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Cyclometallated Platinum(II) Complexes with a Phenylpropene-derived π/σ-Chelator and N-heterocyclic Carbenes

Han Vinh Huynh,*[a] Van Thong Pham,[b] Nguyen Thi Thanh Chi*[b]

Abstract: A series of heteroleptic platinum(II) complexes of the general formula [PtX(ⁱPrEug)(NHC)] (**2**–**7**) bearing the organometallic π/σ chelator ⁱPrEug (isopropyl eugenoxyacetate), varying halido and NHCs ligands derived from imidazole, benzimidazole and triazole have been prepared and fully characterized by elemental analyses, ESI mass spectrometry, IR and NMR spectroscopies. Complexes **3** and **5**–**7** were also characterized by single-crystal X-ray diffraction. The air-stable complexes are rare examples of platinum(II) compounds containing three different types of carbon donors, *i.e.* aryl, carbene and olefin. Unsymmetrical NHCs lead to rotameric pairs of **4** and **5** exhibiting different NMR spectroscopic features. Spectroscopic studies also revealed that the introduction of a NHC leads to a weakening of the metal–olefin bond and strengthening of the metal–aryl bond. Backbone and thus electronic variations among the NHCs on the other hand show little influence on the bonding of the ⁱPrEug chelator.

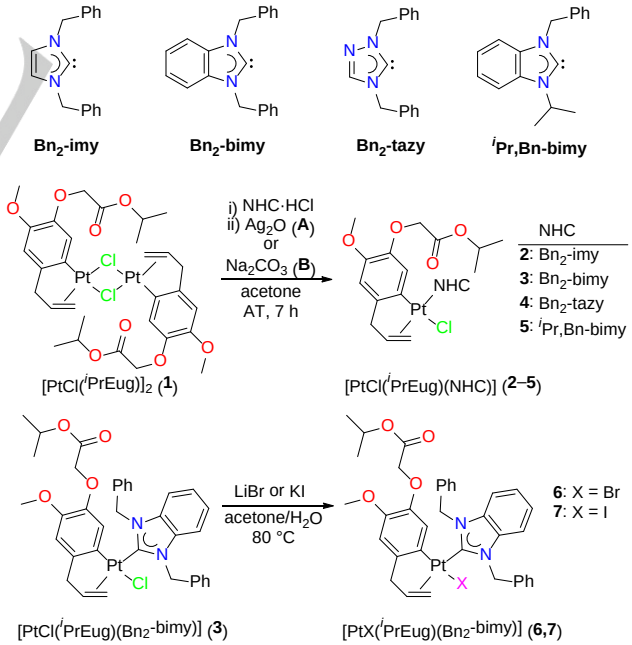
Introduction

The platinum complex K[PtCl$_3$(C$_2$H$_4$)] known as Zeise's salt is the first example of a transition-metal olefin complex.[1] Alkene ligands are indeed very common in organoplatinum chemistry, where they act as two π-electron donors to give rather stable complexes.[2] In addition to olefin-coordination, platinum centers also often show the tendency to undergo ortho-metalation with functionalized aromatic compounds.[3] Thus, olefin-functionalized benzenes such as propenylbenzenes are potentially useful ligand precursors, where pre-coordination of the terminal olefin-function to platinum could assist in the subsequent ortho-C-H activation of the phenyl ring. Such an approach has been used in our previous research to furnish organometallic platinum(II) complexes with ditopic π/σ chelators derived from naturally occurring derivatives such as safrole and eugenol.[4]

Another type of ligand that has received tremendous attention in organometallic chemistry for the last two decades are N-heterocyclic carbenes (NHCs).[5] Given the dominant roles of olefin and NHC ligands in general, it is surprising to note that mixed NHC/olefin complexes are relatively unexplored in platinum chemistry. Most reported examples contain platinum(0) centers, and the respective complexes have found application as hydrosilylation catalysts.[6] Those of platinum(II) are surprisingly rare.[7] The introduction of NHCs into the aforementioned π/σ-complexes would result in complexes with three different types of carbon donors, which could have interesting electronic and structural features of fundamental interest. As a contribution to this area, we herein report on the preparation and characterization of a series of heteroleptic platinum(II) complexes bearing all three types of carbon donors.

Results and Discussion

The dimeric platinum(II) complex containing the isopropyl eugenoxyacetate (ⁱPrEugH) derived chelator [Pt(μ-Cl)(ⁱPrEug)]$_2$ (**1**) can be obtained by ortho-metallation from K[PtCl$_3$(ⁱPrEugH)] in aqueous media. Complexes of this type are prone to bridge-cleavage reactions, which allows the easy introduction of various co-ligands. Thus, mixing complex **1** with azolium salts and a suitable base at ambient temperature (AT) leads to in situ generation of NHCs, which cleave the chlorido bridges in the diplatinum precursor giving the new mononuclear complexes [PtCl(ⁱPrEug)(NHC)] (**2**-**5**) in good yields (Scheme 1). In the case of Ag$_2$O, an intermediate silver(I)-carbene complex may have formed as an NHC transfer agent.



Scheme 1. Preparation of heteroleptic Pt^{II} complexes

Three symmetrically substituted N,N-dibenzylazolium salts derived from imidazole, benzimidazole and 1,2,4-triazole were chosen to study potential electronic influences of the resulting

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classical carbenes differing in their backbones on the properties of the respective complexes. In addition, the unsymmetrical 1-isopropyl-3-benzylbenzimidazolium chloride was included to study potential rotamers.

It was found that both Ag_2O and Na_2CO_3 were suitable bases giving similar and high product yields ranging from 85–95%. In addition, halido exchange reactions were carried out using the chlorido complex [PtCl(ⁱPrEug)(Bn$_2$-bimy)] (**3**) and LiBr and KI, which gave rise to complexes [PtBr(ⁱPrEug)(Bn$_2$-bimy)] (**6**) and [PtI(ⁱPrEug)(Bn$_2$-bimy)] (**7**), respectively. All complexes were obtained as air- and moisture stable, pale-yellow solids that are soluble in $CHCl_3$, CH_2Cl_2, $(CH_3)_2CO$, CH_3CN and DMSO, but insoluble in H_2O, EtOH, and Et_2O. Base peaks for the [M – halide]$^+$ cations were observed in the ESI mass spectra of all complexes, which provide evidence for the proposed NHC coordination (Table 1). Moreover, correct isotopic patterns for [M + Na]$^+$ cations were also detected with different intensities, which allows differentiation of complexes **3**, **6** and **7**.

