# Azametallacycles from Ag(I)- or Cu(II)-Promoted Coupling Reactions of Dialkylcyanamides with Oximes at Pt(II)

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The dialkylcyanamide complexes *cis*-[PtCl(NCNR$_2$)(PPh$_3$)$_2$][BF$_4$] **1** and *cis*-[Pt(NCNR$_2$)$_2$(PPh$_3$)$_2$][BF$_4$]$_2$ **2** (R = Me or Et) have been prepared by treatment of a $CH_2Cl_2$ solution of *cis*-[PtCl$_2$(PPh$_3$)$_2$] with the appropriate dialkylcyanamide and one or two equivalents of Ag[BF$_4$], respectively. Compounds **2** can also be obtained from **1** by a similar procedure. Their reaction with oximes, HON=CR′R″ (R′R″ = Me$_2$ or C$_4$H$_8$), in $CH_2Cl_2$ and in the presence of Ag[BF$_4$] or Cu(CH$_3$COO)$_2$, leads to the novel type of azametallacycles *cis*-[Pt{NH=C(ON=CR′R″)-NR$_2$}(PPh$_3$)$_2$][BF$_4$]$_2$ **4** upon an unprecedented coupling of the organocyanamides with oximes, in a process that proceeds via the mixed oxime−organocyanamide species *cis*-[Pt(NCNR$_2$)(HON=CR′R″)(PPh$_3$)$_2$][BF$_4$]$_2$ **3**, and is catalyzed by either $Ag^+$ or $Cu^{2+}$ which activate the ligating organocyanamide by Lewis acid addition to the amide group. In contrast, in the organonitrile complexes *cis*-[Pt(NCR)$_2$(PPh$_3$)$_2$][BF$_4$]$_2$ **5** (R = C$_6$H$_4$OMe-4 or Et), obtained in a similar way as **2** (but by using NCR instead of the cyanamide), the ligating NCR is not activated by the Lewis acid and does not couple with the oximes. The spectroscopic properties of those complexes are reported along with the molecular structures of **2b** (R = Et), **4a1** (R = Me, R′R″ = Me$_2$), and **4b1** (R = Et, R′R″ = Me$_2$), as established by X-ray crystallography which indicates that in the former complex the amide-N-atoms are trigonal planar, whereas in the latter (**4a1** and **4b1**) the five-membered rings are planar with a localized N=C double bond (imine group derived from the cyanamide) and the exocyclic amide and alkylidene groups (in **4b1**) are involved in two intramolecular H-bonds to the oxygen atom of the ring.

## Introduction

In contrast with the rich coordination chemistry exhibited by the NCR (R = alkyl or aryl) nitriles,[5] that of cyanamides, N≡CNR$_2$ (R = H or alkyl) is still a field that remains to be explored, despite the biological and synthetic significance of such a type of compounds, in particular cyanamide itself (N≡CNH$_2$)[6−8] and its dimeric form, cyanoguanidine, N≡C−N=C(NH$_2$)$_2$.[9−12]

We have previously observed that cyanamide is dehydrogenated by an electron-rich Mo(0) or W(0) center, {M(dppe)$_2$} (M = Mo or W, dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) to form a cyanoimide complex, *trans*-[M(NCN)$_2$(dppe)$_2$],[13] whereas cyanoguanidine at {ReCl(dppe)$_2$} can undergo deprotonation or deamination to give the ligating NCNC(NH)NH$_2^-$ or NCNCN$^-$ (dicyanamide) derivatives, respectively.[14] Moreover, at a dicationic Pt(II) center, {Pt(PPh$_3$)$_2$}$^{2+}$, cyanoguanidine is activated toward nucleophilic addition which, combined with deprotonation of the guanidine unit and its chelation, forms a six-membered azametallacycle, i.e., *cis*-[(PPh$_3$)$_2$Pt{NHC(OMe)=NC(NH$_2$)=NH}][BPh$_4$] derived from the reaction of *cis*-[Pt{NCNC(NH$_2$)$_2$}$_2$(PPh$_3$)$_2$][BPh$_4$]$_2$ with MeOH.[15] These reactions contrast with the usual unreactivity of ligating diorganocyanamides, e.g., NCNR$_2$ (R = Me or Et) at the Pt(II)[16] and Fe(II)[17] complexes we have previously prepared. Moreover, only scarce

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examples of reactions of diorganocyanamides with transition metal complexes (apart from conventional coordination) have been quoted, and they involve, e.g., their insertion into metal−carbon double[18−21] or triple[22] bonds and metathesis like reactions with a metal−metal triple bond[23] to give alkylidyne and nitride complexes.

We now report an unprecedented mode of activation of diorganocyanamides by the combined action of a Pt(II) center (binding the cyano-group) and a catalytic amount of a metal-ion Lewis acid ($Ag^+$ or $Cu^{2+}$) (adduct formation with the amido-group). This activation, that takes advantage of both functional groups of an organocyanamide, promotes its electrophilic character toward nucleophilic addition by an oxime (HON=CR′R″) to give a novel type of azametallacycle, i.e., the amino-functionalized five-membered N,N′-chelates *cis*-[Pt{HN=C(ON=C R′R″)$NR_2$}$(PPh_3)_2$][$BF_4$]$_2$ **4** (R = Me or Et; R′R″ = $Me_2$ or $C_4H_8$) whose formation involves chelation via the imino-nitrogen of the oximate group. These reactions extend to cyanamides and to platinum the behavior of organonitriles we have recently detected at a Rh(III) center,[24] with formation of the chelated iminoacylated species [$RhCl_2${NH=C(R)ON=$C(C_4H_8)$}$_2$]Cl (R = Me or Ph) on reaction of *mer*-[$RhCl_3$-$(NCMe)_3$] with HON=$C(C_4H_8)$. They contrast with all the other known cases of metal mediated [by Pt(IV)[25,26] or Re (IV)[27]] oxime−nitrile coupling reactions which we have recently studied and shown to lead to monodentate iminoacylated products *without* formation of an azametallacycle.

Moreover, the current study also provides a simple method to the formation, under mild conditions, of azametallacycles, a field of coordination and organometallic chemistry that has not yet been adequately explored although particular syntheses and applications in organic chemistry to the preparation of some organonitrogen compounds have already been reported. Hence, e.g., organonitriles[5] or an isocyanide[28] (commonly by insertion reactions into metal−ligand bonds), organoazides (via "NR" insertion into a nickel−C bond),[29] an amino-haloaromatic species (via C−I oxidative addition to Pd(0) of 2′-amino-2-iodobiphenyl with concomitant metal ligation of the amino group),[30] or imido (Ti, Zr or Os) complexes (via cycloaddition reactions with alkenes, alkynes, or organoazides)[31−33] can be precursors for azametallacycles of different types of those we now report, whereas some indoline-[29] or carbazole-[30] derivatives can be obtained from some of those azametallacycle intermediates.

## Results and Discussion

**Organocyanamide Complexes *cis*-[$PtCl(NCNR_2)(PPh_3)_2$][$BF_4$] 1 and *cis*-[$Pt(NCNR_2)_2(PPh_3)_2$][$BF_4$]$_2$ 2.** Treatment of the platinum(II) compound *cis*-[$PtCl_2(PPh_3)_2$] in $CH_2Cl_2$ with the appropriate dialkylcyanamide $NCNR_2$ (R = Me or Et) in an equimolar amount or in a 6-fold molar ratio, under an inert atmosphere and in the presence of Ag[$BF_4$] (equimolar or 2-fold molar ratio, respectively), gives the mono- or the di-alkylcyanamide complexes *cis*-[$PtCl(NCNR_2)(PPh_3)_2$][$BF_4$] **1** or *cis*-[$Pt(NCNR_2)_2(PPh_3)_2$][$BF_4$]$_2$ **2**, respectively [reactions (*i*) and (*ii*), Scheme 1], formed via sequential replacement of the chloride ligands by $NCNR_2$. The silver salt behaves as the halide ligand abstractor, and compounds **2** can also be obtained from **1** via replacement of the chloride ligand by the dialkylcyanamide, in the presence of one equivalent Ag[$BF_4$] [reaction (*iii*), Scheme 1].

Compounds **1** and **2** were obtained in high yields (85−90%) as white solids, and their IR spectra (Nujol mull) show strong bands in the 2275−2250 $cm^{-1}$ range which are assigned to the N≡C stretching mode of the cyanamide ligands, as observed in other Pt(II),[16] Fe(II),[17] or Re(II)[34] compounds. The increase of $\nu$(NC) (by 35−45 $cm^{-1}$) on coordination of $NCNR_2$ is indicative of the $\eta^1$ coordination mode via the cyano group[35,36] which acts as an effective electron donor. The cis geometry of the phosphines is suggested[37] by the detection of a medium intensity (and sharp) band at 540 $cm^{-1}$ and, for compounds **1**, is confirmed by the $^{31}P\{^1H\}$ NMR spectra which consist of two doublets [$\delta$ ca. −131 and ca. −136, relative to $P(OMe)_3$] flanked by $^{195}Pt$ satellites [$^1J_{PPt}$ ca. 3540 and ca. 3800 Hz, respectively]. The former doublet, with the lower $^1J_{PPt}$, is tentatively assigned to the phosphorus trans to the chloride ligand, the other one being trans to the dialkylcyanamide, in view of the slightly lower $^1J_{PPt}$ (3674.0 Hz)[38] and $^2J_{PtF}$ (691 Hz)[39] values for *cis*-[$PtCl_2$-$(PPh_3)_2$] and *trans*-[$Pt(CF_3)Cl(PPh_3)_2$], respectively, in comparison with those observed in our complexes *cis*-[$Pt(NCNR_2)_2$-$(PPh_3)_2$][$BF_4$]$_2$ [3698.5 Hz (**2a**) or 3706.0 Hz (**2b**)] and *trans*-[$Pt(CF_3)(NCNR_2)(PPh_3)_2$][$BF_4$] (717 Hz).[16] Hence, the dialkylcyanamides appear to present a weaker trans influence than chloride. The order of the trans influence of other ligands has been established[40] on the basis of similar relationships with $^1J_{PPt}$, $^2J_{PtF}$, or other coupling constants.

