Reactivity of [*trans*-PtH($C{\equiv}CC_5H_4N$-2)($(PPh_3)_2$] toward [*cis*-Pt($(C_6F_5)_2(thf)_2$]. Synthesis of an Unusual Triplatinum Cluster-Substituted Platinum Complex

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The complex [*trans*-PtH($C{\equiv}CR$)($(PPh_3)_2$] (**1**) (R = 2-pyridyl) reacts with [*cis*-Pt($(C_6F_5)_2(thf)_2$] under mild conditions to afford initially the 1:1 adduct [*trans,cis*-$(PPh_3)_2$(H)Pt(μ-1κC^{α}:$\eta^2{}_{\alpha,\beta}$:2κN-$C{\equiv}CC_5H_4N$-2)Pt$(C_6F_5)_2$] (**2**), which finally rearranges to form a mixture of [*cis,trans*-$(PPh_3)(C_6F_5)_2Pt^-$(μ-1κC^{α}:2κN-$C{\equiv}CC_5H_4N$-2)Pt^+(H)$(PPh_3)_2$] (**5**) (X-ray) and a tetranuclear cluster [{*cis*-Pt$(C_6F_5)_2(PPh_3)$(μ_3-1κC^{α}:2κC^{β}:3κN-$C_2C_5H_4N$-2)}{$Pt_3(C_6F_5)_2$(μ_3-3κC^{α}:$\eta^2{}_{\alpha,\beta}$:2κN-CH=CHC_5H_4N-2)$(PPh_3)_2$}] (**3**). Complex **3**, characterized crystallographically, can be described as a formal zwitterionic cationic Pt_3 cluster-substituted alkynyl platinate complex $[Pt]^-$-$C{\equiv}CC_5H_4\overline{N\text{-}2[Pt_3}]^+$ (**3A**), rather distorted. Another important feature in **3** is the presence of a vinyl group capping the Pt_3 framework. Treatment of **2** with the equimolar amount of PPh_3 allows the synthesis not only of **5** but also of the less polar isomeric complex [*trans,cis*-$(PPh_3)_2$(H)Pt(μ-1κC^{α}:2κN-$C{\equiv}CC_5H_4N$-2)Pt$(C_6F_5)_2(PPh_3)$] (**4**).

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Introduction

The coordination, activation, and subsequent transformation of unsaturated $-C{\equiv}C-$ fragments at two metal sites have been extensively investigated during the past decades.[1] Particular attention has been paid to the transformations in which vinyl and vinylidene ligands[2] are generated, not only due to their wide chemical potential but also due to their relevance as models for species postulated to be present in Fischer−Tropsch chemistry.[3] Many of these studies[1,2] have been based on direct interaction of alkynes or alkynyl reagents with a preformed bimetallic complex, but another attractive route to dinuclear complexes involves their intermediate formation by reaction of mononuclear $-C{\equiv}C-$ containing units with labile-ligand or otherwise reactive species.[2c,4] Thus, whereas hydride-alkynyl complexes of the type [Re_2(μ-H)(μ-$C{\equiv}CR$)$(CO)_7$L] (L = CO, NCMe) are formed (in some cases under severe conditions) by direct oxidative addition of terminal alkynes to metal−metal bonded rhenium carbonyls,[5] similar hetero mixed dicationic species [Cp*(PMe_3)M(μ-H)(μ-$C{\equiv}CPh$)$Pt(PPh_3)_2]^{2+}$ have been prepared (CH bond activation) by Stang and co-workers by interaction under mild

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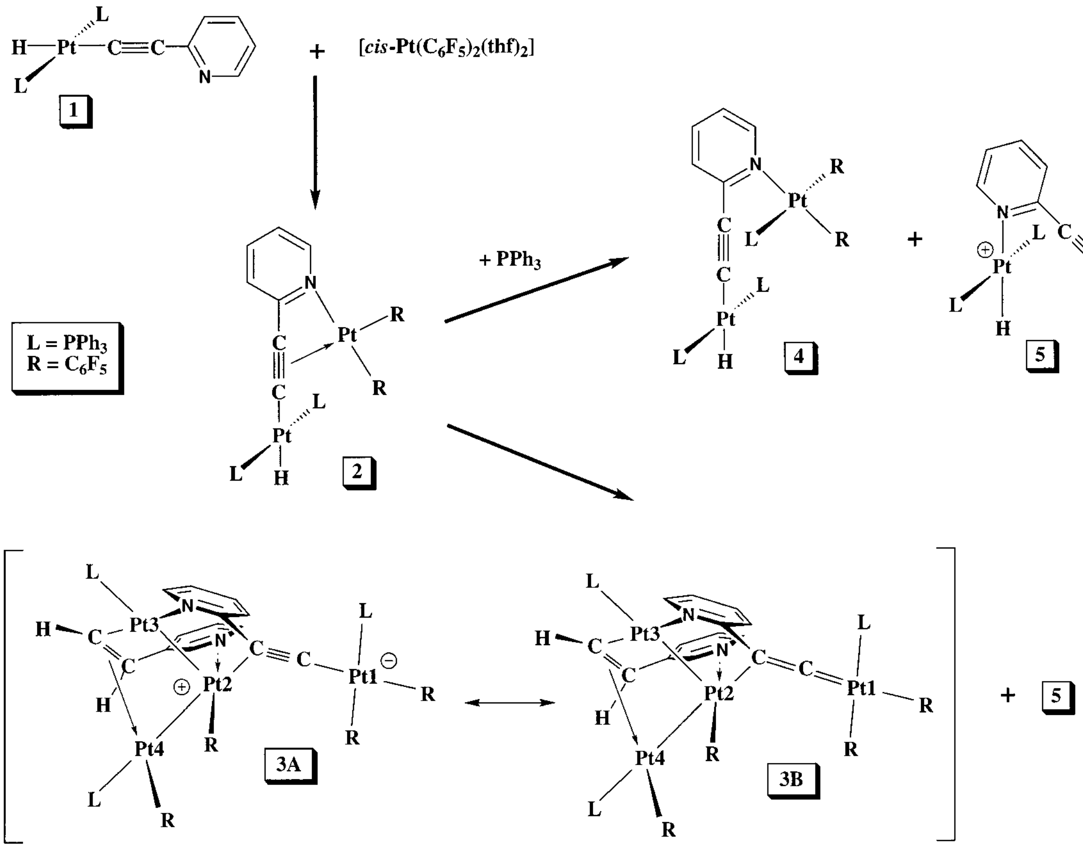
Scheme 1



conditions of [Cp*M(PMe$_3$)(OTf)$_2$] (M = Rh, Ir; OTf = triflate) with the corresponding η^2-complexed Pt(0) acetylene complex [Pt(η^2-HC≡CPh)(PPh$_3$)$_2$].[6] In this context, we have recently found a simple synthetic route to a related diplatinum complex [*trans*-(PPh$_3$)(C$_6$F$_5$)Pt(μ-H)(μ-C≡CPh)Pt(C$_6$F$_5$)(PPh$_3$)] by treatment of [*trans*-PtH(C≡CPh)(PPh$_3$)$_2$] with the solvated species [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$] (thf = tetrahydrofurane).[7] Interestingly, if [*trans*-PtH(C≡CPh)(PPh$_3$)$_2$] is treated with [*cis*-Pt(C$_6$F$_5$)$_2$(CO)(thf)], containing only one labile coordination site, the reaction takes quite another course, yielding the unexpected μ-phenylethenylidene bridging complex [*cis*,*cis*-(OC)(C$_6$F$_5$)$_2$Pt(μ-C=CHPh)Pt(PPh$_3$)$_2$].[8] Lukehart et al.[4i] have also observed that the Pt−H bond of cationic [*trans*-PtH(PEt$_3$)$_2$(acetone)]$^+$ easily adds across the C≡C triple bond of a terminal alkynyl ligand, yielding analogous complexes containing μ-alkenylidene ligands. As a continuation of this work, we have sought to determine whether other hydride alkynyl platinum complexes behave similarly.

In this contribution, we describe the very different behavior of [*trans*-PtH(C≡CR)(PPh$_3$)$_2$] (**1**) (R = 2-pyridyl) toward [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$], probably induced by the presence of one donor N atom on the aromatic ring. In this case, the expected initial adduct formed, [*trans*,*cis*-(PPh$_3$)$_2$(H)Pt(μ-1κC^{α}:$\eta^2_{\alpha,\beta}$:2κN-C≡CC$_5$H$_4$N-2)Pt(C$_6$F$_5$)$_2$] (**2**) (Scheme 1), slowly evolves in solution into a mixture of the dinuclear complex [*cis*,*trans*-(PPh$_3$)(C$_6$F$_5$)$_2$Pt$^-$(μ-1κC^{α}:2κN-C≡CC$_5$H$_4$N-2)Pt$^+$(H)(PPh$_3$)$_2$] (**5**) and the very unusual tetranuclear cluster **3**, the latter generated via formal dimerization of **2** and PPh$_3$ loss.

