Exploring the Transphobia Effect on Heteroleptic NHC Cycloplatinated Complexes.

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ABSTRACT

The synthesis of 1-(4-cyanophenyl)-1*H*-imidazol(**1**) has been carried out by an improved method. Then, its corresponding imidazolium iodide salt, **2**, has been used to prepare the N-heterocyclic carbene (NHC) cycloplatinated compound [{Pt(μ-Cl)(C^C*)}$_2$] (**4**) (HC^C*-κC*=1-(4-cyanophenyl)-3-methyl-1*H*-imidazol-2-ylidene) following a step-by-step protocol. The intermediate complex [PtCl(η^3-2-Me-C_3H_4)(HC^C*-κC*)](**3**) has also been isolated and characterized. Using **4** as precursor, several heteroleptic complexes of stoicheometry [PtCl(C^C*)L] (L = PPh_3 (**5**), pyridine (py, **6**), 2,6-dimethylphenyl isocyanide (CNXyl, **7**) and 2-mercapto-1-methylimidazole (MMI, **8**)) and [Pt(C^C*)LL']PF_6 (L = PPh_3, L' = py (**9**), CNXyl (**10**), MMI (**11**)) have been synthesized. Complexes **6**-**8** were obtained as a mixture of *cis*- and *trans-(C*,L)* isomers, whilst, *trans-(C*,L)* isomer was the only one observed for complexes **5** and **9**-**11**. Their geometries have been discussed in terms of the degree of transphobia (T) of pairs of *trans* ligands and supported by theoretical calculations. The *trans* influence of the two σ Pt–C bonds present in these molecules, Pt–C_{Ar} and Pt–$C^*_{(NHC)}$ have been compared from the J_{Pt-P} values observed in the new complex [Pt(C^C*)(dppe)]PF_6 (dppe = 1, 2-bis(diphenylphosphino)ethane, **12**).

INTRODUCTION

The chemistry of platinum (II) complexes has attracted much interest in the last decade due to their phosphorescence properties and potential use as dopants in LEDS,[1] chemical sensors[2] or bio-labeling agents,[2b,3] with particular consideration given to C^N-cyclometallated derivatives.[1b,4] The C^C* cyclometallated N-heterocyclic carbenes (NHC) may surpass the high ligand field splitting capacity of the conventional C^N-cyclometallated ligands, since they present two C-σ bonds. This implies an even greater heightening of the d-d energy levels on the metal center, enlarging the energy gap with the emissive excited states, avoiding the thermal quenching and improving the quantum yields.[5] Furthermore, as a consequence of the strong metal-ligand binding, metal complexes of C^C* cyclometallated NHCs are very robust and stable which may provide long-term functional materials.

NHCs have been widely used in organometallic chemistry and particularly in the targeted fields of transition-metal catalysis,[6] liquid crystals,[7] bio-medicine,[8] and luminescent materials.[5,8d,9] In particular, platinum(II) compounds containing C^C* cyclometallated NHCs ligands have received much attention in the last decade.[9k,10] Most of them are photoluminescent *β*-diketonates or *β*-ketoiminates derivatives prepared straightforward in one-pot reactions. Variations regarding substituents in the NHC or the *β*-diketonate groups and also regarding the size of the π system have been studied to tune their photophysical properties.[10a-l] However, these preparative methods are slightly limited in terms of reactivity and ligand exchange reactions. Normally, ancillary ligands account for secondary roles within the molecular complex but they could be determinant when modulating their emissive properties[11] or tuning their catalytic activity and selectivity.[10m,10n,12]

In this context, as part of our previous work, we have prepared and studied the photophysical properties of many heteroleptic complexes of Pt(II) with the 7,8-benzoquinolinate and different monodentate auxiliary ligands.[11] Now, we have conducted our ongoing research to new platinum(II) complexes with C^C* cyclometallated NHCs. Generic compounds, such as [{Pt(μ-Cl)(C^C*)}$_2$] are expected to be useful starting materials for complexes containing the "Pt(C^C*)" moiety, because different kinds of ancillary ligands can be coordinated in the vacant sites resulting from the chlorine-bridge cleavage or from the chlorine atoms elimination. We recently reported the synthesis of [{Pt(μ-Cl)(C^C*)}$_2$] (HC^C* = 3-methyl-1-(naphthalen-2-yl)-1*H*-imidazol-2-ylidene).[13] So, the first goal of this work, the synthesis of the generic precursor [{Pt(μ-Cl)(C^C*)}$_2$](**4**) (HC^C*-κC* = 1-(4-cyanophenyl)-3-methyl-1H-imidazol-2-ylidene) following the same strategy, was achieved. Therefore, the use of [{Pt(μ-Cl)(η^3-2-Me-C_3H_4)}$_2$] to accomplish the cyclometallation of the NHCs through the intermediate carbene complex [PtCl(η^3-2-Me-C_3H_4)(HC^C*-κC*)] (**3**) endorses the generality and viability of this step-by-step synthetic protocol for [{Pt(μ-Cl)(C^C*)}$_2$]

Then we explored the use of **4** as a precursor for the preparation of new heteroleptic complexes such as [PtCl(C^C*)L] (L = PPh_3 (**5**), py (**6**) CNXyl (**7**) and 2-mercapto-1-methylimidazole (MMI, **8**) and [Pt(C^C*)LL']$^+$ (L = PPh_3; L' = py (**9**), CNXyl (**10**), MMI (**11**)). Some of them were obtained as a mixture of two isomers, *cis*- and *trans-(C*,L),* while other were obtained selectively as the *trans-(C*,L)* one. The geometries observed for them have been discussed in terms of the degree of transphobia (T) of pairs of *trans* ligands,[14] which has been related with the *trans* influence of the two σ Pt–C bonds present in the molecule, Pt–C_{Ar} and Pt–$C^*_{(NHC)}$. The *trans* influence of σ C_{Ar} and σ C* have been evaluated from the $J_{Pt,P}$ values observed in the new complex [Pt(C^C*)(dppe)]$^+$ (**12**).

EXPERIMENTAL SECTION

General Comments. Information describing materials, instrumental methods used for characterization and spectroscopic studies, DFT computational details and X-ray structures together with the characterization data of **1-12** are contained in the Supporting Information. All chemicals were used as supplied and [{Pt(η^3-2-Me-C_3H_4)(μ-Cl)}$_2$][15] was prepared following the literature procedure.

1-(4-cyanophenyl)-1*H*-imidazole (1). Slight modifications of previous synthetic methods were employed.[16] To a solution of 4-bromobenzonitrile (800.0 mg, 4.35 mmol) in degassed dimethylsulfoxide (12 mL), imidazole (592.5 mg, 8.70 mmol), K_2CO_3 (1202.9 mg, 8.70 mmol) and CuI (165.8 mg, 8.70 mmol) were added in the presence of 4 Å molecular sieves (500.0 mg). After 70 hours at 110 ºC under an argon atmosphere the crude was cooled down to r.t., washed with 100 mL of ethyl acetate and then filtered through Celite. The solution was treated with H_2O (2 x 20 mL) and brine (2 x 20 mL). The organic layer was dried using anhydrous $MgSO_4$. Evaporation under reduced pressure yielded a white solid which was washed with hexane to give **1** as a white-off powder. Yield: 609.5 mg, 83%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.46 (dd, $^3J_{H,H}$ = 1.3, $^3J_{H,H}$ = 0.9, 1H, H_1), 8.09 (d, $^3J_{H6,H7}$ = 8.8, 2H, H_7), 7.99 (d, $^3J_{H6,H7}$ = 8.8, 2H, H_6), 7.98 (m, 1H, Im), 7.16 (dd, $^3J_{H,H}$ = 1.3, $^3J_{H,H}$ = 0.9, 1H, Im). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ = 140.1 (s, C_5), 135.7 (s, C_1), 134.1 (s, 2C, C_7), 130.5 (s, 1C, Im), 120.4 (s, 2C, C_6), 118.3 (s, CN), 117.6 (s, 1C, Im), 109.0 (s, C_8). IR (ATR, cm^{-1}): ν = 2224 (m, C≡N).

1-(4-cyanophenyl)-3-methyl-1*H*-imidazolium Iodide (2). Methyl iodide (0.3 mL, 4.83 mmol) was added to a solution of **1** (544.5 mg, 3.22 mmol) in dried THF (10 mL) under Ar atmosphere. The mixture was refluxed for 48 hours and after cooling, the white precipitate was filtered and washed with THF (5 mL) and diethylether (5 mL) and dried

under vacuum to give **2** as a pure solid. Yield: 967.9 mg, 97%. Anal Calcd for $C_{11}H_{10}IN_3$: C, 42.46; H, 3.24; N, 13.51. Found: C, 42.03; H, 3.33; N, 13.48. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.91 (s, br, 1H, H_1), 8.39 (dd, $^3J_{H2,H3}$ = 1.9, $^3J_{H2,H1}$ = 1.8, 1H, H_2), 8.21 (d, $^3J_{H6,H7}$ = 8.8, 2H, H_7), 8.02 (d, 2H, H_6), 8.00 (m, 1H, H_3), 3.96 (s, 3H, H_4). ^{13}C{^{1}H} NMR plus HMBC and HSQC (101 MHz, DMSO-d_6): δ = 137.9 (s, C_5), 136.5 (s, C_1), 134.4 (s, 2C, C_7), 124.6 (s, C_3), 122.5 (s, 2C, C_6), 120.7 (s, C_2), 117.7 (s, CN), 112.2 (s, C_8), 36.3 (s, C_4). IR (ATR, cm^{-1}): ν = 2235 (m, C≡N). MS (MALDI+): m/z 184.1 $(HC^C*H)^+$.