In the $^{195}Pt$ NMR spectra, a doublet of doublets is observed for **1** (X part of an ABX-type system; A and B = P and X = Pt), whereas for **2** (with two equivalent $^{31}P$ nuclei) they exhibit the expected triplet. The broadness of the signals reveals the influence of the nitrogen nuclei directly bound to the metal, and their chemical shifts of ca. $\delta$ −4400 (relative to $Na_2[PtCl_6]$, by using $K_2[PtCl_4]$, $\delta$ = −1630 ppm, as a standard) are similar to those observed[41] in other Pt(II) complexes with the same geometry.

In the $^{13}C\{^1H\}$ NMR spectra of **1** and **2**, the broad and low intense singlet resonance at $\delta$ ca. 122 (also observed in the $^1H$-


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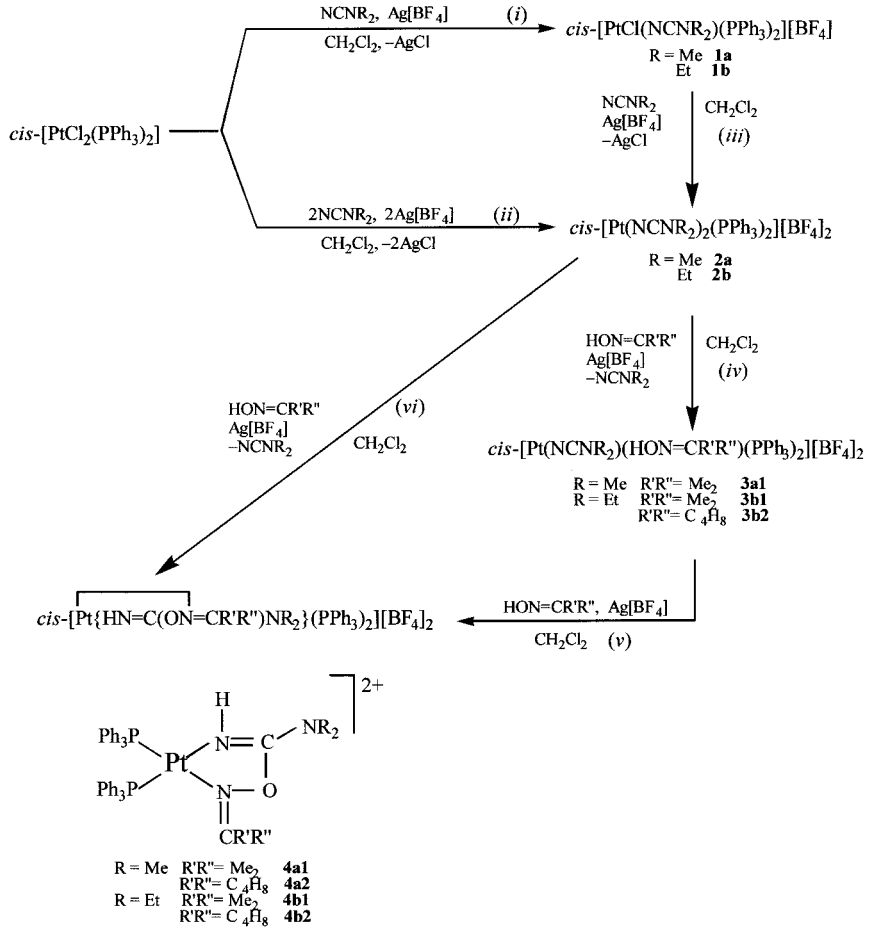
**Scheme 1** . Syntheses of Organocyanamide Complexes and Derived Azametallacycles




undecoupled spectrum) is assigned to the cyanamide N≡*C* carbon, being at a slightly lower field (by ca. 3−5 ppm) relative to that of the corresponding free $NCNR_2$. The two sets of phenyl−carbon resonances for **1** agree with the nonequivalence of the two phosphines, and the complex resonance patterns for both **1** and **2** were assigned to the various aromatic C nuclei. Hence for **2**, the ortho ($C_o$) and meta ($C_m$) carbons present a typical filled doublet for the A part of an AXX′ (X, X′ = P, P′) spin system, whereas the ipso ($C_i$) and the para ($C_p$) carbons give a doublet ($^1J_{CP}$) and a singlet, respectively. The assignments were confirmed by $^{13}C$ NMR whose data are available as Supporting Information (for these and the other complexes).

The molecular structure of the diethylcyanamide complex **2b**, as established by an X-ray diffraction analysis, is depicted in Figure 1. Crystallographic data are given in Table 1, and selected bond lengths and angles are listed in Table 2. The Pt atom has a square-planar environment with the two cyanamide ligands in cis position. The P(1)−Pt−P(2) and P(1)−Pt−N(3) angles of 96.06(7)° and 91.6(2)°, corresponding, are considerably larger than those of N(1)−Pt−N(3) [86.7(3)°] and P(2)−Pt−N(1) [86.0(2)°]. Moreover, the Pt−P distances of 2.255(2) [Pt−P(1)] and 2.276(2) [Pt−P(2)] Å are significantly different, as well as the deviations from the linearity at the ligated cyano-N of the cyanamide ligands, with Pt−N(1)−C(37) and Pt−N(3)−C(42) angles of 163.7(7)° and 149.4(7)°, respectively. These asymmetries are conceivably due to steric congestion at the coordination sphere, and those concerning the phosphine ligands are comparable to the observed ones[16,42] in other Pt(II) diphosphinic compounds.

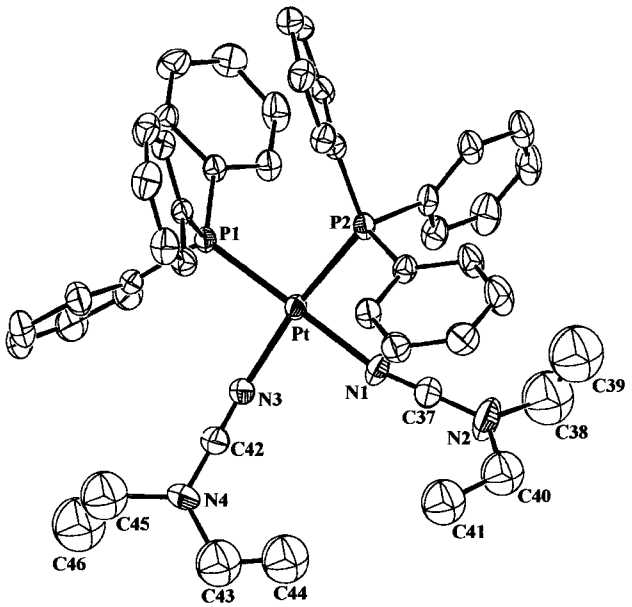



**Figure 1.** Molecular structure of the cationic complex of *cis*-[Pt-$(NCNEt_2)_2(PPh_3)_2][BF_4]_2$ **2b**.

The amide-N atoms of the diethylcyanamide ligands are trigonal planar [the sums of the angles around N(2) and N(4) are 360(1)° and 358(1)°, accordingly] rather than pyramidal as observed in *mer*-$[ReCl_2(NCNEt_2)(PMePh_2)_3]$[34] and in the uncoordinated and related dimethylcyanamide ($NCNMe_2$)[43] and

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**Table 1.** Crystallographic Data for *cis*-$[Pt(NCNEt_2)_2(PPh_3)_2][BF_4]_2$ **2b** and *cis*-$[Pt\{NH{=}C(ON{=}CMe_2)NR_2\}(PPh_3)_2][BF_4]_2$ (R = Me, **4a1**; or Et, **4b1**)

| | **2b** | **4a1** | **4b1** |
|---|---|---|---|
| empirical formula | $C_{42}H_{43}N_3OP_2Pt\ 2(BF_4)$ | $C_{42}H_{43}N_3OP_2Pt\ 2(BF_4)$ | $C_{44}H_{47}N_3OP_2Pt\ 2(BF_4)$ |
| fw | 1089.55 | 1036.46 | 1064.51 |
| temp, °C | 20(2) | 20(2) | 20(2) |
| $\lambda$, Å | 1.54179 | 0.71073 | 0.71073 |
| space group | *P*1 (No. 2) | $P2_1/c$ (No. 14) | $P2_1/c$ (No. 14) |
| *a*, Å | 12.154(2) | 10.277(2) | 10.382(2) |
| *b*, Å | 12.569(3) | 22.992(5) | 23.144(5) |
| *c*, Å | 16.013(3) | 18.377(14) | 18.499(4) |
| α, deg | 102.10(3) | | |
| $\beta$, deg | 100.87(3) | 91.72(3) | 91.23(3) |
| $\gamma$, deg | 93.88(3) | | |
| *V*, Å$^3$ | 2334.3(8) | 4340.3(16) | 4444.2 |
| *Z* | 2 | 4 | 4 |
| $\rho_{calcd}$, g/cm$^3$ | 1.550 | 1.586 | 1.591 |
| $\mu$*, mm$^{-1}$ | 6.862 | 3.377 | 3.301 |
| $R_1$[a] | 0.0351 | 0.0543 | 0.0258 |
| $wR_2$[b] | 0.0946 | 0.1313 | 0.0670 |

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2|F_c^2)^2]/\sum[w(F_o^2)]]^{1/2}$, $w = 1/[\sigma^2(F_o)^2 + (0.0527P)^2 + 9.4133P]$ (for **2b**), $w = 1/[\sigma^2(F_o)^2 + (0.0517P)^2 + 32.4445P]$ (for **4a1**), $w = 1/[\sigma^2(F_o)^2 + (0.0480P)^2 + 7.5223P]$ (for **4b1**); *$\mu$(Cu Kα) for **2b** and $\mu$(Mo Kα) for **4a1** and **4b1**.

