cyclisation of  $\text{DC}\equiv\text{C}(\text{CH}_2)_4\text{ND}_2$  with  $[\text{Pd}(\text{Triphos})][\text{BF}_4]_2$  as an example (Scheme 3). In the first step the substrate is co-ordinated to the empty site in the cationic complex  $\text{Pd}(\text{PPP})^{2+}$  via the triple bond. An equilibrium exists where the substrate is co-ordinated via the amine functionality, but does not lead to further reactions. Co-ordination of  $\pi(\text{C}\equiv\text{C})$  to the palladium centre activates the triple bond for a nucleophilic attack of the free electron pair on nitrogen. The formation of the carbon–nitrogen bond is accompanied by the formation of a palladium–carbon single bond, which is then protonated quickly and irreversibly. The intermediate product  $\text{d}^3\text{-2}$  is formed but is likely to remain co-ordinated to the palladium either via the double bond or the nitrogen or both. Co-

ordination of  $\text{d}^3\text{-2}$  to the palladium centre favours a shift of the C=C double bond from the exocyclic position to an endocyclic position. A further reversible reaction is the formal [1,3] shift of the remaining deuterium on the nitrogen atom and formation of the more stable imine  $\text{d}^3\text{-3}$ . Elimination of  $\text{d}^3\text{-3}$  from the co-ordination sphere of the palladium closes the catalytic cycle.

In the mechanistic cycle proposed a number of formal [1,3]-hydrogen shifts were mentioned. However, the orbital symmetry does not allow the geometrically easy [1,3] suprafacial shift of hydrogen atoms.<sup>20,21</sup> Intramolecular reactions of this type are virtually unknown. Therefore intermolecular reactions are postulated in order to account for the hydrogen shifts observed. The shift of the double bond from the exocyclic position to the endocyclic position as well as the formation of the imine probably involves deprotonation in the  $\alpha$  position which is facilitated by co-ordination of the substrate to the palladium.<sup>22</sup> An intermediate allyl complex is postulated which can easily be protonated to give the product of a formal [1,3]-hydrogen shift.

## Conclusion

The aminoalkyne **1** can be efficiently converted into the cyclic imine **3** with a series of transition metal catalysts. The most active catalysts are the copper(I) compound  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  and Group 12 metal salts. Turnover numbers close to the theoretical limit (up to 96) have been achieved which is much higher than previously known. Slightly less active are the rhodium(I) and palladium(II) complexes  $[\text{Rh}(\text{COD})(\text{DiPAMP})]\text{BF}_4$  and  $[\text{Pd}(\text{Triphos})][\text{BF}_4]_2$ . The connection between the oxidation state of the transition metal, *i.e.* number of d electrons, and the catalytic properties was demonstrated. The trends observed lead to a prediction of catalytic activity and enable a more rational choice of compounds as new catalysts for the hydroamination of alkynes. Preliminary mechanistic studies indicate a common pathway for the intramolecular hydroamination of alkynes with all the late transition metal complexes investigated and a plausible mechanism is proposed. Current work in our laboratories is aimed at further investigating the mechanism as well as to explore the preparative scope of the cyclisation of aminoalkynes.

