

Exploring the Transphobia Effect on Heteroleptic NHC Cycloplatinated Complexes

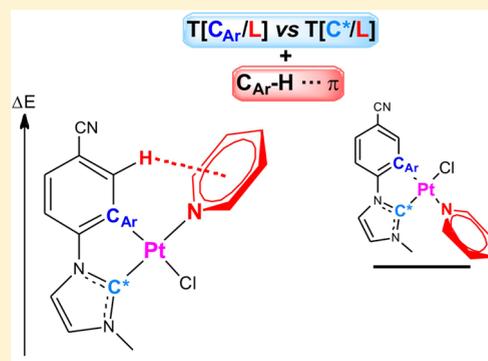
Sara Fuertes,[†] Andrés J. Chueca,[†] and Violeta Sicilia^{*,‡}

[†]Departamento de Química Inorgánica, Facultad de Ciencias, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain

[‡]Departamento de Química Inorgánica, Escuela de Ingeniería y Arquitectura de Zaragoza, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza, Campus Río Ebro, Edificio Torres Quevedo, 50018 Zaragoza, Spain

Supporting Information

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 $[\{\text{Pt}(\mu\text{-Cl})(\text{C}^*\text{C}^*)\}_2]$ (4) ($\text{HC}^*\text{C}^*\text{-}\kappa\text{C}^* = 1\text{-}(4\text{-cyanophenyl})\text{-}3\text{-methyl-}1\text{H-imidazol-}2\text{-ylidene}$) following a step-by-step protocol. The intermediate complex $[\text{PtCl}(\eta^3\text{-}2\text{-Me-C}_3\text{H}_4)(\text{HC}^*\text{C}^*\text{-}\kappa\text{C}^*)]$ (3) has also been isolated and characterized. Using 4 as precursor, several heteroleptic complexes of stoichiometry $[\text{PtCl}(\text{C}^*\text{C}^*)\text{L}]$ (L = PPh_3 (5), pyridine (py, 6), 2,6-dimethylphenyl isocyanide (CNXyl , 7), and 2-mercapto-1-methylimidazole (MMI, 8)) and $[\text{Pt}(\text{C}^*\text{C}^*)\text{LL}']\text{PF}_6$ (L = PPh_3 , L' = py (9), CNXyl (10), and MMI (11)) have been synthesized. Complexes 6–8 were obtained as a mixture of *cis*- and *trans*-($\text{C}^*\text{,L}$) isomers, while *trans*-($\text{C}^*\text{,L}$) 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– $\text{C}^*_{(\text{NHC})}$, has been compared from the $J_{\text{Pt-P}}$ values observed in the new complex $[\text{Pt}(\text{C}^*\text{C}^*)(\text{dppe})]\text{PF}_6$ ($\text{dppe} = 1, 2\text{-bis}(\text{diphenylphosphino})\text{-ethane}$, 12).



INTRODUCTION

The chemistry of platinum(II) complexes has attracted much interest in the past decade due to their phosphorescence properties and potential use as dopants in LEDs,¹ chemical sensors,² or biolabeling agents,^{2b,3} with particular consideration given to C^*N -cyclometalated derivatives.^{1b,4} The C^*C^* -cyclometalated N-heterocyclic carbenes (NHC) may surpass the high ligand field splitting capacity of the conventional C^*N -cyclometalated 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^* -cyclometalated 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 biomedicine,⁸ and luminescent materials.^{5,8d,9} In particular, platinum(II) compounds containing C^*C^* -cyclometalated NHCs ligands have received much attention in the past 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 properties¹¹ or tuning their catalytic activity and selectivity.^{10m,n,12}

In this context, as part of our previous work, we prepared and studied the photophysical properties of many heteroleptic complexes of Pt(II) with the 7,8-benzoquinolate and different monodentate auxiliary ligands.¹¹ Now, we have conducted our ongoing research to new platinum(II) complexes with C^*C^* -cyclometalated NHCs. Generic compounds, such as $[\{\text{Pt}(\mu\text{-Cl})(\text{C}^*\text{C}^*)\}_2]$, 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 chlorine-bridge cleavage or chlorine-atoms elimination. We recently reported the synthesis of $[\{\text{Pt}(\mu\text{-Cl})(\text{C}^*\text{C}^*)\}_2]$ ($\text{HC}^*\text{C}^* = 3\text{-methyl-}1\text{-}(naphthalen\text{-}2\text{-yl})\text{-}1\text{H-imidazol-}2\text{-ylidene}$).¹³ Thus, the first goal of this work, the synthesis of the generic precursor $[\{\text{Pt}(\mu\text{-Cl})(\text{C}^*\text{C}^*)\}_2]$ (4) ($\text{HC}^*\text{C}^*\text{-}\kappa\text{C}^* = 1\text{-}(4\text{-cyanophenyl})\text{-}3\text{-methyl-}1\text{H-imidazol-}2\text{-ylidene}$).

Received: July 23, 2015

ylidene) following the same strategy, was achieved. Therefore, the use of $[\{\text{Pt}(\mu\text{-Cl})(\eta^3\text{-2-Me-C}_3\text{H}_4)\}_2]$ to accomplish the cyclometalation of the NHCs through the intermediate carbene complex $[\text{PtCl}(\eta^3\text{-2-Me-C}_3\text{H}_4)(\text{HC}^*\text{C}^*\text{-}\kappa\text{C}^*)]$ (**3**) endorses the generality and viability of this step-by-step synthetic protocol for $[\{\text{Pt}(\mu\text{-Cl})(\text{C}^*\text{C}^*)\}_2]$.