Table 1. Cations Detected by ESI mass spectroscopy

Complex	[M – X]$^+$ (%)	[M + Na]$^+$ (%)
[PtCl(ⁱPrEug)(Bn$_2$-imy)] (**2**)	706 (100)	765 (8)
[PtCl(ⁱPrEug)(Bn$_2$-bimy)] (**3**)	756 (100)	815 (24)
[PtCl(ⁱPrEug)(Bn$_2$-tazy)] (**4**)	707 (100)	765 (88)
[PtCl(ⁱPrEug)(ⁱPr,Bn-bimy)] (**5**)	708 (100)	766 (24)
[PtBr(ⁱPrEug)(Bn$_2$-bimy)] (**6**)	756 (100)	858 (30)
[PtI(ⁱPrEug)(Bn$_2$-bimy)] (**7**)	756 (100)	906 (62)

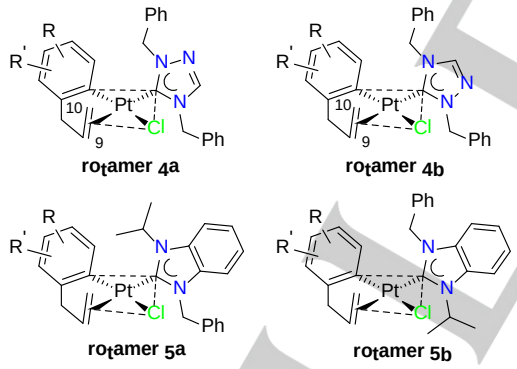


Figure 1. Rotameric forms of complexes **4** and **5**. The assignment to **a** and **b** forms is tentative.

In agreement with the mass spectrometric studies, all ^{1}H and ^{13}C{^{1}H} NMR spectra of the complexes show signals for the NHC and the bidentate ⁱPrEug chelator in a 1:1 ratio. For the complexes **4** and **5** bearing unsymmetrical NHCs, two sets of signals are observed indicative of two inseparable, rotameric complexes **4a/b** and **5a/b**, respectively (Figure 1). For the former, an initial rotameric ratio of 1:0.08 was calculated from the integrals, which reached equilibrium after 6 h with a ratio of 1:0.92 (Figure 2) indicating rotational freedom about the Pt-carbene bond. The essentially equal distribution of both forms of **4** is not surprising, since both N-substituents in the triazolin-5-ylidene are the same offering no steric nor electronic preference for either rotamer.

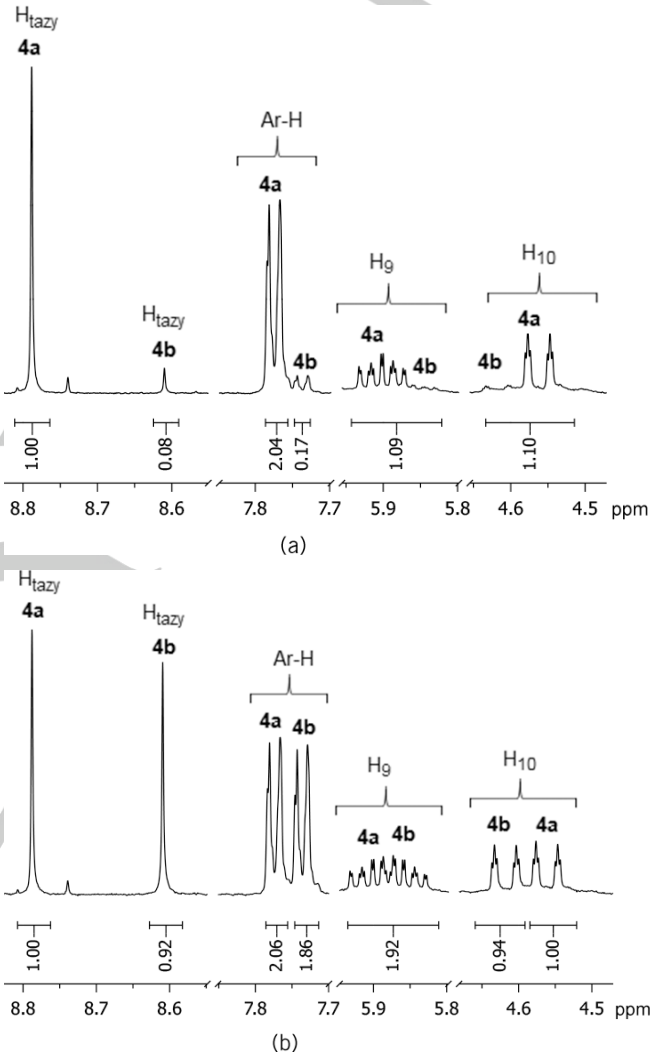


Figure 2: Expanded plots of ^{1}H NMR spectra of [PtCl(ⁱPrEug)(Bn$_2$-tazy)] (**4a** and **4b**) after dissolving the sample (a) and at the equilibrium (b).

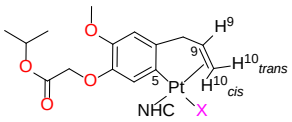
For complex **5**, the ratio equilibrates from initially 1:0.06 to 1:0.65. The slight preference for one form is possibly due to the slightly different steric bulk of the isopropyl and benzyl groups. In rotamer **5a**, the isopropyl group is above the square planar coordination plane and on the same side as the olefinic CH_2 group, while it is pointing away from the latter in form **5b**. Due to the isomerization, a further differentiation between the respective rotamers of **4** and **5** is at the moment not possible.[8]

Of particular interest are potential changes in the resonances of the ⁱPrEug chelator upon NHC binding.

Coordination of the carbene is expected to occur *trans* to the olefin, which would minimize electronic competition between the aryl and NHC as the two strongest donors in these complexes.