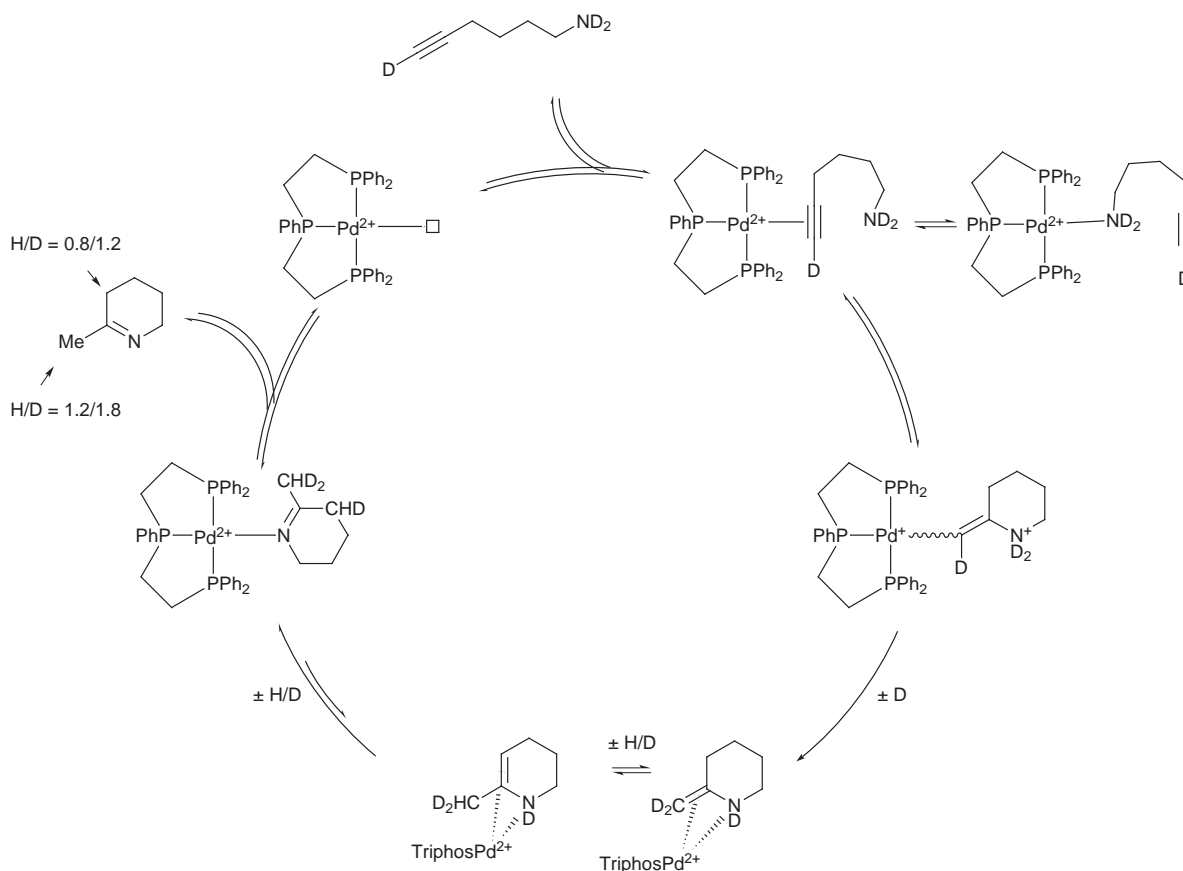
## Experimental

### Materials and methods

All reactions involving air- and/or water-sensitive compounds were performed using standard Schlenk techniques. Solvents were obtained dry from Aldrich except thf, which was dried over KH and distilled prior to use. Catalysts and other chemicals were purchased from Aldrich,  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ ,  $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ , Fluka,  $\text{AgBF}_4$ ,  $\text{Hg}(\text{NO}_3)_2\cdot\text{H}_2\text{O}$ , and Strem,  $[\text{Ir}(\text{COD})(\text{PCy}_3)(\text{py})]\text{PF}_6$ ,  $[\text{Rh}(\text{COD})(\text{DiPAMP})]\text{BF}_4$ ,  $\text{Zn}(\text{O}_3\text{SCF}_3)_2$ , and used as received. Professor W. A. Herrmann is thanked for a gift of  $\text{AuCl}_3$  and  $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ , Dr. P. Dyson for  $[\text{Ru}_3(\text{CO})_{12}]$  and Dr. R. Vilar for  $[\text{Pd}(\text{P}^t\text{Bu}_3)_2]$  and  $[\text{Pd}_2\text{Br}_2(\text{P}^t\text{Bu}_3)_4]$ . The salt  $\text{K}[\text{Co}(\text{CO})_3(\text{PPh}_3)]^{23}$  was prepared as described.

### Physical and analytical methods

The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker AM 400 spectrometer and referenced in ppm relative to the solvent shift<sup>24</sup> or tetramethylsilane, infrared spectra on a Perkin-Elmer 1600 spectrometer as KBr discs if not stated otherwise and mass spectra on a Finnigan MAT 311A instrument by chemical ionisation (CI) or the fast atom bombardment (FAB) method. Elemental analyses were performed by the Microanalytical Laboratory of the Technische Universität München.



**Scheme 3** Mechanism proposed for the intramolecular hydroamination of  $\text{DC}\equiv\text{C}(\text{CH}_2)_4\text{ND}_2$  with the palladium catalyst  $[\text{Pd}(\text{Triphos})][\text{BF}_4]$  ( $\square$  represents an empty co-ordination site).