Then we explored the use of **4** as a precursor for the preparation of new heteroleptic complexes such as $[\text{PtCl}(\text{C}^*\text{C}^*)\text{L}]$ ($\text{L} = \text{PPh}_3$ (**5**), py (**6**), CNXyl (**7**), and 2-mercapto-1-methylimidazole (MMI, **8**)) and $[\text{Pt}(\text{C}^*\text{C}^*)\text{LL}']^+$ ($\text{L} = \text{PPh}_3$; $\text{L}' = \text{py}$ (**9**), CNXyl (**10**), and MMI (**11**)). Some of them were obtained as a mixture of two isomers, *cis*- and *trans*-(C^*L), while others 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– $\text{C}^*(\text{NHC})$. The trans influence of σ C_{Ar} and σ C^* has been evaluated from the $J_{\text{Pt,P}}$ values observed in the new complex $[\text{Pt}(\text{C}^*\text{C}^*)(\text{dppe})]^+$ (**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 $[\{\text{Pt}(\mu\text{-Cl})(\eta^3\text{-2-Me-C}_3\text{H}_4)\}_2]$ ¹⁵ was prepared following the literature procedure.

1-(4-Cyanophenyl)-1H-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 dimethyl sulfoxide (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 h at 110 °C under an argon atmosphere the crude was cooled down to rt, washed with 100 mL of ethyl acetate, and then filtered through Celite. The solution was treated with H_2O (2 × 20 mL) and brine (2 × 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%. ¹H NMR (400 MHz, $\text{DMSO-}d_6$): $\delta = 8.46$ (dd, $^3J_{\text{H,H}} = 1.3$, $^3J_{\text{H,H}} = 0.9$, 1H, H_1), 8.09 (d, $^3J_{\text{H}_6\text{H}_7} = 8.8$, 2H, H_7), 7.99 (d, $^3J_{\text{H}_6\text{H}_7} = 8.8$, 2H, H_6), 7.98 (m, 1H, Im), 7.16 (dd, $^3J_{\text{H,H}} = 1.3$, $^3J_{\text{H,H}} = 0.9$, 1H, Im). ¹³C{¹H} NMR (101 MHz, $\text{DMSO-}d_6$): $\delta = 140.1$ (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}): $\nu = 2224$ (m, CN).

1-(4-Cyanophenyl)-3-methyl-1H-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 h, and after cooling, the white precipitate was filtered and washed with THF (5 mL) and diethyl ether (5 mL) and dried under vacuum to give **2** as a pure solid. Yield: 967.9 mg, 97%. Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{IN}_3$: C, 42.46; H, 3.24; N, 13.51. Found: C, 42.03; H, 3.33; N, 13.48. ¹H NMR (400 MHz, $\text{DMSO-}d_6$): $\delta = 9.91$ (s, br, 1H, H_1), 8.39 (dd, $^3J_{\text{H}_2\text{H}_3} = 1.9$, $^3J_{\text{H}_2\text{H}_1} = 1.8$, 1H, H_2), 8.21 (d, $^3J_{\text{H}_6\text{H}_7} = 8.8$, 2H, H_7), 8.02 (d, 2H, H_6), 8.00 (m, 1H, H_3), 3.96 (s, 3H, H_4). ¹³C{¹H} NMR plus HMBC and HSQC (101 MHz, $\text{DMSO-}d_6$): $\delta = 137.9$ (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}): $\nu = 2235$ (m, CN). MS (MALDI+): m/z 184.1 (HCAC^*H)⁺.

$[\text{PtCl}(\eta^3\text{-2-Me-C}_3\text{H}_4)(\text{HC}^*\text{C}^*\text{-}\kappa\text{C}^*)]$ (3**) ($\text{HC}^*\text{C}^* = 1\text{-}(4\text{-Cyanophenyl})\text{-3-methyl-1H-imidazol-2-ylidene}$).** 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 rt, $[\{\text{Pt}(\eta^3\text{-2-Me-C}_3\text{H}_4)(\mu\text{-Cl})\}_2]$ (779.1 mg, 1.36 mmol) was added and the mixture was allowed to

react for 3 h 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 × 15 mL) to afford **3** as a pale-yellow solid. Yield: 1.1222 g, 83%. Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{ClN}_3\text{Pt}$: C, 38.42; H, 3.43; N, 8.96. Found: C, 38.23; H, 3.35; N, 8.52. ¹H NMR (400 MHz, methylene chloride- d_2): $\delta = 7.95$ (d, $^3J_{\text{H,H}} = 8.8$, 2H, H_7), 7.74 (d, $^3J_{\text{H,H}} = 8.8$, 2H, H_6), 7.26 (d, $^3J_{\text{H}_2\text{H}_3} = 2.1$, $^4J_{\text{H,Pt}} = 13.4$, 1H, H_2), 7.15 (d, $^4J_{\text{H,Pt}} = 10.6$, 1H, H_3), 3.91 (s, 3H, Me (NHC)), 3.64 (m, 1 H_{syn} , $\eta^3\text{-2-Me-C}_3\text{H}_4$), 2.63 (m, $^2J_{\text{H,Pt}} = 28.3$, 1 H_{syn} , $\eta^3\text{-2-Me-C}_3\text{H}_4$), 2.37 (m, $^2J_{\text{H,Pt}} = 34.1$, 1 H_{anti} , $\eta^3\text{-2-Me-C}_3\text{H}_4$), 1.74 (s, $^3J_{\text{H,Pt}} = 64.7$, 3H, Me, $\eta^3\text{-2-Me-C}_3\text{H}_4$), 1.44 (m, 1 H_{anti} , $\eta^3\text{-2-Me-C}_3\text{H}_4$). ¹³C{¹H} NMR plus HMBC and HSQC (101 MHz, methylene chloride- d_2): $\delta = 177.4$ (s, C_1), 144.1 (s, C_5), 133.2 (s, 2C, C_6), 126.2 (s, 2C, C_7), 123.6 (s, $^3J_{\text{C,Pt}} = 41.3$, C_3), 120.7 (s, $^3J_{\text{C,Pt}} = 42.4$, C_2), 118.6 (s, CN), 118.4 (s, $\text{C}^{2'}$, $\eta^3\text{-2-Me-C}_3\text{H}_4$), 112.1 (s, C_8), 58.1 (s, $^1J_{\text{C,Pt}} = 77.6$, $\text{C}^{1'}$, $\eta^3\text{-2-Me-C}_3\text{H}_4$), 38.3 (s, C_4 (Me), NHC), 37.1 (s, $\text{C}^{3'}$, $\eta^3\text{-2-Me-C}_3\text{H}_4$), 23.4 (s, $^2J_{\text{C,Pt}} = 40.1$, $\text{C}^{4'}$ (Me), $\eta^3\text{-2-Me-C}_3\text{H}_4$). ¹⁹⁵Pt{¹H} NMR (85.6 MHz, methylene chloride- d_2): $\delta = -4460$. IR (ATR, cm^{-1}): $\nu = 285$ (s, Pt–Cl), 2228 (w, CN).