Results and Discussion

The hydride-alkynyl derivative [*trans*-PtH(C≡CR)(PPh$_3$)$_2$] (**1**) (R = 2-pyridyl) (see Experimental Section), prepared following a procedure similar to that employed for the preparation of other hydride σ-alkynyl platinum complexes[9] by treatment of [*trans*-PtHCl(PPh$_3$)$_2$] with 2-ethynylpyridine in the presence of NEt$_2$H and CuI as catalyst, reacts with [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$] in CH$_2$Cl$_2$ at room temperature to give instantaneously the corresponding alkyne adduct [*trans*,*cis*-(PPh$_3$)$_2$(H)Pt(μ-1κC^{α}:$\eta^2_{\alpha,\beta}$:2κN-C≡CC$_5$H$_4$N-2)Pt(C$_6$F$_5$)$_2$] (**2**) (61% isolated yield). Although the formation of **2** is not unexpected, due to the presence of the nitrogen atom on the aromatic ring (chelate effect), this result contrasts with the easy reorganization of ligands that we have observed in the reactions of other mononuclear hydride complexes [*trans*-PtHXL$_2$] (X = C≡CPh, C$_6$F$_5$, Cl; L = PPh$_3$) with [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$], yielding dinuclear derivatives stabilized by a mixed bridging system H/X.[7]

Complex **2** was characterized by elemental analysis, MS FAB(+), IR, and ^{1}H and ^{31}P NMR spectroscopy. The

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most noteworthy absorptions in the IR spectrum are two bands at 2125 and at 2012 cm^{-1} (the latter with a shoulder at 2038 cm^{-1}), which are tentatively assigned to terminal ν(Pt−H) and bridging ν(C≡C) vibrations.[10] The corresponding absorptions in **1** are seen at 2044 [ν(Pt−H)] and at 2109 cm^{-1} (ν(C≡C)]. The shift of the ν(C≡C) to lower frequencies is in accord with η^2-side-on coordination of the alkyne function, and the displacement of the ν(Pt−H) to higher frequencies is consistent with a weaker trans influence for the bridging alkynyl ligand relative to the terminal one in **1**.[10] The retention of the geometries around the platinum centers can be inferred from NMR spectroscopy. Thus, as was expected, the ^{19}F NMR spectrum of **2** displays signals due to two inequivalent C_6F_5 groups (AA′MXX′ systems). In addition, both the chemical shifts of the hydride ligand (δ −6.75) and of the phosphine ligands (δ 25.7), as well as the value of the coupling constants in **2** ($^1J_{\text{Pt-H}} = 671$ Hz; $^2J_{(\text{P-H})cis} = 13.6$ Hz; $^1J_{\text{Pt-P}} = 2898$ Hz), are very similar to those observed in **1** (δ(hydride) −6.3, $^2J_{\text{P-H}}$/$^1J_{\text{Pt-H}} = 15.5/645$ Hz; δ(P) 26.5, $^1J_{\text{Pt-P}} = 2917$ Hz), implying that little structural rearrangement has taken place. Interestingly, only two of the pyridyl hydrogen resonances (H^3, H^5) are clearly observed in the ^{1}H NMR spectrum of **2**. The signals due to H^4 and H^6 are obscured by the protons of the PPh_3 [δ 7.57, 7.35 (m)] ligands. The considerable upfield shift of the pyridyl-N-deshielded H^6 signal, which appears at δ 8.8 in **1**, clearly suggests that the pyridyl group is involved in coordination, as shown in Scheme 1. Complex **2** is stable in the solid state, at least for several weeks if stored in a freezer, but unstable in solution, evolving over a period of approximately 10 h at room temperature into an approximately equimolar mixture of complexes **3** and **5** (Scheme 1). An identical mixture is obtained if the initial equimolar mixture of **1** and [*cis*-Pt$(C_6F_5)_2$(thf)$_2$] in CH_2Cl_2 is refluxed for 30 min. No products other than **3** and **5** were detected when the reaction was monitored by NMR spectroscopy. Complex **3** can be isolated pure and in low yield (16%) as a microcrystalline orange solid by slow diffusion of *n*-hexane into a solution of the crude mixture (**3** and **5**) in CH_2Cl_2 or acetone. Upon workup of the mother liquors, only mixtures of **3** and **5** are obtained. However, the dinuclear zwitterionic complex **5** can alternatively be obtained as a white microcrystalline solid by treatment of solutions of complex **2** with PPh_3; this reaction can easily be monitored by NMR spectroscopy. As shown in Scheme 1, the addition of 1 equiv of PPh_3 to a solution of **2** in CH_2Cl_2 instantaneously yields a mixture of the isomeric complexes [*trans*,*cis*-$(PPh_3)_2$(H)Pt(μ-1κC^{α}:2κN-C≡CC_5H_4N-2)Pt$(C_6F_5)_2(PPh_3)$] (**4**) and **5** in a ratio of 3.5:1. Complex **4**, formed by simple displacement of the η^2-alkyne interaction, can be isolated in high yield (70%) as a pale yellow solid by slow crystallization of this mixture at low temperature (CH_2Cl_2/*n*-hexane). The proportion of the isomeric zwitterionic complex **5** remains unaltered over time, and a similar mixture was obtained by dissolving a solid equimolar mixture of **2** and PPh_3 in $CDCl_3$. Moreover, when a solution of **4** in $CDCl_3$ is monitored by ^{31}P NMR no evidence of formation of **5** was observed. All these data strongly suggest that **4** is not an intermediate in the formation of **5**, which is formed by an intramolecular transfer of the alkynyl fragment between the platinum centers, probably through an intermediate species type of **A** (Scheme 2). This suggestion seems to be reinforced by the obtention of a mixture containing a higher proportion of **5** (molar ratio **4**/**5** ∼ 1:1.5) if the dicloromethane solution of **2** is stirred for 15 min before the PPh_3 is added. From this mixture complex **5** can be isolated as a white microcrystaline solid in moderate yield (47%, see Experimental Section). Surprisingly, the nitrogen−platinum bonding interaction in both derivatives seems to be quite stable. Thus, treatment of the resulting mixtures with an excess of PPh_3 (two additional equivalents) only causes broadening of the ^{31}P resonance of the phosphorus atoms of the [PtH(C≡CR)$(PPh_3)_2$] fragment of complex **4**, suggesting some dynamic ligand exchange process; but the **4**/**5** ratio was not modified and no other phosphorus-containing species was detected. The reason for the alkynyl ligand migration is unclear,[4g,11] but we postulate that the zwitterionic nature of **5** plays an important role. Similar zwitterionic complexes have been obtained previously by unexpected alkynylation of [*cis*-Pt$(C_6F_5)_2$(CO)(thf)] with several alkynyl complexes L$_n$MC≡CR.[11d]

All of the new complexes **3**−**5** have been characterized by the usual spectroscopic and analytical methods and, in the cases of **3** and **5**, by single-crystal X-ray analyses. The IR spectra of **4** and **5** show two bands in the expected region for terminal ν(C≡C) and ν(Pt−H) stretching vibrations (2094, 2045 cm^{-1} **4**; 2090, 2063 cm^{-1} **5**). By comparison with those observed for **1** and those reported for other pyridyl or bipyridyl akynylmetal complexes,[12] the higher frequency band can be tentatively assigned to ν(C≡C). The high-frequency shift of 18 cm^{-1} for ν(Pt−H) in **5** is consistent with the fact that the trans influence of the pyridyl group is smaller than that of the σ-C alkynyl ligand.[13] The presence of the pyridyl group trans to H in **5** is clearly evident from the ^{1}H NMR data, which displays the hydride resonance shifted significantly (10 ppm) to high field (δ −17.0 in **5** vs −6.66 in **4**), with a larger $^1J_{\text{Pt-H}}$ value (982 Hz in **5** vs 608 Hz in **4**). The hydride resonance in **4** is similar to those seen in **1** and **2** and falls in the range previously reported for Pt(II) hydrides having a C atom (alkynyl, alkyl, carbene) trans to the hydride ligand.[9,14] In contrast, the chemical shift observed in **5** compares well

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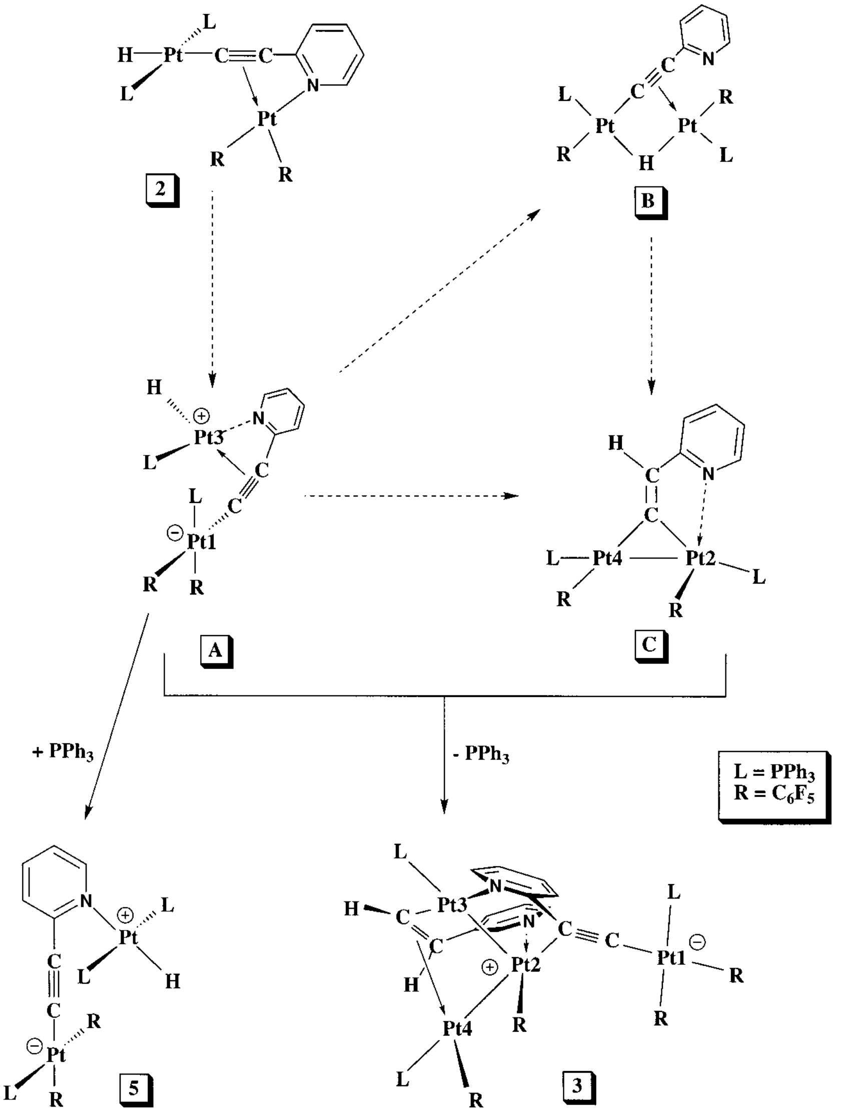
Scheme 2