### Preparations

**$\text{H}_2\text{N}(\text{CH}_2)_4\text{C}\equiv\text{CH}$ .** 5-Cyanopent-1-yne (0.269 mol, 25.0 g) was dissolved in  $\text{Et}_2\text{O}$  (100  $\text{cm}^3$ ) and added over a period of 60 min to a magnetically stirred mixture of 0.289 mol  $\text{LiAlH}_4$  (11.0 g) in  $\text{Et}_2\text{O}$  (400  $\text{cm}^3$ ) at  $0^\circ\text{C}$ . The mixture was refluxed overnight, the excess of  $\text{LiAlH}_4$  destroyed by addition of 75  $\text{cm}^3$  water, the mixture filtered and the organic layer separated. The  $\text{Et}_2\text{O}$  was removed to yield a yellow liquid. Addition of 300  $\text{cm}^3$  1 M  $\text{HCl}$  in  $\text{Et}_2\text{O}$  (0.300 mol) precipitated the product as the hydrochloride which was filtered off and dried *in vacuo*. The hydrochloride (23.3 g) was dissolved in methanol (100  $\text{cm}^3$ ), 18.5 g  $\text{Na}_2\text{CO}_3$  (0.175 mol) were added and the mixture stirred at room temperature for 1 h. The solvent was removed and the product distilled (69–70  $^\circ\text{C}$  at 18 mmHg). Yield: 10.6 g, 41% (Found: C, 74.3; H, 11.4; N, 14.2. Calc. for  $\text{C}_6\text{H}_{11}\text{N}$ : C, 74.2; H, 11.3; N, 14.4%).  $d = 0.852 \text{ g cm}^{-3}$ .  $^{13}\text{C}\{-^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  84.3 (s, C2), 68.4 (s, C1), 41.7 (s, C6), 32.8 (s, C5), 25.8 (s, C4) and 18.3 (s, C3).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.72 (t, 2 H,  $\text{CH}_2\text{N}$ ), 2.22 (td, 2 H,  $\text{CH}_2\text{C}\equiv\text{C}$ ), 1.96 (t, 1 H,  $\text{HC}\equiv\text{C}$ ), variable 1.9–1.6 (m, 2 H,  $\text{NH}_2$ ) and 1.57 (m, 4 H,  $\text{CH}_2\text{CH}_2$ ).  $m/z$  (CI) 98 ( $\text{M}^+ + 1$ ). IR (film): 3295vs, 2934vs, 2862s, 2115m, 1596s, 1455s, 1392w, 1328w, 1037s, 943w, 896w and 635s  $\text{cm}^{-1}$ .

**$\text{H}_2\text{N}(\text{CH}_2)_4\text{C}\equiv\text{CH}\cdot\text{HCl}$ .** 6-Aminohex-1-yne (100  $\mu\text{l}$ , 0.88 mmol) was dissolved in  $\text{Et}_2\text{O}$ , 5  $\text{cm}^3$  1 M  $\text{HCl}$  in  $\text{Et}_2\text{O}$  (5 mmol) were added and the solvent removed *in vacuo*. Yield: 10.6 mg, 91% (Found: C, 53.9; H, 9.0; Cl, 26.3; N, 10.4. Calc. for  $\text{C}_6\text{H}_{13}\text{ClN}$ : C, 53.9; H, 9.0; Cl, 26.6; N, 10.5%).  $^{13}\text{C}\{-^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  84.1 (s, C2), 70.4 (s, C1), 40.3 (s, C6), 27.5 (s, C5), 26.4 (s, C4) and 18.6 (s, C3).  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  4.8 (s, 3 H,  $\text{NH}_3^+$ ), 2.96 (t, 2 H,  $\text{CH}_2\text{N}$ ), 2.27 (m, 1 H,  $\text{HC}\equiv\text{C}$ ), 2.25 (m, 2 H,  $\text{CH}_2\text{C}\equiv\text{C}$ ), 1.80 (qnt, 2 H,  $\text{CH}_2\text{CN}$ ) and 1.60 (qnt, 2 H,  $\text{CH}_2\text{CC}\equiv\text{C}$ ).  $m/z$  (FAB) 98 ( $\text{M}^+ - \text{Cl}$ ). IR: 3228vs, 3094vs, 2981vs, 2892vs, 2722m 1609s, 1490s, 1466s, 988s, 880m, 778s, 715s, 684s and 416s  $\text{cm}^{-1}$ .