[PtCl(η^3-2-Me-C_3H_4)(HC^C*-κC*)] (3) (HC^C* = 1-(4-cyanophenyl)-3-methyl-1*H*-imidazol-2-ylidene). To a suspension of **2** (893.7 mg, 2.87 mmol) in anhydrous dichloromethane (30 mL), Ag_2O (332.8 mg, 1.44 mmol) was added in the absence of light under an argon atmosphere. After 3 h of stirring at r.t., [{Pt(η^3-2-Me-C_3H_4)(μ-Cl)}$_2$] (779.1 mg, 1.36 mmol) was added and the mixture was allowed to react for 3 hours to give a yellow precipitate (AgI), which was separated by filtration through Celite under Ar. The resulting solution was evaporated to dryness and treated with n-hexane (3 x 15 mL) to afford **3** as a pale-yellow solid. Yield: 1.1222 g, 83%. Anal Calcd for $C_{15}H_{16}ClN_3Pt$: C, 38.42; H, 3.43; N, 8.96. Found: C, 38.23; H, 3.35; N, 8.52. ^{1}H NMR (400 MHz, Methylene Chloride-d_2): δ = 7.95 (d, $^3J_{H,H}$ = 8.8, 2H, H_7), 7.74 (d, $^3J_{H,H}$ = 8.8, 2H, H_6), 7.26 (d, $^3J_{H2,H3}$ = 2.1, $^4J_{H,Pt}$ = 13.4, 1H, H_2), 7.15 (d, $^4J_{H,Pt}$ = 10.6, 1H, H_3), 3.91 (s, 3H, Me (NHC)), 3.64 (m, 1H$_{syn}$, η^3-2-Me-C_3H_4), 2.63 (m, $^2J_{H,Pt}$ = 28.3, 1H$_{syn}$, η^3-2-Me-C_3H_4), 2.37 (m, $^2J_{H,Pt}$ = 34.1, 1H$_{anti}$, η^3-2-Me-C_3H_4), 1.74 (s, $^3J_{H,Pt}$ = 64.7, 3H, Me, η^3-2-Me-C_3H_4), 1.44 (m, 1H$_{anti}$, η^3-2-Me-C_3H_4). ^{13}C{^{1}H} NMR plus HMBC and HSQC (101 MHz, Methylene Chloride-d_2) : δ = 177.4 (s, C_1), 144.1 (s, C_5), 133.2 (s, 2C, C_6), 126.2 (s, 2C, C_7), 123.6 (s, $^3J_{C,Pt}$ = 41.3, C_3), 120.7 (s, $^3J_{C,Pt}$ = 42.4, C_2), 118.6 (s, CN), 118.4 (s, $C^{2'}$, η^3-2-Me-C_3H_4), 112.1 (s, C_8), 58.1 (s, $^1J_{C,Pt}$ = 77.6, $C^{1'}$,

η^3-2-Me-C_3H_4), 38.3 (s, C_4 (Me), NHC)), 37.1 (s, $C^{3'}$, η^3-2-Me-C_3H_4), 23.4 (s, $^2J_{C,Pt}$ = 40.1, $C^{4'}$ (Me), η^3-2-Me-C_3H_4). $^{195}Pt\{^1H\}$ NMR (85.6 MHz, Methylene Chloride-d_2): δ = – 4460. IR (ATR, cm^{-1}): ν = 285 (s, Pt-Cl), 2228 (w, CN).

[{Pt(μ-Cl)(C^C*)}$_2$] (4). Compound **3** (500.0 mg, 1.07 mmol) was refluxed in 2-methoxyethanol (15 mL) for 3 hours and then it was cooled down to r.t. The resulting solid was filtered and washed with dichloromethane (10 mL) and diethylether (15 mL). Then, it was treated with activated carbon in hot acetonitrile (3 x 40 mL) and the suspension was filtered through Celite. The resulting solution was evaporated to dryness and the residue was washed with hexane to give a yellow solid, **4**. Yield: 357.6 mg, 81%. Anal Calcd for $C_{22}H_{16}Cl_2N_6Pt_2$: C, 32.01; H, 1.95; N, 10.18. Found: C, 31.63; H, 2.33; N, 10.16. ^1H NMR (400 MHz, DMSO-d_6): δ = 8.72 (s, br, $^3J_{H7,Pt}$ = 60, 1H, H_7), 8.14 (d, $^3J_{H2,H3}$ = 1.7, 1H, H_2), 7.63 (dd, $^3J_{H9,H10}$ = 8.0, $^4J_{H9,H7}$ = 1.5, 1H, H_9), 7.57 (d, 1H, H_{10}), 7.53 (d, 1H, H_3), 4.14 (s, 3H, H_4). $^{13}C\{^1H\}$ NMR plus HMBC and HSQC (101 MHz, DMSO-d_6): δ = 156.0 (s, C_1), 149.8 (s, C_5), 137.0 (s, C_7), 129.3 (s, C_9), 127.9 (s, C_6), 125.51 (s, C_3), 119.6 (s, CN), 115.7 (s, C_2), 112.3 (s, C_{10}), 106.9 (s, C_8), 37.6 (s, C_4). IR (ATR, cm^{-1}): ν = 266 (s, Pt-Cl), 2250 (w, CN), 2215 (w, CN).

***trans*-(C*,P)[Pt(Cl)(C^C*)(PPh_3)] (5).** PPh_3 (128.1 mg, 0.48 mmol) was added to a suspension of **4** (177.8 mg, 0.22 mmol) in dichloromethane (30 mL) at -8 ºC (ice/brine bath). After 1 hour of reaction, the solvent was removed under reduced pressure. The residue was treated with MeOH (5 mL), filtered and washed with MeOH (3 mL) to give **5** as a pale yellow solid. Yield: 193.5 mg, 67%. Anal Calcd for $C_{29}H_{23}ClN_3PPt$: C, 51.60; H, 3.43; N, 6.22. Found: C, 51.26; H, 3.49; N, 6.18. ^1H NMR (400 MHz, Methylene Chloride-d_2): δ = 7.72 (m, 6H, H*o* (PPh_3)), 7.52–7.35 (m, 10H, H*m*, H*p* (PPh_3)) and H_2), 7.24 (dd, $^3J_{H9,H10}$ = 8.0, $^4J_{H9,H7}$ = 1.6, 1H, H_9), 7.05 (d, $^4J_{H10,Pt}$ = 14.2, 1H, H_{10}), 6.99 (m, 1H, H_3), 6.88 (m, $^3J_{H7,Pt}$ = 64.0, 1H, H_7), 4.29 (s, 3H, H_4). $^{13}C\{^1H\}$

NMR plus HMBC and HSQC (101 MHz, Methylene Chloride-d_2): δ = 170.1 (s, C_1), 150.5 (s, C_5), 141.0 (d, $^3J_{C7,P}$ = 8.7, $^2J_{C7,Pt}$ = 57.0, C_7), 135.5 (d, $^2J_{C,P}$ = 11.3, $^3J_{C,Pt}$ = 20.7, 6C, C*o* (PPh_3)), 130.7 (s, 3C, C*p* (PPh_3)), 130.1 (d, $^1J_{C,P}$ = 53.6, 3C, C*i* (PPh_3)), 128.5 (s, C_6), 128.1 (d, $^3J_{C,P}$ = 10.6, 6C, C*m* (PPh_3)), 127.8 (s, C_9), 124.3 (d, $^4J_{C,P}$ = 6.1, $^4J_{C3,Pt}$ = 26.0, C_3), 118.8 (s, CN), 113.9 (s, $^4J_{C2,Pt}$ = 40.1, C_2), 111.0 (s, $^3J_{C10,Pt}$ = 32.5, C_{10}), 108.0 (s, C_8), 38.6 (s, C_4). $^{31}P\{^1H\}$ NMR (162 MHz, Methylene Chloride-d_2): δ = 28.6 (s, $^1J_{P,Pt}$ = 2868.0). $^{195}Pt\{^1H\}$ NMR (85.6 MHz, Methylene Chloride-d_2): δ = –4227.0 (d). IR (ATR, cm^{-1}): ν = 279 (m, Pt-Cl), 2218 (w, CN). MS (MALDI+): m/z 639.1 $[Pt(C\hat{}C^*)(PPh_3)]^+$.

cis/trans*-(C*,N) [Pt(Cl)(C^C*)(py)] (6).** Pyridine (Py) (24.8 μL, 0.30 mmol) was added to a suspension of **4** (115.2 mg, 0.14 mmol) in dichloromethane (30 mL) at -8 ºC (ice/brine bath). After 2 h stirring, the solvent was removed under reduced pressure. The residue was treated with MeOH (5 mL), filtered and washed with MeOH (3 mL) to give **6-*t (92%) / **6-*c*** (8%) as a yellow solid. Yield: 99.9 mg, 73%. Anal Calcd for $C_{16}H_{13}ClN_4Pt$: C, 39.07; H, 2.66; N, 11.39. Found: C, 38.67; H, 2.73; N, 11.22. ^1H NMR data for **6-*t*** (400 MHz, Methylene Chloride-d_2): δ = 8.81 (dd, $^3J_{H,H}$ = 6.4, $^4J_{H,H}$ = 1.6, $^3J_{H,Pt}$ = 28.0, 2H, H*o* (py)), 7.97 (tt, $^3J_{H,H}$ = 7.7, $^4J_{H,H}$ = 1.6, 1H, H*p* (py)), 7.56 (m, 2H, H*m* (py)), 7.38 (dd, $^3J_{H9,H10}$ = 8.0, $^4J_{H9,H7}$ = 1.7, 1H, H_9), 7.33 (d, $^3J_{H2,H3}$ = 2.1, 1H, H_2), 7.06 (d, $^4J_{H10,Pt}$ = 16.8, 1H, H_{10}), 6.94 (d, $^4J_{H3,Pt}$ = 9.1, 1H, H_3), 6.69 (d, $^3J_{H7,Pt}$ = 61.8, 1H, H_7), 4.24 (s, 3H, H_4). ^1H NMR data for **6-*c***: δ = 8.91 (dd, $^3J_{H,H}$ = 6.3, $^4J_{H,H}$ = 1.6, $^3J_{H,Pt}$ = 20.7, 2H, H*o* (py)), 8.41 (d, $^3J_{H7,H9}$ = 1.6, $^3J_{H7,Pt}$ = 55.1, 1H, H_7), 7.91 (tt, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.6, 1H, H*p* (py)), 3.06 (s, 3H, H_4). $^{13}C\{^1H\}$ NMR plus HMBC and HSQC for **6-*t*** (101 MHz, Methylene Chloride-d_2): δ = 152.7 (s, C_1), 152.0 (s, $^2J_{C,Pt}$ = 12.2, 2C, C*o* (py)), 150.3 (s, C_5), 138.5 (s, C*p* (py)), 135.2 (s, $^2J_{C7,Pt}$ = 37.8, C_7), 131.3 (s, C_6), 128.3 (s, C_9), 126.1 (s, $^3J_{C,Pt}$ = 31.2, 2C, C*m* (py)), 123.1 (s, $^3J_{C3,Pt}$ = 38.4, C_3),

119.4 (s, CN), 114.4 (s, $^{3}J_{C2,Pt}$ = 47.2, C_2), 110.7 (s, $^{3}J_{C10,Pt}$ = 36.1, C_{10}), 108.1 (s, C_8), 37.6 (s, C_4). $^{195}Pt\{^{1}H\}$ NMR (85.6 MHz, Methylene Chloride-d_2): δ = –3731.9 (s, br, **6-*t***); –3775.4 (s, **6-*c***). IR (ATR, cm^{-1}): ν = 271 (m, Pt-Cl), 2220 (w, CN). MS (MALDI+): m/z 456.0 $[Pt(C\hat{}C^*)(py)]^+$.