$[\{\text{Pt}(\mu\text{-Cl})(\text{C}^*\text{C}^*)\}_2]$ (4**).** Compound **3** (500.0 mg, 1.07 mmol) was refluxed in 2-methoxyethanol (15 mL) for 3 h, and then it was cooled down to rt. The resulting solid was filtered and washed with dichloromethane (10 mL) and diethyl ether (15 mL). Then it was treated with activated carbon in hot acetonitrile (3 × 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 $\text{C}_{22}\text{H}_{16}\text{Cl}_2\text{N}_2\text{Pt}_2$: C, 32.01; H, 1.95; N, 10.18. Found: C, 31.63; H, 2.33; N, 10.16. ¹H NMR (400 MHz, $\text{DMSO-}d_6$): $\delta = 8.72$ (s, br, $^3J_{\text{H}_7\text{Pt}} = 60$, 1H, H_7), 8.14 (d, $^3J_{\text{H}_2\text{H}_3} = 1.7$, 1H, H_2), 7.63 (dd, $^3J_{\text{H}_9\text{H}_{10}} = 8.0$, $^4J_{\text{H}_9\text{H}_7} = 1.5$, 1H, H_9), 7.57 (d, 1H, H_{10}), 7.53 (d, 1H, H_3), 4.14 (s, 3H, H_4). ¹³C{¹H} NMR plus HMBC and HSQC (101 MHz, $\text{DMSO-}d_6$): $\delta = 156.0$ (s, C_1), 149.8 (s, C_5), 137.0 (s, C_7), 129.3 (s, C_9), 127.9 (s, C_6), 125.5 (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}): $\nu = 266$ (s, Pt–Cl), 2250 (w, CN), 2215 (w, CN).

***trans*-(C^*P) $[\text{Pt}(\text{Cl})(\text{C}^*\text{C}^*)(\text{PPh}_3)]$ (**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 °C (ice/brine bath). After 1 h 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 $\text{C}_{29}\text{H}_{23}\text{ClN}_3\text{PPt}$: 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): $\delta = 7.72$ (m, 6H, Ho (PPh_3)), 7.52–7.35 (m, 10H, Hm , Hp (PPh_3) and H_2), 7.24 (dd, $^3J_{\text{H}_9\text{H}_{10}} = 8.0$, $^4J_{\text{H}_9\text{H}_7} = 1.6$, 1H, H_9), 7.05 (d, $^4J_{\text{H}_{10}\text{Pt}} = 14.2$, 1H, H_{10}), 6.99 (m, 1H, H_3), 6.88 (m, $^3J_{\text{H}_7\text{Pt}} = 64.0$, 1H, H_7), 4.29 (s, 3H, H_4). ¹³C{¹H} NMR plus HMBC and HSQC (101 MHz, methylene chloride- d_2): $\delta = 170.1$ (s, C_1), 150.5 (s, C_5), 141.0 (d, $^3J_{\text{C}_7\text{P}} = 8.7$, $^2J_{\text{C}_7\text{Pt}} = 57.0$, C_7), 135.5 (d, $^2J_{\text{C}_3\text{P}} = 11.3$, $^3J_{\text{C}_3\text{Pt}} = 20.7$, 6C, C_6 (PPh_3)), 130.7 (s, 3C, C_p (PPh_3)), 130.1 (d, $^1J_{\text{C}_9\text{P}} = 53.6$, 3C, C_i (PPh_3)), 128.5 (s, C_6), 128.1 (d, $^3J_{\text{C}_6\text{P}} = 10.6$, 6C, C_m (PPh_3)), 127.8 (s, C_9), 124.3 (d, $^4J_{\text{C}_3\text{P}} = 6.1$, $^4J_{\text{C}_3\text{Pt}} = 26.0$, C_3), 118.8 (s, CN), 113.9 (s, $^4J_{\text{C}_2\text{Pt}} = 40.1$, C_2), 111.0 (s, $^3J_{\text{C}_{10}\text{Pt}} = 32.5$, C_{10}), 108.0 (s, C_8), 38.6 (s, C_4). ³¹P{¹H} NMR (162 MHz, methylene chloride- d_2): $\delta = 28.6$ (s, $^1J_{\text{P,Pt}} = 2868.0$). ¹⁹⁵Pt{¹H} NMR (85.6 MHz, methylene chloride- d_2): $\delta = -4227.0$ (d). IR (ATR, cm^{-1}): $\nu = 279$ (m, Pt–Cl), 2218 (w, CN). MS (MALDI+): m/z 639.1 $[\text{Pt}(\text{C}^*\text{C}^*)(\text{PPh}_3)]^+$.