**$\text{D}_2\text{N}(\text{CH}_2)_4\text{C}\equiv\text{CD}\cdot\text{HCl}$ .**  $^{13}\text{C}\{-^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  83.6 [t, C2,  $^1J(^{13}\text{C}, ^2\text{D}) = 7$ ], 70.1 [t, C1,  $^1J(^{13}\text{C}, ^2\text{D}) = 38 \text{ Hz}$ ], 40.3 (s, C6), 27.5 (s, C5), 26.4 (s, C4), 18.6 (s, C3).  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  4.8 [s, 1.4 H,  $\text{N}(\text{H}/\text{D})_3^+$ ], 2.96 (t, 2 H,  $\text{CH}_2\text{N}$ ), 2.27 (m, 0.2 H,  $\text{H}/\text{DC}\equiv\text{C}$ ), 2.25 (m, 2 H,  $\text{CH}_2\text{C}\equiv\text{C}$ ), 1.80 (qnt, 2 H,  $\text{CH}_2\text{CN}$ ) and 1.60 (qnt, 2 H,  $\text{CH}_2\text{CC}\equiv\text{C}$ ).

**Catalysis and hydrochloride of 2-methyl-1,2-dehydropiperidine.** In a typical procedure, a mixture of 6-aminohex-1-yne (0.10  $\text{cm}^3$ , 0.88 mmol),  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (3.2 mg, 8.8  $\mu\text{mol}$ ) and acetonitrile (25  $\text{cm}^3$ ) was heated at reflux for 20 h. The product, 2-methyl-1,2-dehydropiperidine, was isolated together with the remaining starting material as a mixture of hydrochlorides (0.11 g, 93% yield). The product distribution was analysed by  $^1\text{H}$  NMR spectroscopy using the following signals for the integration: at  $\delta$  3.0, 2.3 and 1.6 for the starting material and at  $\delta$  3.6, 2.8 and 2.4 for the product. For  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  a quantitative conversion into the product was observed (Found: C, 53.5; H, 9.1; Cl, 10.4. Calc. for  $\text{C}_6\text{H}_{12}\text{ClN}$ : C, 53.9; H, 9.1; Cl, 10.5%).  $^{13}\text{C}\{-^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  191.8 (s, C2), 45.7 (s, C6), 32.1 (s, C3), 24.9 (s, Me), 20.2 (s, C5) and 17.9 (s, C4).  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  4.8 (s, 1 H,  $\text{NH}^+$ ), 3.64 (s, 2 H,  $\text{CH}_2\text{N}$ ), 2.83 (t, 2 H,  $\text{CH}_2\text{C}=\text{N}$ ), 2.39 (s, 3 H, Me), 1.89 (m, 2 H,  $\text{CH}_2\text{CC}=\text{N}$ ) and 1.85 (m, 2 H,  $\text{CH}_2\text{CN}$ ).  $m/z$  (FAB) 98 ( $\text{M}^+ - \text{Cl}$ ). IR: 2960s, 2876s, 1696vs, 1637s, 1450s, 1026s  $\text{cm}^{-1}$ .

**Hydrochloride of 2-methyl-1,2-dehydropiperidine- $d^3$ .**  $^{13}\text{C}\{-^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  191.8 (s, C2), 45.7 (s, C6), 31.7 [t, C3,  $^1J(^{13}\text{C}, ^2\text{D}) = 20$ ], 24.4 [qnt, Me,  $^1J(^{13}\text{C}, ^2\text{D}) = 21$ ], 20.2 (s, C5) and 17.8 [t, C4,  $^2J(^{13}\text{C}, ^2\text{D}) = 10 \text{ Hz}$ ].  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  4.8 (s, 1 H,  $\text{NH}^+$ ), 3.64 (s, 2 H,  $\text{CH}_2\text{N}$ ), 2.83 [t, 1.0 H,  $\text{C}(\text{H}/\text{D})_2\text{C}=\text{N}$ ], 2.39 (s, 1.4 H, Me), 1.89 (m, 2 H,  $\text{CH}_2\text{CC}=\text{N}$ ) and 1.85 (m, 2 H,  $\text{CH}_2\text{CN}$ ).