cis/trans*-(C*,C) [Pt(Cl)(C^C*)(CNXyl)] (7).** 2,6-Dimethylphenyl isocyanide (CNXyl) (35.7 mg, 0.27 mmol) was added to a suspension of **4** (100.0 mg, 0.12 mmol) in dichloromethane (30 mL) at -8 ºC (ice/brine bath). After 2.5 hours stirring, the solvent was removed under reduced pressure. The residue was treated with MeOH (0ºC, 5 mL), filtered and washed with MeOH (3 mL) to give **7-*t (86%) / **7-*c*** (14%) as a yellow solid. Yield: 61.8 mg, 47%. Anal Calcd for $C_{20}H_{17}ClN_4Pt$: C, 44.16; H, 3.15; N, 10.30. Found: C, 44.09; H, 3.02; N, 9.92. ^{1}H NMR data for **7-*t*** (400 MHz, Methylene Chloride-d_2): δ = 7.97 (d, $^{4}J_{H9,H7}$ = 1.7, $^{3}J_{H7,Pt}$ = 77.3, 1H, H_7), 7.47 (dd, $^{3}J_{H9,H10}$ = 8.0, 1H, H_9), 7.36 (d, $^{3}J_{H2,H3}$ = 2.0, $^{4}J_{H2,Pt}$ = 5.3, 1H, H_2), 7.33 (t, $^{3}J_{Hp,Hm}$ = 7.7, 1H, H_p (Xyl)), 7.21 (d, 2H, H_m (Xyl)), 7.14 (d, $^{4}J_{H10,Pt}$ = 15.4, 1H, H_{10}), 6.97 (d, $^{4}J_{H3,Pt}$ = 7.9, 1H, H_3), 4.28 (s, 3H, H_4), 2.51 (s, 6H, Me (Xyl)). ^{1}H NMR data for **7-*c***: δ = 8.45 (d, $^{4}J_{H7,H10}$ = 1.7, $^{3}J_{H,Pt}$ = 47.2, 1H, H_7), 7.43 (dd, $^{3}J_{H9,H10}$ = 8.0, 1H, H_9), 7.09 (d, 1H, H_{10}), 7.00 (d, $^{4}J_{H3,Pt}$ = 12.3, 1H, H_3), 3.92 (s, 3H, H_4), 2.45 (s, 6H, Me (Xyl)). $^{13}C\{^{1}H\}$ NMR plus HMBC and HSQC for **7-*t*** (101 MHz, Methylene Chloride-d_2): δ = 167.7 (s, C_1), 149.5 (s, C_5), 140.8 (s, $^{2}J_{C7\text{-}Pt}$ = 72.4, C_7), 135.8 (s, 2C, C_o (Xyl)), 129.7 (s, C_p (Xyl)), 128.7 (s, C_9), 128.1 (s, 2C, C_m (Xyl)), 123.9 (s, $^{3}J_{C3,Pt}$ = 30.9, C_3), 119.0 (s, CN), 114.8 (s, C_2), 111.6 (s, $^{3}J_{C10,Pt}$ = 32.9, C_{10}), 109.5 (s, C_8), 37.3 (s, C_4), 18.7 (s, 2C, Me (Xyl)). $^{195}Pt\{^{1}H\}$ NMR (85.6 MHz, Methylene Chloride-d_2): δ = –4042.7 (t, $^{2}J_{Pt,N}$ = 89.7 Hz, **7-*t***); –4160.2 (m, **7-*c***). IR (ATR, cm^{-1}): ν = 285 (m, Pt-Cl), 2161 (s, CN, CNXyl), 2217 (w, CN, NHC). MS (MALDI+): m/z 508.1 $[Pt(C\hat{}C^*)(CNXyl)]^+$.

cis/trans*-(C*,S) [Pt(Cl)(C^C*)(MMI)] (8).** 2-Mercapto-1-methylimidazole (MMI) (37 mg, 0.32 mmol) was added to a suspension of **4** (120.0 mg, 0.15 mmol) in acetone (30 mL) at -8 ºC (ice/brine bath). After 1 h stirring, the mixture was filtered through Celites and the filtrated was evaporated to dryness. The residue was treated with diethylether (5 mL), filtered and washed with diethylether (3 mL). The resulting orange solid was recrystallized from CH_2Cl_2/Et_2O to give **8-*t (86%) / **8-*c*** (14%)**.** Yield: 78.6 mg, 51%. Anal Calcd for $C_{15}H_{14}ClN_5PtS$: C, 34.19; H, 2.68; N, 13.29; S, 6.09. Found: C, 34.57; H, 2.97; N, 13.13; S, 6.75. ^{1}H NMR data for **8-*t*** (400 MHz, Methylene Chloride-d_2): δ = 12.72 (s, 1H, NH, MMI), 8.27 (s, $^3J_{H7,Pt}$ = 65.9, 1H, H_7), 7.41 (d, $^3J_{H9,H10}$ = 7.6, 1H, H_9), 7.30 (d, $^3J_{H2,H3}$ = 2.1, 1H, H_2), 7.04 (d, $^4J_{H10,Pt}$ = 14.3, 1H, H_{10}), 6.92 (d, $^4J_{H3,Pt}$ = 8.9, 1H, H_3), 6.87 (m, 1H, $H_{4'}$, MMI), 6.84 (m, 1H, $H_{5'}$, MMI), 4.19 (s, 3H, H_4), 3.75 (s, 3H, NMe, MMI). ^{1}H NMR data for **8-*c***: δ = 8.47 (d, $^4J_{H7,H9}$ = 1.1, $^3J_{H7,Pt}$ = 57.5, 1H, H_7), 4.04 (s, 3H, H_4), 3.68 (s, 3H, NMe, MMI). ^{13}C{^{1}H} NMR plus HMBC and HSQC (101 MHz, Methylene Chloride-d_2) for **8-*t***: δ = 159.3 (s, C_1), 156.1 (s, C=S, MMI), 149.9 (s, C_5), 135.4 (s, $^2J_{C7,Pt}$ = 37.1, C_7), 126.7 (s, C_6), 128.4 (s, C_9), 123.6 (s, $^3J_{C3,Pt}$ = 37.3, C_3), 120.4 (s, $C_{5'}$, MMI), 119.8 (s, CN), 115.1 (s, $C_{4'}$, MMI), 113.6 (s, $^3J_{C2,Pt}$ = 45.2, C_2), 110.7 (s, $^3J_{C10,Pt}$ = 35.8, C_{10}), 107.5 (s, C_8), 37.9 (s, C_4), 34.5 (s, NMe, MMI). ^{195}Pt{^{1}H} NMR (85.6 MHz, Methylene Chloride-d_2): δ = – 3856.5 (s, **8-*t***); – 3884.2 (s, **8-*c***). IR (ATR, cm^{-1}): ν = 268 (m, Pt-Cl), 2216 (w, CN), 3100 (w, NH). MS (MALDI+): m/z 491.0 $[Pt(C^C*)(MMI)]^+$.

***trans*-(C*,P) [Pt(C^C*)(py)(PPh_3)]PF_6 (9).** Pyridine (15.8 μL, 0.20 mmol) and KPF_6 (36.9 mg, 0.20 mmol) were added to a pale yellow suspension of **5** (132.6 mg, 0.20 mmol) in acetone (30 mL). After 1 h of stirring at room temperature, the solvent was evaporated to dryness and the residue treated with dichloromethane (35 mL) and filtered through Celite. Then, the solvent was removed under reduced pressure and the residue

was treated with diethylether (10 mL), filtered and washed with diethylether (5 mL). The solid was recrystallized from acetone (0ºC)/Et_2O to give **9** as a pale yellow solid. Yield: 88.3 mg, 49%. Anal Calcd for $C_{34}H_{28}F_6N_4P_2Pt$: C, 47.28; H, 3.27; N, 6.49. Found: C, 46.86; H, 3.05; N, 6.47. ^{1}H NMR (400 MHz, Methylene Chloride-d_2): δ = 8.40 (dd, $^3J_{H,H}$ = 6.2, $^4J_{H,H}$ = 1.1, $^3J_{H,Pt}$ = 23.0, 2H, H*o* (py)), 7.69 (tt, $^3J_{H,H}$ = 7.7, $^4J_{H,H}$ = 1.4, 1H, H*p* (py)), 7.59 (m, 6H, H*o* (PPh_3)), 7.53 – 7.45 (m, 4H, H_2, H*p* (PPh_3)), 7.36 (m, 6H, H*m* (PPh_3)), 7.31 (dd, $^3J_{H9,H10}$ = 8.1, $^4J_{H9,H7}$ = 1.7, 1H, H_9), 7.19 (m, 3H, H_{10}, H*m* (py)), 7.03 (m, 1H, H_3), 6.85 (m, $^3J_{H7,Pt}$ = 58.8, 1H, H_7), 2.87 (s, 3H, H_4). ^{13}C{^{1}H} NMR plus HMBC and HSQC (101 MHz, Methylene Chloride-d_2): δ = 171.2 (d, $^2J_{C,P}$ = 136.2, C_1), 151.9 (s, $^2J_{C,Pt}$ = 10.0, 2C, C*o* (py)), 150.8 (s, C_5), 142.9 (d, $^3J_{C7,P}$ = 9.6, $^2J_{C7,Pt}$ = 55.4, C_7), 139.3 (s, C*p* (py)), 134.7 (d, $^2J_{C,P}$ = 11.7, 6C, C*o* (PPh_3)), 131.7 (s, 3C, C*p* (PPh_3)), 129.9 (s, C_9), 129.0 (d, $^3J_{C,P}$ = 10.0, 6C, C*m* (PPh_3)), 127.5 (s, 2C, C*p* (py)), 124.6 (d, $^4J_{C3,P}$ = 4.8, $^3J_{C3,Pt}$ = 31.3, C_3), 118.4 (s, CN), 115.1 (s, br, $^3J_{C2,Pt}$ = 40.2, C_2), 111.7 (s, $^3J_{C10,Pt}$ = 29.2, C_{10}), 108.3 (s, C_8), 35.3 (s, C_4). ^{31}P{^{1}H} NMR (162 MHz, Methylene Chloride-d_2): δ = 28.2 (s, $^1J_{P\text{-}Pt}$ = 2881.6). ^{195}Pt{^{1}H} NMR (85.6 MHz, Methylene Chloride-d_2): δ = – 4274.6 (d). Λ_M (5x10^{-4} M acetone solution) = 76.87 Ω^{-1} cm^2 mol^{-1}. IR (ATR, cm^{-1}): ν = 2226 (w, C≡N). MS (MALDI+): m/z 639.1 $[Pt(C^C^*)(PPh_3)]^+$.

***trans*-(C*,P) [Pt(C^C*)(CNXyl)(PPh_3)]PF_6 (10). Method a)** 2,6-Dimethylphenyl isocyanide (CNXyl) (20.6 mg, 0.15 mmol) and KPF_6 (28.9 mg, 0.15 mmol) were added to a pale yellow suspension of **5** (103.8 mg, 0.15 mmol) in acetone (30 mL). After 1 h of stirring at room temperature, the solvent was evaporated to dryness and the residue treated with dichloromethane (20 mL) and filtered through Celite. Then, the solvent was removed under reduced pressure and the residue was treated with diethylether (5 mL),

filtered and washed with diethylether (3 mL) to give **10** as a pale yellow solid. Yield: 124.9 mg, 89%.