***cis/trans*-(C^*N) $[\text{Pt}(\text{Cl})(\text{C}^*\text{C}^*)(\text{py})]$ (**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 °C (ice/brine bath). After 2 h of 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 $\text{C}_{16}\text{H}_{13}\text{ClN}_4\text{Pt}$: 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): $\delta = 8.81$ (dd, $^3J_{\text{H,H}} = 6.4$, $^4J_{\text{H,H}} = 1.6$, $^3J_{\text{H,Pt}} = 28.0$, 2H, Ho (py)), 7.97 (tt, $^3J_{\text{H,H}} = 7.7$, $^4J_{\text{H,H}} = 1.6$, 1H, Hp (py)), 7.56 (m, 2H, Hm (py)), 7.38 (dd, $^3J_{\text{H}_9\text{H}_{10}} = 8.0$, $^4J_{\text{H}_9\text{H}_7} = 1.7$, 1H, H_9), 7.33 (d, $^3J_{\text{H}_2\text{H}_3} =$

2.1, 1H, H₂), 7.06 (d, ⁴J_{H10,Pt} = 16.8, 1H, H₁₀), 6.94 (d, ⁴J_{H3,Pt} = 9.1, 1H, H₃), 6.69 (d, ³J_{H7,Pt} = 61.8, 1H, H₇), 4.24 (s, 3H, H₄). 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, Ho (py)), 8.41 (d, ³J_{H7,H9} = 1.6, ³J_{H7,Pt} = 55.1, 1H, H₇), 7.91 (tt, ³J_{H,H} = 7.8, ⁴J_{H,H} = 1.6, 1H, Hp (py)), 3.06 (s, 3H, H₄). ¹³C{¹H} NMR plus HMBC and HSQC for 6-t (101 MHz, methylene chloride-d₂): δ = 152.7 (s, C₁), 152.0 (s, ²J_{C,Pt} = 12.2, 2C, C_o (py)), 150.3 (s, C₅), 138.5 (s, C_p (py)), 135.2 (s, ²J_{C7,Pt} = 37.8, C₇), 131.3 (s, C₆), 128.3 (s, C₉), 126.1 (s, ³J_{C,Pt} = 31.2, 2C, C_m (py)), 123.1 (s, ³J_{C3,Pt} = 38.4, C₃), 119.4 (s, CN), 114.4 (s, ³J_{C2,Pt} = 47.2, C₂), 110.7 (s, ³J_{C10,Pt} = 36.1, C₁₀), 108.1 (s, C₈), 37.6 (s, C₄). ¹⁹⁵Pt{¹H} NMR (85.6 MHz, methylene chloride-d₂): 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[∧]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 °C (ice/brine bath). After 2.5 h of stirring, the solvent was removed under reduced pressure. The residue was treated with MeOH (0 °C, 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 C₂₀H₁₇ClN₄Pt: C, 44.16; H, 3.15; N, 10.30. Found: C, 44.09; H, 3.02; N, 9.92. ¹H NMR data for 7-t (400 MHz, methylene chloride-d₂): δ = 7.97 (d, ⁴J_{H9,H7} = 1.7, ³J_{H7,Pt} = 77.3, 1H, H₇), 7.47 (dd, ³J_{H9,H10} = 8.0, 1H, H₉), 7.36 (d, ³J_{H2,H3} = 2.0, ⁴J_{H2,Pt} = 5.3, 1H, H₂), 7.33 (t, ³J_{H9,Hm} = 7.7, 1H, H_p (Xyl)), 7.21 (d, 2H, H_m (Xyl)), 7.14 (d, ⁴J_{H10,Pt} = 15.4, 1H, H₁₀), 6.97 (d, ⁴J_{H3,Pt} = 7.9, 1H, H₃), 4.28 (s, 3H, H₄), 2.51 (s, 6H, Me (Xyl)). ¹H NMR data for 7-c: δ = 8.45 (d, ⁴J_{H7,H10} = 1.7, ³J_{H,Pt} = 47.2, 1H, H₇), 7.43 (dd, ³J_{H9,H10} = 8.0, 1H, H₉), 7.09 (d, 1H, H₁₀), 7.00 (d, ⁴J_{H3,Pt} = 12.3, 1H, H₃), 3.92 (s, 3H, H₄), 2.45 (s, 6H, Me (Xyl)). ¹³C{¹H} NMR plus HMBC and HSQC for 7-t (101 MHz, methylene chloride-d₂): δ = 167.7 (s, C₁), 149.5 (s, C₅), 140.8 (s, ²J_{C7,Pt} = 72.4, C₇), 135.8 (s, 2C, C_o (Xyl)), 129.7 (s, C_p (Xyl)), 128.7 (s, C₉), 128.1 (s, 2C, C_m (Xyl)), 123.9 (s, ³J_{C3,Pt} = 30.9, C₃), 119.0 (s, CN), 114.8 (s, C₂), 111.6 (s, ³J_{C10,Pt} = 32.9, C₁₀), 109.5 (s, C₈), 37.3 (s, C₄), 18.7 (s, 2C, Me (Xyl)). ¹⁹⁵Pt{¹H} NMR (85.6 MHz, methylene chloride-d₂): δ = -4042.7 (t, ²J_{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[∧]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 °C (ice/brine bath). After 1 h of stirring, the mixture was filtered through Celite, and the filtrate was evaporated to dryness. The residue was treated with diethyl ether (5 mL), filtered, and washed with diethyl ether (3 mL). The resulting orange solid was recrystallized from CH₂Cl₂/Et₂O to give 8-t (86%)/8-c (14%). Yield: 78.6 mg, 51%. Anal. Calcd for C₁₃H₁₄ClN₃PS: 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. ¹H NMR data for 8-t (400 MHz, methylene chloride-d₂): δ = 12.72 (s, 1H, NH, MMI), 8.27 (s, ³J_{H7,Pt} = 65.9, 1H, H₇), 7.41 (d, ³J_{H9,H10} = 7.6, 1H, H₉), 7.30 (d, ³J_{H2,H3} = 2.1, 1H, H₂), 7.04 (d, ⁴J_{H10,Pt} = 14.3, 1H, H₁₀), 6.92 (d, ⁴J_{H3,Pt} = 8.9, 1H, H₃), 6.87 (m, 1H, H₄, MMI), 6.84 (m, 1H, H₅, MMI), 4.19 (s, 3H, H₄), 3.75 (s, 3H, NMe, MMI). ¹H NMR data for 8-c: δ = 8.47 (d, ⁴J_{H7,H9} = 1.1, ³J_{H7,Pt} = 57.5, 1H, H₇), 4.04 (s, 3H, H₄), 3.68 (s, 3H, NMe, MMI). ¹³C{¹H} NMR plus HMBC and HSQC (101 MHz, methylene chloride-d₂) for 8-t: δ = 159.3 (s, C₁), 156.1 (s, C=S, MMI), 149.9 (s, C₅), 135.4 (s, ²J_{C7,Pt} = 37.1, C₇), 126.7 (s, C₆), 128.4 (s, C₉), 123.6 (s, ³J_{C3,Pt} = 37.3, C₃), 120.4 (s, C₅, MMI), 119.8 (s, CN), 115.1 (s, C₄, MMI), 113.6 (s, ³J_{C2,Pt} = 45.2, C₂), 110.7 (s, ³J_{C10,Pt} = 35.8, C₁₀), 107.5 (s, C₈), 37.9 (s, C₄), 34.5 (s, NMe, MMI). ¹⁹⁵Pt{¹H} NMR (85.6 MHz, methylene chloride-d₂): 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)]⁺.