**$[\text{Ag}(\text{Triphos})]\text{BF}_4$ .** The compound Triphos (0.47 mmol, 0.25 g) was dissolved in  $\text{CH}_2\text{Cl}_2$  (20  $\text{cm}^3$ ) and added to a magnetic-

ally stirred solution of 0.47 mmol  $\text{AgBF}_4$  (92 mg) in  $\text{CH}_2\text{Cl}_2$  (100  $\text{cm}^3$ ). The solution was filtered, the volume reduced in a partial vacuum and the product precipitated with pentane. The product was recrystallised from  $\text{CH}_2\text{Cl}_2$ -pentane and dried *in vacuo*. Yield: 0.32 g, 93% (Found: C, 55.4; H, 4.6. Calc. for  $\text{C}_{34}\text{H}_{33}\text{AgBF}_4\text{P}_3$ : C, 56.0; H, 4.6%).  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  5.9 (br, 1P), 4.6 (br, 1P) and 1.7 (br, 1P).  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  133.4–130.2 (mm, Ph), 25.5 (m,  $\text{CH}_2$ ) and 24.8 (m,  $\text{CH}_2$ ).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  7.4–7.2 (mm, 25 H, Ph), 2.4 (br, 4 H,  $\text{CH}_2$ ) and 2.2 (br, 4 H,  $\text{CH}_2$ ). *m/z* (FAB) 641 ( $\text{M}^+ - \text{BF}_4$ ). IR: 3053m, 1482m, 1435s, 1084vs ( $\text{BF}_4^-$ ), 742s, 695s and 511  $\text{cm}^{-1}$ .

**$\text{AuCl}_3$ -Triphos.** The compound Triphos (0.470 mmol, 0.251 g) was dissolved in  $\text{CH}_2\text{Cl}_2$  (15  $\text{cm}^3$ ) and added to a magnetically stirred solution of 0.470 mmol  $\text{AuCl}_3$  (0.143 g) in  $\text{CH}_2\text{Cl}_2$  (50  $\text{cm}^3$ ). The volume was increased to 100  $\text{cm}^3$  and 1.9  $\text{cm}^3$  of the solution used for catalysis.

**$\text{Ni}(\text{PPh}_3)_4$ .** The complex  $\text{Ni}(\text{COD})_2$  (8.8  $\mu\text{mol}$ , 2.4 mg) was dissolved in thf (5  $\text{cm}^3$ ), 35  $\mu\text{mol}$   $\text{PPh}_3$  (9.2 mg) were added, the solution filtered and the volatiles removed. The remaining solid was dried *in vacuo* and used without further characterisation.

**$[\text{Pd}(\text{dppf})][\text{NO}_3]_2 \cdot \text{CH}_2\text{Cl}_2$ .** The compound dppf (0.35 mmol, 0.19 g) was dissolved in  $\text{CH}_2\text{Cl}_2$  (5  $\text{cm}^3$ ) and added to a magnetically stirred solution of 0.35 mmol  $[\text{PdCl}_2(\text{COD})]$  (0.10 g) in  $\text{CH}_2\text{Cl}_2$  (25  $\text{cm}^3$ ). The solvent was removed and the residue dried *in vacuo*. The solid was redissolved in  $\text{CH}_2\text{Cl}_2$  (15  $\text{cm}^3$ ) and a solution of 0.70 mmol  $\text{AgNO}_3$  (0.12 g) in MeOH (35  $\text{cm}^3$ ) added. The resulting suspension was stirred for 1 h in the dark and filtered over Celite. The filtrate was taken to dryness, the residue recrystallised from  $\text{CH}_2\text{Cl}_2$ -MeOH (3:1)- $\text{Et}_2\text{O}$  and dried *in vacuo*. Yield: 0.23 g, 83% (Found: C, 48.3; H, 3.5; N, 3.2. Calc. for  $\text{C}_{35}\text{H}_{30}\text{Cl}_2\text{FeN}_2\text{O}_6\text{P}_2\text{Pd}$ : C, 48.3; H, 3.5; N, 3.2%).  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ - $\text{CD}_3\text{CN}$ , 1:1):  $\delta$  40.6 (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ - $\text{CD}_3\text{CN}$ , 1:1):  $\delta$  7.8 (br, 8 H, Ph), 7.7 (m, 4 H, Ph), 7.5 (s, 8 H, Ph), 5.4 (s, 2 H,  $\text{CH}_2\text{Cl}_2$ ), 3.8 (s, 4 H, cp) and 3.3 (s, 4 H, cp). *m/z* (FAB) 722 ( $\text{M}^+ - \text{NO}_3$ ) and 660 ( $\text{M}^+ - 2\text{NO}_3$ ). IR: 3055w, 1477vs, 1436s, 1384vs ( $\text{NO}_3^-$ ), 1275vs, 1168w, 1097m, 1000m, 749m, 693m, 558w, 493m and 467  $\text{cm}^{-1}$ .