Generally, all olefinic ^{1}H and ^{13}C NMR resonances of complexes **2-7** shift significantly downfield upon carbene coordination compared to the parent complex **1** (Table 2). The resemblance of their H^{9}, H^{10}_{cis} and H^{10}_{trans} resonances to those of the free isopropyl eugenoxyacetate (*i.e.* δ_H 5.96, 5.08, 5.01 ppm) indicates weaker olefin-binding due to the strong *trans* influences of the NHCs compared to the μ-chlorido ligand in complex **1**. The magnitude of change is the largest for the H^{9} nucleus compared to the two H^{10} hydrogen atoms, while the chemical shift differences are in the same range for the C9 and C10 nuclei. Comparison among complexes **2**–**4**, which solely differ in the carbene backbone does not reveal any notable trend. Apparently, the decreasing donor ability[9] in the order Bn_2-imy > Bn_2-bimy > Bn_2-tazy is insufficient to induce clear trends in olefinic resonances. Comparison between complexes **3**, **6** and **7** containing different halido ligands, however, shows a deshielding (downfield) trend on the olefinic protons with increasing electron density of the *cis*-halido ligands in the order Cl < Br < I. The increasing pile-up of electron density going from **3** via **6** to **7** leads to a notable weakening of the platinum–olefin bonds.

Table 2. Selected ^{1}H and ^{13}C NMR signals[a] of complexes **1–7**



Complex	H^{9}	H^{10}_{cis}	H^{10}_{trans}	C9	C10	C5	C_{NHC}
1	5.09	4.00	4.27	91.2	64.2	141.1	-
2	5.79	4.52	4.82	111.0	84.1	127.7	172.9
3	5.92	4.67	4.95	113.0	86.4	127.8	184.2
4a	5.92	4.58	4.90	112.3,	85.4,	127.7,	177.0
4b	5.85	4.62	4.88	112.2	85.1	127.3	
5a[b]	5.98	4.72	5.00	112.9_8,	86.3,	125.9,	181.8,
5b[b]		4.70	4.99	112.9_7	85.9	125.2	181.7
6	5.93	4.73	5.05	112.1	85.4	129.9	184.3
7	5.98	4.83	5.18	111.4	83.9	135.0	184.5

[a] acetone-d_6, [b] $CDCl_3$.

On the other hand, all aryl carbon donors (C5) *cis* to the NHC experience an upfield shift upon NHC coordination, which would indicate stronger binding possibly to compensate for the weaker olefin coordination of the chelator. However, with increasing electron density and thus better *trans* influences of the *trans*-halido ligands, these resonances gradually shift downfield again.

The good solubility of complexes allows for detection of all $^{13}C_{carbene}$ NMR resonances, which are in the range of 172.9–184.5 ppm and primarily influenced by their different backbones. Comparison of complexes **3**, **6** and **7**, which contain the same NHC, but different *cis*-halido ligands does not reveal any significant halido effect. In comparison to other mono- and bis(NHC) complexes of platinum(II),[10] these resonances are notably more downfield. This indicates that all complexes are significantly electron-rich complexes, which needs to be considered for their future applications.

Overall, the conclusion can be made that the bonding of the ^{i}PrEug π/σ chelator is similar in complexes with different classical NHCs derived from imidazole, benzimidazole and triazole.

Single crystals of complexes **3**, **5**, **6** and **7** suitable for X-ray analyses could be obtained from evaporation of their concentrated solutions in acetone/water (**3**, **6**, **7**) or chloroform/isopropanol (**5**). Their molecular structures depicted in Figure 3 confirm the distorted square planar geometry of all complexes. The platinum centers are coordinated by the ^{i}PrEug chelator, a halido ligand and the carbene. The latter is indeed bound *trans* to the olefin, which places the two strongest donors in the electronically more favorable *cis* arrangement to each other. The complexes are rare examples of complexes containing three different types of carbon donors, *i.e.* anionic aryl, neutral carbene and η^2-olefin. The carbene plane is oriented almost perpendicularly to the square planar coordination plane with dihedral angles ranging from 68.9–72.80°. The orientation of the C=C bond vector of the olefin donor with respect to the coordination plane is similar with dihedral angles from 79.3–86.1°. Because of this orientation, the space above and below the coordination becomes inequivalent.

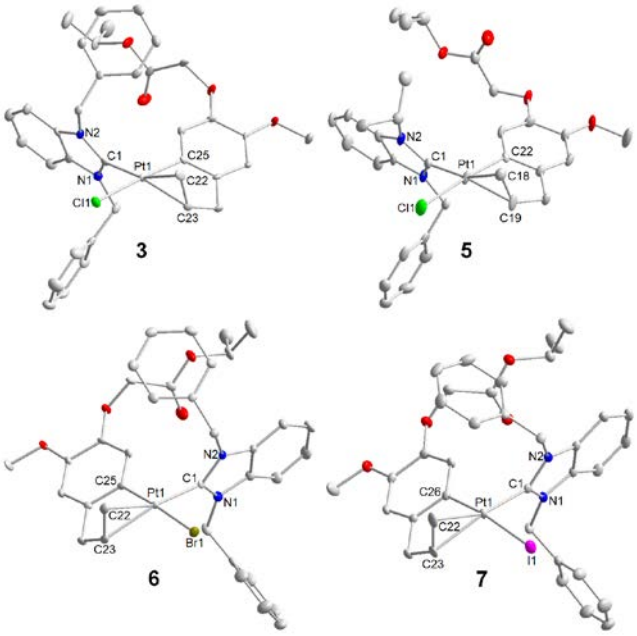


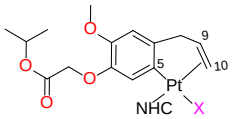
Figure 3. Solid state molecular structures of complexes **3**, **5**, **6** and **7** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

For example, all depictions in Figure 3 show the CH_2 group of the terminal olefin on the upper side of the square plane. This makes the complexes axially chiral. Nevertheless, the compounds with symmetrical NHCs were obtained as racemates due to lack of chiral induction, while unsymmetrical NHCs gives rise to rotameric (diastereomers) pairs (vide supra). Complex **5**

is an example, which crystallized as rotamer **5a**, where the isopropyl and the olefinic CH_2 groups are on the same side with respect to the square plane.