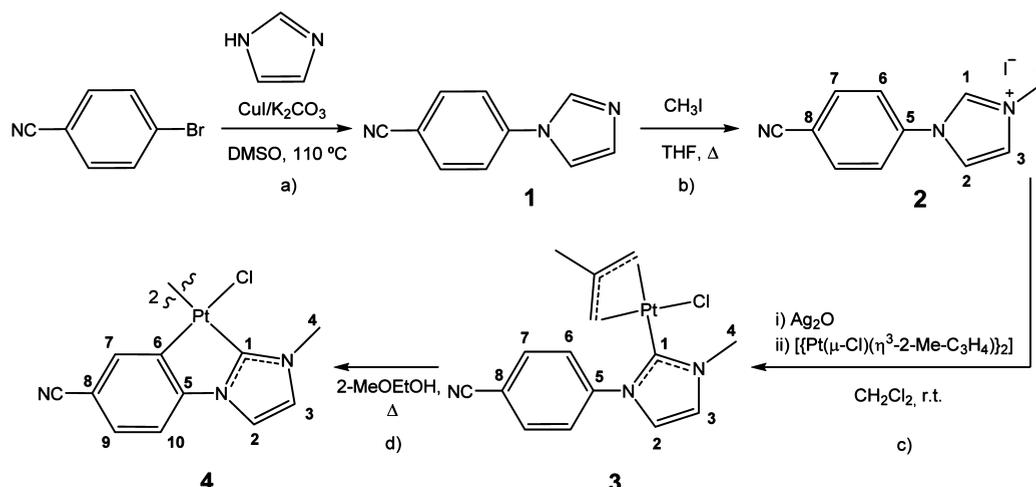
trans-(C,P) [Pt(C[∧]C*)(py)(PPh₃)]PF₆ (9)*. Pyridine (15.8 μL, 0.20 mmol) and KPF₆ (36.9 mg, 0.20 mmol) were added to a pale yellow suspension of 5 (132.6 mg, 0.20 mmol) in acetone (30 mL). After 1 h of stirring at room temperature, the solvent was evaporated to dryness and the residue treated with dichloromethane (35 mL) and filtered