**$[\text{Pd}(\text{Triphos})][\text{BF}_4]_2 \cdot 0.5\text{CH}_3\text{CN}$ .** The compound Triphos (0.224 mmol, 0.120 g) was dissolved in  $\text{CH}_2\text{Cl}_2$  (20  $\text{cm}^3$ ) and added to a magnetically stirred mixture of 0.224 mmol  $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$  (0.100 g) in  $\text{CH}_2\text{Cl}_2$  (100  $\text{cm}^3$ ). The mixture was stirred overnight, filtered, the volume reduced in a partial vacuum and the product precipitated with pentane. The product was recrystallised from  $\text{CH}_2\text{Cl}_2$ -pentane and dried *in vacuo*. Yield: 0.120 g, 64% (Found: C, 50.5; H, 4.9; N, 1.0. Calc. for  $\text{C}_{35}\text{H}_{34.5}\text{B}_2\text{F}_8\text{N}_{0.5}\text{P}_3\text{Pd}$ : C, 50.3; H, 4.2; N, 0.8%).  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  117.4 (s, 1P) and 54.2 (s, 2P).  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  135.4s, 134.6s, 134.5s, 134.0–133.7m, 131.1–130.7m, 129.2s, 128.5s, 127.8s and 30.2 [d,  $^2J(^{13}\text{C}, ^{31}\text{P}) = 37$  Hz] and 28.2s.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta$  7.9 (dd, 3 H), 7.7–7.5 (mm, 22 H), 3.4 [dd, 2 H,  $^3J(^1\text{H}, ^{31}\text{P}) = 54$  Hz], 3.1 (br, 2 H), 3.0 (m, 2 H), 2.4 (br, 2 H) and 2.1 (s, 1.5 H,  $\text{CH}_3\text{CN}$ ). *m/z* (FAB) 659 ( $\text{M}^+ - \text{BF}_4 - \text{BF}_3$ ) and 640 ( $\text{M}^+ - 2\text{BF}_4$ ). IR: 3053m, 1436s, 1084vs ( $\text{BF}_4^-$ ), 747s, 692s, 522s and 481  $\text{cm}^{-1}$ .

**$[\text{PtH}(\text{PEt}_3)]\text{NO}_3$ .** The complex  $[\text{PtCl}_2(\text{COD})]$  (0.815 mmol, 0.305 g) was dissolved in 25  $\text{cm}^3$   $\text{CH}_2\text{Cl}_2$ , 1.63 mmol  $\text{PEt}_3$  (1 M in thf, 1.63  $\text{cm}^3$ ) added and stirred for 10 min. Hexane (25  $\text{cm}^3$ ) were added, the volume reduced in a partial vacuum and the precipitate filtered off. The solid was suspended in 20  $\text{cm}^3$  hexane for 1 h. The product *cis*- $[\text{PtCl}_2(\text{PEt}_3)_2]$  was dried *in vacuo*, dissolved in a mixture of 20  $\text{cm}^3$  MeOH and 6.9  $\text{cm}^3$   $\text{Et}_2\text{NH}$ ;

0.82 mmol  $\text{NaBH}_4$  (31 mg) was added. After 10 min the volatiles were removed, the residue extracted with pentane and the product  $[\text{PtCl}(\text{H})(\text{PEt}_3)_2]$  isolated (0.13 g). The white powder was dissolved in 5  $\text{cm}^3$   $\text{CH}_3\text{CN}$ , 76.2 mg  $\text{TINO}_3$  in a mixture of 2  $\text{cm}^3$  water and 10  $\text{cm}^3$   $\text{CH}_3\text{CN}$  added and the mixture stirred for 5 min. Filtration, followed by removal of the solvent, resulted in a white powder which was recrystallised from pentane. Overall yield: 69 mg, 18% (Found: C, 29.1; H, 6.3; N, 2.7. Calc. for  $\text{C}_{12}\text{H}_{31}\text{NO}_3\text{Pt}$ : C, 31.1; H, 6.7; N, 3.0%).  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  24.9 [t,  $^2J(^{31}\text{P}, ^{195}\text{Pt}) = 2819$  Hz].  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  18.0 (tt) and 8.4 (t).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.53 (m, 12 H), 1.00 (qnt, 18 H) and 0.39 (s, 1 H). *m/z* (FAB) 431 ( $\text{M}^+ - \text{NO}_3$ ). IR: 2962vs, 2934s, 2876s, 2218s (Pt-H), 1448vs, 1383vs ( $\text{NO}_3^-$ ), 1285vs, 1051s, 1020m, 1002m, 767vs and 696  $\text{cm}^{-1}$ .

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