Method b) PPh_3 (34 mg, 0.129 mmol) and KPF_6 (23 mg, 0.125 mmol) were added to a yellow suspension of **7-*c*** / **7-*t*** (14 / 86%) (70 mg, 0.128 mmol) in acetone (10 mL). After 1 h of stirring at room temperature, the solvent was evaporated to dryness and the residue treated with dichloromethane (20 mL) and filtered through Celite. Then, the solvent was removed under reduced pressure and treated with diethylether (5 mL), filtered and washed with diethylether (3 mL) to give **10** as a pale yellow solid. Yield: 91.1 mg, 77%. Anal Calcd for $C_{38}H_{32}F_6N_4P_2Pt$: C, 49.84; H, 3.52; N, 6.12. Found: C, 49.59; H, 3.34; N, 6.05. ^{1}H NMR (400 MHz, Methylene Chloride-d_2): δ = 7.67 (m, 6H, H*o* (PPh_3)), 7.56 (d, $^3J_{H2,H3}$ = 2.1, 1H, H_2), 7.46 – 7.35 (m, 10H, H*m*, H*p* (PPh_3)) and H_9), 7.30 (d, $^3J_{H10,H9}$ = 8.8, 1H, H_{10}), 7.28 (d, $^3J_{H2,H3}$ = 2.1, 1H, H_3), 7.26 (t, $^3J_{H,H}$ = 7.7, 1H, H*p* (Xyl)), 7.08 (d, $^3J_{H,H}$ = 7.7, 2H, H*m* (Xyl)), 7.02 (s, br, $^3J_{H7,Pt}$ = 50.7, 1H, H_7), 3.91 (s, 3H, H_4), 2.12 (s, 6H, Me (Xyl)). ^{13}C{^{1}H} NMR plus HMBC and HSQC (101 MHz, Methylene Chloride-d_2): δ = 169.3 (d, $^2J_{C,P}$ = 127.7, C_1), 151.6 (s, C_5), 143.5 (d, $^3J_{C7,P}$ = 9.2, $^2J_{C7,Pt}$ = 51.0, C_7), 138.6 (s, C_6), 134.8 (s, 2C, C*o* (Xyl)), 134.5 (d, $^2J_{C,P}$ = 11.7, 6C, C*o* (PPh_3)), 132.4 (s, 3C, C*p* (PPh_3)), 131.4 (s, C_9), 130.8 (s, C*p* (Xyl)), 129.5 (d, $^3J_{C,P}$ = 11.0, 6C, C*m* (PPh_3)), 128.7 (d, $^1J_{C,P}$ = 57.2, 3C, C*i* (PPh_3)), 128.6 (s, 2C, C*m* (Xyl)), 125.3 (s, br, C_3), 118.7 (s, CN), 116.1 (s, C_2), 112.4 (s, $^3J_{C10,Pt}$ = 25.8 ,C_{10}), 109.7 (s, C_8), 39.2 (s, C_4), 18.2 (s, Me (Xyl)). ^{31}P{^{1}H} NMR (162 MHz, Methylene Chloride-d_2): δ = 19.3 (s, $^1J_{P,Pt}$ = 2585.2). ^{195}Pt{^{1}H} NMR (85.6 MHz, Methylene Chloride-d_2): δ = – 4697 (dt, $^2J_{Pt,N}$ = 61.7 Hz,). Λ_M (5x10^{-4} M acetone solution) = 70.63 Ω^{-1} cm^2 mol^{-1}. IR (ATR, cm^{-1}): ν = 2231 (m, C≡N), 2187 (s, C≡NXyl). MS (MALDI+): m/z 770.1 [Pt(C^C*)(CNXyl)(PPh_3)]$^+$.

***trans*-(C*,P) [Pt(C^C*)(PPh$_3$)(MMI)]PF$_6$ (11).** 2-Mercapto-1-methylimidazole (MMI) (22.0 mg, 0.19 mmol) and KPF_6 (34.8 mg, 0.19 mmol) were added to a pale yellow suspension of **5** (125.0 mg, 0.19 mmol) in acetone (30 mL). After 1.5 h of stirring at room temperature, the solvent was evaporated to dryness and the residue was treated with dichloromethane (7 x 10 mL) and filtered through Celite. Then, the solvent was removed under reduced pressure and the residue was treated with diethylether (10 mL), filtered and washed with 5 mL more. The orange solid was washed with dichloromethane (3 x 4 mL) to give **11** as a pale yellow solid. Yield: 59.2 mg, 36%. Anal Calcd for $C_{33}H_{29}F_6N_5P_2PtS$: C, 44.10; H, 3.25; N, 7.79; S, 3.57. Found: C, 43.72; H, 3.27; N, 7.69; S, 3.85. ^{1}H NMR (400 MHz, Acetone-d_6) δ = 11.70 (s, 1H, NH (MMI)), 8.06 (d, $^3J_{H2,H3}$ = 1.7, 1H, H_2), 7.77 (m, 6H, H*o* (PPh_3)), 7.61 – 7.54 (m, 4H, H_{10} and H*p* (PPh_3)), 7.49 (m, 7H, H_3 and H*m* (PPh_3)), 7.43 (dd, $^3J_{H9,H10}$ = 8.2, $^4J_{H9,H7}$ = 1.6, 1H, H_9), 7.18 (m, 1H, $H_{5'}$, MMI), 7.05 (m, 1H, $H_{4'}$, MMI), 6.97 (m, $^3J_{H7,Pt}$ = 59.4, 1H, H_7), 4.08 (s, 3H, H_4), 3.32 (s, 3H, NMe, MMI). ^{13}C NMR (101 MHz, Acetone-d_6) δ 170.7 (d, $^2J_{C1,P}$ = 144.4, C_1), 153.7 (s, C=S (MMI)), 151.8 (s, C_5), 142.6 (d, $^3J_{C7,Pt}$ = 56.1, $^3J_{C7,P}$ = 8.9, C_7), 136.1 (d, $^2J_{C,P}$ = 11.2, 6C, C*o* (PPh_3)), 132.3 (d, $^4J_{C,P}$ = 11.2, 3C, C*p* (PPh_3)), 130.5 (d, $^1J_{C,P}$ = 54.38, 3C, C*i* (PPh_3)), 130.4 (s, C_9) 129.2 (d, $^3J_{C,P}$ = 10.7, 6C, C*m* (PPh_3)), 126.7 (d, $^4J_{C,P}$= 5.1, C_3), 123.2 (s, $C_{5'}$, MMI), 119.2 (s, CN), 116.7 (s, $C_{4'}$, MMI), 116.5 (s, br, C_2), 113.1 (s, $^3J_{C10,Pt}$ = 29.2, C_{10}), 109.2 (s, C_8), 38.3 (s, C_4), 34.7 (s, NMe, MMI). ^{31}P{^{1}H} NMR (162 MHz, Acetone-d_6): δ = 26.1 (s, $^1J_{P,Pt}$ = 2786.3). ^{195}Pt{^{1}H} NMR (85.6 MHz, Acetone-d_6): δ = – 4533.7 (d). Λ_M (5x10^{-4} M acetone solution) = 84.26 Ω^{-1} cm^2 mol^{-1}. IR (ATR, cm^{-1}): ν = 2224 (m, C≡N). MS (MALDI+): m/z 753.2 [Pt(C^C*)(MMI)(PPh$_3$)]$^+$, 639.1 [Pt(C^C*)(PPh$_3$)]$^+$.

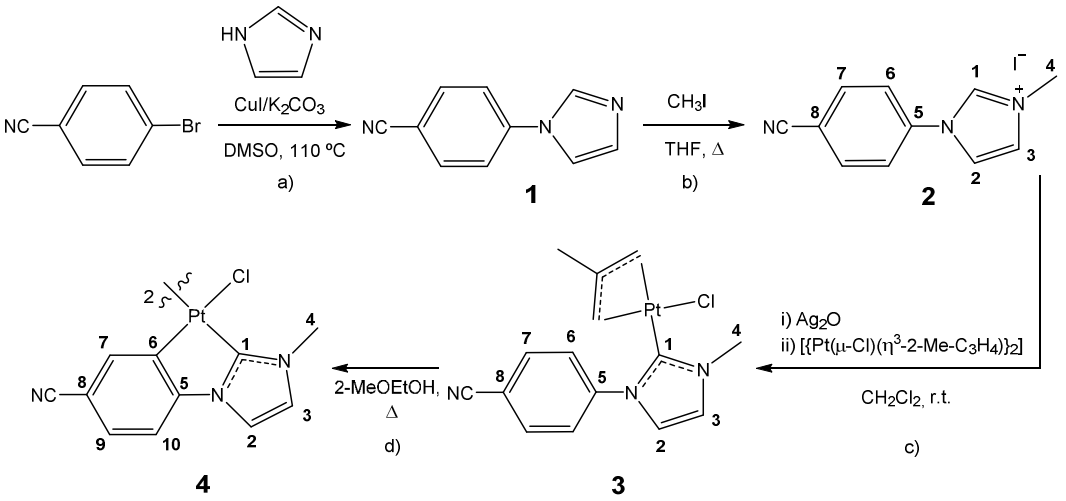
[Pt(C^C*)(dppe)]PF$_6$ (12). 1, 2-Bis(diphenylphosphino)ethane (dppe) (118.3 mg, 0.30 mmol) and KPF_6 (55.8 mg, 0.30 mmol) were added to a suspension of **4** (122.6 mg, 0.15

mmol) in acetone (30 mL). After 2.5 h of stirring at r.t. the solvent was removed in vacuo. Dichloromethane (50 mL) was then added and the resulting suspension was filtered through Celite. The solvent was removed under reduced pressure and Et_2O (20 mL) was added to the residue to obtain **12** as a white solid. Yield: 245.3 mg, 90%. Anal Calcd for $C_{37}H_{32}F_6N_3P_3Pt$: C, 48.27; H, 3.50; N, 4.56. Found: C, 47.93; H, 3.35; N, 4.49. ^{1}H NMR (400 MHz, Methylene Chloride-d_2): δ = [7.96–7.80] (m, 8H, H_o (dppe)), [7.69–7.54] (m, 13H, H_2 and H_m, H_p (dppe)), 7.43 (dd, $^3J_{H9,10}$ = 8.4, $^4J_{H9,7}$ = 1.7, 1H, H_9), 7.34 (m, $^3J_{H7,Pt}$ = 50.6, 1H, H_7), 7.31 (dd, $^3J_{H10,9}$ = 8.4, $^5J_{H10,P}$ = 2.3, 1H, H_{10}), 7.05 (m, $^4J_{H3,Pt}$ = 9.1, 1H, H_3), 3.04 (s, 3H, H_4), 2.37 (m, 4H, CH_2 (dppe)). ^{13}C{^{1}H} NMR plus HMBC and HSQC (101 MHz, Methylene Chloride-d_2): δ = 172.7 (dd, $^2J_{C1,Ptrans}$ = 126.9; $^2J_{C1,Pcis}$ = 8.8, C_1), 151.0 (s, C_5), 143.9 (dd, $^2J_{C6,Ptrans}$ = 103.5, $^2J_{C1,Pcis}$ = 6.0, C_6), 142.5 (dd, $^3J_{C7,Ptrans}$ = 9.9; $^3J_{C7,Pcis}$ = 2.8, $^2J_{C7,Pt}$ = 54, C_7), 134.1 (d, $^2J_{C,P}$ = 12.1, 4C, C_o (dppe)), 133.6 (d, $^2J_{C,P}$ = 12.3, 4C, C_o (dppe)), 132.8 (s, 4C, C_p (dppe)), 131.1 (s, C_9), 130.0 (d, $^3J_{C,P}$ = 11.0, 4C, C_m (dppe)), 129.7 (d, $^3J_{C,P}$ = 11.0, 4C, C_m (dppe)), 124.9 (d, $^4J_{C3,P}$ = 4.0, $^3J_{C3,Pt}$ = 29.0, C_3), 118.5 (s, CN), 116.4 (d, $^4J_{C2,P}$ = 2.0, $^3J_{C3,Pt}$ = 33.0, C_2), 112.04 (s, $^3J_{C10,Pt}$ = 21.7, C_{10}), 110.7 (m, C_8), 38.9 (s, C_4), 31.7 (dd, $^1J_{C,P}$ = 37.6, $^2J_{C,P}$ = 10.0, CH_2 (dppe)), 30.6 (dd, $^1J_{C,P}$ = 39.8, $^2J_{C,P}$ = 12.4, CH_2 (dppe)). ^{31}P{^{1}H} NMR (162 MHz, Methylene Chloride-d_2): δ = 50.2 (d, $^2J_{P,P}$ = 7.0, $^1J_{P,Pt}$ = 2673.8, *trans C**), 43.1 (d, $^1J_{P,Pt}$ = 2014.6, *trans* C_{ph}). ^{195}Pt{^{1}H} NMR (85.6 MHz, Methylene Chloride-d_2): δ = – 4996 (dd). Λ_M (5x10^{-4} M acetone solution) = 69.01 Ω^{-1} cm^2 mol^{-1}. IR (ATR, cm^{-1}): ν = 2223 (m, C≡N). (m, C≡N). MS (MALDI+): m/z 775.2 $[Pt(C\hat{}C^*)(dppe)]^+$