**Table 2.** Selected Lengths (Å) and Angles (deg) for *cis*-$[Pt(NCNEt_2)_2(PPh_3)_3][BF_4]_2$ **2b** and *cis*-$[Pt\{NH{=}C(ON{=}CMe_2)NR_2\}(PPh_3)_2][BF_4]_2$ (R = Me, **4a1**; or Et, **4b1**) with ESD in Parentheses

| **2b** | | **4a1** | | **4b1** | |
|---|---|---|---|---|---|
| Pt−N(3) | 2.054(7) | Pt−P(2) | 2.267(3) | Pt−P(2) | 2.261(2) |
| Pt−N(1) | 2.061(6) | Pt−P(1) | 2.269(3) | Pt−P(1) | 2.272(2) |
| Pt−P(1) | 2.255(2) | Pt−N(2) | 2.105(8) | Pt−N(1) | 2.078(7) |
| Pt−P(2) | 2.276(2) | Pt−N(1) | 2.050(10) | Pt−N(2) | 2.050(7) |
| N(1)−C(37) | 1.134(10) | N(2)−O | 1.428(12) | N(1)−O(1) | 1.454(9) |
| N(2)−C(37) | 1.308(11) | O−C(37) | 1.352(14) | O(1)−C(1) | 1.348(12) |
| N(2)−C(40) | 1.50(2) | N(1)−C(37) | 1.278(14) | N(2)−C(1) | 1.271(12) |
| N(2)−C(38) | 1.71(2) | N(2)−C(38) | 1.274(15) | N(1)−C(42) | 1.274(11) |
| N(3)−C(42) | 1.136(10) | N(3)−C(37) | 1.323(15) | N(3)−C(1) | 1.341(12) |
| N(4)−C(42) | 1.291(12) | N(1)−H1 | 0.66 | N(2)−H2 | 0.9086 |
| N(4)−C(43) | 1.51(2) | N(3)−C(42) | 1.46(2) | N(3)−C(38) | 1.45(2) |
| N(4)−C(45) | 1.66(2) | N(3)−C(40) | 1.47(2) | N(3)−C(40) | 1.46(2) |
| N(3)−Pt−N(1) | 86.7(3) | N(2)−Pt−N(1) | 74.0(4) | N(2)−Pt−N(1) | 75.0(3) |
| N(3)−Pt−P(1) | 91.6(2) | N(2)−Pt−P(2) | 161.9(3) | N(1)−Pt−P(2) | 162.9(2) |
| N(1)−Pt−P(1) | 176.5(2) | N(1)−Pt−P(2) | 89.5(3) | N(1)−Pt−P(1) | 98.9(2) |
| N(3)−Pt−P(2) | 170.3(2) | N(2)−P−P(1) | 100.3(3) | N(2)−Pt−P(2) | 89.5(2) |
| N(1)−Pt−P(2) | 86.0(2) | N(1)−P−P(1) | 169.5(3) | N(2)−Pt−P(1) | 168.7(2) |
| P(1)−Pt−P(2) | 96.06(7) | P(2)−P−P(1) | 97.07(10) | P(2)−P−P(1) | 97.50(8) |
| C(37)−N(1)−Pt | 163.7(7) | C(37)−N(1)−H1 | 116 | C(1)−N(2)−H2 | 118.78 |
| C(37)−N(2)−C(40) | 123.0(10) | P−N(1)−H1 | 120 | Pt−N(2)−H2 | 126.87 |
| C(37)−N(2)−C(38) | 119.9(10) | C(37)−N(1)−Pt | 115.0(9) | C(1)−N(2)−Pt | 114.7(7) |
| C(40)−N(2)−C(38) | 116.9(11) | C(38)−N(2)−O | 111.5(9) | C(1)−O(1)−N(1) | 110.0(7) |
| C(42)−N(3)−Pt | 149.4(7) | C(38)−N(2)−Pt | 138.7(9) | C(42)−N(1)−O(1) | 109.7(7) |
| C(42)−N(4)−C(43) | 122.3(10) | O−N(2)−Pt | 109.5(6) | C(42)−N(1)−Pt | 141.3(7) |
| C(42)−N(4)−C(45) | 120.3(9) | C(37)−N(3)−C(42) | 123.6(12) | O(1)−N(1)−Pt | 108.7(5) |
| C(43)−N(4)−C(45) | 114.4(11) | C(37)−N(3)−C(40) | 119.3(11) | C(1)−N(3)−C(38) | 120.3(11) |
| N(1)−C(37)−N(2) | 177.3(10) | C(42)−N(3)−C(40) | 117.1(11) | C(1)−N(3)−C(40) | 118.8(9) |
| N(3)−C(42)−N(4) | 175.7(11) | C(37)−O−N(2) | 109.9(8) | C(38)−N(3)−C(40) | 120.6(11) |
| | | N(1)−C(37)−N(3) | 128.4(12) | N(2)−C(1)−N(3) | 128.2(11) |
| | | N(1)−C(37)−O | 119.6(11) | N(2)−C(1)−O(1) | 119.7(9) |
| | | N(3)−C(37)−O | 112.0(10) | N(3)−C(1)−O(1) | 112.1(9) |

cyanamide ($NCNH_2$).[44,45] The NC−$NEt_2$ distances [C(37)−N(2) = 1.308(11) Å and C(42)−N(4) = 1.291(12) Å] indicate some double bond character,[46] being shorter than the corresponding ones in free $NCNMe_2$ [1.351 Å][43] and $NCNH_2$ [1.346 Å].[44] These features indicate that the lone pair of the amide N atom of each ligating diethylcyanamide participates in $\pi$-bonding to the cyano carbon atom, the canonical form

$$\overset{-}{Pt} \leftarrow N = C = \overset{+}{N}Et_2$$

presenting a significant contribution in the VB representation of that ligand. A related behavior is observed for *trans*-$[Pt(CF_3)(L)(PPh_3)_2][BF_4]$ (L = $NCNEt_2$),[16] *trans*-$[Cr(L)(CO)_5]$,[47] and *trans*-$[Fe(L)_2(Et_2PCH_2CH_2PEt_2)_2][BF_4]_2$.[17]

**Oxime and Derived Azametallacycle Complexes *cis*-$[Pt(NCNR_2)(HON{=}CR'R'')(PPh_3)_2][BF_4]_2$ 3 and *cis*-$[Pt\{NH{=}$**

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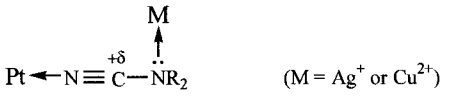
**C(ON=CR′R″)NR$_2$}(PPh$_3$)$_2$][BF$_4$]$_2$ 4.** When a $CH_2Cl_2$ solution of *cis*-[Pt(NCNEt$_2$)$_2$(PPh$_3$)$_2$][BF$_4$]$_2$ **2b** is stirred with the oxime HON=CR′R″ (2-fold molar ratio) in the presence of Ag[BF$_4$] (either catalytic or stoichiometric amounts), at room temperature, the corresponding mixed oxime−cyanamide complexes *cis*-[Pt(NCNEt$_2$)(HON=CR′R″)(PPh$_3$)$_2$][BF$_4$]$_2$ **3b1** (R′R″ = Me$_2$) or **3b2** (R′R″ = $C_4H_8$) are obtained [reaction (*iv*), Scheme 1] (ca. 90% yield) via replacement of one of the diethylcyanamides by the oxime. Complex *cis*-[Pt(NCNMe$_2$)$_2$(PPh$_3$)$_2$][BF$_4$]$_2$ **2a** leads similarly to the formation of *cis*-[Pt(NCNMe$_2$)(HON=CMe$_2$)(PPh$_3$)$_2$][BF$_4$]$_2$ **3a1** on treatment with HON=CMe$_2$, but the reaction is faster than the reaction for **2b** and proceeds to the formation [reaction (*v*), Scheme 1] of the corresponding product **4** (see below) of oxime−cyanamide coupling, which is the isolated complex. However, the formation of **3a1** as an intermediate was clearly established by monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy. In accord, compounds **4** can be prepared from **3** [reaction (*v*), Scheme 1] (ca. 85% yield) in the presence of additional amounts of the oxime and the silver salt (either catalytic or stoichiometric amount).

Following a similar procedure with an excess of the oxime and in the presence of Ag[BF$_4$], the related complexes **4a1** and **4a2** are obtained (ca. 70% yield) in a single-pot synthesis from **2a** [reaction (*vi*), Scheme 1].

It is noteworthy to mention that the presence of Ag[BF$_4$] is essential for both the selective replacement of the organocyanamide by the oxime [reaction (*iv*), Scheme 1] and the cyanamide-oxime coupling [reaction (*v*), Scheme 1]. Without the silver salt we observed the formation of the intermediate **3a1** along with a broad mixture of unidentified products. Moreover, the silver salt can be replaced by copper(II) acetate. These observations suggest that $Ag^+$ (or $Cu^{2+}$) is behaving as an abstracting agent of one of the cyanamide ligands in the dicyanamide complexes **2** and as an activating agent of the remaining cyanamide in **3** toward nucleophilic addition of the oxime. The latter behavior conceivably results from interaction of the Lewis acid metal-ion with the amido-N of the cyanamide ligand in **3**, hampering its electron release to the cyano group (see above) and enhancing the electrophilic character of the cyano-C, in an intermediate moiety of the following type:




(M = $Ag^+$ or $Cu^{2+}$)

We favor such a Lewis acid−base interaction relative to the alternative interaction of $Ag^+$ or $Cu^{2+}$ with the platinum(II) center in the reacting complex (a type of interaction known[48−58] to occur in other cases and which could, in principle, also lead to an enhanced activation of the cyanamide ligand) on the basis of the following evidence: (i) Neither $Ag^+$ nor $Cu^{2+}$ promoting effect toward nitrile−oxime coupling was detected for the ligating organonitriles (without amide substituent) in *cis*-[Pt(NCR)$_2$(PPh$_3$)$_2$][BF$_4$]$_2$ (R = $C_6H_4$OMe-4 **5a** or Et **5b**) which we have prepared similarly to **2** (by using the appropriate nitrile instead of the cyanamide) and that do *not* undergo any nitrile−oxime coupling (either in the presence or in the absence of $Ag^+$ or $Cu^{2+}$) although these organonitriles would be expected to be more susceptible than organocyanamides to nucleophilic attack by the oxime if the activation would merely result from coordination to the Pt(II) center either with or without interaction of this metal with the $Ag^+$ or $Cu^{2+}$ ions; the reactions of **5a** or **5b** with the oximes resulted in replacement of NCR and formation of unidentified final products. Moreover, all our attempts to add ketoximes, including acetoxime, to other platinum(II) compounds [PtX$_2$(NCR)$_2$] (X = Cl, R = Me, Ph; X = Br, R = Me) failed and only formation of a broad spectrum of unidentified products was detected. (ii) The coupling reaction is faster in the presence of $Cu^{2+}$ than $Ag^+$ in agreement with the stronger Lewis acid character of the former ion (the reaction is complete within a few minutes in the presence of a catalytic amount, ca. 10%, of the former ion, whereas ca. 2 h is required for the latter).