The bond parameters of the first coordination sphere and the C=C double bond are summarized in Table 3. They show that all four complexes have very similar bond distances and angles. The Pt–carbene distances are identical with an average value of 2.0 Å, which is not surprising since all contain benzimidazolin-2-ylidene ligands. Moreover, they are in the typical range of other benzimidazolin-2-ylidene complexes.[10a] The Pt–aryl and Pt–olefin bonds are also indistinguishable within 3σ with averaged values of 2.0, 2.2 and 2.2 Å, respectively. In comparison to the precursor **1**, the Pt–olefin bonds have become elongated (*cf.* Pt–C9 2.141(3) and Pt–C10 2.108(3) Å) and slightly weakened, which is in agreement with observations made by ^{1}H NMR spectroscopy in solution (vide supra). As such the olefinic character has marginally increased compared to that in the parent complex **1** {C9–C10 1.393(5) Å} as well.

Table 3. Selected bond parameters of complexes **3** and **5**–**7**



bond parameter[a]	**3** (X = Cl)	**5** (X = Cl)	**6** (X = Br)	**7** (X = I)
Pt−C_{NCN}	2.000(5)	1.996(6)	2.006(5)	2.002(2)
Pt−C5	1.997(5)	2.011(6)	2.012(5)	2.010(2)
Pt−X	2.409(1)	2.401(2)	2.5316(6)	2.7020(2)
Pt−C9	2.219(5)	2.223(6)	2.222(5)	2.227(2)
Pt−C10	2.205(6)	2.207(7)	2.205(6)	2.212(2)
C9−C10	1.378(8)	1.36(1)	1.372(8)	1.376(3)
X−Pt−C5	176.1(2)	175.2(2)	176.5(1)	172.96(5)
X−Pt−C_{NCN}	91.2(2)	90.0(2)	90.6(1)	92.19(5)
C5−Pt−C_{NCN}	92.5(2)	92.5(2)	92.7(2)	91.33(8)
PtC_2X/NHC	70.2(2)	68.9(2)	70.5(1)	72.80(5)
PtC_2X/alkene	81.8(3)	79.3(3)	81.5(3)	86.1(1)

[a] bond distances in [Å] and angles in [deg].

Conclusions

Six new platinum complexes of the general formula [PtX(^{i}PrEug)(NHC)] (**2**-**7**) bearing three different types of carbon donors, *i.e.* anionic aryl, neutral carbene and olefin, have been prepared and fully characterized by various spectroscopic and spectrometric means. Solid-state molecular structures have also been determined for four complexes. The introduction of a NHC *trans* to the olefin leads to a weakening of the olefin coordination. On the other hand, variation of the three classical NHCs derived from imidazole, benzimidazole and 1,2,4-triazole does not show any significant effect on the π/σ chelating ^{i}PrEug ligand. The unusual coordination sphere results in axially-chiral complexes, which were obtained as racemates due to the lack of chiral induction from the achiral ligands. Moreover, the use of unsymmetrical NHCs leads to rotameric pairs.

The good stability of this new family of organometallic compounds warrants their further extension, which will involve chiral predetermination studies using chiral NHCs and detailed characterizations of their rotamers. Moreover, attempts will be made to explore potential applications of such complexes.

Experimental Section

General Considerations. Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture. All solvents and chemicals were used as received without any further treatment if not noted otherwise. Ag_2O was purchased from Sigma-Aldrich. The azolium salts[11] Bn_2-imy·HCl, Bn_2-bimy·HCl and Bn_2-tazy·HCl and the complexes K[$PtCl_3$(^{i}PrEugH)][4a] and [PtCl(^{i}PrEug)]$_2$ (**1**)[4b,4c] were prepared as previously reported. Mass spectra were measured using a Finnigan MAT LCQ (ESI) and Finnigan/MAT 95XL-T (FAB) spectrometer. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer. Infrared spectra were recorded on IMPACK-410 NICOLET spectrometer as KBr discs in the range 400–4000 cm^{-1}. ^{1}H, ^{13}C, and 2D NMR spectra were recorded on a Bruker AVANCE 500 MHz at 298–300 K, and the chemical shifts (δ) were internally referenced using the residual protio-solvent signals relative to tetramethylsilane. The following abbreviations were used to designate the multiplicities: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, t-d = triplet of doublets, m = multiplet, ov = overlap.

General procedure for the synthesis of [PtCl(^{i}PrEug)(NHC)] complexes (2-5). All the complexes of the general formula [PtCl(^{i}PrEug)(NHC)] (**2**–**5**) were prepared according to Method A. Besides, the complexes **3**–**5** were also synthesized following Method B.

Method A. A mixture of [PtCl(^{i}PrEug)]$_2$ (99 mg, 0.1 mmol), NHC·HCl (0.2 mmol) and Ag_2O (27 mg, 0.12 mmol) was suspended in acetone (5 mL), stirred and shielded from light at ambient temperature (AT) for 7 h. The reaction mixture was then filtered through Celite, and the residue was repeatedly washed by acetone until the filtrate was colorless. The solvent of the filtrate was removed under vacuum to give solids, which were subsequently washed with warm water (3 × 3 mL) and cold ethanol (2 × 2 mL). Drying under vacuum for 2 h afforded the products as a pale-yellow powder.

Method B. The procedure was similar to that of Method A, but Na_2CO_3 (12 mg, 0.11 mmol) was used instead of Ag_2O. The yields of the preparations according to Method A and B were similar.

General procedure for the synthesis of [PtX(^{i}PrEug)(NHC)] complexes (6, 7). A mixture of **3** (79 mg, 0.1 mmol) and either LiBr (for **6**) or KI (for **7**) (0.5 mmol) was dissolved in an acetone-water mixture (15 mL; 2:1, *v/v*) and stirred at 80 °C under reflux for 10 h. The mixture was concentrated down to ~3 mL under reduced pressure, and the resulting yellow suspension was filtered. Washing the precipitate with water (3 × 3 mL) and drying under vacuum for 2 h afforded the product as a yellow solid.