RESULTS

Improved method of preparation of a NHC ligand and its use in the stepwise synthesis of [{Pt(μ-Cl)(C^C*)}$_2$] (HC^C*-κC*= 1-(4-cyanophenyl)-3-methyl-1*H*-imidazol-2-ylidene).

The synthesis of the N-heterocyclic carbene (NHC) 1-(4-cyanophenyl)-1*H*-imidazol(**1**) has been previously reported.[16a,16b] However, we have prepared it by a slightly modified method (Scheme 1, path a, Experimental Section) to avoid the use of co-ligands (pyrrolidinylmethylimidazole) and the purification step by column chromatography. 4-Bromobenzonitrile was coupled with imidazole in DMSO at 110ºC using copper(I) iodide and potassium carbonate in the presence of 4 Å molecular sieves. After work-up, **1** was obtained by precipitation with *n*-hexane in good yield (83%). Then, the addition of methyl iodide to a refluxing THF solution of **1** rendered the corresponding imidazolium salt: 1-(4-cyanophenyl)-3-methyl-1*H*-imidazolium iodide (**2**) (Scheme 1, path b and Experimental Section).



Scheme 1. Synthesis of compounds **1-4.** Numerical scheme for NMR purporses.

Compound **2** was reacted with silver(I) oxide for 3 h and subsequently with [{Pt(μ-Cl)(η^3-2-Me-C_3H_4)}$_2$] (η^3-2-Me-C_3H_4 = η^3-2-methylallyl) to yield the neutral complex

[PtCl(η^3-2-Me-C_3H_4)(HC^C*-κC*)] (**3**), which was isolated as a pale yellow and air stable solid in very good yield (83%, see Experimental Section and Scheme 1, path c). Spectroscopic IR and NMR data support the proposed structure for complex **3.** Its IR spectrum shows an absorption band at 285 cm^{-1} which is consistent with the presence of a terminal Pt-Cl bond in *trans* disposition to a ligand with a large *trans* influence such as η^3-2-Me-C_3H_4[13,14c] and another one at 2228 cm^{-1} due to the cyano group of the HC^C* ligand.

The disappearance of the signal attributed to H1 in the free ligand **2** (9.91 ppm) and the presence of Pt satellites in the signals corresponding to the H2 and H3 protons of the imidazolyl moiety (see Figure S1 in the SI) indicates that the imidazolium salt has been successfully anchored to the Pt center through the C1 of the N-heterocyclic carbene (HC^C*-κC*). This statement was confirmed by the similarities of the $^{195}Pt\{^1H\}$ resonance (δ = –4460 ppm) and the ^1H and $^{13}C\{^1H\}$ ones corresponding to the imidazolyl moiety and the methyl allyl group (η^3-2-Me-C_3H_4) with those of [PtCl(η^3-C_4H_7)(HC^C*-κC*)](HC^C* = 3-methyl-1-(naphthalen-2-yl)-1*H*-imidazol-2-ylidene).[13]

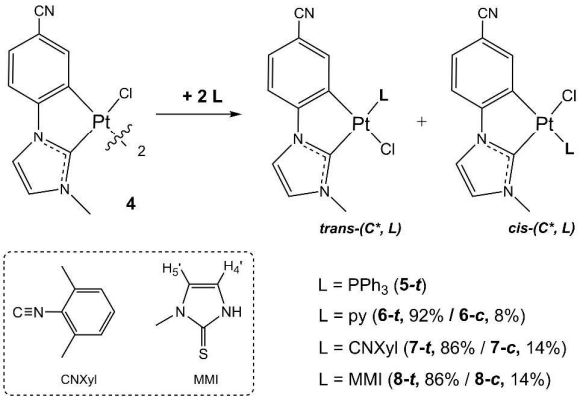
A refluxing suspension of **3** in 2-methoxyethanol yielded the precipitation of a dark colored solid which was recrystallized in hot acetonitrile solution (see Scheme 1 path d and Experimental Section) to render **4** as a pure yellow solid in very good yield (81%). Compound **4** was not soluble in the common organic solvents, only in DMSO. The NMR data of **4** in DMSO-d_6 show the absence of the allyl group and the metalation of the 1-(4-cyanophenyl)-3-methyl-1*H*-imidazol-2-ylidene) (HC^C*-κC*) through the C6 (see Experimental Section and figures S2 in the SI). This is evident by the lack of the H6 resonance and by the presence of a broad singlet corresponding to H7 at 8.72 ppm with a Pt-H coupling constant of *ca* 60 Hz. The observed C1 resonance (δ = 156.0 ppm)

is in good agreement with the literature values[10a-c,10e,10h,13,17] for related cyclometallated platinum (II) compounds.

These results embrace the feasibility of this stepwise synthetic pathway for [{Pt(μ-Cl)(C^C*)}$_2$] systems, since in this work, we have been able to reproduce the same strategy described by ourselves to prepare C^N[14b,14c] and more recently C^C*[13] cyclometallated complexes of platinum (II).

Reactivity of 4. Synthesis and Characterization of [PtCl(C^C*)L] (L = PPh_3 (5); py (6-*t* / 6-*c*), CNXyl (7-*t* / 7-*c*),MMI (8-*t* / 8-*c*))

The dinuclear complex [{Pt(μ-Cl)(C^C*)}$_2$] (**4**) reacts with several neutral P, N, C and S donor ligands, such as PPh_3, py, CNXyl and MMI in a 1:2 molar ratio at low temperature (–8ºC) (Scheme 2 and Experimental Section) to give the mononuclear complexes [PtCl(C^C*)L] (L = PPh_3 (**5**); py (**6-*t*** / **6-*c***), CNXyl (**7-*t*** / **7-*c***), MMI (**8-*t*** / **8-*c***)). X-ray and spectroscopic data discussed below indicate that compound **5** was obtained as a solid with the *trans*-(C*,L) being the only isomer observed. Whilst, in all other cases (**6-8**), the cleavage of the bridging system rendered both isomers *cis*- and *trans*-(C*,L) with the *trans* isomer being the main one, especially when L is py (**6**).



Scheme 2. Synthetic pathway to compounds **5-8.**

For compound **7**, several reaction conditions were tested at room temperature and also in refluxing chloroform. End results were *cis*/*trans* mixtures with the same ratios. Analytical and spectroscopic data of compounds **5**-**8** are consistent with the proposed stoicheometry for them (See Experimental Section in the SI). Relevant structural information was provided by multinuclear NMR spectra (See Experimental Section in the SI and Table 1). It deserves to be noted that the ^{1}H-NMR resonances corresponding to both cyanophenyl and imidazole fragments of C^C* are clearly altered by the coordination of the ancillary ligands (L). Especially sensitive to both, the nature of L and the geometric disposition of the ligands around the Pt centre, are the H7 and the H4 resonances. In all cases, as depicted in Figure 1, the H7 resonances of the *trans*-(C*,L) isomers appear more shielded than those of the *cis*- derivatives.

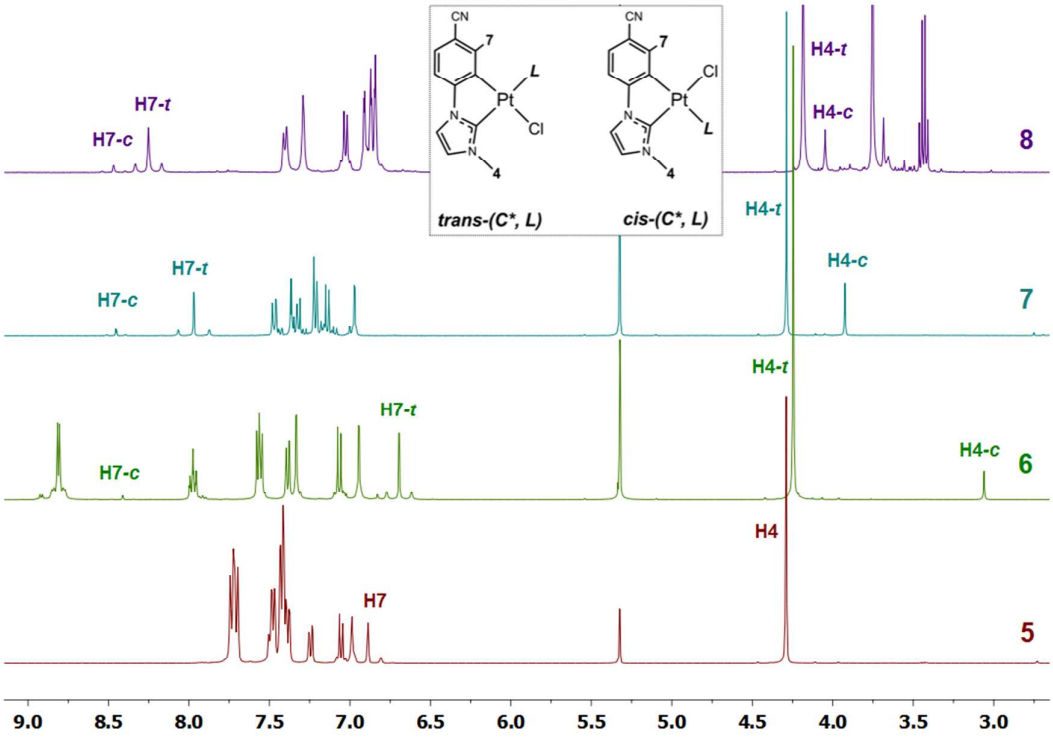


Figure 1. ^{1}H NMR spectra of **5**-**8** in CD_2Cl_2

Table 1. Significant NMR data for compound characterization[a]