The formation of complexes **4** involves the nucleophilic attack of an oxime to an organocyanamide ligand, a type of reaction that is now reported for the first time for the latter ligand which thus is shown to exhibit a similar behavior to that which we have observed[24] for organonitriles at the Rh(III) complexes *mer*-[RhCl$_3$(NCR)$_3$] (R = Me or Ph) which give, e.g., [RhCl$_2$\{NH=C(R)ON=C($C_4H_8$)\}$_2$]Cl on the reaction with HON=C($C_4H_8$).

The reaction can be viewed as an iminoacylation of the oxime by the organocyanamide, to form an iminoacylated species [it can also be considered as an (alkylideneaminooxy)imine] which chelates via the imine-N atoms. This chelation constitutes a driving force for the oxime−organocyanamide coupling and contrasts with the oxime−acetonitrile coupling reactions we have observed at the higher oxidation state Pt(IV) or Re(IV) complexes *trans*-[PtCl$_4$(NCMe)$_2$][25,26] or *cis*-[ReCl$_4$(NCMe)$_2$],[27] which, on reaction with HON=CR′R″, lead to monodentate iminoacylated species, i.e., *trans*-[PtCl$_4$\{NH=C(Me)ON=CR′R″\}$_2$] [R′R″ = Me$_2$, $C_4H_8$, $C_5H_{10}$, (H)Ph, (H)$C_6H_4$(OH)-2 or (Me)C(Me)=NOH] or *cis*-[ReCl$_4$\{NH=C(Me)ON=CR′R″\}$_2$] [R′R″ = Me$_2$, $C_4H_8$, $C_5H_{10}$, $C_9H_{18}$, $C_9H_{16}$ or (Me)(C(Me)NOH)].

The lower metal oxidation state of the Pt(II) complexes of the current study (therefore with an expected weaker activation of N≡CNR$_2$ toward nucleophilic attack) and the weaker electrophilic character of the organocyanamides (with the $\pi$-electron-donor amine group, see above) in comparison with organonitriles are compensated by the above activating effect of $Ag^+$ or $Cu^{2+}$ and the capacity for chelation of the iminoacylated product; the coupling occurs smoothly in mild conditions at room temperature to give a five-membered azametallacycle.

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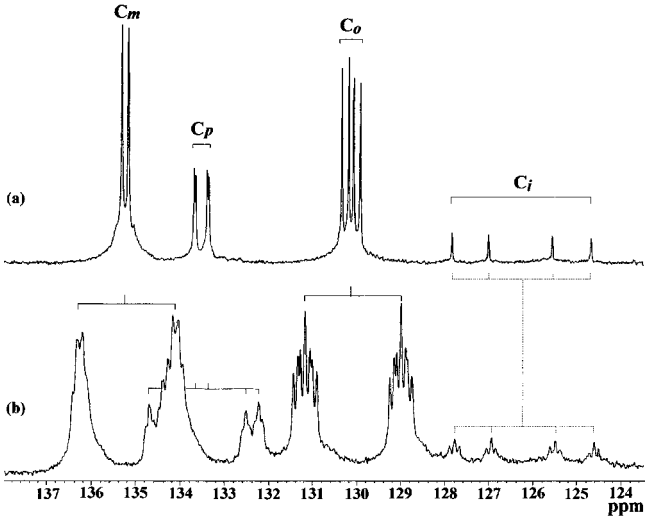



**Figure 2.** (*a*) $^{13}C\{^1H\}$ NMR and (*b*) $^{13}C$ NMR spectra (phenyl region) of *cis*-[Pt{NH=C(ON=$CC_4H_8$)$NMe_2$}$(PPh_3)_2$][$BF_4$]$_2$ **4a2** in $CD_2Cl_2$.

In the IR spectra of compounds **3** (KBr pellet), the bands at ca. 2260, ca. 3300, and 1630 $cm^{-1}$ are assigned to $\nu$(N≡C) of the cyanamide ligand (values similar to those of compounds **1** and **2**), $\nu$(OH), and $\nu$(N=C)/$\delta$(OH) of the ligating oxime, respectively. In their $^1H$ NMR spectra, the low field ($\delta$ ca. 10) resonance of the OH group is diagnostic[24] for coordinated oxime. The $^{31}P\{^1H\}$ NMR spectra present two well-separated doublets with corresponding $^{195}Pt$ satellites (see below).

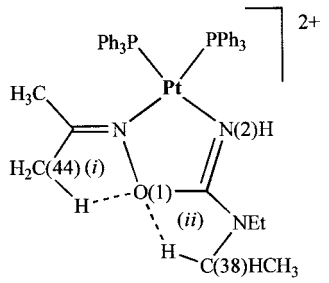
The IR spectra of all compounds **4** show one strong and broad band in the 1640−1620 $cm^{-1}$ range which is assigned to unresolved $\nu$(N=C) of the chelated ligand, as well as a weak band at 3420−3400 $cm^{-1}$ attributable to $\nu$(NH). Their $^1H$ NMR spectra show the NH resonance as a broad singlet at $\delta$ ca. 4.2, flanked by $^{195}Pt$ satellites ($^2J_{PtH}$ ca. 63 Hz); intermolecular exchange of this proton with added $D_2O$ supported this attribution. As expected, the two methyl groups of the N=$CMe_2$ moiety in **4a1** and **4b1** are nonequivalent as a result of rotational hindrance about the CN double bond. The four distinct resonances and their splittings also reveal the nonequivalency of the methylene groups of **4a2**.

In the $^{13}C\{^1H\}$ and $^{13}C$ NMR spectra (the latter available as Supporting Information), the two low field resonances ($\delta$ 182−195 and 168−163) are assigned to the two N=C groups associated to the metallacycle. The complex phenyl-carbon resonances, as observed for compounds **1**, appear as two sets of multiplets (in accord with the nonequivalency of the two phosphines) which were clearly assigned to the various types of aromatic carbons (Figure 2 for **4a2**).

The $^{31}P\{^1H\}$ NMR spectra of compounds **4** exhibit the expected pair of doublets (with $^{195}Pt$ satellites) and their formation via the corresponding intermediate **3** was monitored by this technique. The $^{195}Pt$ spectra of those compounds show a clear doublet of doublets [$^1J(PtP_A) = 3396$, $^1J(PtP_B) = 3709$ Hz].

The crystal structures of **4a1** and **4b1** were determined by X-ray diffraction analyses, and the molecular structures of the corresponding cationic complexes are depicted in Figure 3. Crystallographic data are presented in Table 1 and selected bond distances and angles are given in Table 2. In these compounds, the platinum ion shows the typical square-planar coordination geometry and belongs to the five-membered ring, which includes the NC and the ON groups of the alkylcyanamide and of the oxime, respectively. This ring is planar and contains a localized C=N double bond, without $\pi$-electron delocalization. In fact, the two C=N distances of the iminoacyl ligands are identical and typical for the double bonds. It appears that the bidentate coordination of the iminoacylated species observed in the present study does not affect the C=N and N−O bond lengths as compared to *trans*-[$PtCl_4${NH=C(Me)ON=CRR′}$_2$][25] where such species are monodentate ligands. This is in accord with what has been reported[24] for the related five-membered azametallacyclic Rh complexes. The N−Pt−N bond angles of 74−75° are smaller, as expected, than those known for the six-[15] or the seven-membered rings[59] [ca. 85° or ca. 92°, correspondingly] in *cis*-[$(PPh_3)_2$Pt{NHC(OMe)=NC$(NH_2)$=NH}][$BPh_4$] and [Pt(NH=C(Ph)NHC$H_2$C$H_2$N$H_2)_2$][$SbF_6$]$_2$. In **4a1** and **4b1**, the Pt−P and the Pt−N(H) bond lengths are comparable to those[15] of the former metallacycle, but the Pt−N(O) distances are slightly longer conceivably due to steric reasons and/or the high electronegativity of the adjacent oxygen atom.

The data obtained for **4b1** indicate the existence of two weak (i and ii see **a**) intramolecular hydrogen bonds between the oxygen, O(1), of the ring and the exocyclic alkylidene [one hydrogen of one methyl unit, C(44)−H] and amide groups [one methylene hydrogen, i.e., C(38)−H]. They lead to two five-membered rings involving two nonmetallic sides of the azametallacycle, and the relevant structural parameters are as follows: (i) for the alkylidene group, the C(44)···O(1), C(44)−H and H···O(1) distances are 2.567(15), 0.95 and 2.09 Å, respectively, and the C(44)−H···O(1) angle is 109.0°; (ii) for the amide group and the oxygen of the ring, O(1), the C(38)···O(1), C(38)−H, and H···O(1) distances are 2.58(3), 1.02, and 2.17 Å, correspondingly, and the C(38)−H···O(1) angle is 101.5°. These values are comparable with those reported for H-bonding between the NH and the imine or amine groups of the iminoacylated ligands in complexes [$PtCl_4$(NH=C(Me)-ON=CR′R″)$_2$] [R′R″ = $Me_2$ or {$C_5H_{10}$}][25] and *trans*-[$PtCl_4$-{NH=C(Me)ON$Et_2$}$_2$].[60]




(**a**)

## Concluding Remarks

This study reports a novel type of activation of organocyanamides ($NCNR_2$) by showing that, despite the electron-releasing character of their $NR_2$ moiety, the cyano group can be activated toward nucleophilic addition (even by a weak nucleophile such as an oxime) by the combined cyano-coordination to a Pt(II) center and catalytic adduct formation of a metal ion Lewis-acid with the amido group thus hampering the electron donation of this group to the cyano center. This