with those observed in complexes [*trans*-PtHNP$_2$] with ionic nitrogen ligands trans to H.[15] In both complexes the signal appears as a triplet due to coupling to mutually trans phosphines [$^2J_{P-H}$ (Hz) 15.3 **4**; 12.7 **5**]. The two phosphorus environments are visible in their ^{31}P NMR spectra, which exhibit two signals in the expected ratio. The lower field resonance, assigned to the two mutually trans phosphines, is sharp and seems to be affected by the electron density on the platinum center (δ 25.46 **4**; 29.71 **5**), while the higher field signal is broad, probably due to long-range unresolved coupling to fluorine atoms and appears at ca. δ 16.5 for both **4** and **5**. The ^{19}F NMR spectra confirm the presence of two inequivalent C_6F_5 groups unsymmetrically disposed with respect to the Pt coordination plane. Complex **5** exhibits two multiplets in the *o*-F region centered at δ -117.01 (2 *o*-F) and -117.61 (2 *o*-F), a triplet at δ -161.78 (1 *p*-F), and three additional multiplets due to the remaining *m*-F and 1 *p*-F resonances (δ -165.48, -166.27, and -166.59). The complexity of the *o*-F signals and the fact that the spectrum remains unchanged over the temperature range 223−303 K suggest that the expected nonequivalent halves of each C_6F_5 group (AFMRX systems) are essentially coincident (degenerate). By contrast, the asymmetry caused by coordination of the pyridyl group to the bis(pentafluorophenyl) platinum fragment in complex **4** is more pronounced. Its ^{19}F NMR spectrum is temperature dependent and similar to that previously observed in other compounds in which the "*cis*-Pt(C_6F_5)$_2$" fragment is stabilized by different ligands trans to the C_6F_5 rings.[8,11d,16] At 223 K **4** displays two different sets of five fluorine signals (4 *o*-F, 2 *p*-F, and 4 *m*-F; AFMRX systems), confirming the presence of two inequivalent and rigid C_6F_5 groups; but upon heating only the two *o*-F and two *m*-F signals of one of them broaden. The *m*-F resonances coalesce at ca. 303 K, while the *o*-F signals remain very broad, finally disappearing at the highest accessible temperature (near 323 K) in $CDCl_3$. The other set of five signals remains sharp even at high temperature. As has been previously suggested,[8,16] this behavior can be explained by assuming that the pres-

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for $5{\cdot}0.75C_6H_{14}$

Pt(1)–C(13)	1.972(19)	Pt(1)–C(7)	2.06(2)	Pt(1)–C(1)	2.074(18)
Pt(1)–P(1)	2.283(6)	Pt(2)–N	2.120(16)	Pt(2)–P(3)	2.280(6)
Pt(2)–P(2)	2.282(6)	N–C(19)	1.33(2)	N–C(15)	1.39(2)
C(13)–C(14)	1.19(2)	C(14)–C(15)	1.47(3)	C(15)–C(16)	1.40(2)
C(16)–C(17)	1.31(2)	C(17)–C(18)	1.44(2)	C(18)–C(19)	1.36(2)

C(13)–Pt(1)–C(1)	89.5(7)	C(7)–Pt(1)–C(1)	82.8(8)
C(13)–Pt(1)–P(1)	94.4(5)	C(7)–Pt(1)–P(1)	93.3(6)
N–Pt(2)–P(3)	94.7(4)	N–Pt(2)–P(2)	93.0(4)
P(3)–Pt(2)–P(2)	172.2(2)	C(19)–N–C(15)	121.0(17)
C(19)–N–Pt(2)	118.5(12)	C(15)–N–Pt(2)	120.5(13)
C(14)–C(13)–Pt(1)	174.0(16)	C(13)–C(14)–C(15)	167(2)
N–C(15)–C(16)	116.5(17)	N–C(15)–C(14)	122.0(17)
C(16)–C(15)–C(14)	121.4(17)		

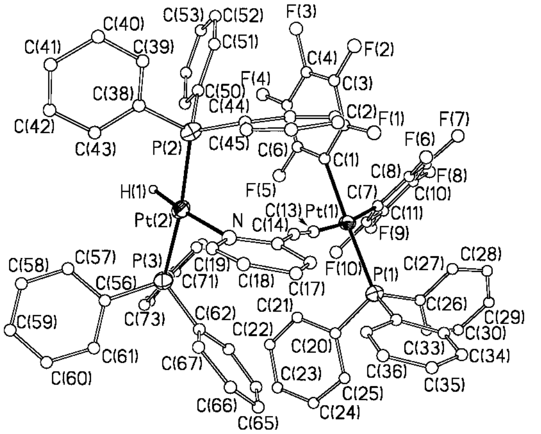

Figure 1. Molecular structure with the numbering scheme for [*cis,trans*-$(PPh_3)(C_6F_5)_2Pt^-(\mu\text{-}1\kappa C^{\alpha}{:}2\kappa N\text{-}C{\equiv}CC_5H_4N\text{-}2)\text{-}Pt^+(H)(PPh_3)_2$], $\mathbf{5}{\cdot}0.75C_6H_{14}$.

ence of different ligands trans to the Pt-*ipso*-C(C_6F_5) bonds (PPh_3 and pyridyl) induces different energy barriers to the rotation of C_6F_5 groups. In addition, the considerably different sizes of the ligands [PPh_3 and Pt(H)$(PPh_3)_2$(C≡CPy)] probably cause different degrees of steric hindrance around the C_6F_5 rings. Thus, rotation is prevented even at high temperature for one of the rings and is frozen at a lower temperature for the other. An estimation of the activation barrier for this process using the coalescence of the *o*-F signals gives a $\Delta G_1^{\ddagger}{}_{323}$ of 57.4 kJ·mol^{-1}, which compares well with other reported values.[17]

Crystals of **5** suitable for a single-crystal X-ray diffraction study were obtained by slow diffusion of *n*-hexane into dichloromethane solutions of this complex at −30 °C. This study supports the spectroscopic data and confirms the zwitterionic nature of **5**, which is shown in Figure 1 (see also Table 1). The molecule consists of two organometallic moieties, *cis*-Pt(1)$(C_6F_5)_2$(PPh_3) and *trans*-Pt(2)H$(PPh_3)_2$, connected by a μ-κC^{α}:κN-C≡C(pyridyl) ligand, bonded by the C_α atom (C(13)) to the former and by the N atom of the pyridyl group to the latter. Although an alkynylation process has occurred between the platinum atoms, both of them retain their respective cis and trans geometries and are in approximately square-planar environments. The structural data of both platinum fragments are similar to those found in other Pt(II) complexes containing C_6F_5 and PPh_3 groups;[4k,10,11d] the three Pt–P bond distances present in the molecule are equal to within experimental error [Pt(1)–P(1) 2.283(6) Å, Pt(2)–P(2) 2.282(6) Å, Pt(2)–P(3) 2.280(6) Å]. Pt(2) is also bonded to the N atom of the pyridyl group, with a Pt(2)–N bond distance [2.120(16) Å] similar to those reported in other [*trans*-$PtHNP_2$] complexes,[15d] and completes its coordination plane with a hydride ligand whose position (trans to the N atom) has not been well established by this analysis but can be inferred from the NMR data. Due to the lesser steric demand of the hydride ligand, the P(2)–Pt(2)–P(3) angle [172.2(2)°] is somewhat smaller than 180°. This angle, although larger than that found in the complex *trans,trans,trans*-{[Pt$(C_6F_5)_2(\mu\text{-}1\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CPh)_2$][PtH$(PEt_3)_2$]$_2$},[10] compares well with that found for other, similar structures.[9a,b,15d]

Coordination of the alkynyl ligand to Pt(2) through the N atom of the pyridyl group is responsible for the very long separation between the Pt atoms (5.745 Å) and causes a perceptible bending of the alkyne fragment, which is more pronounced at C_β [C(13)–C(14)–C(15) 167(2)° vs Pt(1)–C(13)–C(14) 174.0(16)°]. However, as expected, the ligand has a C–C triple bond of length 1.19(2) Å, similar to those found in σ-alkynyl complexes of platinum.[9a,b] The alkynyl unit [C(13)≡C(14) and pyridyl ring], which remains nearly planar, is oriented practically perpendicular to the local coordination plane of Pt(2) [dihedral angle 85.3°] and inclined by 54.4° to the corresponding plane around Pt(1). The dihedral angle between the platinum coordination planes is 78.5°.