	δH (J_{Pt-H})		δC (J_{Pt-C})			δP (J_{Pt-P})	δPt
Comp.	H7	H4	C1	C7	C3		
5[b]	6.88 (64.0)	4.29	170.1	141(57.0)	124.3 (26.0)	28.6 (2868.0)	- 4227.0
6-*t*	6.69(61.8)	4.24	152.7	135.2 (37.8)	123.1 (38.4)		
6-*c*	8.41 (55.1)	3.06					
7-*t*	7.97 (77.3)	4.28	167.7	140.8 (72.4)	123.9 (30.9)		
7-*c*	8.45 (47.2)	3.92					
8-*t*	8.27 (65.9)	4.19	159.3	135.4 (37.1)	123.6 (37.3)		
8-*c*	8.47 (57.5)	4.04					
9[b]	6.85 (58.8)	2.87	171.2	142.9 (55.4)	124.6 (31.3)	28.2 (2881.6)	- 4274.6
10[b]	7.02 (50.7)	3.91	169.3	143.5 (51.0)	125.3	19.3(2585.2)	- 4697.0
11[b]	6.97 (59,4)	4.08	170.7	142.6 (56.1)	126.7	26.1 (2786.3)	- 4533.7
12	7.34 (50.6)	3.04	172.7	142.5 (54.0)	124.9 (29.0)	(*t*-C*): 50.2 (2673.8) (*c*-C*): 43.1 (2014.6)	- 4996.0

[a]δ (ppm), J (Hz), [b] = *trans*-(C*,P) isomer is the only one observed

Within the *trans* isomer complexes, in particular, when L = PPh_3 (**5**) and py (**6-*t***), the H7 resonance undergoes an important upfield shift comparing with that in complexes with L = CNXyl (**7-*t***) and MMI (**8-*t***) (Table 1). This effect has been associated with the anisotropic shielding effect caused by the proximity in space of the aromatic ring current of the phenyl (**5**) and pyridine (**6-*t***) groups to the H7.[14b,14c,18] This C–H7 ⋯ π interaction was also observed in the X-ray structure of **5**, as discussed below. Likewise, in the *cis*-(C*,L) isomers of complexes **6**–**8**, the H4 resonance is the one that suffers the anisotropic effect since it moves upfield in relation to the *trans* isomers, the effect being more intense when L is pyridine (3.06 **6-*c***; 4.24 **6-*t***). In both geometric isomers, the H7 signal appears accompanied by platinum satellites. The Pt-H7 coupling constants of the *trans* isomers are larger than those of the *cis* derivatives, which is in agreement with the higher *trans* influence of the L ligands comparing to the Cl.[11c,14a,19]

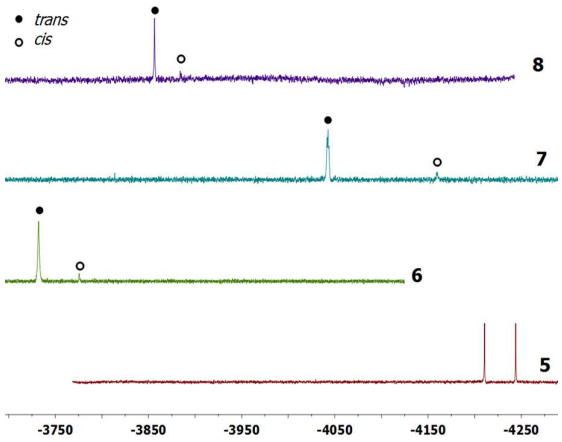


Figure 2. $^{195}Pt\{^{1}H\}$ spectra of **5**-**8** in CD_2Cl_2.

It is worth noting that the *cis/trans* isomer ratios of **6**–**8** from the worked up solids match with those from the crude reaction mixtures, as proven by NMR experiments. We have also confirmed that these ratios do not change over the time.

As expected, the $^{195}Pt\{^{1}H\}$ spectrum of **5** exhibits only a doublet at –4227 ppm with a ^{195}Pt-^{31}P coupling constant of 2868 Hz, while two ^{195}Pt resonances were observed for each one of the complexes **6**–**8**, due to the existence of both isomers (Figure 2). The main one, which corresponds to the *trans* isomer, appears less shielded than the *cis* one, in all three cases.

In agreement with its formulation, the $^{31}P\{^{1}H\}$ NMR spectrum of **5** shows only one sharp signal at 28.6 ppm flanked by platinum satellites. The ^{195}Pt–^{31}P coupling constant value is typical of a P–Pt–C *trans* arrangement[19-20] making evident the strong *trans* influence of the carbene atom (C*).

The molecular structure of **5** (see Figure 3), obtained by X-ray diffraction analysis of a single crystal of it, confirmed the complex to be the isomer *trans*-(C*,P)[Pt(C^C*)Cl(PPh_3)]; The data analysis is discussed below.

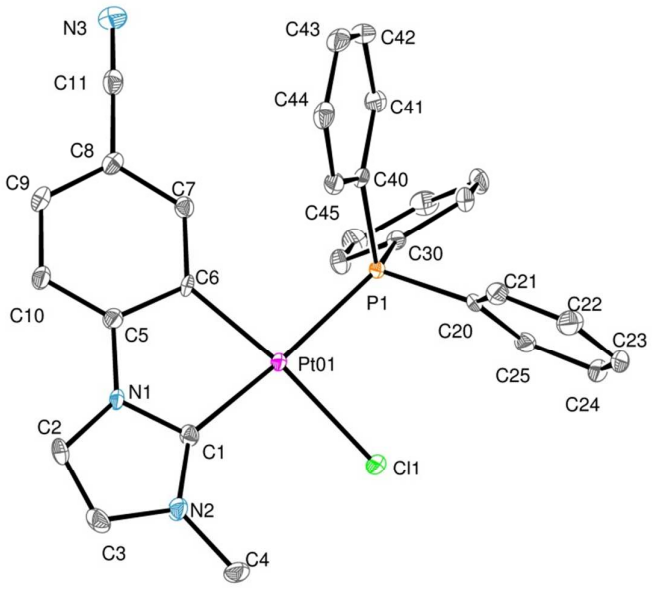
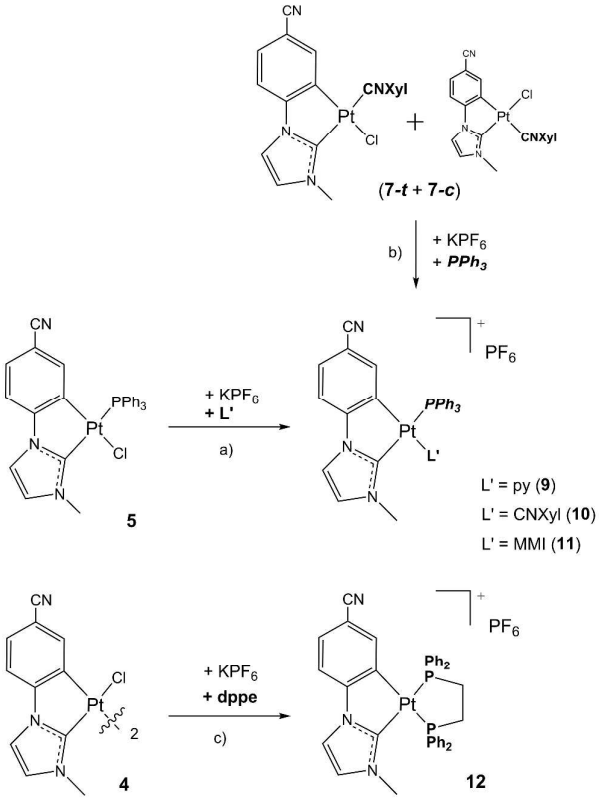


Figure 3. Molecular structure of complex **5·MeOH**. Thermal ellipsoids are drawn at the 50% probability level. Solvent molecules and hydrogen atoms have been omitted for clarity.

Synthesis and Characterization of the new Cationic "Pt(C^C*)" Complexes: *trans*-(C*,P)-[Pt(C^C*)(PPh_3)L']PF_6 (L' = py (9), CNXyl (10), MMI (11)) and [Pt(C^C*)(dppe)]PF_6 (12)

With the aim of preparing new heteroleptic compounds with the N-heterocyclic carbene {Pt(C^C*)LL'}, various strategies were followed (see scheme 3). Using different starting materials **4**, **5** or **7**, we have been able to prepare the first cationic complexes with the "Pt(C^C*)" moiety. Hence, the addition of equimolecular amounts of KPF_6 and L' to a solution of **5** in acetone rendered the compounds **9 – 11** as pure solids (scheme 3, path a). The formulation and geometry proposed are in agreement with the spectroscopic and crystallographic data discussed below. As inferred from these data, the PPh_3 remains coordinated *trans* to the C*. Interestingly, compound **10** can also be prepared by adding KPF_6 and PPh_3 to the mixture of *cis/trans* isomers of complex **7** (see scheme 3, path b). Therefore, in this case, the main fraction of this reaction does not proceed with stereoretention, since the CNXyl ligand, that is located *trans* to C* in **7-*t***, migrates to the *cis* position by the coordination of the PPh_3. When a suspension of **4** in acetone was treated with KPF_6 and dppe (1:2 molar ratio) compound **12** was formed, a mononuclear species with the dppe acting as a chelate ligand.

Relevant structural information arises from the multinuclear NMR spectra (see Experimental Section, Table 1 and Figures S4 in the SI). The $^{31}P\{^1H\}$ NMR spectra of **9-11** show a singlet flanked by platinum satellites. The δP and ^{195}Pt-^{31}P coupling constants values are quite similar to those found in complex **5**, indicating a *trans*-(C*,PPh_3) arrangement in these complexes. In the ^{31}P NMR spectrum of **12**, the two different P atoms appear as two doublet signals accompanied by Pt satellites. The chemical shifts and the observed P-P coupling of 7 Hz confirm the chelating arrangement of the dppe around the platinum center.[21]



Scheme 3. Synthethic pathway to cationic complexes **9**–**12**.

According to the geometry proposed (see scheme 3), H7 resonances appear in the range of 6.80 – 7.30 ppm due to the anisotropic shielding effect caused by the proximity in space of the phenyl groups of the PPh_3. When L' is pyridine and dppe, the H4 resonance also suffers the anisotropic shielding effect, since it moves upfield (2.87 **9**, 3.04 **12**) comparing with that in complexes **10** and **11** (3.91 **10**, 4.08 **11**).

Significant are also the $^{195}Pt\{^{1}H\}$ spectra (see Figure 4 and Table 1) which confirm the presence of a single isomer in each case. They exhibit doublets for compounds **9**–**11** and a doublet of doublets for **12** due to the coupling with the ^{31}P nuclei, these chemical shifts are ranging from –4274 to –4996 ppm.

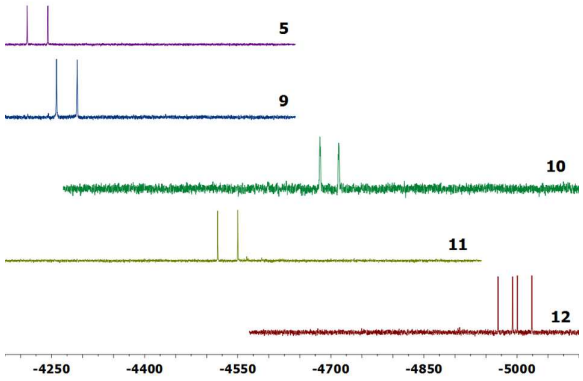


Figure 4. $^{195}Pt\{^{1}H\}$ spectra of **5** and **9**–**12** in CD_2Cl_2.