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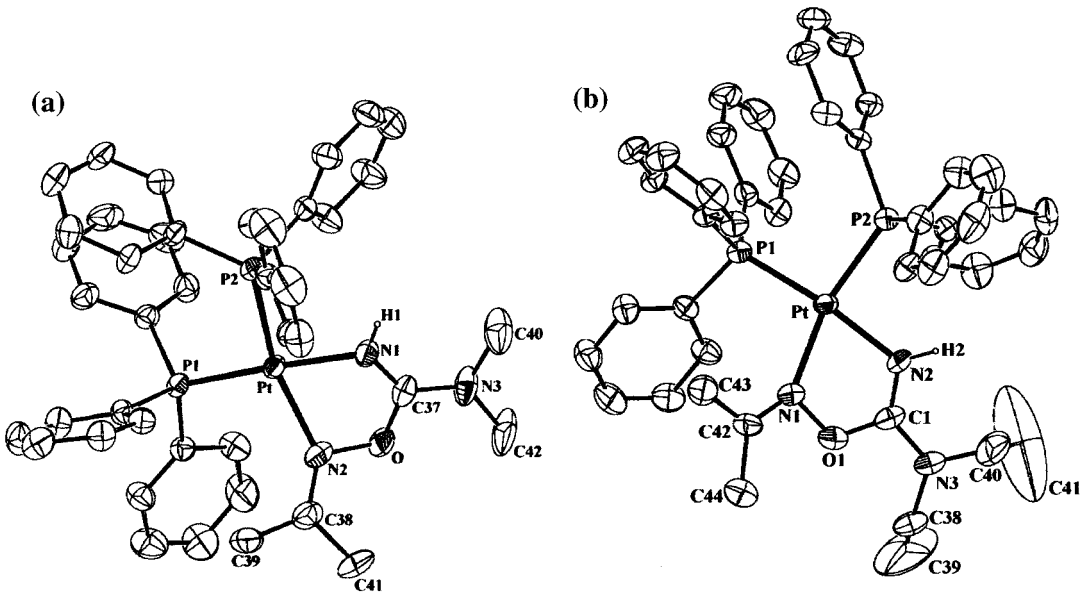


**Figure 3.** Molecular structures of the cationic complexes (*a*) *cis*-[Pt{NH=C(ON=CMe$_2$)NMe$_2$}(PPh$_3$)$_2$][BF$_4$]$_2$ **4a1** and (*b*) *cis*-[Pt{NH=C(ON=CMe$_2$)NEt$_2$}(PPh$_3$)$_2$][BF$_4$]$_2$ **4b1**.

bifunctional mode of activation of organocyanamides is expected to be extended to a variety of nucleophiles other than oximes.

The reaction is also assisted by the driving effect of chelation of the iminoacylated product, and further stabilization of the derived azametallacycle can be achieved by intramolecular H-bonding. Hence, by taking advantage of the properties and the proximity of the various functional groups of the substrates (NC, NR$_2$, and {NO}), via the combined effects of the cyano-ligating Pt(II) site, of the amido-ligating $Ag^+$ or $Cu^{2+}$ ion (even in catalytic amount) and of the coordinating ability of the imido nitrogen of the oxime-derived moiety, a novel type of reaction involving coupling of a cyanamide with an oxime was achieved. This reaction also constitutes a simple route to the synthesis, under mild conditions, of heterometallacycles and shows, for the first time, that organocyanamides, with oximes, can be convenient starting materials for such species, in particular, of the new amino-functionalized five-membered azametallacycle type.

## Experimental Section

All reactions were carried out in the absence of air using standard vacuum and inert gas flow techniques. Solvents were purified by standard procedures. IR spectra were recorded on Perkin-Elmer 683 or Bio-Rad FTS 3000 MX spectrophotometers and were run in KBr pellet or in Nujol mull (values in cm$^{-1}$; intensity of bands are referred as w = weak, m = medium, s = strong, vs = very strong, or br = broad). $^1$H, $^{31}$P{$^1$H}, $^{195}$Pt, $^{13}$C{$^1$H}, or $^{13}$C NMR spectra were recorded on a Varian Unity 300 spectrometer [$\delta$ values in ppm relative to SiMe$_4$ ($^1$H and $^{13}$C), P(OMe)$_3$ ($^{31}$P), or Na$_2$[PtCl$_6$] (by using K$_2$[PtCl$_4$], $\delta$ = −1630 ppm, as a standard) ($^{195}$Pt), at ambient temperature]. The $^{13}$C NMR data are not included but are available in Supporting Information. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets. The fast-atom bombardment (FAB) mass spectrometric measurements were performed on a Trio 2000 instrument and the positive-ion FAB spectra were obtained by bombarding 3-nitrobenzyl alcohol (NOBA) matrixes of the samples with 8 keV xenon atoms. Mass calibration for the data acquisition system was achieved using CsI. The complex *cis*-[PtCl$_2$(PPh$_3$)$_2$] was prepared by a published method,[38] whereas other reagents were purchased from Aldrich.

**Syntheses of *cis*-[PtCl(NCNR$_2$)(PPh$_3$)$_2$][BF$_4$] [R = Me (1a) or Et (1b)].** The general procedure followed in the synthesis of complexes **1** involved stirring of a solution of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (0.10 g, 0.13 mmol) in CH$_2$Cl$_2$ (10 mL), at room temperature for 2 h, with equimolar amounts of the appropriate dialkylcyanamide NCNR$_2$ (10.4 or 15.1 $\mu$L for R = Me or Et, respectively) and Ag[BF$_4$] (0.13 mmol, 0.60 mL of a 0.22 M acetone solution). A gray suspension was formed, the solution was filtered, and the filtrate was concentrated in a vacuum. Addition of Et$_2$O led to the precipitation of complex **1a** or **1b** as a white solid, which was separated by filtration, washed with Et$_2$O, and dried in a vacuum. Yield ca. 85% (ca. 0.095 or 0.10 g for **1a** or **1b**, respectively).

**1a.** IR (KBr pellet): 2275 [s, $\nu$(NC)], 1100 [s, br, $\nu$(BF)], ca. 305 [m, $\nu$(PtCl)]. $^1$H NMR (CDCl$_3$): $\delta$ 7.45−7.15 (m, 30H, P*Ph*$_3$), 2.58 (s, 6H, C*H*$_3$). $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 135.31 [d, $^3J_{CP}$ = 10.2 Hz, C$_m$ (PPh$_3$)], 134.54 [d, $^3J_{CP}$ = 10.8 Hz, C$_{m'}$ (PPh$_3$)], 132.94 [d, $^4J_{CP}$ = 2.1 Hz, C$_p$ (PPh$_3$)], 132.43 [d, $^4J_{CP}$ = 2.2 Hz, C$_{p'}$ (PPh$_3$)], 129.66 [d, $^2J_{CP}$ = 11.8 Hz, C$_o$ (PPh$_3$)], 128.99 [d, $^2J_{CP}$ = 11.8 Hz, C$_{o'}$ (PPh$_3$)], 127.69 [d, $^1J_{CP}$ = 64.6 Hz, C$_i$ (PPh$_3$)], 127.66 [d, $^1J_{CP}$ = 68.9 Hz, C$_{i'}$ (PPh$_3$)], 122.20 (s, br, N≡*C*), 40.01 (s, *C*H$_3$). $^{31}$P{$^1$H} NMR: $\delta$ −130.7 (d, $^2J_{PP}$ = 18.5 Hz, $^1J_{PPt}$ = 3553.1 Hz), −136.8 (d, $^2J_{PP}$ = 18.5 Hz, $^1J_{PPt}$ = 3800.0 Hz). $^{195}$Pt NMR: $\delta$ −4409.3 (dd). Anal. Calcd for C$_{39}$H$_{36}$N$_2$BClF$_4$P$_2$Pt·$^1/_4$CH$_2$Cl$_2$: C, 50.5; H, 3.9; N, 3.0. Found: C, 50.5; H, 4.2; N, 3.6. FAB MS: *m*/*z* 825 [*M*]$^+$ and 755 [*M* − NCNMe$_2$]$^+$.

**1b.** IR (Nujol mull): 2260 [s, $\nu$(NC)] 1100 [s, br, $\nu$(BF)], ca. 305 [m, $\nu$(PtCl)]. $^1$H NMR (CDCl$_3$): $\delta$ 7.48−7.20 (m, 30H, P*Ph*$_3$), 2.85 (q, $^3J_{HH}$ = 7.2 Hz, 4H, C*H*$_2$CH$_3$), 0.99 (t, $^3J_{HH}$ = 7.2 Hz, 6H, CH$_2$C*H*$_3$). $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 135.21 [d, $^3J_{CP}$ = 10.2 Hz, C$_m$ (PPh$_3$)], 134.61 [d, $^3J_{CP}$ = 10.8 Hz, C$_{m'}$ (PPh$_3$)], 132.95 [d, $^4J_{CP}$ = 2.7 Hz, C$_p$ (PPh$_3$)], 132.46 [d, $^4J_{CP}$ = 2.7 Hz, C$_{p'}$ (PPh$_3$)], 129.65 [d, $^2J_{CP}$ = 11.3 Hz, C$_o$ (PPh$_3$)], 129.02 [d, $^2J_{CP}$ = 11.8 Hz, C$_{o'}$ (PPh$_3$)], 127.73 [d, $^1J_{CP}$ = 64.6 Hz, C$_i$ (PPh$_3$)], 127.64 [d, $^1J_{CP}$ = 68.9 Hz, C$_{i'}$ (PPh$_3$)], 122.46 (s, br, N≡*C*), 46.50 (s, *C*H$_2$CH$_3$), 13.49 (s, CH$_2$*C*H$_3$). $^{31}$P{$^1$H} NMR: $\delta$ −131.3 (d, $^2J_{PP}$ = 18.5 Hz, $^1J_{PPt}$ = 3528.6 Hz), −135.9 (d, $^2J_{PP}$ = 18.5 Hz, $^1J_{PPt}$ = 3807.6 Hz). $^{195}$Pt NMR: $\delta$ −4403.7 (dd). Anal. Calcd for C$_{41}$H$_{40}$N$_2$BClF$_4$P$_2$Pt·$^1/_4$CH$_2$Cl$_2$: C, 51.5; H, 4.3; N, 2.9. Found: C, 51.3; H, 4.2; N, 3.5. FAB MS: *m*/*z* 755 [*M* − NCNEt$_2$]$^+$ (*M*$^+$, calcd 853).