The elemental analyses and FAB(+) mass spectrum (*m/z* 2441, 3%) of **3** suggest formal dimerization of **2** with the loss of one molecule of PPh_3. The IR spectrum of **3** shows a broad band at 1940 cm^{-1}, indicating the presence of alkynyl bridging ligands. The ^{19}F NMR spectrum is very complex, showing at least four inequivalent C_6F_5 groups, as evidenced by the presence of seven *o*-F resonances in the ratio (1:1:1:2:1:1:1). Complex **3** is only moderately soluble in common solvents, but after prolonged accumulation (12 h) three different phosphorus resonances are clearly seen in its ^{31}P NMR ($CDCl_3$) spectrum, suggesting three chemically distinct environments. The highest frequency resonance (δ 12.3) is the narrowest and exhibits only one set of short-range platinum satellites ($^1J_{Pt-P}$ = 2321 Hz). The other two sets are centered at δ −13.9 and −14.7, considerably shifted to higher field compared to those in **2** and also in **4** and **5**. It is noteworthy that both signals were flanked by two sets of platinum satellites, evidencing coupling to near and far platinum atoms. But the most prominent feature is the extremely pronounced long-range coupling observed (δ −13.9, $^1J_{Pt-P}$ = 2454

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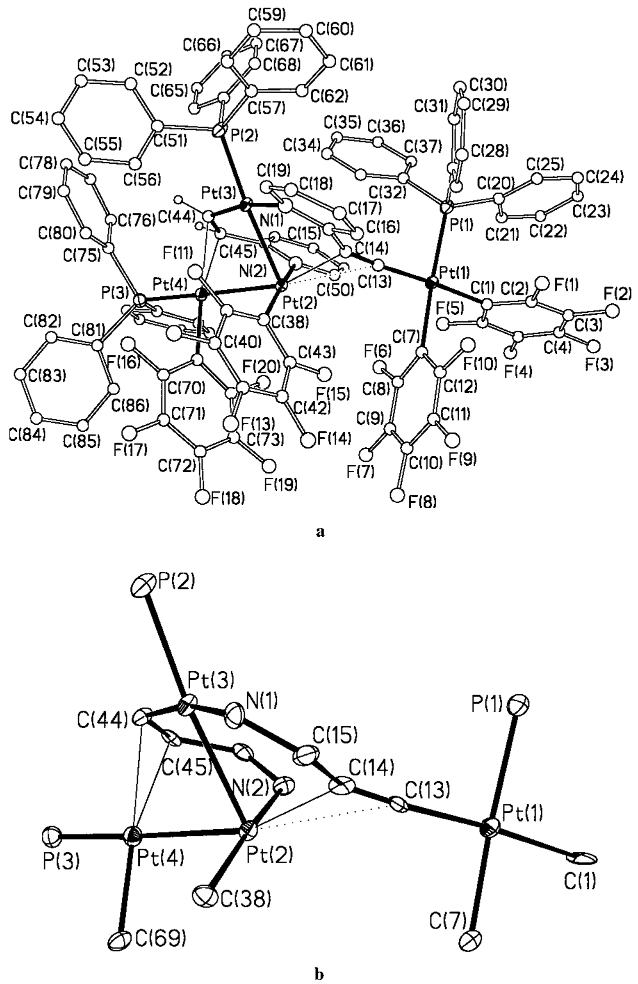

Figure 2. (a) Structure of the complex $[\{cis\text{-Pt}(C_6F_5)_2(PPh_3)(\mu_3\text{-}1\kappa C^{\alpha}{:}2\kappa C^{\beta}{:}3\kappa N\text{-}C_2C_5H_4N\text{-}2)\}\{Pt_3(C_6F_5)_2(\mu_3\text{-}3\kappa C^{\alpha}{:}\eta^2{}_{\alpha,\beta}{:}2\kappa N\text{-}CH{=}CHC_5H_4N\text{-}2)(PPh_3)_2\}]$, $\mathbf{3}\cdot 1.25CH_2Cl_2\cdot 0.75C_6H_{14}$, showing the atom-labeling scheme. (b) View of the core.

Hz, $^2J_{\text{Pt-P}} = 1186$ Hz; δ −14.7, $^1J_{\text{Pt-P}} = 4393$ Hz, $^2J_{\text{Pt-P}} = 1192$ Hz), signaling the presence of "$PPh_3{-}Pt{-}Pt$" fragments.[18] A single-crystal X-ray diffraction study was undertaken in order to identify **3**, and the resulting molecular structure is shown in Figure 2 (see also Table 2). Complex **3** is a tetranuclear derivative formed by a triplatinum (I, I, II) $[Pt_3(C_6F_5)_2(PPh_3)_2(CH{=}CH{-}Py)]$ cluster unit and a mononuclear $[cis\text{-Pt}(1)(C_6F_5)_2(PPh_3)]$ fragment linked through one $C_\alpha{\equiv}C_\beta{-}Py$ group.

As indicated in Figure 2b, which shows a perspective view of the central core, complex **3** comprises a central cationic cluster $[Pt_3]^+$ framework with one edge-bridging platinum "$[Pt(1)]^-C{\equiv}CC_6H_5N\text{-}2$" $\{[Pt(1)] = cis\text{-Pt}(C_6F_5)_2(PPh_3)\}$ anionic unit. As can be seen, the mononuclear Pt(1) fragment is linked to the rest of the molecule through the alkynyl C≡C(pyridyl) group, which is σ bonded to Pt(1) and $\mu\text{-}\eta^1C^{\beta}\text{-}\kappa N$ bridging between two platinum atoms [Pt(2), Pt(3)] of the $[Pt_3]$ cluster. Bridging alkynyls are capable of a broad range of bonding modes, typically adopting $\mu\text{-}\kappa C^{\alpha}{:}\eta^2{}_{\alpha,\beta}$ and $\mu\text{-}\kappa C^{\alpha}$ bridging arrangements.[1a,b,h,19] Metal-substituted vinylidene disposed as $\mu\text{-}\kappa C^{\alpha}{:}\kappa C^{\beta}$ is rather rare,[20] although several examples containing considerable distortion toward this arrangement have been described.[2c,10,11a,b,21] In complex **3**, the bond lengths $Pt(2){-}C_\beta$ [Pt(2)−C(14) = 2.381(8) Å] and C≡C triple bond [C(13)−C(14) = 1.229(12) Å], the latter shorter than the C=C in the vinyl group [C(44)−C(45) = 1.390(13) Å], are similar to those reported for η^2-alkynides.[1h,4k,7,10,16] These data and the observed ν(C≡C) absorption in the IR spectrum indicate that complex **3** can be adequately viewed using the zwitterionic description **3A**, $[Pt]^-{-}C{\equiv}CC_5H_4\overbracket{N\text{-}2[Pt_3]}^+$ Scheme 1). Although the apparent lack of interaction between Pt(2) and C_α (Pt(2)−C(13) = 2.852 Å) and between Pt(1) and Pt(2) (4.386 Å), and the angles associated with the bridging fragment $Pt(1),Pt(2){-}C{\equiv}CC_6H_4N\text{-}2$, nearly linear at C^{α} [175.2(8)°] and strongly distorted at C_β [150.4(9)°], which are comparable to the corresponding metric data observed in metal-substituted vinylidene complexes,[20,21] could suggest some degree of participation of the vinylidene form **3B** with a triplatinum neutral $[Pt_3]$ cluster coordinated to a Pt(1) center $[Pt]{=}C{=}C[Pt_3](C_5H_4N\text{-}2)$ (Scheme 1); the rest of the parameters associated with this fragment indicate a bonding type **3A** rather than **3B**. The very long Pt(2)−C(13) distance and the value of the C(13)−C(14)−C(15) angle, 150(4)°, can be due to the steric hindrance introduced by the ligands bonded to Pt(1) and $[Pt_3]^+$ fragments.

On the other hand, if we assume that the alkynyl group donates four electrons to the central cationic $[Pt_3]^+$ core and the $\mu_3\text{-}\kappa C^{\alpha}{:}\eta^2{}_{\alpha,\beta}{:}\kappa N\text{-}CH{=}CHC_6H_5N\text{-}2$ is treated as a five-electron donor, then the platinum atoms are in formal oxidation states (II, I, I), and the valence electron count for this fragment cluster is 44 e^-. A large number of planar platinum triangle neutral (with 42 or 44 valence electron count), anionic, or cationic (44 valence electron count) clusters are presently known,[22,23] but complex **3** is unique, not only due to its unprecedented formation but also in that it displays very unusual ligands. In particular, the presence of the face-capping vinyl and edge-bridging metallaalkynyl structures is novel. μ-Vinyl species have been previously suggested as intermediates in processes occurring during chemisorption of ethyne on Pt(111)

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $3 \cdot 1.25CH_2Cl_2 \cdot 0.75C_6H_{14}$