The structural information obtained from the NMR spectra was confirmed by X-ray diffraction studies on compounds **9**–**12**, as can be seen in Figures 5 and 6 (for complexes **10** and **12**) and Figures S6, S8 for complexes **9** and **11**).

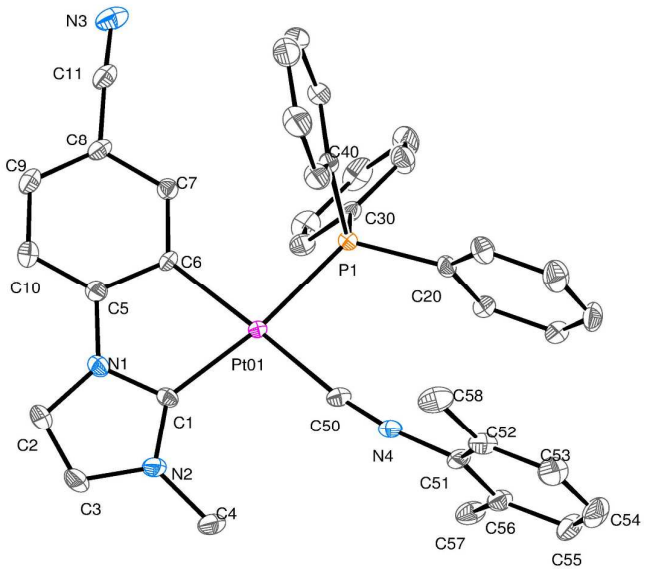


Figure 5. Molecular structure of the complex **10·0.5 OEt_2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, PF_6 and solvent molecules have been omitted for clarity.

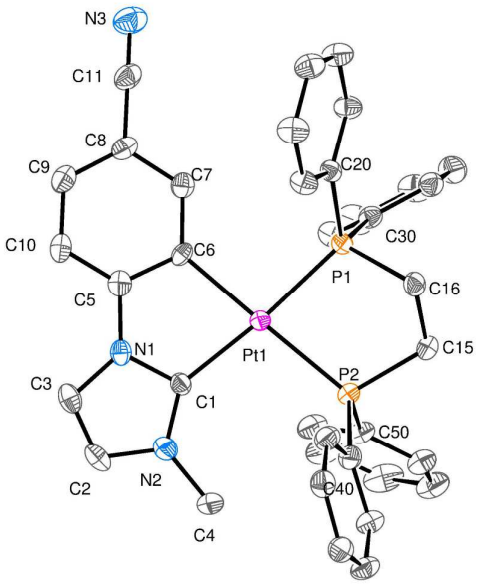


Figure 6. Molecular structure of complex **12·CH_2Cl_2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, PF_6 and solvent molecules have been omitted for clarity.

Crystal structures determination

Single crystal X-ray diffraction studies were performed on compounds **5** and **9**–**12** to confirm their molecular structures. Crystallographic data are given in Table S1 and a selection of bond lengths and angles is shown in Table 2. As shown in Figures 3, 5, 6 and S5-S9 (in the SI), the Pt centre lies in a distorted square planar coordination environment as a consequence of the small bite angle of the NHC cyclometallated ligand (C^C*) ligand [79.83(11)º–78.54(13)º]. This angle together with the Pt–C6 and Pt–C1(C*) distances are similar to those found in other five membered metalacycles of Pt(II) with N-heterocyclic carbenes.[10a-h,13] PPh_3 and L (L = Cl **5**, py **9**, CNXyl **10** and MMI **11**) complete the coordination sphere of platinum (II), whereas in **12**, a chelate dppe ligand does.

The Pt–Cl,[14b,14c,22] Pt–N,[23] Pt–C,[11c,11f] Pt–S[24] and Pt–P[19,25] distances are within the typical range for platinum(II) compounds with these *trans* to σ-bonded carbon atoms.

The Pt–C6 bond lengths are clearly altered by the ancillary ligand coordinated at the *trans* position [2.015(3) Å (Cl, **5**)–2.080(4) Å (P, **12**)]; whilst the Pt–C1 ones are practically the same regardless of the neutral (**5**) or cationic (**9**–**12**) nature of the complexes. These are the first examples of $[Pt(C\hat{}C^*)L'L]^{0,+}$ heteroleptic complexes studied by X-ray diffraction. So far, all crystal structures of NHC cycloplatinated compounds have been reported with diketonate derivatives.[10a-h]

Table 2. Selected bond lengths (Å) and angles (º) for **5** and **9**–**12**

	5·MeOH (X= Cl(1))	**9**·H_2O (X= N(4))	**10**·0.5 Et_2O (X= C(50))	**11** (X= S(1))	**12**·CH_2Cl_2 (X= P(2))
Pt(1)–C(1)	2.030(3)	2.033(3)	2.035(4)	2.037(3)	2.055(4)
Pt(1)–C(6)	2.015(3)	2.035(3)	2.065(4)	2.047(3)	2.080(4)
Pt(1)–P(1)	2.3024(7)	2.3075(9)	2.3171(11)	2.3046(8)	2.2787(13)
Pt(1)–X	2.3860(7)	2.099(3)	1.974(4)	2.3781(13)	2.3218(13)
C(1)–Pt(1)–C(6)	79.83(11)	78.54(13)	78.58(17)	79.54(10)	79.05(17)
C(6)–Pt(1)–P(1)	96.60(8)	95.90(10)	93.35(12)	94.67(7)	96.00(12)
C(1)–Pt(1)–X	95.85(8)	94.94(12)	98.74(17)	97.45(8)	101.91(13)
P(1)–Pt(1)–X	88.92(2)	89.45(8)	89.39(13)	89.28(3)	83.15(5)

The chelating dppe ligand adopts the *gauche* conformation with a P–CH_2–CH_2–P torsion angle of 46.7º. The Pt–P2 bond length is slightly longer than the Pt–P1 one, due to the higher *trans* influence of the C_{Ar}. Nevertheless, both distances and the small bite angle (83.15º) are similar to those of related compounds.[21c,26]

The cyclometallated NHC carbene ligand itself is not completely planar; it exhibits a small interplanar angle between the cyanophenyl and the imidazole fragments of 2.45(10)º (**5**), 6.42(9)º (**9**), 12.35(13)º (**10**), 5.79(8)º (**11**) and 5.81(14)º (**12**). As well as the molecular complexes that show dihedral angles between the platinum coordination plane (Pt01, C1, C6, P1, X) and the NHC ligand (N1–N3, C1–C11) of 10.7(2)º (**5**), 10.9(8)º (**9**), 8.83(8)º (**10**), 10.39(3)º (**11**) and 10.27(5) (**12**).[27] The rings of the ancillary ligands are almost perpendicular to the platinum coordination plane with dihedral angles

of 78.94(9)º (N4, C12–C16, **9**), 82.48(12)º (N4, C50–C56, **10**), 89.18(4)º (N4, N5, C50–C53, **11**).

Further inspection of the molecule packing within the crystal structures revealed the presence of weak intra- and inter-molecular interactions (see the SI), however, no Pt···Pt contacts were observed. In all crystal structures, (Figures 3, 5, 6 and S5-S9) we find an edge to – face, also known as T-shaped, C–H···π interaction: the H7 hydrogen atom is pointing to phenyl ring of the PPh_3 ligand, showing moderately short distances (C–H··· π; C7···C_{ph} (PPh_3) = 3.22 **5**, 3.28 **9**, 3.35 **10**, 3.15 **11** and 3.23 Å **12**). Only in **9** and **12**, there is a C–H···π interaction between the Me group (C4) and the pyridine or phenyl rings (C4···C_{py} = 3.42 Å (**9**), C4···C_{ph} = 3.23 Å (**12**)). Also in **9-11**, the phenyl group of the PPh_3 displays short intramolecular π ···π interactions (3.11 - 3.58 Å) with the rings of the ancillary ligands (py, CNXyl, MMI), which are placed almost parallel to each other [15.30(11)º **9**, 5.42(16)º **10**, 9.47(9)º **11**]. Additionally, compound **9** crystallizes with one water molecule, which is holding a hydrogen bond with the CN group of the cyclometallated NHC fragment (see Figure S6). Finally, in **9** and **12**, the molecules arrange themselves in pairs in a head-to-tail fashion supported by π ···π intermolecular contacts between the NHC fragments (3.70 Å **9**, 3.32 Å **12**), see Figures S6 and S9).

DISCUSSION

As shown above, the cleavage of the chlorine-bridge system in [{Pt(μ-Cl)(C^C*)}$_2$] (**4**) by different ancillary ligands (L) led to the clean formation of *trans*-(C*,L)-[PtCl (C^C*)L] when L is PPh_3 (**5**). If L is py, CNXy and MMI, the bridge-splitting reaction gave mixtures of *cis*/*trans* isomers (**6-8**).

In an attempt to explain this behavior we have used the term transphobia degree (T) of pairs of trans ligands, which has been accepted by many authors to explain the geometries of stable square-planar complexes of d^8 transition metals. The degree of T, has been assumed to be related to the *trans* influence, in such a way that the greater the *trans* influence of two ligands, the greater the transphobia and the cis disposition of them will be the favored geometry. In this sense the heteroleptic complexes [PtCl(C^N)L] (HC^N = 3,8-dinitro-6-phenylphenanthridine, 2-(4-bromophenyl)imidazol[1,2-a]pyridine; L= PPh_3, tht, C≡NR (R = ^{t}Bu, 2,6-dimethylphenyl)) and [Pt(C^P)(C≡CPh)L] (C^P= $CH_2C_6H_4P(o\text{-tolyl})_2$-κC,P; L = CO, py, tht) exist as the *trans*-(C,Cl) isomer as expected on the basis of the transphobia degree (T) of pairs of trans ligands.[14a,14b] However, the steric requirements of the ligands involved can also play an important role in determining the geometries of these complexes. In this sense, complex [Pt(C^P)(C≡CPh)PPh_3], exhibits the *trans*-(C,C≡CPh) geometry instead of the expected one considering electronic preferences (*trans*-C,PPh_3), which was attributed to the crowding associated with the cis disposition of the P(o-tolyl)$_2$ and the PPh_3 group.[14a]

Therefore, we have tried to explain the preferred geometry for complexes [PtCl(C^C*)L] (**5**-**8**) and [Pt(C^C*)(PPh_3)L]$^+$ (**9**-**11**) on the basis of the transphobia effect (T). With this purpose we have studied the relative trans influences of the two σ Pt-C bonds present in the Pt(C^C*) unit, both expected to have a great trans influence, and those of the auxiliary ligands (Cl, PPh_3, py, CNXyl, MMI), comparing the $^1J_{Pt,P}$, $^2J_{Pt,C}$ and $^3J_{Pt,H}$ values affected by the ligands located at their trans positions.