**Syntheses of *cis*-[Pt(NCNR$_2$)$_2$(PPh$_3$)$_2$][BF$_4$]$_2$ [R = Me (2a) or Et (2b)]. Method A, from *cis*-[PtCl$_2$(PPh$_3$)$_2$].** Complexes **2** were prepared by adding the appropriate dialkylcyanamide NCNR$_2$ in a 6-fold molar ratio [62 $\mu$L, 0.78 mmol (R = Me); 91 $\mu$L, 0.78 mmol (R = Et$_2$)] and Ag[BF$_4$] in a 2-fold ratio (0.26 mmol, 1.2 mL of a 0.22 M acetone solution) to a solution of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (0.10 g, 0.13 mmol), and the mixture was left stirring for ca. 5 h at room temperature. A gray suspension was formed. The solution was filtered, and the filtrate was concentrated in a vacuum. Addition of Et$_2$O led to the precipitation of

the corresponding complex **2** as a white solid, which was separated by filtration, washed with $Et_2O$, and dried in a vacuum. Yield ca. 65% (ca. 0.085 or 0.090 g for **2a** or **2b**, respectively).

**Method B, from 1a or 1b.** The stirring of a $CH_2Cl_2$ solution (10 mL) of **1a** (0.050 g, 0.055 mmol) or **1b** (0.040 g, 0.043 mmol), at room temperature for 2 h, with the appropriate dialkylcyanamide $NCNR_2$ [4.4 $\mu$L, 0.055 mmol (R = $Me_2$) or 4.9 $\mu$L, 0.043 mmol (R = $Et_2$)] and $Ag[BF_4]$ [0.055 mmol, 0.25 mL (R = $Me_2$) or 0.044 mmol, 0.20 mL (R = $Et_2$) of a 0.22 M acetone solution] led to the formation of a gray suspension which was isolated by filtration and discarded. The filtrate was then concentrated in a vacuum, and upon addition of $Et_2O$, the corresponding complex **2** precipitated as a white solid. Yield ca. 90% (0.050 or 0.040 g for **2a** or **2b**, respectively).

Crystallization by slow diffusion of diethyl ether over a solution of **2b** in dichloromethane produced white crystals suitable for X-ray crystallographic analysis.

**2a.** IR (Nujol mull): 2260 [s, br, $\nu$(NC)]. $^1$H NMR ($CDCl_3$): $\delta$ 7.53−7.32 (m, 30H, P*Ph*$_3$), 2.61 (s, 12H, C*H*$_3$). $^{13}$C{$^1$H} ($CD_2Cl_2$): $\delta$ 135.19 [m, $C_m$ ($PPh_3$)], 133.40 [s, $C_p$ ($PPh_3$)], 129.99 [m, $C_o$ ($PPh_3$)], 126.60 [d, $^1J_{CP}$ = 68.9 Hz, $C_i$ ($PPh_3$)], 123.60 (s, br, N≡*C*), 39.97 (s, *C*H$_3$). $^{31}$P{$^1$H} NMR: $\delta$ −138.6 (s, $^1J_{PPt}$ = 3698.5 Hz). $^{195}$Pt NMR: $\delta$ −4379.6 (t, br). Anal. Calcd for $C_{42}H_{42}N_4B_2F_8P_2Pt$: C, 48.8; H, 4.1; N, 5.4. Found: C, 48.4; H, 4.1; N, 5.5. FAB MS: *m*/*z* 878 [*M* + F]$^+$ and 808 [*M* + F − $NCNMe_2$]$^+$ (*M*$^+$, calcd 859).

**2b.** IR (Nujol mull): 2250 [s, br, $\nu$(NC)]. $^1$H NMR ($CDCl_3$): $\delta$ **7**.60−7.38 (m, 30H, P*Ph*$_3$), 2.92 (q, $^3J_{HH}$ = 7.3 Hz, 8H, C*H*$_2$CH$_3$), 0.99 (t, $^3J_{HH}$ = 7.3 Hz, 12H, CH$_2$C*H*$_3$). $^{13}$C{$^1$H} ($CD_2Cl_2$): $\delta$ 135.14 [m, $C_m$ ($PPh_3$)], 133.44 [s, $C_p$ ($PPh_3$)], 130.03 [m, $C_o$ ($PPh_3$)], 126.29 [d,$^1J_{CP}$ = 68.9 Hz, $C_i$ ($PPh_3$)], 121.28 (s, br, N≡*C*), 46.28 (s, *C*H$_2$CH$_3$), 13.18 (s, CH$_2$*C*H$_3$). $^{31}$P{$^1$H} NMR: $\delta$ −138.6 (s, $^1J_{PPt}$ = 3706.0 Hz). $^{195}$Pt NMR: $\delta$ −4375.7 (t, br). Anal. Calcd for $C_{46}H_{50}N_4B_2F_8P_2Pt$: C, 50.7; H, 4.6; N, 5.1. Found: C, 51.0; H, 4.6; N, 5.0. FAB MS: *m*/*z* 836 [*M* + F − $NCNEt_2$]$^+$ (*M*$^+$, calcd 915).

**Syntheses of *cis*-[Pt(NCNEt$_2$)(HON=CR′R″)(PPh$_3$)$_2$][BF$_4$]$_2$ [R′R″ = Me$_2$ (3b1) or C$_4$H$_8$ (3b2)] and of *cis*-[Pt(NCNMe$_2$)(HON=CMe$_2$)(PPh$_3$)$_2$][BF$_4$]$_2$ (3a1).** A solution of *cis*-[Pt($NCNEt_2$)$_2$($PPh_3$)$_2$][$BF_4$]$_2$ **2b** (0.070 g, 0.064 mmol) with a 2-fold excess of the appropriate oxime [9.4 mg, 0.130 mmol (R′R″ = $Me_2$) or 12.7 mg, 0.130 mmol (R′R″ = $C_4H_8$)] and of $Ag[BF_4]$ (0.13 mmol, 0.57 mL of a 0.23 M acetone solution) in $CH_2Cl_2$ (10 mL) was stirred for ca. 12 h at room temperature. A gray suspension was formed. After the silver salts were filtered off, concentration of the filtered mother solution in a vacuum and addition of $Et_2O$ led to the precipitation of **3b1** or **3b2** as a pale gray solid which was isolated by filtration, washed with $Et_2O$, dried in a vacuum, and then recrystallized from $CH_2Cl_2$/$Et_2O$ to give a white solid. Yield ca. 90% (ca. 0.060 or 0.063 g for **3b1** or **3b2**, respectively).

When a similar procedure was followed for complex **2a**, the reaction proceeded to the formation of the final compounds **4** (see below). However, the formation of **3a1** and its subsequent conversion into **4a1** were monitored by $^{31}$P{$^1$H} NMR.

**3b1.** IR (KBr pellet): 2260 [s, $\nu$(N≡C)], 3309 [vs, br, $\nu$(OH)], 1630 [m, $\nu$(N=C)]. $^1$H NMR ($CDCl_3$): $\delta$ 10.14 (s, br, 1H, O*H*), 7.71−7.38 (m, 30H, P*Ph*$_3$), 2.84 (q, $^3J_{HH}$ = 7.4 Hz, 4H, NCN(C*H*$_2$CH$_3$)$_2$), 2.63 (s, 3H, C*H*$_3$ oxime), 1.54 (s, 3H, C*H*$_3$ oxime), 0.86 (t, $^3J_{HH}$ = 7.4 Hz, 4H, NCN(CH$_2$C*H*$_3$)$_2$). $^{31}$P{$^1$H} NMR: $\delta$ −135.2 (d, $^1J_{PPt}$ = 3872.7 Hz, $^2J_{PP}$ = 20.4 Hz), −143.6 (d, $^1J_{PPt}$ = 3200.4 Hz, $^2J_{PP}$ = 21.4 Hz).

**3b2.** IR (KBr pellet): 2265 [s, $\nu$(N≡C)], 3300 [vs, br, $\nu$(OH], 1629 [m, $\nu$(N=C)]. $^1$H NMR ($CDCl_3$): $\delta$ 10.19 (s, br, 1H, O*H*), 7.71−7.43 (m, 30H, P*Ph*$_3$), 2.85 (q, $^3J_{HH}$ = 7.4 Hz, 4H, NCN(C*H*$_2$CH$_3$)$_2$, 1.75 (s, br, 8H, C*H*$_2$ oxime), 0.86 (t, $^3J_{HH}$ = 7.4 Hz, 4H, NCN(CH$_2$C*H*$_3$)$_2$). $^{31}$P{$^1$H} NMR: $\delta$ −134.9 (d, $^1J_{PPt}$ = 3881.9 Hz, $^2J_{PP}$ = 21.4 Hz), −143.5 (d, $^1J_{PPt}$ = 3164.5 Hz, $^2J_{PP}$ = 21.4 Hz). Anal. Calcd for $C_{46}H_{49}N_3B_2F_8OP_2Pt$: C, 50.6; H, 4.5; N, 3.9. Found: C, 49.9; H, 4.5; N, 3.9. FAB MS: *m*/*z* 935 [*M* + F]$^+$, 916 [*M*]$^+$ and 818 [*M* − $NCNEt_2$]$^+$ or [*M* − HON=C($C_4H_8$)]$^+$.

**3a1.** $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ −135.2 (d, $^1J_{PPt}$ = 3887.7 Hz, $^2J_{PP}$ = 18.1 Hz), −143.8 (d, $^1J_{PPt}$ = 3197.1 Hz, $^2J_{PP}$ = 20.3 Hz).