Pt(1)−C(13)	1.986(9)	Pt(1)−C(1)	2.052(10)	Pt(1)−C(7)	2.067(10)
Pt(1)−P(1)	2.303(3)	Pt(2)−C(38)	2.037(9)	Pt(2)−N(2)	2.110(8)
Pt(2)−C(14)	2.381(8)	Pt(2)−Pt(3)	2.5671(5)	Pt(2)−Pt(4)	2.5974(6)
Pt(3)−C(44)	1.966(9)	Pt(3)−N(1)	2.117(8)	Pt(3)−P(2)	2.226(3)
Pt(4)−C(69)	2.014(10)	Pt(4)−C(45)	2.223(8)	Pt(4)−P(3)	2.277(3)
Pt(4)−C(44)	2.288(9)	N(1)−C(19)	1.338(12)	N(1)−C(15)	1.346(12)
N(2)−C(46)	1.346(12)	N(2)−C(50)	1.352(13)	C(13)−C(14)	1.229(13)
C(14)−C(15)	1.418(13)	C(15)−C(16)	1.402(13)	C(16)−C(17)	1.364(14)
C(17)−C(18)	1.379(15)	C(18)−C(19)	1.387(13)	C(44)−C(45)	1.390(13)
C(45)−C(46)	1.478(13)	C(46)−C(47)	1.378(13)	C(47)−C(48)	1.377(15)
C(48)−C(49)	1.391(14)	C(49)−C(50)	1.346(14)		

C(13)−Pt(1)−C(7)	89.6(4)	C(1)−Pt(1)−C(7)	86.1(4)
C(13)−Pt(1)−P(1)	91.6(3)	C(1)−Pt(1)−P(1)	92.5(3)
C(38)−Pt(2)−N(2)	170.2(3)	C(38)−Pt(2)−C(14)	85.0(4)
N(2)−Pt(2)−C(14)	102.7(3)	C(38)−Pt(2)−Pt(3)	95.8(3)
N(2)−Pt(2)−Pt(3)	91.7(2)	C(14)−Pt(2)−Pt(3)	79.2(2)
C(38)−Pt(2)−Pt(4)	94.3(3)	N(2)−Pt(2)−Pt(4)	80.6(2)
C(14)−Pt(2)−Pt(4)	159.6(2)	Pt(3)−Pt(2)−Pt(4)	80.55(2)
C(44)−Pt(3)−P(2)	91.4(3)	N(1)−Pt(3)−P(2)	97.4(2)
C(44)−Pt(3)−Pt(2)	84.7(3)	N(1)−Pt(3)−Pt(2)	87.5(2)
P(2)−Pt(3)−Pt(2)	170.92(7)	C(69)−Pt(4)−P(3)	95.6(3)
C(45)−Pt(4)−P(3)	88.6(2)	C(69)−Pt(4)−C(44)	154.7(4)
P(3)−Pt(4)−C(44)	100.6(2)	C(69)−Pt(4)−Pt(2)	88.7(3)
C(45)−Pt(4)−Pt(2)	85.3(2)	P(3)−Pt(4)−Pt(2)	170.99(7)
C(44)−Pt(4)−Pt(2)	78.1(2)	C(19)−N(1)−C(15)	118.1(8)
C(19)−N(1)−Pt(3)	121.8(6)	C(15)−N(1)−Pt(3)	119.7(6)
C(46)−N(2)−C(50)	118.0(8)	C(46)−N(2)−Pt(2)	123.3(6)
C(50)−N(2)−Pt(2)	118.2(6)	C(14)−C(13)−Pt(1)	175.2(8)
C(13)−C(14)−C(15)	150.4(9)	C(13)−C(14)−Pt(2)	99.4(6)
C(15)−C(14)−Pt(2)	109.9(7)	N(1)−C(15)−C(16)	120.4(9)
N(1)−C(15)−C(14)	119.8(9)	C(16)−C(15)−C(14)	119.8(9)
C(45)−C(44)−Pt(3)	131.0(7)	C(45)−C(44)−Pt(4)	69.5(5)
Pt(3)−C(44)−Pt(4)	103.1(4)	C(44)−C(45)−C(46)	126.2(8)
C(44)−C(45)−Pt(4)	74.6(5)	C(46)−C(45)−Pt(4)	103.7(6)
N(2)−C(46)−C(47)	120.6(9)	N(2)−C(46)−C(45)	119.9(8)
C(47)−C(46)−C(45)	119.3(9)		

surfaces and have been implicated in H−D exchange processes within the terminal vinyl group on triplatinum clusters $[Pt_3(CH{=}CHR)(\mu_3\text{-}\eta^2\text{-}CH{\equiv}CR)(\mu\text{-dppm})_3]$ (R = H, Me).[24] However, as far as we know, complex **3** is the first example in which a triplatinum fragment is stabilized by a μ-vinyl (CH═CHR) ligand. In addition, the presence of a functionalized group (R = pyridyl) allows a very unusual $\mu_3\text{-}\kappa C^{\alpha}{:}\eta^2{}_{\alpha,\beta}{:}\kappa N$ coordination mode.

The $[Pt_3]$ framework core shows, as expected for a 44 valence electron count cluster,[22] an open triangle of Pt atoms [Pt(3)−Pt(2)−Pt(4) = 88.55(2)°], with two very short Pt(2)−Pt(3) [2.5671(5) Å] and Pt(2)−Pt(4) [2.5974(6) Å] distances and one very long Pt(3)−Pt(4) [3.338(1) Å] separation, which clearly has to be considered as a nonbonding distance. The bonding Pt(2)−Pt(3,4) distances are somewhat shorter than those previously reported for 44-electron (2.708−3.066 Å) and even for 42-electron Pt_3 clusters (2.62−2.74 Å),[22b] although comparisons are complicated by the varying ligands that bridge these bonds. The triangle is face-capped by a formally reduced pyridyl-vinyl ligand, which interacts with all three Pt atoms. The vinyl ligand is σ bonded to Pt(3) [Pt(3)−C(44) = 1.966(9) Å] and η^2-bonded to Pt(4) [Pt(4)−C(44) = 2.288(9) Å, Pt(4)−C(45) = 2.223(8) Å] and interacts with the central platinum atom through the N atom of the pyridyl group [Pt(2)−N(2) = 2.110(8) Å]. The bond lengths [Pt(3)−C(44) = 1.966(9) Å and C(44)−C(45) = 1.390(13) Å] found in compound **3** are comparable to those observed in $[(PPh_3)_2Pt(\mu\text{-}CH{=}CH_2)(\mu\text{-}H)ML_n]^+$ [Pt−C/C═C (Å), ML_n = $Ir(CO)(PPh_3)_2$[25a] 2.014(4)/1.415(6); ML_n = Cp^*IrPMe_3[6] 2.01(1)/1.38(2)]. The angle Pt(3)−C(44)−C(45) [131.0(7)°] is substantially greater than those seen for the lattter binuclear complexes [ML_n = $Ir(CO)(PPh_3)_2$ 120.7°; Cp^*IrPMe_3 125(1)°] probably due to the constraint imposed by coordination of the pydidyl group [torsion angle C(44)−C(45)−C(46)−N(2) 39.5°]. The angle C(44)−C(45)−C(46) [126.2(8)°] is also slightly larger than those reported for related μ-vinyl cluster complexes (∼120°).[25] A PPh_3 ligand [trans to Pt(3)−Pt(2)] and a N atom of a μ-C≡C-pyridyl complete a distorted square-planar coordination about Pt(3), while the coordination at Pt(4) is completed by the *ipso*-C atom of a C_6F_5 ligand and by one PPh_3 trans to Pt(4)−Pt(2). The Pt(3)−P(2) bond distance [2.226(3) Å] is slightly shorter than the Pt(4)−P(3) bond length [2.277(3) Å], reflecting the very different ligands around the platinum centers, but both fall within the normal range for this type of cluster.[22]

The geometry around Pt(2) is very unusual since it is five coordinate. It can be viewed as a very distorted square pyramid with the apical position occupied by Pt(3) and the basal plane formed by four different donor atoms: the ipso-C atom of one C_6F_5 group and the N atom of the pyridyl vinyl group, which are essentially

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in mutually trans positions [C(38)−Pt(2)−N(2) 170.2(3)°], and the C_β atom of the alkynyl ligand and Pt(4) [C(14)−Pt(2)−Pt(4) 159.6(2)°]. In the basal plane, the angles between cis-atoms around Pt(2) range from 80.6(2)° for N(2)−Pt(2)−Pt(4) to 102.7(3)° for N(2)Pt(2)C(14), and the dihedral angle between the planes Pt(4)Pt(2)N(2) and N(2)−Pt(2)−C(14) is 20.5°. Finally, it should be mentioned that the Pt−*ipso*-C(C_6F_5) distances in **3** are very similar, the shortest being those corresponding to the two C_6F_5 groups associated with the triplatinum [Pt_3] framework.