through Celite. Then the solvent was removed under reduced pressure, and the residue was treated with diethyl ether (10 mL), filtered, and washed with diethyl ether (5 mL). The solid was recrystallized from acetone (0 °C)/Et₂O to give 9 as a pale yellow solid. Yield: 88.3 mg, 49%. Anal. Calcd for C₃₄H₂₈F₆N₄P₂Pt: C, 47.28; H, 3.27; N, 6.49. Found: C, 46.86; H, 3.05; N, 6.47. ¹H NMR (400 MHz, methylene chloride-d₂): δ = 8.40 (dd, ³J_{H,H} = 6.2, ⁴J_{H,H} = 1.1, ³J_{H,Pt} = 23.0, 2H, Ho (py)), 7.69 (tt, ³J_{H,H} = 7.7, ⁴J_{H,H} = 1.4, 1H, Hp (py)), 7.59 (m, 6H, Ho (PPh₃)), 7.53–7.45 (m, 4H, H₂, Hp (PPh₃)), 7.36 (m, 6H, Hm (PPh₃)), 7.31 (dd, ³J_{H9,H10} = 8.1, ⁴J_{H9,H7} = 1.7, 1H, H₉), 7.19 (m, 3H, H₁₀, Hm (py)), 7.03 (m, 1H, H₃), 6.85 (m, ³J_{H7,Pt} = 58.8, 1H, H₇), 2.87 (s, 3H, H₄). ¹³C{¹H} NMR plus HMBC and HSQC (101 MHz, methylene chloride-d₂): δ = 171.2 (d, ²J_{C,P} = 136.2, C₁), 151.9 (s, ²J_{C,Pt} = 10.0, 2C, C_o (py)), 150.8 (s, C₅), 142.9 (d, ³J_{C7,P} = 9.6, ²J_{C7,Pt} = 55.4, C₇), 139.3 (s, C_p (py)), 134.7 (d, ²J_{C,P} = 11.7, 6C, C_o (PPh₃)), 131.7 (s, 3C, C_p (PPh₃)), 129.9 (s, C₉), 129.0 (d, ³J_{C,P} = 10.0, 6C, C_m (PPh₃)), 127.5 (s, 2C, C_p (py)), 124.6 (d, ⁴J_{C3,P} = 4.8, ³J_{C3,Pt} = 31.3, C₃), 118.4 (s, CN), 115.1 (s, br, ³J_{C2,Pt} = 40.2, C₂), 111.7 (s, ³J_{C10,Pt} = 29.2, C₁₀), 108.3 (s, C₈), 35.3 (s, C₄). ³¹P{¹H} NMR (162 MHz, methylene chloride-d₂): δ = 28.2 (s, ¹J_{P,Pt} = 2881.6). ¹⁹⁵Pt{¹H} NMR (85.6 MHz, methylene chloride-d₂): δ = -4274.6 (d). Λ_M (5 × 10⁻⁴ M acetone solution) = 76.87 Ω⁻¹ cm² mol⁻¹. IR (ATR, cm⁻¹): ν = 2226 (w, CN). MS (MALDI+): m/z 639.1 [Pt(C[∧]C*)(PPh₃)]⁺.

trans-(C,P) [Pt(C[∧]C*)(CNXyl)(PPh₃)]PF₆ (10)*. Method a. 2,6-Dimethylphenyl isocyanide (CNXyl) (20.6 mg, 0.15 mmol) and KPF₆ (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 diethyl ether (5 mL), filtered, and washed with diethyl ether (3 mL) to give 10 as a pale yellow solid. Yield: 124.9 mg, 89%.

Method b. PPh₃ (34 mg, 0.129 mmol) and KPF₆ (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, treated with diethyl ether (5 mL), filtered, and washed with diethyl ether (3 mL) to give 10 as a pale yellow solid. Yield: 91.1 mg, 77%. Anal. Calcd for C₃₈H₃₂F₆N₄P₂Pt: C, 49.84; H, 3.52; N, 6.12. Found: C, 49.59; H, 3.34; N, 6.05. ¹H NMR (400 MHz, methylene chloride-d₂): δ = 7.67 (m, 6H, Ho (PPh₃)), 7.56 (d, ³J_{H2,H3} = 2.1, 1H, H₂), 7.46–7.35 (m, 10H, Hm, Hp (PPh₃)) and H₉), 7.30 (d, ³J_{H10,H9} = 8.8, 1H, H₁₀), 7.28 (d, ³J_{H2,H3} = 2.1, 1H, H₃), 7.26 (t, ³J_{H,H} = 7.7, 1H, Hp (Xyl)), 7.08 (d, ³J_{H,H} = 7.7, 2H, Hm (Xyl)), 7.02 (s, br, ³J_{H7,Pt} = 50.7, 1H, H₇), 3.91 (s, 3H, H₄), 2.12 (s, 6H, Me (Xyl)). ¹³C{¹H} NMR plus HMBC and HSQC (101 MHz, methylene chloride-d₂): δ = 169.3 (d, ²J_{C,P} = 127.7, C₁), 151.6 (s, C₅), 143.5 (d, ³J_{C7,P} = 9.2, ²J_{C7,Pt} = 51.0, C₇), 138.6 (s, C₆), 134.8 (s, 2C, C_o (Xyl)), 134.5 (d, ²J_{C,P} = 11.7, 6C, C_o (PPh₃)), 132.4 (s, 3C, C_p (PPh₃)), 131.4 (s, C₉), 130.8 (s, C_p (Xyl)), 129.5 (d, ³J_{C,P} = 11.0, 6C, C_m (PPh₃)), 128.7 (d, ¹J_{C,P} = 57.2, 3C, C_i (PPh₃)), 128.6 (s, 2C, C_m (Xyl)), 125.3 (s, br, C₃), 118.7 (s, CN), 116.1 (s, C₂), 112.4 (s, ³J_{C10,Pt} = 25.8, C₁₀), 109.7 (s, C₈), 39.2 (s, C₄), 18.2 (s, Me (Xyl)). ³¹P{¹H} NMR (162 MHz, methylene chloride-d₂): δ = 19.3 (s, ¹J_{P,Pt} = 2585.2). ¹⁹⁵Pt{¹H} NMR (85.6 MHz, methylene chloride-d₂): δ = -4697 (dt, ²J_{Pt,N} = 61.7 Hz). Λ_M (5 × 10⁻⁴ M acetone solution) = 70.63 Ω⁻¹ cm² mol⁻¹. IR (ATR, cm⁻¹): ν = 2231 (m, CN), 2187 (s, C≡NXyl). MS (MALDI+): m/z 770.1 [Pt(C[∧]C*) (CNXyl) (PPh₃)]⁺.

trans-(C,P) [Pt(C[∧]C*)(PPh₃)(MMI)]PF₆ (11)*. 2-Mercapto-1-methylimidazole (MMI) (22.0 mg, 0.19 mmol) and KPF₆ (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 × 10 mL) and filtered through Celite. Then the solvent was removed under reduced pressure, and the residue was treated with diethyl ether (10 mL), filtered, and washed