[PtCl(^{i}PrEug)(Bn_2-imy)] (2). Yield: 126 mg (0.17 mmol, 85%). ^{1}H NMR (500 MHz, acetone-d_6): δ 7.73 (d, ^3J(H,H) = 7.5 Hz, 2H, Ar−H), 7.43 (d, ^3J(H,H) = 2 Hz, 1H, H_{imy}), 7.41–7.32 (m, 5H, Ar–H), 7.29 (dd, ^3J(H,H) = 5 Hz, ^4J(H,H) = 1.5 Hz, 3H, Ar−H), 7.20 (d, ^3J(H,H) = 2 Hz, 1H, H_{imy}), 6.70 (s, 1H, Ar-H), 5.97/5.53/5.35/4.93 (d, ^2J(H,H) = 14.5 Hz, 4H, NCH_2), 5.79 (m, $^2J_{PtH}$ = 65 Hz, 1H, CH=C), 5.57 (s, $^3J_{PtH}$ = 65, 1H, Ar-H), 4.97 (m, 1H, O-CH), 4.82 (d, ^3J(H,H) = 8 Hz, $^2J_{PtH}$ = 50 Hz, 1H, C=CH_2), 4.52 (d, ^3J(H,H) = 16.5 Hz, $^2J_{PtH}$ = 65 Hz, 1H, C=CH_2), 4.21/4.07 (d, ^2J(H,H) = 16 Hz, 2H, OCH_2), 3.75–3.68 (ov, 4H, CH_2-CH, OCH_3), 3.05 (d, ^3J(H,H) =

17.5 Hz, $^3J_{PtH}$ = 90 Hz, 1H, CH_2-CH), 1.19 (d, ^3J(H,H) = 6.5, 6H, C-(CH_3)$_2$). ^{13}C NMR (125.8 MHz, acetone-d_6): 172.9 (NCN), 168.7 (C=O), 147.4, 145.1, 144.4, 137.4, 136.9, 129.6, 129.5, 129.4, 129.1, 128.9, 128.8, 128.6, 128.3, 127.7, 122.3, 121.9, 121.8, 111.1 (Ar-C), 111.0 (*C*H=CH$_2$), 84.1 (CH=*C*H$_2$), 68.3 (O-CH), 66.8 (O*C*H$_2$), 55.9 (O*C*H$_3$), 54.5/54.3 (N*C*H$_2$), 38.7 (*C*H$_2$-CH), 21.6/21.5$_9$ (C-(*C*H$_3$)$_2$). Anal. Calcd for $C_{32}H_{35}N_2O_4ClPt$: C, 51.79; H, 4.72; N, 3.78. Found: C, 51.48; H, 4.30; N, 3.95. MS (ESI) Calcd for [M − Cl]$^+$, $C_{32}H_{35}N_2O_4Pt$: *m/z* 706. Found (%): *m/z* 706 (100). Calcd for [M + Na]$^+$, $C_{32}H_{35}N_2O_4ClPtNa$: *m/z* 764. Found (%): *m/z* 764 (8). FT-IR (KBr pellet, cm^{-1}): ῦ 1748 (C=O); 1562, 1458 (C=C).

[PtCl(*i*PrEug)(Bn$_2$-bimy)] (3). Yield: 143 mg (0,18 mmol, 90%). Yellowish crystals were obtained by slow evaporation within 16 hours from a concentrated acetone/water solution at RT. ^{1}H NMR (500 MHz, acetone-d_6): δ 7.80 (d, ^3J(H,H) = 7.5 Hz, 2H, Ar−H), 7.69 (d, ^3J(H,H) = 7.5 Hz, 1H, Ar−H), 7.56 (d, ^3J(H,H) = 7.5 Hz, 2H, Ar−H), 7.43 (d, ^3J(H,H) = 7.5 Hz, 1H, Ar−H), 7.39 (t, ^3J(H,H) = 7.5 Hz, 2H, Ar−H), 7.35–7.29 (m, 2H, Ar−H), 7.29−7.25 (m, 4H, Ar−H), 6.72 (s, 1H, Ar-H), 6.34/6.05/5.80/5.41 (d, ^2J(H,H) = 15 Hz, 4H, N*C*H$_2$), 5.92 (m, $^2J_{PtH}$ = 65 Hz, 1H, CH=C), 5.78 (s, $^3J_{PtH}$ = 65 Hz, 1H, Ar-H), 4.95 (d, ^3J(H,H) = 8.5 Hz, $^2J_{PtH}$ = 50 Hz, 1H, C=CH$_2$), 4.67 (d, ^3J(H,H) = 15 Hz, $^2J_{PtH}$ = 60 Hz, 1H, C=CH$_2$), 4.30 (m, 1H, O-CH), 4.21/4.04 (d, ^2J(H,H) = 16 Hz, 2H, OCH$_2$), 3.75 (dd, ^2J(H,H) = 17 Hz, ^3J(H,H) = 6.5 Hz, 1H, CH_2-CH), 3.70 (s, 3H, OCH$_3$), 3.11 (d, ^3J(H,H) = 17 Hz, $^3J_{PtH}$ = 90 Hz, 1H, CH_2-CH), 0.97/0.87 (d, ^3J(H,H) = 6.5, 6H, C-(CH$_3$)$_2$). ^{13}C NMR (125.8 MHz, acetone-d_6): 184.2 (NCN), 169.4 (C=O), 148.2, 145.8, 145.0, 137.4, 136.8, 135.6, 135.1, 129.8, 129.7, 129.5, 129.2, 129.0, 128.9, 127.8, 124.8, 124.6, 122.9, 113.1, 112.6, 111.7 (Ar-C), 113.0 (*C*H=CH$_2$), 86.4 (CH=*C*H$_2$), 68.8 (O-CH), 67.5 (OCH$_2$), 56.4 (OCH$_3$), 53.0/52.7 (NCH$_2$), 39.2 (*C*H$_2$-CH), 21.9$_6$/21.9$_5$ (C-(*C*H$_3$)$_2$). Anal. Calc. for $C_{36}H_{37}N_2O_4ClPt$: C, 54.58; H, 4.67; N, 3.54. Found: C, 54.87; H, 4.37; N, 3.85. MS (ESI) Calcd for [M − Cl]$^+$, $C_{36}H_{37}N_2O_4$ Pt: *m/z* 756. Found (%): *m/z* 756 (100). Calcd for [M + Na]$^+$, $C_{36}H_{37}N_2O_4ClPtNa$: *m/z* 814. Found (%): *m/z* 814 (24). FT-IR (KBr pellet, cm^{-1}): ῦ 1748 (C=O); 1590, 1562, 1485 (C=C).