Having established the structure, the interpretation of the NMR data is more facile. Thus, in the ^{31}P NMR spectrum the low-field signal at δ 12.3, with only one set of Pt satellites, is attributed to P(1), and we tentatively assign the high-field signal at δ −13.9, showing a smaller value of $^1J_{Pt-P}$ (2454 Hz) to P(3), which exhibits a longer Pt(4)−P(3) distance [2.277(3) Å], and the signal at δ −14.7 to P(2) [Pt(3)−P(2) 2.226(3) Å]. This latter signal is seen as a badly resolved triplet ($J \sim 14.8$ Hz) probably due to long-range coupling to two *o*-F atoms. The two-bond platinum−phosphorus coupling constants observed in **3** (1186, 1192 Hz) are considerably larger than those reported for triangular Pt_3 clusters displaying typical P−Pt−Pt−L arrangements[22] (e.g., $^2J_{Pt-P} = 252$ Hz for terminal PPh_3 in [$Pt_3(PPh_2)_3Ph(PPh_3)_2$]),[22a,b] but similar and even larger values have been found for P atoms lying trans to coordinatively unsaturated Pt centers (e.g., $^2J_{Pt-P} = 1632$ Hz and $^3J_{Pt-P} = 283$ Hz have been reported in [{Pt(dppen)(XylNC)$_2$}$_2$Pt]$^+$ containing a P−Pt−Pt−Pt−P arrangement).[18c] The assignment of the pyridyl and vinyl protons was facilitate by using a $^1H-^1H$ correlation spectrum (see Experimental Section). Although the spectrum is poorly resolved, the ^1H NMR signals of the vinyl group could be located at δ 6.01 and 5.4. Both resonances are seen as multiplets due to proton−proton and proton−phosphorus coupling, and only for the low-field (δ 6.01) signal are ^{195}Pt satellites clearly visible ($^2J_{Pt-H} \sim 43$ Hz). Therefore, this was assigned to the α-proton. Similar ^1H NMR patterns have been reported for related μ-vinyl complexes, in which the α-protons are more deshielded than the β-protons:[2i,6,25] e.g., [PtW(μ-CH$_\alpha$=CH$_\beta$Ph)(PEt$_3$)$_2$(dppe)(CO)$_3$]$^+$ (δ 6.30 H$_\alpha$; 5.65 H$_\beta$)[25g] and [Cp*WOs$_3$(μ_4-C)(μ-H)$_2$(μ-CH=CHOMe)(CO)$_9$] (δ 6.32, 5.38).[25b] The values of $^3J_{H-H} = 8.6$ Hz, $^3J_{P-H\alpha} = 10.4$ Hz, and $^4J_{P-H\beta} = 6.9$ Hz have been assigned on the basis of selective decoupling of phosphorus signals due to P(3) and P(2) (δ −13.9 and −14.7) while observing the proton spectrum. With this treatment both signals simplify to the expected AB splitting pattern ($^3J_{H-H} = 8.6$ Hz), and the ^{195}Pt satellites on the H$_\beta$ protons are clearly seen ($^3J_{Pt-H\beta} \sim 48$ Hz).

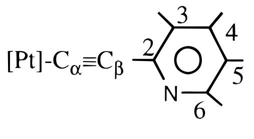
An unresolved question concerns the mechanism by which complex **3** is formed. It is well-known that alkenyl derivatives can easily be formed by hydride transfer to the C$_\alpha$ carbon atom of either terminal[26] or bridging[2g,25b,d] μ-vinylidene ligands. This and the unsymmetrical structure of **3** suggest that compounds of type **A** and **C** are probably intermediates (Scheme 2). The formation of **3** could be envisaged as involving simple migratory insertion of the C$_\alpha$ carbon atom of the vinylidene bridging ligand of **C** into the platinum−hydride bond of **A**, followed by a slight rearrangement of the resulting vinyl group. The formation of a new platinum−platinum bond [Pt(3)−Pt(2)] could be compensated for by loss of PPh$_3$. We note that the reaction of **A** with PPh$_3$ should lead to the simultaneous formation of **5**. The polarized species **A** could be accessible through a slight rearrangement of the ligands on the initial adduct **2**, probably favored by the electron-withdrawing nature of the C_6F_5 groups. In fact, compound **A** could be considered as a "frozen" intermediate in the formation (in seconds) of type **B** complexes, as previously observed in the reaction of [*trans*-PtH(C≡CPh)(PPh$_3$)$_2$] with [*cis*-Pt(C_6F_5)$_2$(thf)$_2$].[7] The formation of a μ-vinylidene compound of type **C** is less clear, but the involvement of acetylide−hydride intermediates in the final formation of vinylidene-bridging dinuclear complexes has been previously observed.[2f,j,m] Unfortunately, we have not been able to observe any of these proposed species, and therefore, the mechanism is very speculative.

In summary, we have observed a new and interesting reactivity between the solvated species [*cis*-Pt(C_6F_5)$_2$(thf)$_2$] and [*trans*-PtH(C≡C−C_5H_4N-2)(PPh$_3$)$_2$] yielding unusual products. We are currently studying the scope of these reactions and exploring the reactivity of [*cis*-Pt(C_6F_5)$_2$(thf)L] (L = thf or CO) toward new alkynyl-substituted hydride derivatives [*trans*-PtH(C≡CR)(PPh$_3$)$_2$].

Experimental Section

General Considerations. All reactions were carried out with rigorous exclusion of air by using Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. Complexes [*trans*-PtHCl(PPh$_3$)$_2$],[27] [*cis*-Pt(C_6F_5)$_2$(thf)$_2$],[28] and 2-ethynylpyridine[29] were prepared by literature methods. For additional general information, including a list of spectrometers and equipment used for the physical characterizations, see ref 7. NMR coupling constants are given in hertz.

The following notation was used in the assignment of proton and ^{13}C NMR resonances on the pyridyl fragments.



Preparation of [*trans*-PtH(C≡C−C_5H_4N-2)(PPh$_3$)$_2$], 1. A solution of [*trans*-PtHCl(PPh$_3$)$_2$] (0.4 g, 0.529 mmol) in CHCl$_3$ (10 mL) was treated with 0.3 mL of 2-ethynylpyridine (3.05 mmol) and 0.5 mL of NEt$_2$H. After the mixture was refluxed for 30 min, it was concentrated to small volume. By addition of methanol (20 mL) and cooling for ~12 h, complex **1** precipitates as a white microcrystalline solid in 74% yield. Anal. Calcd for $C_{43}H_{35}NP_2Pt$: C, 62.77; H, 4.28; N, 1.70. Found: C, 62.28; H, 3.87; N, 1.73. MS (FAB +): m/z = 823 [M + H]$^+$ 35; 719 [Pt(PPh$_3$)$_2$]$^+$ 100. Ir (Nujol, cm^{-1}): ν(C≡C) 2109(s); ν(Pt−H) 2044(m). ^1H NMR (CDCl$_3$, δ): at room temperature (rt) 8.28 (d, $J_{H-H} = 4.2$, H^6); 7.71 (m, *o*-H, Ph); 7.35 (m,

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m-H, *p*-H, Ph); 7.23 (t, $J_{H-H} = 7.6$, H^4); 6.82 (m, H^5); 6.42 (d, $J_{H-H} = 7.8$, H^3); −6.30 (t, $^{2}J_{P-H} = 15.5$; $^{1}J_{Pt-H} = 645$, Pt−H). Assignment based on a COSY experiment. ^{13}C NMR ($CDCl_3$, δ): at rt 148.52 (s, C^6); 147.25 (s, $^{3}J_{Pt-C} = 23$, C^2); 134.6 (s, *o*-C, Ph, PPh_3); 133.13 (t, $^{1}J_{P-C}+^{3}J_{P-C} = 54$, *i*-C, Ph, PPh_3); 130.14 (s, *p*-C, Ph, PPh_3 and probably C^4 or C^5); 127.99 (s, *m*-C, Ph, PPh_3); 126.04 (s, $^{4}J_{Pt-C} = 6.4$, C^3); 118.95 (s, C^4 or C^5); 115.01 (s, $^{2}J_{Pt-C\beta} = 236$, C_β); C_α is not observed. ^{31}P NMR ($CDCl_3$, δ): at rt 26.5 (s, $^{1}J_{Pt-P} = 2917$).

Preparation of [*trans,cis*-$(PPh_3)_2(H)Pt(\mu\text{-}1\kappa C^{\alpha}:\eta^{2}{}_{\alpha,\beta}:2\kappa N\text{-}C{\equiv}CC_5H_4N\text{-}2)Pt(C_6F_5)_2$], 2. [*cis*-$Pt(C_6F_5)_2(thf)_2$] (0.123 g, 0.182 mmol) was added to a colorless solution of **1** (0.15 g, 0.182 mmol) in 15 mL of CH_2Cl_2, and the mixture stirred for 5 min at room temperature. The solvent was removed under vacuum and the residue treated with diethyl ether, affording **2** as a white solid (61%). Anal. Calcd for $C_{55}H_{35}F_{10}NP_2Pt_2$: C, 48.86; H, 2.61; N, 1.04. Found: C, 48.64; H, 1.88; N, 1.04. MS (FAB +): $m/z = 1350$ $[M - 2H]^+$ 3; 1184 $[M - C_6F_5 - H]^+$ 5; 719 $[Pt(PPh_3)_2]^+$ 100. Ir (Nujol, cm^{-1}): ν(Pt−H) 2125(m); $\nu(C{\equiv}C)$ 2038(sh), 2012(s); $\nu(C_6F_5)_{x-sens}$ 808(s), 797(s). ^{1}H NMR ($CDCl_3$, δ): at rt 7.57 (m), 7.35 (m) (Ph, PPh_3, H^6 and H^4); 7.01 (m, H^5); 6.46 (d, $J_{H-H} = 8$, H^3); −6.75 (t, $^{2}J_{P-H} = 13.9$; $^{1}J_{Pt-H} = 671$, Pt−H). Assignment based on a COSY experiment. Due to its low stability in solution, the ^{13}C NMR of **2** could not be registered. ^{19}F NMR ($CDCl_3$, δ): at rt −114.72 (d, $^{3}J_{Pt-o-F} = 448$), −119.25 (d, $^{3}J_{Pt-o-F} = 541$) (*o*-F); −162.31 (t), −162.5 (t) (*p*-F); −164.8 (m), −165.22 (m) (*m*-F). A similar spectrum was observed at −50 °C. ^{31}P NMR ($CDCl_3$, δ): at rt 25.7 (s, $^{1}J_{Pt-P} = 2898$).