**Syntheses of *cis*-[Pt(NH=C(ON=CR′R″)NMe$_2$)(PPh$_3$)$_2$][BF$_4$]$_2$ [R′R″ = Me$_2$ (4a1) or C$_4$H$_8$ (4a2)] and *cis*-[Pt(NH=C(ON=CR′R″)-NEt$_2$)(PPh$_3$)$_2$][BF$_4$]$_2$ [R′R″ = Me$_2$ (4b1) or C$_4$H$_8$ (4b2)].** The general procedure for obtaining compounds **4a** consists of the addition, to a solution of *cis*-[Pt($NCNMe_2$)$_2$($PPh_3$)$_2$][$BF_4$]$_2$ **2a** (0.10 g, 0.097 mmol) in $CH_2Cl_2$ (10 mL), of $Ag[BF_4]$ (0.097 mmol, 0.44 mL of a 0.22 M acetone solution) followed (upon stirring the mixture for some minutes at room temperature) by the addition of the appropriate oxime HON=CR′R″ [0.014 g (R′R″ = $Me_2$) or 0.019 g (R′R″ = $C_4H_8$), 0.19 mmol]. The mixture was left stirring at room temperature for 2 h. The solid (containing silver salts) was filtered off, and the solution was concentrated in a vacuum. Dropwise addition of *n*-pentane led to the formation of a pale gray oil. Isolation of this oily residue by decantation of the supernatant solution, addition of *n*-pentane followed by application of the freeze−thaw technique, and vigorous stirring resulted in the formation of a pale gray powder of the corresponding compound **4a** which was filtered off, washed with *n*-pentane, dried in a vacuum, and recrystallized from $CH_2Cl_2$/$Et_2O$ to give a white solid. Yield ca. 70% (0.070 g for **4a1** and 0.075 g for **4a2**).

The preparative reaction can also be performed by using a catalytic amount of $Ag[BF_4]$ or $Cu(CH_3COO)_2$·$H_2O$ (ca. 10% relative to the starting Pt complex) instead of the stoichiometric amount of $Ag[BF_4]$ mentioned above. It is then completed after ca. 2 h or within a few minutes, with the silver(I) or the copper(II) catalyst, respectively, as indicated by monitoring the reaction solution by $^{31}$P{$^1$H} NMR.

Compound **4b1** was obtained by reacting *cis*-[Pt($NCNEt_2$)(HON=$CMe_2$)($PPh_3$)$_2$][$BF_4$]$_2$ **3b1** (0.060 g, 0.056 mmol) in $CH_2Cl_2$ (10 mL) with an excess (1:4) of the oxime (0.016 g, 0.219 mmol) and $Ag[BF_4]$ (0.12 mmol, 0.50 mL of a 0.23 M acetone solution). The mixture was stirred for ca. 24 h at room temperature and became gray. The silver salts were filtered off, and the solution concentrated in a vacuum. $Et_2O$ was added and the product **4b1** was obtained as a pale gray solid which was filtered off, washed with $Et_2O$, dried in a vacuum, and then recrystallized from $CH_2Cl_2$/$Et_2O$ to give a white solid. Yield ca. 85% (0.052 g).

Compound **4b2** was obtained by reacting *cis*-[Pt($NCNEt_2$)$_2$($PPh_3$)$_2$]-[$BF_4$]$_2$ **2b** with an excess of the oxime and $Ag[BF_4]$, in $CDCl_3$, a reaction that was only performed in the NMR tube and monitored by $^{31}$P-{$^1$H} NMR. The formation of the intermediate **3b2** was also observed.

Crystallization by slow diffusion of diethyl ether into a solution of **4a1** or **4b1** in dichloromethane produced white crystals suitable for X-ray crystallographic analysis.

**4a1.** IR (KBr pellet): 3390 [w, $\nu$(NH)], 1650−1620 [vs, br, $\nu$(N=C), $\delta$(NH)], 540 [m, $\delta$ ($PPh_3$)]. $^1$H NMR ($CDCl_3$): $\delta$ 7.99−7.40 (m, 30H, P*Ph*$_3$), 4.29 (s, $^2J_{HPt}$ = 63.0 Hz, 1H, N*H*), 3.21 [s, br, 6H, NH=C(ON=C*Me*$_2$)*Me*$_2$], 2.08 [s, 3H, NH=C(ON=C*Me*$_2$)Me$_2$], 1.68 [s, 3H, NH=C(ON=C*Me*$_2$)Me$_2$]. $^{13}$C{$^1$H} NMR: $\delta$ 182.28 [s, br, NH=*C*(ON=CMe$_2$)Me$_2$], 167.87 [s, NH=C(ON=*C*Me$_2$)Me$_2$], 135.35 [d, $^3J_{CP}$ = 11.3 Hz, $C_m$ ($PPh_3$)], 134.76 [d, $^3J_{CP}$ = 10.7 Hz, $C_{m'}$ ($PPh_3$)], 133.41 [d, $^4J_{CP}$ = 2.7 Hz, $C_p$ ($PPh_3$)], 133.01 [d, $^4J_{CP}$ = 2.6 Hz, $C_{p'}$ ($PPh_3$)], 130.16 [d, $^2J_{CP}$ = 11.8 Hz, $C_o$ ($PPh_3$)], 129.96 [d, $^2J_{CP}$ = 11.8 Hz, $C_{o'}$ ($PPh_3$)], 126.90 [d, $^1J_{CP}$ = 62.5 Hz, $C_i$ ($PPh_3$)], 125.10 [d, $^1J_{CP}$ = 66.3 Hz, $C_{i'}$ ($PPh_3$)], 37.05 [s, NH=C(ON=CMe$_2$)*Me*$_2$], 36.53 [s, NH=C(ON=CMe$_2$)*Me*$_2$], 27.76 [s, NH=C(ON=C*Me*$_2$)Me$_2$], 20.97 [s, NH=C(ON=C*Me*$_2$)Me$_2$]. $^{31}$P{$^1$H} NMR: $\delta$ −138.0 (d, $^1J_{PPt}$ = 3439.3 Hz, $^2J_{PP}$ = 25.6 Hz), −141.0 (d, $^1J_{PPt}$ = 3692.6 Hz, $^2J_{PP}$ = 25.6 Hz). $^{195}$Pt NMR: $\delta$ −4279.7 (dd, $^1J_{PtPA}$ = 3395.9 Hz, $^1J_{PtPB}$ = 3708.7 Hz). Anal. Calcd for $C_{42}H_{43}N_3B_2F_8OP_2Pt$: C, 48.7; H, 4.2; N 4.1. Found: C, 48.6; H, 4.2; N, 4.0. FAB MS: *m*/*z* 881 [*M* + F]$^+$, 808 [*M* + F − HON=$CMe_2$]$^+$ and 789 [*M* − HON=$CMe_2$]$^+$ (*M*$^+$, calcd 862).

**4a2.** IR (KBr pellet): 3390 [w, $\nu$(NH)], 1650−1620 [vs, br, $\nu$(N=C), $\delta$(NH)], 540 [m, $\delta$(PPh$_3$)]. $^1$H NMR ($CDCl_3$): $\delta$ 7.81−7.35 (m, 30H, P*Ph*$_3$), 4.12 (s, $^2J_{HPt}$ = 64.2 Hz, 1H, N*H*), 3.13 [t, br, 6H, NH=C(ON=C{$C_4H_8$})*Me*$_2$], 2.71 [t, 2H, $^3J_{HH}$ = 7.4 Hz, NH=C(ON=C{$C_4H_8$})Me$_2$], 1.88 [t, 2H, $^3J_{HH}$ = 7.1 Hz, NH=C(ON=C{$C_4H_8$})-Me$_2$], 1.59 [q, 2H, $^3J_{HH}$ = 6.9 Hz, NH=C(ON=C{$C_4H_8$})Me$_2$], 1.12 [q, 2H, $^3J_{HH}$ = 6.9 Hz, NH=C(ON=C{$C_4H_8$})Me$_2$]. $^{13}$C{$^1$H} NMR: $\delta$ 194.75 [d, $^3J_{CPtrans}$ = 4.3 Hz, $^2J_{CPt}$ = 49.6 Hz, NH=*C*(ON=C{$C_4H_8$})-Me$_2$], 162.68 [s, NH=C(ON=*C*{$C_4H_8$})Me$_2$], 135.23 [d, $^3J_{CP}$ = 10.8 Hz, $C_m$ ($PPh_3$)], 133.66 [d, $^4J_{CP}$ = 2.7 Hz, $C_p$ ($PPh_3$)], 133.36 [d, $^4J_{CP}$ = 3.2 Hz, $C_{p'}$ ($PPh_3$)], 130.28 [d, $^2J_{CP}$ = 11.9 Hz, $C_o$ ($PPh_3$)], 130.01 [d, $^2J_{CP}$ = 11.3 Hz, $C_{o'}$ ($PPh_3$)], 127.43 [d, $^1J_{CP}$ = 62.5 Hz, $C_i$ ($PPh_3$)], 125.13 [d, $^1J_{CP}$ = 66.8 Hz, $C_{i'}$ ($PPh_3$)], 40.00 [s, br, NH=C(ON=

C{$C_4H_8$})$Me_2$], 38.20 [s, br, NH=C(ON=C{$C_4H_8$})$Me_2$], 36.70 [s, NH=C(ON=C{$C_4H_8$})$Me_2$], 35.41 [s, NH=C(ON=C{$C_4H_8$})$Me_2$], 25.08 [s, NH=C(ON=C{$C_4H_8$})$Me_2$], 24.08 [s, NH=C(ON=C{$C_4H_8$})-$Me_2$]. $^{31}P\{^1H\}$ NMR: $\delta$ −138.4 (d, $^1J_{PPt}$ = 3382.5 Hz, $^2J_{PP}$ = 26.7 Hz), −140.1 (d, $^1J_{PPt}$ = 3721.5 Hz, $^2J_{PP}$ = 25.7 Hz). Anal. Calcd for $C_{44}H_{45}N_3B_2F_8OP_2Pt$: C, 49.7; H, 4.2; N, 4.0. Found: C, 49.2; H, 4.6; N, 4.5. FAB MS: *m*/*z* 907 [*M* + F]$^+$, 888 [*M*]$^+$ and 808 [*M* + F − HON=C($C_4H_8$)]$^+$.