The $^1J_{Pt,P}$ values observed for complexes *trans*-(C*,P) [PtCl(C^C*)(PPh_3)] (**5**), and [Pt(C^C*)(PPh_3)L']PF_6 (L' = py (**9**), CNXyl (**10**), MMI (**11**)) range from 2585.2 to 2881.6 Hz, which are typical of a P–Pt–C *trans* arrangement.[19-20] These values are also

very similar to those observed in Q[Pt(CH_2-C_6H_4-P(o-tolyl)$_2$)(C≡CPh)$_2$] (Q = Li^+ (2746 Hz), NBu_4^+ (2603 Hz)) with the Pt–P bond trans to a Pt–Cacetylide one.[14a] In addition, the $J_{Pt\text{-}P}$ corresponding to the P trans to C* (2673.8 Hz) in [Pt(C^C*)(dppe)]PF_6 (**12**), resulted to be similar to that observed in complexes with phosphine ligands located in the trans position, such as [Pt(C^P)(dppe)]$^+$[C^P = {(R)-1-[1-diphenylphosphino]ethyl}naphthyl-C,P; $J_{Pt\text{-}P\ (transP)}$ =2770 Hz,[21c] or [Pt(dppe)(PAn-H)]$^+$ [PAn = 9-diphenylphosphinoanthracene; $J_{Pt\text{-}P\ (transP)}$ =2796],[26d] indicating that the C* displays a great trans influence, similar to alkynyl or phosphine ligands.

Then, we focused again on complex [Pt(C^C*)(dppe)]PF_6 (**12**) and we observed the $^1J_{Pt\text{-}P}$ for the P trans to C_{Ar} and C* are 2014.6 and 2673.8 Hz respectively. These values indicate that the *trans* influence of C_{Ar} is slightly greater than that of C*. The same assessment was inferred from the $^3J_{Pt\text{-}Ho(py)}$ in complex **6** which exhibits different values when pyridine is facing C_{Ar} (**6-*c*,** 20.7 Hz) or C* (**6-*t*,** 28.0 Hz). Moreover, an evaluation of the electronic effects of the different L ligands can be undertaken by comparison of the spectroscopic and crystallographic data of complexes with the same stoichiometry and configuration, such as *trans*-(C*,P)-[Pt(C^C*)(PPh_3)L]$^{0,+}$ (L = Cl (**5**), py (**9**), CNXyl (**10**), MMI (**11**)) or *cis*-(C*,L)-[PtCl(C^C*)L] (L = py (**6-*c***), CNXyl (**7-*c***), MMI (**8-*c***)) (Table 1). On the basis of the observed $^3J_{Pt\text{-}H7}$ (64.0 **5**, 58.8 **9,** 50.7 **10**, and 59.4 Hz, **11**) and $^2J_{Pt\text{-}C7}$ (57.0 **5,** 55.4 **9**, 51.0 **10** and 56.1 Hz **11**) in the *trans*-(C*,P) named complexes, the trans influence order seems to be CNXyl > py ~ MMI > Cl. An additional comparison of the values of δC1 (170.1 ppm **5**, 152.7 **6-*t***; 167.7, **7-*t*;**159.3, **8-*t***) and $^3J_{Pt\text{-}C3}$ (26.0 Hz **5**, 38.4 **6-*t***; 30.9, **7-*t*;** 37.3, **8-*t***) in complexes *trans*-(C*,L)-[PtCl(C^C*)L] (L = PPh_3 (**5**), py (**6-*t***), CNXyl (**7-*t***), MMI (**8-*t***)) indicates that the trans influence of PPh_3 is even greater than that of CNXyl. Finally, the X-ray data analysis of **5** and **9**–**12** (Table 2) indicate that the longest Pt–C6 distances correspond to those of **12**

and **10**, with the dppe and CNXyl located at the trans position. Therefore, the trans influence of all the used ancillary ligands seems to follow the order: PPh_3 / dppe > CNXyl > py ~ MMI > Cl.

Taking into account all these assumptions the $T[C_{Ar}/L)] > T[C^*/L]$ and $T[C_{Ar}/PPh_3)] > T[C_{Ar}/CNXyl)] > T[C_{Ar}/py)] \sim T[C_{Ar}/MMI)] > T[C_{Ar}/Cl)]$. Therefore, the $T[C_{Ar}/PPh_3)]$ should be greatest one and the experimental results seem to indicate that the difference between $T[C_{Ar}/PPh_3)]$ and $T[C^*/PPh_3]$ is big enough to direct the clean formation of *trans*-(C*,PPh_3)- complexes **5**, **9**–**11**.

However, the difference between $T[C_{Ar}/L)]$ and T[C*/L] (L = py, CNXyl, MMI, Cl) is, in each case, not big enough to avoid the formation of mixtures of isomers. Based on the order of $T[C_{Ar}/L]$ named above, the cleavage of the chlorine-bridge system in $[\{Pt(\mu\text{-}Cl)(C\hat{}C^*)\}_2]$ (**4**) by py to give complex **6** was expected to be no more stereoselective than that with CNXyl or MMI, but it is. Other factors to promote the greater stability of **6-*t***, such as the steric hindrance between py and the imidazol fragment of C^C* in the *cis* isomer can be excluded. Given that the H7 and H4 resonances in **6-*t*** and **6-*c*** suffer a great anisotropic shielding effect, which was discussed in the NMR section, we considered the C–H···π (py) interactions to be involved in it. C–H···π interactions have been known to play a key role in the stereoselectivity of coordination compounds amongst other fields in chemistry.[28] It has been widely reported that intramolecular C–H···π hydrogen bonds can induce the formation of single linkage isomers.[29] In both isomers of **6**, a C–H···π interaction could be possible: Csp^3–H4 (Me) ··· π (py) in **6-*c*** and a T-shaped Csp^2–H7 (Ar) ··· π (py) in **6-*t***. As reported before, the interaction energy involving a T-shaped aromatic C–H is somewhat stronger than that of the aliphatic ones.[28a,30] So, we would expect **6-*t*** to be more stable than **6-*c***. DFT calculations for models of **6-*c*/-*t*** in solution of CH_2Cl_2 were

carried out (see Figure 7). In effect, isomer **6-*t*** with the C–H7 pointing at the pyridine ring is 1.01 Kcal mol^{-1} more stable than **6-*c***. This subtle difference in energy added to the bigger T[C_{Ar}/py)] vs T[C*/py] results to be reasonably determining for the high stereo selectivity of isomers in **6**.

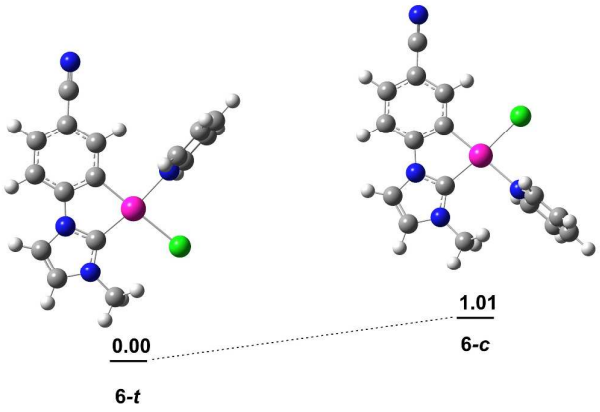


Figure 7. DFT- computed energies for the **6-c/-t** isomers (ΔE, kcal mol^{-1})

In complexes **5** and **9-11**, their X-ray structures and NMR data also show the presence of Csp^2–H7 (Ar) ⋯ π interactions, which will contribute together with the difference of T[C_{Ar}/L)] vs T[C*/L] to the selective formation of the *trans*-(C*,PPh_3) isomer, as experimentally observed.

CONCLUSIONS

The synthetic method for **1** has been greatly improved and the corresponding imidazolium salt, **2**, has been successfully anchored and subsequently cyclometallated to the Pt center, which endorse the generality and viability of this step-by-step synthetic pathway for cyclometallated NHCs complexes, [{Pt(μ-Cl)(C^C*)}$_2$]. The chlorine-bridge complex, **4** has been revealed as a useful starting material for neutral and cationic heteroleptic complexes containing the "Pt(C^C*)" moiety, **5-12**.

The transphobia degree (T) of pairs of trans ligands, as inferred from spectroscopic data, resulted to be: T[C_{Ar}/L)] > T[C*/L] and T[C_{Ar}/PPh_3)] > T[C_{Ar}/CNXyl)] > T[C_{Ar}/py)] ~ T[C_{Ar}/MMI)] > T[C_{Ar}/Cl)]. The difference between T[C_{Ar}/L)] and T[C*/L] (L = py, CNXyl, MMI) is not enough to avoid the formation of mixtures of *cis*/*trans* isomers during the splitting of the chlorine-bridge in **4** by L but, in all cases, the *trans*-(C*,L)-[PtCl(C^C*)L] isomer is the major species, especially when L is py. In this case, the intramolecular T-shaped C_{Ar}–H$\cdots$ π (py) interaction seems to contribute to the stabilization of this isomer, as proven by DFT calculations. Otherwise, the greatest T[C_{Ar}/PPh_3)] together with the intramolecular T-shaped C_{Ar}–H$\cdots$ π (Ph) interactions present in the *trans*-(C*, PPh_3)-[Pt(C^C*)(PPh_3)L] complexes (L = Cl **5,** py **9**, CNXyl **10**, MMI **11**) would account for the stereo-selective formation of this isomer in each case, as experimentally observed.

ASSOCIATED CONTENT

Supporting information: General procedures and materials, computational and crystallographic details. Crystallographic data. Full NMR spectra of **3** and **4**. Full NMR spectra of **6** and **10** (Selected as examples of the neutral and cationic derivatives). X-ray

structures. Tables of atomic coordinates of compounds. This material is available free of charge via the Internet at http://pubs.acs.org."

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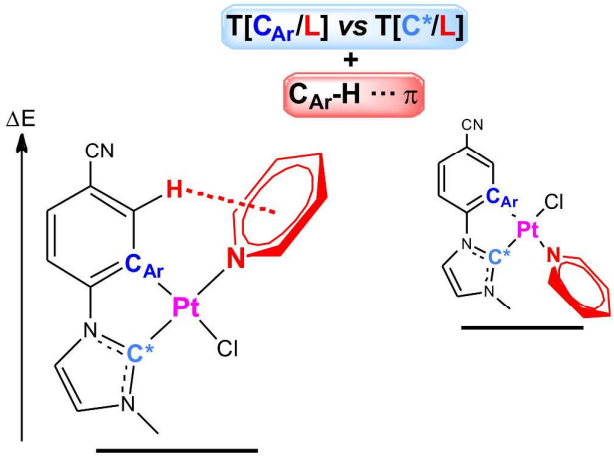
Exploring the Transphobia Effect on Heteroleptic NHC Cycloplatinated Complexes.



Synopsis

Neutral and cationic heteroleptic NHC cycloplatinated complexes $[Pt(C\hat{}C^*)LL']^{0,+}$ (L' = Cl, L= PPh_3, py, CNXyl, MMI; L= PPh_3, L' = py, CNXyl, MMI) were prepared and characterized. The more stable *trans*-(C*,L) geometry is assessed in terms of the T[C_{Ar}/L] vs T[C*/L] and the feasibility of T–shaped C_{Ar}–H··· π interactions.