[PtCl(*i*PrEug)(Bn$_2$-tazy)] (4). Yield: 134 mg (0.18 mmol, 90%). ^{1}H NMR (500 MHz, acetone-d_6): **4a**: δ 8.81 (s, 1H, H$_{tazy}$), 7.79 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.5 Hz, 2H, Ar−H), 7.45–7.36 (m, 5H, Ar−H), 7.29–7.28 (m, 3H, Ar−H), 6.73 (s, 1H, Ar-H), 6.01/5.61/5.39/5.05 (d, ^2J(H,H) = 14.5 Hz, 4H, N*C*H$_2$), 5.92 (m, 1H, CH=C), 5.37 (s, $^3J_{PtH}$ = 65 Hz, 1H, Ar-H), 4.98 (m, 1H, O-CH), 4.90 (d, ^3J(H,H) = 8.5 Hz, $^2J_{PtH}$ = 50 Hz, 1H, C=CH$_2$), 4.58 (d, ^3J(H,H) = 15 Hz, $^2J_{PtH}$ = 60 Hz, 1H, C=CH$_2$), 4.19/4.02 (d, ^2J(H,H) = 16.5 Hz, 2H, OCH$_2$), 3.82 (dd, ^2J(H,H) = 17 Hz, ^3J(H,H) = 6.5 Hz, 1H, CH$_2$-C), 3.72 (s, 3H, OCH$_3$), 3.10 (d, ^3J(H,H) = 17 Hz, $^3J_{PtH}$ = 90 Hz, 1H, CH$_2$-C), 1.23/1.22 (d, ^3J(H,H) = 5.5 Hz, 6H, C-(CH$_3$)$_2$). **4b**: 8.63 (s, 1H, H$_{tazy}$), 7.73 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.5 Hz, 2H, Ar−H), 7.45–7.40 (m, 5H, Ar−H), 7.32–7.31 (m, 3H, Ar−H), 6.73 (s, 1H, Ar-H), 6.12/5.62/5.24/5.07 (d, ^2J(H,H) = 14.5 Hz, 4H, N*C*H$_2$), 5.85 (m, 1H, CH=C), 5.45 (s, $^3J_{PtH}$ = 65 Hz, 1H, Ar-H), 4.98 (m, 1H, O-CH), 4.88 (d, ^3J(H,H) = 8.5 Hz, $^2J_{PtH}$ = 50 Hz, 1H, C=CH$_2$), 4.62 (d, ^3J(H,H) = 15 Hz, $^2J_{PtH}$ = 60 Hz, 1H, C=CH$_2$), 4.20/4.00 (d, ^2J(H,H) = 16.5 Hz, 2H, OCH$_2$), 3.82 (dd, ^2J(H,H) = 17 Hz, ^3J(H,H) = 6.5 Hz, 1H, CH_2-CH), 3.71 (s, 3H, OCH$_3$), 3.10 (d, ^3J(H,H) = 17 Hz, $^3J_{PtH}$ = 90 Hz, 1H, CH_2-CH), 1.23/1.22 (d, ^3J(H,H) = 5.5 Hz, 6H, C-(CH$_3$)$_2$). ^{13}C NMR (125.8 MHz, acetone-d_6) for the mixture of **4a** and **4b** at the equilibrium: 177.0 (NCN), 169.2/169.1 (C=O), 148.0, 147.9, 145.6$_3$, 145.5$_9$, 144.8, 144.7, 144.5, 136.9, 136.7, 136.2$_3$, 136.1$_7$, 130.3$_3$, 130.3, 129.8, 129.6, 129.5$_2$, 129.4$_8$, 129.4, 129.3, 129.2, 128.9, 127.7, 127.3, 122.0, 121.7, 111.6, 111.5$_6$ (Ar-C), 112.2$_5$/112.1$_6$ (*C*H=CH$_2$), 85.4/85.1 (CH=*C*H$_2$), 68.8$_7$/68.8$_4$ (O-CH), 67.0/66.9 (O*C*H$_2$), 57.0$_3$/56.9$_8$/52.6$_3$/52.5 (N*C*H$_2$), 56.3 (O*C*H$_3$), 39.1$_5$/39.0$_9$ (*C*H$_2$-CH), 22.0$_7$/22.0$_5$/22.0$_2$/22.0 (C-(*C*H$_3$)$_2$). Anal. Calc. for $C_{31}H_{34}N_3O_4ClPt$: C, 50.10; H, 4.58; N, 5.66. Found: C, 50.11; H, 4.47; N, 5.64. MS (ESI) Calcd for [M − Cl]$^+$, $C_{31}H_{34}N_3O_4Pt$: *m/z* 707. Found (%): *m/z* 707. Calcd for [M + Na]$^+$, $C_{31}H_{34}N_3O_4ClPtNa$: *m/z* 765. Found (%): *m/z* 765 (90). FT-IR (KBr pellet, cm^{-1}): ῦ 1740 (C=O); 1585, 1535, 1489 (C=C).