**4b1.** IR (KBr pellet): 3420 [w, $\nu$(NH)], 1627 [vs, br, $\nu$(N=C), $\delta$-(NH)], 540 [m, $\delta$($PPh_3$)]. $^1H$ NMR ($CDCl_3$): $\delta$ 7.82−7.38 (m, 30H, P*Ph*$_3$), 4.26 (s, $^2J_{HPt}$ = 61.5 Hz, 1H, N*H*), 3.48 [s, br, 2H, NH=C(ON=CMe$_2$)*Et*$_2$], 2.78 [s, br, 3H, NH=C(ON=C*Me*$_2$)Et$_2$], 1.25 [s, br, 3H, NH=C(ON=C*Me*$_2$)Et$_2$], 0.76 [s, br, 3H, NH=C(ON=CMe$_2$)*Et*$_2$]. $^{13}C\{^1H\}$ NMR: $\delta$ 183.15 [s, NH=*C*(ON=CMe$_2$)Et$_2$], 164.61 [s, NH=C(ON=*C*Me$_2$)Et$_2$], 135.30 [d, $^3J_{CP}$ = 10.6 Hz, $C_m$ ($PPh_3$)], 134.96 [d, $^3J_{CP}$ = 10.6 Hz, $C_{m'}$ ($PPh_3$)], 133.72 [d, $^4J_{CP}$ = 2.5 Hz, $C_p$ ($PPh_3$)], 133.33 [d, $^4J_{CP}$ = 2.5 Hz, $C_{p'}$ ($PPh_3$)], 130.27 [d, $^2J_{CP}$ = 11.7 Hz, $C_o$ ($PPh_3$)], 130.01 [d, $^2J_{CP}$ = 11.2 Hz, $C_{o'}$ ($PPh_3$)], 126.79 [d, $^1J_{CP}$ = 63.3 Hz, $C_i$ ($PPh_3$)], 125.00 [d, $^1J_{CP}$ = 67.0 Hz, $C_{i'}$ ($PPh_3$)], 46.43 [s, br, NH=C(ON=CMe$_2$)(*C*H$_2$CH$_3$)$_2$], 44.73 [s, br, NH=C(ON=CMe$_2$)(*C*H$_2$-CH$_3$)$_2$], 25.68 [s, NH=C(ON=C*Me*$_2$)Et$_2$], 16.62 [s, NH=C(ON=C*Me*$_2$)Et$_2$], 13.56 [s, NH=C(ON=CMe$_2$)(CH$_2$*C*H$_3$)$_2$], 12.24 [s, NH=C(ON=CMe$_2$)(CH$_2$*C*H$_3$)$_2$]. $^{31}P\{^1H\}$ NMR: $\delta$ −138.3 (d, $^1J_{PPt}$ = 3382.6 Hz, $^2J_{PP}$ = 26.7 Hz), −141.7 (d, $^1J_{PPt}$ = 3721.5 Hz, $^2J_{PP}$ = 25.7 Hz). Anal. Calcd for $C_{44}H_{47}N_3B_2F_8OP_2Pt$: C, 49.5; H, 4.4; N, 3.9. Found: C, 49.2; H, 4.6; N, 3.8. FAB MS: *m*/*z* 909 [*M* + F]$^+$ and 836 [*M* + F − HON=CMe$_2$]$^+$ (*M*$^+$, calcd 890).

**4b2.** $^{31}P\{^1H\}$ NMR ($CDCl_3$) : $\delta$ −138.5 (d, $^1J_{PPt}$ = 3361.2 Hz, $^2J_{PP}$ = 24.5 Hz), −140.1 (s, br, $^1J_{PPt}$ = 3716.7 Hz).

**Syntheses of *cis*-[Pt(NCR)$_2$(PPh$_3$)$_2$][BF$_4$]$_2$ [R = C$_6$H$_4$OMe-4 (5a) or Et (5b)].** Complexes **5** were prepared by adding the appropriate nitrile NCR in a 2-fold molar ratio [0.035 g, 0.26 mmol (R = $C_6H_4$-OMe-4); 18.8 $\mu$L, 0.26 mmol (R = Et)] and Ag[$BF_4$] (0.26 mmol, 0.90 mL of a 0.29 M acetone solution) to a $CH_2Cl_2$ (20 mL) solution of *cis*-[$PtCl_2(PPh_3)_2$] (0.10 g, 0.13 mmol), and the mixture left stirring for 20 h at room temperature. A gray suspension was formed. The solution was filtered, and the filtrate was concentrated in a vacuum. Addition of $Et_2O$ led to the precipitation of the corresponding complex **5** as a white solid, which was separated by filtration, washed with $Et_2O$, and dried in a vacuum. Yield ca. 55% (ca. 0.080 or 0.070 g for **5a** or **5b**, respectively).

**5a.** IR (KBr pellet): 2280 [s, $\nu$(NC)]. $^1H$ NMR ($CDCl_3$): $\delta$ 7.69−7.40 [m, 34H, P*Ph*$_3$ + H$_o$ (nitrile)], 6.84 [d, $^3J_{HH}$ = 8.7 Hz, 4H, H$_m$ (nitrile)], 3.82 (s, 6H, OC*H*$_3$); $^{13}C\{^1H\}$ ($CDCl_3$): $\delta$ 165.03 [s, $C_p$ (nitrile)], 136.25 [s, $C_o$ (nitrile)], 134.37 [m, $C_m$ ($PPh_3$)], 132.64 [s, $C_p$ ($PPh_3$)], 129.33 (m, $C_o$ ($PPh_3$)], 124,75 [dd, $^1J_{CP}$ = 78.1 and $^3J_{CP}$ = 6.8 Hz, $C_i$ ($PPh_3$)], 122.20 (s, br, N*C*), 114.80 [s, $C_m$ (nitrile)], 98.03 [s, $C_i$ (nitrile)], 55.67 (s, O*C*H$_3$). $^{31}P\{^1H\}$ NMR: $\delta$ −139.6 (s, $^1J_{PPt}$ = 3692.1 Hz). Anal. Calcd for $C_{52}H_{44}N_2B_2F_8O_2P_2Pt\cdot{}^1/_2CH_2Cl_2$: C, 52.5; H 3.7; N 2.3. Found: C, 52.7; H, 3.5; N, 2.3. FAB MS: *m*/*z* 885 [*M* − CC$_6$H$_4$-OMe + F]$^+$, 884 [*M* − NCC$_6$H$_4$OMe + 2O]$^+$ (*M*$^+$, calcd 985).

**5b.** IR (KBr pellet): 2315 [m, $\nu$(NC)]. $^1H$ NMR ($CDCl_3$): $\delta$ 7.72−7.40 (m, 30H, P*Ph*$_3$), 2.44 (q, $^3J_{HH}$ = 7.3 Hz, 4H, NCC*H*$_2$CH$_3$), 0.91 (t, br, $^3J_{HH}$ = 6.3 Hz, 6H, NCCH$_2$C*H*$_3$). $^{31}P\{^1H\}$ NMR: $\delta$ −138.0 (s, $^1J_{PPt}$ = 3694.3 Hz). Anal. Calcd for $C_{42}H_{40}N_2B_2F_8P_2Pt\cdot{}^1/_2CH_2Cl_2$: C, 48.8; H 3.9; N 2.7. Found: C, 49.0; H, 3.9; N, 2.4.

**X-ray Structure Determination of *cis*-[Pt(NCNEt$_2$)$_2$(PPh$_3$)$_2$][BF$_4$]$_2$ 2b and *cis*-[Pt{NH=C(ON=CMe$_2$)NR$_2$)(PPh$_3$)$_2$][BF$_4$]$_2$ (R = Me 4a1 or Et 4b1).** Diffraction data were collected on a Syntex P-1 (for **2b** and **4a1**) and a Enraf-Nonius CAD 4 for **4b1** diffractometers. Cell parameters were obtained from centered reflections with $\theta$ between 10° and 13°. Range of *hkl*: $h = -12$ to 0, $k = -13$ to 13, $l = -16$ to 17 (for **2b**); $h = 0$ to 11, $k = 0$ to 24, $l = -20$ to 20 (for **4a1**); and $h = -11$ to 12, $k = 0$ to 26, $l = 0$ to 22 (for **4b1**). Standard reflections were measured every 60 min and showed practically no change with time (±1%). Diffractometer data were processed by the program PROFIT[61] with profile analysis of reflections. The structures were solved by means of Fourier synthesis based upon the Pt-atom coordinates obtained from the Patterson syntheses using the SHELXTL package.[62] After that, all reflections with $I < 3\sigma(I)$ were excluded from calculations. Refinement was done by full-matrix least squares based on $F^2$ using the SHELX-97 package.[63] All non-H atoms were treated anisotropically. H atoms were located in a difference Fourier map and refined isotropically, except for the hydrogen atoms of the ethyl group in **2b** because the ethyl carbons have strong thermal vibrations and therefore hydrogens cannot be localized. An extinction correction has been applied. Lorentz, polarization, and absorption corrections were made.[64] Crystal size: 0.45 mm × 0.20 mm × 0.05 mm (for **2b**), 0.30 mm × 0.20 mm × 0.15 mm (for **4a1**), and 0.42 mm × 0.18 mm × 0.17 mm (for **4b1**). $T_{min}$ and $T_{max}$ are 0.210 and 0.706 for **2b**, 0.255 and 0.383 for **4a1**, 0.5510 and 0.5911 for **4b1**. Scattering factors are from ref 65. Crystal data are given in Table 1 and distances and angles in Table 2 (for **2b**, **4a1,** and **4b1**).

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**Supporting Information Available:** X-ray crystallographic files in CIF format for the structure determinations of *cis*-[Pt(NCNEt$_2$)$_2$-(PPh$_3$)$_2$][BF$_4$]$_2$ **2b** and *cis*-[Pt{NH=C(ON=CMe$_2$)NR$_2$)(PPh$_3$)$_2$][BF$_4$]$_2$ (R = Me **4a1** or Et **4b1**) and $^{13}C$ ($^1H$-coupled) NMR data for complexes *cis*-[PtCl(NCNR$_2$)(PPh$_3$)$_2$][BF$_4$] [R = Me (**1a**) or Et (**1b**)], *cis*-[Pt-(NCNR$_2$)$_2$(PPh$_3$)$_2$][BF$_4$]$_2$ [R = Me (**2a**) or Et (**2b**)], *cis*-[Pt(NH=C(ON=CR′R″)NMe$_2$)(PPh$_3$)$_2$][BF$_4$]$_2$ [R′R″ = Me$_2$ (**4a1**) or $C_4H_8$ (**4a2**)], *cis*-[Pt(NH=C(ON=CMe$_2$)NEt$_2$)(PPh$_3$)$_2$][BF$_4$]$_2$ (**4b1**), and *cis*-[Pt(NC-$C_6H_4$OMe-4)$_2$(PPh$_3$)$_2$][BF$_4$]$_2$ (**5a**). This material is available free of charge via Internet at http://pubs.acs.org.

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