Scheme 1. Synthesis of Compounds 1–4^a

^aNumerical scheme for NMR purposes.

with 5 mL more. The orange solid was washed with dichloromethane (3 × 4 mL) to give **11** as a pale yellow solid. Yield: 59.2 mg, 36%. Anal. Calcd for C₃₃H₂₉F₆N₅P₂PtS: 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. ¹H NMR (400 MHz, acetone-*d*₆) δ = 11.70 (s, 1H, NH (MMI)), 8.06 (d, ³J_{H₂,H₃} = 1.7, 1H, H₂), 7.77 (m, 6H, H_o (PPh₃)), 7.61–7.54 (m, 4H, H₁₀ and H_p (PPh₃)), 7.49 (m, 7H, H₃ and H_m (PPh₃)), 7.43 (dd, ³J_{H₉,H₁₀} = 8.2, ⁴J_{H₉,H₇} = 1.6, 1H, H₉), 7.18 (m, 1H, H₅, MMI), 7.05 (m, 1H, H₄, MMI), 6.97 (m, ³J_{H₇,Pt} = 59.4, 1H, H₇), 4.08 (s, 3H, H₄), 3.32 (s, 3H, NMe, MMI). ¹³C NMR (101 MHz, acetone-*d*₆) δ = 170.7 (d, ²J_{C₁,P} = 144.4, C₁), 153.7 (s, C=S (MMI)), 151.8 (s, C₅), 142.6 (d, ³J_{C₇,Pt} = 56.1, ³J_{C₇,P} = 8.9, C₇), 136.1 (d, ²J_{C₆,P} = 11.2, 6C, C₆ (PPh₃)), 132.3 (d, ⁴J_{C₆,P} = 11.2, 3C, C_p (PPh₃)), 130.5 (d, ¹J_{C₆,P} = 54.38, 3C, C_i (PPh₃)), 130.4 (s, C₉), 129.2 (d, ³J_{C₉,P} = 10.7, 6C, C_m (PPh₃)), 126.7 (d, ⁴J_{C₉,P} = 5.1, C₃), 123.2 (s, C₅, MMI), 119.2 (s, C₅, MMI), 116.7 (s, C₄, MMI), 116.5 (s, br, C₂), 113.1 (s, ³J_{C₁₀,Pt} = 29.2, C₁₀), 109.2 (s, C₄), 38.3 (s, C₄), 34.7 (s, NMe, MMI). ³¹P{¹H} NMR (162 MHz, acetone-*d*₆): δ = 26.1 (s, ¹J_{P,Pt} = 2786.3). ¹⁹⁵Pt{¹H} NMR (85.6 MHz, acetone-*d*₆): δ = -4533.7 (d). Λ_M (5 × 10⁻⁴ M acetone solution) = 84.26 Ω⁻¹ cm² mol⁻¹. IR (ATR, cm⁻¹): ν = 2224 (m, CN). MS (MALDI+): *m/z* 753.2 [Pt(C^{*}C*)(MMI) (PPh₃)]⁺, 639.1 [Pt(C^{*}C*)(PPh₃)]⁺.

[Pt(C^{*}C*)(dppe)]PF₆ (**12**). 1,2-Bis(diphenylphosphino)ethane (dppe) (118.3 mg, 0.30 mmol) and KPF₆ (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 rt 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 Et₂O (20 mL) was added to the residue to obtain **12** as a white solid. Yield: 245.3 mg, 90%. Anal. Calcd for C₃₇H₃₂F₆N₃P₃Pt: C, 48.27; H, 3.50; N, 4.56. Found: C, 47.93; H, 3.35; N, 4.49. ¹H NMR (400 MHz, methylene chloride-*d*₂): δ = [7.96–7.80] (m, 8H, H_o (dppe)), [7.69–7.54] (m, 13H, H₂ and H_m, H_p (dppe)), 7.43 (dd, ³J_{H₉,H₁₀} = 8.4, ⁴J_{H₉,H₇} = 1.7, 1H, H₉), 7.34 (m, ³J_{H₇,Pt} = 50.6, 1H, H₇), 7.31 (dd, ³J_{H₁₀,P} = 8.4, ⁵J_{H₁₀,P} = 2.3, 1H, H₁₀), 7.05 (m, ⁴J_{H₃,Pt} = 9.1, 1H, H₃), 3.04 (s, 3H, H₄), 2.37 (m, 4H, CH₂ (dppe)). ¹³C{¹H} NMR plus HMBC and HSQC (101 MHz, methylene chloride-*d*₂): δ = 172.7 (dd, ²J_{C₁,P_{trans}} = 126.9; ²J_{C₁,P_{cis}} = 8.8, C₁), 151.0 (s, C₅), 143.9 (dd, ²J_{C₆,P_{trans}} = 103.5, ²J_{C₁,P_{cis}} = 6.0, C₆), 142.5 (dd, ³J_{C₇,P_{trans}} = 9.9; ³J_{C₇,P_{cis}} = 2.8, ²J_{C₇,Pt} = 54, C₇), 134.1 (d, ²J_{C₆,P} = 12.1, 4C, C₆ (dppe)), 133.6 (d, ²J_{C₉,P} = 12.3, 4C, C₉ (dppe)), 132.8 (s, 4C, C_p (dppe)), 131.1 (s, C₉), 130.0 (d, ³J_{C₉,P} = 11.0, 4C, C_m (dppe)), 129.7 (d, ³J_{C₉,P} = 11.0, 4C, C_m (dppe)), 124.9 (d, ⁴J_{C₃,Pt} = 4.0, ³J_{C₃,Pt} = 29.0, C₃), 118.5 (s, CN), 116.4 (d, ⁴J_{C₂,P} = 2.0, ³J_{C₃,Pt} = 33.0, C₂), 112.04 (s, ³J_{C₁₀,Pt} = 21.7, C₁₀), 110.7 (m, C₈), 38.9 (s, C₄), 31.7 (dd, ¹J_{C₆,P} = 37.6, ²J_{C₆,P} = 10.0, CH₂ (dppe)), 30.6 (dd, ¹J_{C₆,P} = 39.8, ²J_{C₆,P} = 12.4, CH₂ (dppe)). ³¹P{¹H} NMR (162 MHz, methylene chloride-*d*₂): δ = 50.2 (d, ²J_{P,Pt} =