[PtCl(*i*PrEug)(*i*Pr,Bn-bimy)] (5). Yield: 129 mg (0.174 mmol, 87%). Yellow crystals were obtained by slow evaporation within 10 hours from a concentrated chloroform/isopropanol solution at ambient temperature. ^{1}H NMR (500 MHz, chloroform-d_1): **5a**: δ 7.67 (d, ^3J(H,H) = 8 Hz, 1H, Ar−H), 7.30–7.20 (m, 6H, Ar−H), 7.15−7.14 (m, 2H, Ar−H), 6.64 (s, 1H, Ar-H), 6.14 (m, 1H, NCH), 6.08 (s, 1H, Ar−H), 5.98 (m, $^2J_{PtH}$ = 65 Hz, 1H, CH=C), 5.74/5.42 (d, ^2J(H,H) = 16 Hz, 2H, NCH$_2$), 5.00 (d, ^3J(H,H) = 8 Hz, $^2J_{PtH}$ = 50 Hz, 1H, C=CH$_2$), 4.72 (d, ^3J(H,H) = 15 Hz, $^2J_{PtH}$ = 60 Hz, 1H, C=CH$_2$), 4.60 (m, 1H, O-CH), 4.36/4.26 (d, ^2J(H,H) = 16 Hz, 2H, OCH$_2$), 3.78−3.74 (ov, 4H, CH_2-CH, OCH$_3$), 3.09 (d, ^3J(H,H) = 17 Hz, $^3J_{PtH}$ = 90 Hz, 1H, CH_2-CH), 1.88/1.87 (d, ^3J(H,H) = 7 Hz, 6H, NCH-(CH_3)$_2$), 1.03/1.01 (d, ^3J(H,H) = 6 Hz, 6H, C-(CH$_3$)$_2$). **5b**: ^{1}H NMR (500 MHz, chloroform-d_1): δ 7.61−7.56 (ov, 2H, Ar−H), 7.40–7.33 (m, 4H, Ar−H), 7.30−7.11 (ov, 3H, Ar−H), 6.65 (s, 1H, Ar−H), 6.23/5.84 (d, ^2J(H,H) = 15.5 Hz, 2H, NCH$_2$), 5.98 (m, $^2J_{PtH}$ = 65 Hz, 1H, CH=C), 5.66–5.63 (ov, 2H, Ar−H, NCH), 4.99 (d, ^3J(H,H) = 8 Hz, $^2J_{PtH}$ = 50 Hz, 1H, C=CH$_2$), 4.70 (d, ^3J(H,H) = 15 Hz, $^2J_{PtH}$ = 60 Hz, 1H, C=CH$_2$), 4.52 (m, 1H, O-CH), 4.20/4.01 (d, ^2J(H,H) = 16 Hz, 2H, OCH$_2$), 3.86 (dd, ^2J(H,H) = 16.5 Hz, ^3J(H,H) = 6.5 Hz, 1H, CH_2-CH), 3.75 (s, 3H, OCH$_3$), 3.14 (d, ^3J(H,H) = 16.5 Hz, $^3J_{PtH}$ = 90 Hz, 1H, CH_2-CH), 1.64/1.29 (d, ^3J(H,H) = 7, 6H, NCH-(CH_3)$_2$), 1.05/0.94 (d, ^3J(H,H) = 6, 6H, C-(CH$_3$)$_2$). ^{13}C NMR (125.8 MHz, acetone-d_6) for the mixture of **5a** and **5b** at the equilibrium: 181.7$_5$/181.6$_9$ (NCN), 168.7/168.5 (C=O), 147.4, 146.9, 145.1, 144.4, 144.0, 143.9, 135.7, 135.4, 135.2, 134.9, 132.6, 132.5, 128.9, 128.8, 128.7, 128.3$_4$, 128.2$_9$, 128.2, 128.0, 127.7, 125.9, 125.2, 123.4, 123.3, 123.1$_3$, 123.1$_0$, 122.9, 121.8, 112.2$_0$, 112.1$_7$, 112.1, 111.1, 110.4, 110.0 (Ar-C), 112.9$_8$/112.9$_7$ (*C*H=CH$_2$), 86.3/85.9 (CH=*C*H$_2$), 68.4$_4$/68.4$_3$ (O-CH), 67.7/67.1 (O*C*H$_2$), 56.0/55.9 (O*C*H$_3$), 54.48/54.43 (NCH), 52.6/52.1 (N*C*H$_2$), 38.5$_7$/38.5$_3$ (*C*H$_2$-CH), 21.6$_3$, 21.6, 21.5$_6$, 21.4, 21.2$_8$, 21.2$_5$, 20.3 (CH-(*C*H$_3$)$_2$). Suitable elemental analysis could not be obtained despite several recrystallization attempts. MS (ESI) Calcd for [M − Cl]$^+$, $C_{32}H_{37}N_2O_4Pt$: *m/z* 708. Found (%): *m/z* 708 (100). Calcd for [M + Na]$^+$, $C_{32}H_{37}N_2O_4ClPtNa$: *m/z* 766. Found (%): *m/z* 766 (88). FT-IR (KBr pellet, cm^{-1}): ῦ 1755 (C=O); 1562, 1485 (C=C).

[PtBr(*i*PrEug)(Bn$_2$-bimy)] (6). Yield: 80 mg (0.095 mmol, 95%). Yellow crystals were obtained by slow evaporation within 12 hours from a concentrated acetone/water solution at ambient temperature. ^{1}H NMR (500 MHz, acetone-d_6): δ 7.80 (d, ^3J(H,H) = 7.5 Hz, 2H, Ar−H), 7.68 (d, ^3J(H,H) = 7.5 Hz, 1H, Ar−H), 7.52 (d, ^3J(H,H) = 7.5 Hz, 2H, Ar−H), 7.41–7.37 (m, 3H, Ar−H), 7.33 (t, ^3J(H,H) = 7.5, 2H, Ar−H), 7.28−7.23 (m, 4H, Ar−H), 6.74 (s, 1H, Ar-H), 6.32/6.05/5.79/5.46 (d, ^2J(H,H) = 15.5 Hz, 4H, N*C*H$_2$), 5.93 (m, $^2J_{PtH}$ = 65 Hz, 1H, CH=C), 5.77 (s, $^3J_{PtH}$ = 65 Hz, 1H, Ar-H), 5.05 (d, ^3J(H,H) = 8.5 Hz, $^2J_{PtH}$ = 50 Hz, 1H, C=CH$_2$), 4.73 (d, ^3J(H,H) = 15 Hz, $^2J_{PtH}$ = 60 Hz, 1H, C=CH$_2$), 4.29 (m, 1H, O-CH), 4.21/4.04 (d, ^2J(H,H) = 16.5 Hz, 2H, OCH$_2$), 3.74 (dd, ^2J(H,H) = 16.5 Hz, ^3J(H,H) = 6.5 Hz, 1H, CH_2-CH), 3.70 (s, 3H, OCH$_3$), 3.13 (d, ^2J(H,H) = 16.5 Hz, $^3J_{PtH}$ = 90 Hz, 1H, CH_2-CH), 0.96/0.89 (d, ^3J(H,H) = 6 Hz, 6H, C-(CH$_3$)$_2$). ^{13}C NMR (125.8 MHz, acetone-d_6): 184.3 (NCN), 169.2 (C=O), 148.2, 145.7, 143.9, 137.1, 136.5, 135.6, 135.1, 129.9, 129.6, 129.4, 129.1, 128.9, 128.7, 124.6, 124.4, 122.4, 112.9, 112.8, 111.5 (Ar-C), 112.1 (*C*H=CH$_2$), 85.4 (CH=*C*H$_2$), 68.7 (O-CH), 67.5 (OCH$_2$), 56.2 (OCH$_3$), 52.9$_4$/52.8$_6$ (NCH$_2$), 39.2 (*C*H$_2$-CH), 21.8$_5$/21.8$_2$ (C-(*C*H$_3$)$_2$). Anal. Calc. for $C_{36}H_{37}N_2O_4BrPt$: C, 51.67; H, 4.43; N, 3.36. Found: C, 52.10; H, 3.83; N, 3.48. MS (ESI) Calcd for [M − Br]$^+$, $C_{36}H_{37}N_2O_4Pt$: *m/z* 756. Found (%): *m/z* 756 (100). Calcd for [M + Na]$^+$, $C_{36}H_{37}N_2O_4BrPtNa$: *m/z* 859. Found (%): *m/z* 859 (30). FT-IR (KBr pellet, cm^{-1}): ῦ 1755 (C=O); 1562, 1485 (C=C).