Formation of [{*cis*-$Pt(C_6F_5)_2(PPh_3)(\mu_3\text{-}1\kappa C^{\alpha}:2\kappa C^{\beta}:3\kappa N\text{-}C_2C_5H_4N\text{-}2)$}{$Pt_3(C_6F_5)_2(\mu_3\text{-}3\kappa C^{\alpha}:\eta^{2}{}_{\alpha,\beta}:2\kappa N\text{-}CH{=}CHC_5H_4N\text{-}2)(PPh_3)_2$}], 3. To a solution of **1** (0.13 g, 0.158 mmol) in CH_2Cl_2 (15 mL) was added [*cis*-$Pt(C_6F_5)_2(thf)_2$] (0.106 g, 0.158 mmol), and the mixture was refluxed for 30 min. The resulting dark orange solution was evaporated to dryness and the residue dissolved in acetone (∼5 mL). Slow diffusion of *n*-hexane into this solution causes the crystallization of complex **3** as an orange crystalline solid in ∼16% yield. From the mother liquors an additional fraction of **3** (total yield ∼40%) contaminated with small amounts of **5** was obtained by treatment of the resulting residue with 2-propanol. Similar results were obtained when the initial mixture of **1** and [*cis*-$Pt(C_6F_5)_2(thf)_2$] was stirred at room temperature for 10 h. Anal. Calcd for $C_{92}H_{55}F_{20}N_2P_3Pt_4\cdot 1.25CH_2Cl_2\cdot 0.75n\text{-}Hex$ ($C_{97.75}Cl_{2.5}H_{68}F_{20}N_2P_3Pt_4$): C, 44.94; H, 2.62; N, 1.07. Found: C, 45.25; H, 2.27; N, 1.14. MS (FAB +): $m/z = 2441$ $[M]^+$ 3; 2275 $[M - C_6F_5]^+$ 3; 1649 $[Pt_3(C_6F_5)_2(PPh_3)_2(C{\equiv}CR)_2]^+$ 10; 561 $[Pt(PPh_3)(HC{\equiv}CC_5H_4N\text{-}2)]^+$ 100; 456 $[Pt(PPh_3)\text{-}H]^+$ 68; 378 $[Pt(PPh_2)\text{-}2H]^+$ 57%. Ir (Nujol, cm^{-1}): $\nu(C{\equiv}C)$ 1940(br). ^{1}H NMR (HDA, δ): at rt 11.6 (H^6 CH=CHPy), 7.96 (t, $J_{H-H} = 7.5$, H^4 CH=CHPy); 7.62−7.12 (m, Ph, PPh_3, H^5 and H^3 CH=CHPy, H^6 C≡CPy); 6.92 (t, $J_{H-H} = 7.4$, H^4 C≡CPy); 6.40 (d, $J_{H-H} = 7.9$, H^3 C≡CPy); 6.24 (t, $J_{H-H} = 6.5$, H^5 C≡CPy); 6.01 (m, $^{2}J_{Pt-H} = 43$, $^{3}J_{H-H} = 8.6$, $^{3}J_{P-H} = 10.4$, $C_\alpha H$, $C_\alpha H{=}C_\beta HPy$); 5.4 (m, $^{2}J_{Pt-H} \sim 48$, $^{3}J_{H-H} = 8.6$, $^{4}J_{P-H} = 6.9$, $C_\beta H$, $C_\alpha H{=}C_\beta HPy$). Assignment based on COSY and $^{1}H\{^{31}P\}$ NMR experiments. The ^{13}C NMR spectrum could not be recorded due to the low solubility of this complex. ^{19}F NMR ($CDCl_3$, δ): at rt −114.08 (d), −115.12 (d), −117.27 (m), −117.87 (m), −118.71 (d), −120.25 (m), −121.29 (m) (8 *o*-F, 1:1:1:2:1:1:1); −163.73 (t, 1 *p*-F); −164.69 (m), −165.11 (m), −165.8 (m), −166.43 (m) (3 *p*-F, 8*m*-F). ^{31}P NMR ($CDCl_3$, δ): at rt 12.3 [s, $^{1}J_{Pt-P} = 2321$ Hz, P(1)]; −13.9 (s, $^{1}J_{Pt-P} = 2454$, $^{2}J_{Pt-P} = 1186$), −14.7 (t, $J_{P-F} = 14.8$, $^{1}J_{Pt-P} = 4393$, $^{2}J_{Pt-P} = 1192$) [P(2), P(3)]. Similar spectra were obtained in CD_3COCD_3.

Reaction of 2 with PPh_3: Formation of 4 and 5. A solution of **2** (0.185 g, 0.137 mmol) in CH_2Cl_2 (25 mL) was treated with 1 equiv of PPh_3 (0.036 g, 0.137 mmol), and the reaction was followed by NMR spectroscopy (^{1}H, ^{19}F, and ^{31}P), showing the formation of both isomers **4** and **5** in the ratio 3.5:1, respectively. This molar ratio proved to be unchanged over time. Complex **4** can be obtained as a pale-yellow solid by partial evaporation of the solvent (∼5 mL) and slow diffusion of *n*-hexane into this solution at −30 °C. Isolated yield: 70%.

A similar mixture was obtained by dissolving a solid equimolar mixture of **2** and PPh_3 in $CDCl_3$.

Alternatively, when a solution of **2** (0.125 g, 0.09 mmol) in CH_2Cl_2 was first stirred for 15 min and then treated with PPh_3 (0.024 g, 0.09 mmol), the formation of an ∼1:1.5 mixture of **4** and **5** was observed, from which complex **5** could be isolated as a pure white microcrystalline solid following workup similar to that described for **4**. Isolated yield: 47%.

Data for 4. Anal. Calcd for $C_{73}H_{50}F_{10}NP_3Pt_2$: C, 54.32; H, 3.12; N, 0.87. Found: C, 54.67; H, 3.39; N, 0.88. MS (FAB +): $m/z = 1612$ $[M - H]^+$ 1; 1446 $[M - C_6F_5]^+$ 1; 1350 $[M - PPh_3 - H]^+$ 2; 1184 $[M - PPh_3 - C_6F_5]^+$ 2; 822 $[PtH(C_2Py)(PPh_3)_2]^+$ 5; 719 $[Pt(PPh_3)_2]^+$ 100; 560 $[PtH(C_2Py)(PPh_3)]^+$ 17; 455 $[Pt(PPh_3) - 2H]^+$ 30; 378 $[Pt(PPh_2) - 2H]^+$ 38. Ir (Nujol, cm^{-1}): $\nu(C{\equiv}C)$ 2094(s), ν(Pt−H) 2045(m). ^{1}H NMR ($CDCl_3$, δ): at rt 8.09 (d, $J_{H-H} = 5.1$, H^6); 7.54−7.13 (m, Ph, PPh_3); 6.77 (t, $J_{H-H} = 7.4$, H^4); 6.23 (d, $J_{H-H} = 7.9$, H^3); 6.16 (t, $J_{H-H} = 6.4$, H^5); −6.66 (t, $^{2}J_{P-H} = 15.3$; $^{1}J_{Pt-H} = 608$, Pt−H). Assignment based on a COSY experiment. ^{13}C NMR ($CDCl_3$, δ): at rt 151.27 (s, C^6); 150.11 (s, $^{3}J_{Pt-C} = 26.7$, C^2); 149.51, 146.66, 137.92 (m, C_6F_5); 134.36 (m, *o*-C, Ph, PPh_3); 133.09 (t, $^{1}J_{P-C}+^{3}J_{P-C} = 56.6$, *i*-C, Ph, 2 PPh_3); 131.02 (d $^{1}J_{P-C} = 43.9$, *i*-C, Ph, PPh_3); 130.21 (s, C^3); 130.05 (s br, *p*-C, Ph, PPh_3); 129.33 (s, C^4 or C^5); 127.84 (m, *m*-C, Ph, PPh_3); 118.81 (s, C^4 or C^5); 115.23 (s, $^{2}J_{Pt-C\beta} = 246.5$, C_β); C_α is not observed. ^{19}F NMR ($CDCl_3$, δ): at −50 °C −111.56 (d, $^{3}J_{Pt-o-F} \sim 315$); −114.90 (d, $^{3}J_{Pt-o-F} \sim 350$); −119.03 (d, $^{3}J_{Pt-o-F} \sim 450$); −124.64 (d, $^{3}J_{Pt-o-F} \sim 370$) (4 *o*-F); −162.11 (m, 1 *m*-F); −163.5 (t, 1 *p*-F); −164.06 (t, 1 *p*-F); −165.77, −166.79, −166.97 (m, *m*-F). The *o*-F signals −119.03 and −124.64 coalesce at ∼ 50 °C and the *m*-F −162.11 and −166.79 at ∼ 30 °C. At rt −112.3 (br, 1 *o*-F); −113.77 (d, $^{3}J_{Pt-o-F} = 350$, 1 *o*-F); −119.11(d, $^{3}J_{Pt-o-F} = 458$, 1 *o*-F); −123.8 (br, 1 *o*-F); −163.43 (t, 1 *p*-F); −165.16 (t, 1 *p*-F); −166.21 (m, 1 *m*-F); −166.7 (m, 1 *m*-F). The other two *m*-F are very broad, nearly disappearing into the baseline, around −164.4 and −166.4. ^{31}P NMR ($CDCl_3$, δ): at rt 25.46 (s, $^{1}J_{Pt-P} = 2929$, 2P); 16.46 (br, $^{1}J_{Pt-P} = 2506$, 1P trans to C_6F_5).