[PtI(ⁱPrEug)(Bn₂-bimy)] (7). Yield: 84 mg (0.095 mmol, 95%). Light yellow crystals were obtained by slow evaporation within 10 hours from a concentrated acetone/water solution at ambient temperature. ^{1}H NMR (500 MHz, acetone-d_6): δ 7.79 (d, ^3J(H,H) = 7.5 Hz, 2H, Ar−H), 7.64 (d, ^3J(H,H) = 7.5 Hz, 1H, Ar−H), 7.44 (d, ^3J(H,H) = 7.5 Hz, 2H, Ar−H), 7.40−7.30 (m, 5H, Ar−H), 7.25 (dd, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1 Hz, 1H, Ar−H), 7.24–7.20 (m, 3H, Ar−H), 6.78 (s, 1H, Ar-H), 6.28/6.08/5.73/5.53 (d, ^2J(H,H) = 15.5 Hz, 4H, NCH_2), 5.98 (m, $^2J_{PtH}$ = 65 Hz, 1H, CH=C), 5.79 (s, $^3J_{PtH}$ = 65 Hz, 1H, Ar-H), 5.18 (d, ^3J(H,H) = 7.5 Hz, $^2J_{PtH}$ = 50 Hz, 1H, C=CH_2), 4.83 (t-d, ^3J(H,H) = 15 Hz, ^2J(H,H) = 1.5 Hz, $^2J_{PtH}$ = 60 Hz, 1H, C=CH_2), 4.32 (m, 1H, O-CH), 4.19/4.04 (d, ^2J(H,H) = 16.5 Hz, 2H, OCH_2), 3.73 (dd, ^2J(H,H) = 17 Hz, ^3J(H,H) = 6.5 Hz, 1H, CH_2-CH), 3.71 (s, 3H, OCH_3), 3.14 (dd, ^2J(H,H) = 17 Hz, ^3J(H,H) = 1.5 Hz, $^3J_{PtH}$ = 90 Hz, 1H, CH_2-CH), 0.96/0.92 (d, ^3J(H,H) = 6 Hz, 6H, C-$(CH_3)_2$). ^{13}C NMR (125.8 MHz, acetone-d_6): 184.5 (NCN), 169.2 (C=O), 148.3, 145.6, 142.2, 136.8, 136.3, 135.7, 135.0, 129.7, 129.6, 129.3, 129.1, 128.9, 128.6, 124.5, 124.4, 122.0, 112.9, 112.8, 111.3 (Ar-C), 111.4 (*C*H=CH_2), 83.9 (CH=*C*H_2), 68.7 (O-CH), 67.6 (OCH_2), 56.2 (OCH_3), 53.3/53.0 (NCH_2), 39.5 (CH_2-CH), 21.8$_5$/21.8$_1$ (C-$(CH_3)_2$). Suitable elemental analysis could not be obtained despite several recrystallization attempts. MS (ESI) Calcd for $[M - I]^+$, $C_{36}H_{37}N_2O_4Pt$: *m/z* 756. Found (%): *m/z* 756 (100). Calcd for $[M + Na]^+$, $C_{36}H_{37}N_2O_4IPtNa$: *m/z* 906. Found (%): *m/z* 906 (62). FT-IR (KBr pellet, cm^{-1}): ṽ 1751 (C=O); 1612, 1520, 1485 (C=C).

X-ray Crystallography. Single crystal X-ray diffraction was carried out on a Bruker AXS SMART APEX diffractometer using graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å). The software used was as follows: SMART for collecting frames of data, indexing reflections, and determining lattice parameters;[12] SAINT for integration of intensity of reflections and scaling;[13] SADABS for empirical absorption correction;[14] SHELXTL for space group determination, structure solution, and least-squares refinements on $|F|^2$.[15] Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. The hydrogen atoms were placed in their ideal positions.

CCDC 1563498–1563501 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +441223 336033.

Supporting Information: Crystallographic data for **3** and **5**–**7** (CIF); Experimental details for ⁱPr,Bn-bimy·HCl, K[$PtCl_3$(ⁱPrEugH)] and [PtCl(ⁱPrEug)]$_2$ (**1**); ^{1}H, ^{13}C{^{1}H}, HMQC and HMBC NMR spectra of the salt ⁱPr,Bn-bimy·HCl and complexes **2**–**7** (PDF).

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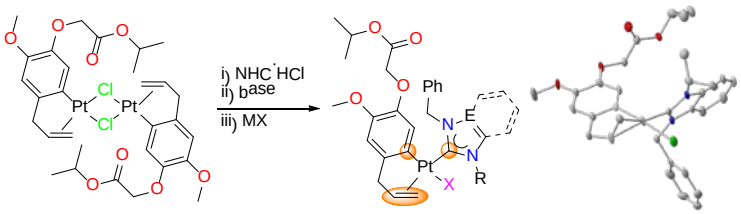

Six platinum(II) complexes of general formula [PtX(ⁱPrEug)(NHC)] bearing three different types of carbon donors have been prepared and fully characterized. The introduction of a NHC *trans* to the olefin leads to a weakening of the metal–olefin bond and strengthening of the metal–aryl bond in the axially chiral complexes.

Organometallic

Han Vinh Huynh, Van Thong Pham, Nguyen Thi Thanh Chi**

Page No. – Page No.

Cyclometallated Platinum(II) Complexes with a Phenylpropene-derived π/σ-Chelator and N-heterocyclic Carbenes