Data for 5. Anal. Calcd for $C_{73}H_{50}F_{10}NP_3Pt_2$: C, 54.32; H, 3.12; N, 0.87. Found: C, 54.90; H, 3.89; N, 1.23. MS (FAB +): $m/z = 1614$ $[M + H]^+$ 1; 1446 $[M - C_6F_5]^+$ 1; 1351 $[M - PPh_3]^+$ 1; 1184 $[M - PPh_3 - C_6F_5]^+$ 2; 719 $[Pt(PPh_3)_2]^+$ 100; 560 $[PtH(C_2Py)(PPh_3)]^+$ 7; 455 $[Pt(PPh_3) - 2H]^+$ 26; 378 $[Pt(PPh_2) - 2H]^+$ 40. Ir (Nujol, cm^{-1}): 2090(s), 2063(s); $\nu(C_6F_5)_{x-sens}$ 787(s), 778(s). ^{1}H NMR ($CDCl_3$, δ): at rt 7.58−7.02 (m, Ph PPh_3, H^6 Py); 6.5 (t, $J_{H-H} = 7.5$, H^4); 6.11 (t, $J_{H-H} = 6.3$, H^5); 5.19 (d, $J_{H-H} = 8$, H^3); −17.01 (t, $^{2}J_{P-H} = 12.7$; $^{1}J_{Pt-H} = 982$, Pt−H). Assignment based on a COSY experiment. Due to the low solubility of complex **5**, its ^{13}C NMR spectrum is poorly resolved ($CDCl_3$, δ): at rt 148.09 (s, C^6); 134.54 (d, $^{2}J_{P-C} = 11.1$, *o*-C, Ph, PPh_3); 134.18 (t, $^{2}J_{P-C} = 6.9$, *o*-C, Ph, 2 PPh_3); 132.83 (d, $^{1}J_{P-C} = 50.6$, *i*-C, Ph, PPh_3); 130.75 (s, *p*-C, Ph, 2 PPh_3); 130.60 (t, $^{1}J_{P-C}+^{3}J_{P-C} = 56.0$, *i*-C, Ph, 2 PPh_3); 130.37 (s, py); 129.39 (s, *p*-C, Ph, PPh_3); 128.46 (t, $^{3}J_{P-C} = 5.4$, *m*-C, Ph, 2 PPh_3); 127.38 (d, $^{3}J_{P-C} = 10.1$, *m*-C, Ph, PPh_3); 119.0 (s, py). ^{19}F NMR ($CDCl_3$, δ): at rt −117.01 (m, $^{3}J_{Pt-o-F} = 401$); −117.61 (m, $^{3}J_{Pt-o-F} = 350$) (4 *o*-F); −161.78 (t, 1 *p*-F); −165.48 (m), −166.27 (m), −166.59 (m) (1 *p*-F, 4 *m*-F). A similar spectrum was observed at −50 °C. ^{31}P NMR ($CDCl_3$, δ): at rt 29.71 (s, $^{1}J_{Pt-P} = 3074$, 2P); 16.48 (br, $^{1}J_{Pt-P} = 2504$, 1P trans to C_6F_5).

X-ray Crystal Structure Determinations. Suitable crystals of $\mathbf{3}\cdot 1.25CH_2Cl_2\cdot 0.75C_6H_{14}$ were obtained by slow diffusion of *n*-hexane in CH_2Cl_2 solutions of complex **3** at −30 °C. Suitable crystals of $\mathbf{5}\cdot 0.75C_6H_{14}$ were obtained by slow diffusion of *n*-hexane in dichloromethane solutions of complex **5** at −30 °C.

Table 3. Crystal Data and Structure Refinement for $3\cdot1.25CH_2Cl_2\cdot0.75C_6H_{14}$ and $5\cdot0.75C_6H_{14}$

complex	$\mathbf{3}\cdot1.25CH_2Cl_2\cdot0.75C_6H_{14}$	$\mathbf{5}\cdot0.75C_6H_{14}$
empirical formula	$C_{92}H_{55}F_{20}N_2P_3Pt_4\cdot1.25CH_2Cl_2\cdot0.75C_6H_{14}$	$C_{73}H_{50}F_{10}NP_3Pt_2\cdot0.75C_6H_{14}$
fw	2612.44	1678.86
unit cell dimens		
a (Å)	33.503(5)	11.993(19)
b (Å)	20.5925(14)	15.56(2)
c (Å)	29.366(4)	23.23(4)
α (deg)	90	71.75(10)
β (deg)	113.654(14)	86.81(5)
γ (deg)	90	67.63(10)
volume (Å^3), *Z*	18558(4), 8	3797(10), 2
wavelength (Å)	0.71073	0.71073
temp (K)	150(2)	173(2)
radiation	graphite-monochromated Mo Kα	
cryst syst	monoclinic	triclinic
space group	*C*2/*c*	$P\bar{1}$
abs coeff (mm^{-1})	6.223	3.808
transmission factors	0.866, 0.396	0.996, 0.603
abs corr	ψ scans	ψ scans
diffractometer	Enraf-Nonius CAD4	Siemens STOE/AED2
2θ range for data collect. (deg)	4−50 ($+h$, $+k$, $\pm l$)	4−50 ($+h$, $\pm k$, $\pm l$)
no. of reflns collected	18 433	14 070
no. of indep reflns	18 068 (R(int) = 0.0534)	13 373 (R(int) = 0.1269)
refinement method	full-matrix least-squares on F^2	
goodness-of-fit on F^2 [b]	1.028	1.010
final *R* indices ($I > 2\sigma(I)$)[a]	$R1 = 0.0461$, $wR2 = 0.1060$	$R1 = 0.0905$, $wR2 = 0.1556$
R indices (all data)	$R1 = 0.0984$, $wR2 = 0.1841$	$R1 = 0.2535$, $wR2 = 0.2021$

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_c^2)^2]^{1/2}$. [b] Goodness-of-fit $= [\sum w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$. $w = [\sigma^2(F_o) + (g_1P)^2 + g_2P]^{-1}$; $P = [\max(F_o^2; 0) + 2F_c^2]/3$.

Crystal data and other details of the structure analyses are presented in Table 3. Crystals were fixed on top of glass or quartz fibers and mounted on the diffractometers. Unit cell constants were determined from 25 accurately centered reflections with 22.0° < 2θ < 27.9° for $\mathbf{3}\cdot1.25CH_2Cl_2\cdot0.75C_6H_{14}$, and 32 reflections in the range 21.4° < 2θ < 28.5° for $\mathbf{5}\cdot0.75C_6H_{14}$. Data were collected using ω/θ scans for $\mathbf{3}\cdot1.25CH_2Cl_2\cdot0.75C_6H_{14}$ and using ω scans for $\mathbf{5}\cdot0.75C_6H_{14}$. Three check reflections were measured at regular intervals, and no loss of intensity was observed in either case. The positions of the heavy atoms were determined from the Patterson maps. The remaining atoms were located in successive difference Fourier syntheses. H atoms were added at calculated positions (C−H = 0.96 Å) with isotropic displacement parameters assigned as 1.2 times the equivalent isotropic *U*'s of the corresponding C atoms. For $\mathbf{3}\cdot1.25CH_2Cl_2\cdot0.75C_6H_{14}$, the carbon atom (C(94)) of one molecule of dichloromethane lies on a 2-fold axis; thus only half of the atoms are present in the asymmetric unit, and these with only 0.5 occupancy. Also, one complete and one half molecule of *n*-hexane are present (the other half being generated by an inversion center); all the carbon atoms for these molecules were refined with 0.5 occupancy. For the dichloromethane molecule on the special position and the *n*-hexane molecules, the interatomic distances were restrained to idealized geometries, and for each *n*-hexane molecule all of the atoms were refined with a common set of anisotropic thermal parameters. The hydrogen atoms were not included for the dichloromethane and *n*-hexane molecules in the special positions. For the solvent molecules of $\mathbf{5}\cdot0.75C_6H_{14}$, isotropic displacement parameters were used. A common set of anisotropic displacement parameters was refined for each of the rings C(7) to C(12), N to C(19), C(20) to C(25), C(26) to C(31), and C(38) to C(43). A peak of electron density consistent with the geometry expected for the hydride group was found in the electron density maps and named as H(1). The distance Pt(2)−H(1) was restrained to 1.6 Å, and the isotropic displacement parameter for H(1) was fixed to 1.2 times the U_{iso} value of Pt(2). The interatomic bond lengths and angles for the *n*-hexane molecules were fixed to sensible geometries, and all the carbon atoms in each of these molecules were given common anisotropic thermal parameters. For $\mathbf{3}\cdot1.25CH_2Cl_2\cdot0.75C_6H_{14}$ a final difference electron density map showed eight peaks above 1 e Å^{-3} (max 1.46; largest diff hole −1.45), all within 1.1 Å of the Pt atoms. For $\mathbf{5}\cdot0.75C_6H_{14}$ a final difference electron density map showed 18 peaks above 1 e Å^{-3} (max 1.76; largest diff hole −1.01) in the vicinity of the platinum atoms or the solvent molecules. All calculations were carried out using the program SHELXL-93.[30]

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Supporting Information Available: Tables giving positional and thermal parameters, bond distances, and bond angles for $\mathbf{3}\cdot1.25CH_2Cl_2\cdot0.75C_6H_{14}$ and $\mathbf{5}\cdot0.75C_6H_{14}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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[30] Sheldrick, G. M. *SHELXL-93*, a program for crystal structure determination; University of Göttingen: Germany, 1993.

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