7.0, ¹J_{P,Pt} = 2673.8, trans C^{*}), 43.1 (d, ¹J_{P,Pt} = 2014.6, trans C_p). ¹⁹⁵Pt{¹H} NMR (85.6 MHz, methylene chloride-*d*₂): δ = -4996 (dd). Λ_M (5 × 10⁻⁴ M acetone solution) = 69.01 Ω⁻¹ cm² mol⁻¹. IR (ATR, cm⁻¹): ν = 2223 (m, CN). MS (MALDI+): *m/z* 775.2 [Pt(C^{*}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-1H-imidazol-2-ylidene). The synthesis of the N-heterocyclic carbene (NHC) 1-(4-cyanophenyl)-1H-imidazol (**1**) has been previously reported.^{16a,b} However, we prepared it by a slightly modified method (Scheme 1, path a, Experimental Section) to avoid the use of coligands (pyrrolidinylmethylimidazole) and the purification step by column chromatography. 4-Bromobenzonitrile was coupled with imidazole in DMSO at 110 °C using copper(I) iodide and potassium carbonate in the presence of 4 Å molecular sieves. After workup, **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-1H-imidazolium iodide (**2**) (Scheme 1, path b, and Experimental Section).

Compound **2** was reacted with silver(I) oxide for 3 h and subsequently with [Pt(μ-Cl)(η³-2-Me-C₃H₄)₂] (η³-2-Me-C₃H₄ = η³-2-methylallyl) to yield the neutral complex [PtCl(η³-2-Me-C₃H₄)(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 η³-2-Me-C₃H₄^{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 imidazolium moiety (see Figure S1 in the SI) indicate that the imidazolium salt has been successfully anchored to the Pt center through the C1 of the N-heterocyclic carbene (HC^{*}C^{*}-

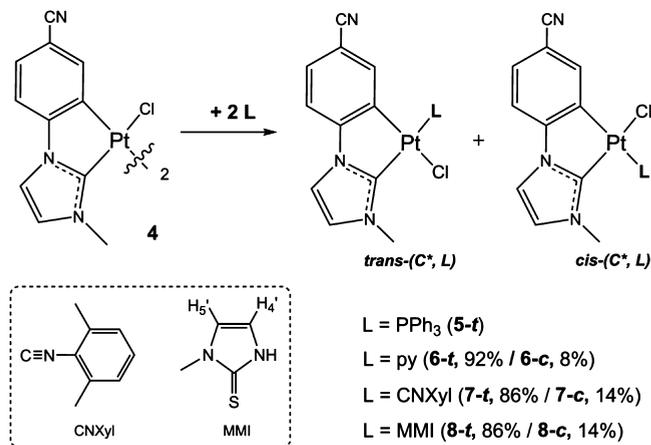
κC^*). This statement was confirmed by the similarities of the $^{195}\text{Pt}\{^1\text{H}\}$ resonance ($\delta = -4460$ ppm) and the ^1H and $^{13}\text{C}\{^1\text{H}\}$ ones corresponding to the imidazolyl moiety and the methyl allyl group ($\eta^3\text{-2-Me-C}_3\text{H}_4$) with those of $[\text{PtCl}(\eta^3\text{-C}_4\text{H}_7)(\text{HC}^*\text{C}^*\text{-}\kappa\text{C}^*)]$ ($\text{HC}^*\text{C}^* = 3\text{-methyl-1-(naphthalen-2-yl)-1H-imidazol-2-ylidene}$).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-1H-imidazol-2-ylidene ($\text{HC}^*\text{C}^*\text{-}\kappa\text{C}^*$) through the C6 (see Experimental Section and Figure 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 ($\delta = 156.0$ ppm) is in good agreement with the literature value- $s_{10a-c,e,h,13,17}$ for related cyclometalated platinum(II) compounds.

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

Reactivity of 4. Synthesis and Characterization of $[\text{PtCl}(\text{C}^*\text{C}^*)\text{L}]$ (L = PPh₃ (5**), py (**6-t**/**6-c**), CNXyl (**7-t**/**7-c**), MMI (**8-t**/**8-c**)).** The dinuclear complex $[\{\text{Pt}(\mu\text{-Cl})(\text{C}^*\text{C}^*)\}_2]$ (**4**) reacts with several neutral P, N, C, and S donor ligands, such as PPh₃, py, CNXyl, and MMI in a 1:2 molar ratio at low temperature (-8 °C) (Scheme 2 and Experimental Section) to

Scheme 2. Synthetic Pathway to Compounds 5–8



give the mononuclear complexes $[\text{PtCl}(\text{C}^*\text{C}^*)\text{L}]$ (L = PPh₃ (**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 *trans*-(C*,L) being the only isomer observed, while in all other cases (**6–8**), 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**).

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 stoichiometry 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 ^1H 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 center are the H7 and 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.

Within the *trans* isomer complexes, in particular, when L = PPh₃ (**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,c,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 from 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}

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 also confirmed that these ratios do not change over the time.

As expected, the $^{195}\text{Pt}\{^1\text{H}\}$ 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 $^{31}\text{P}\{^1\text{H}\}$ 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*).

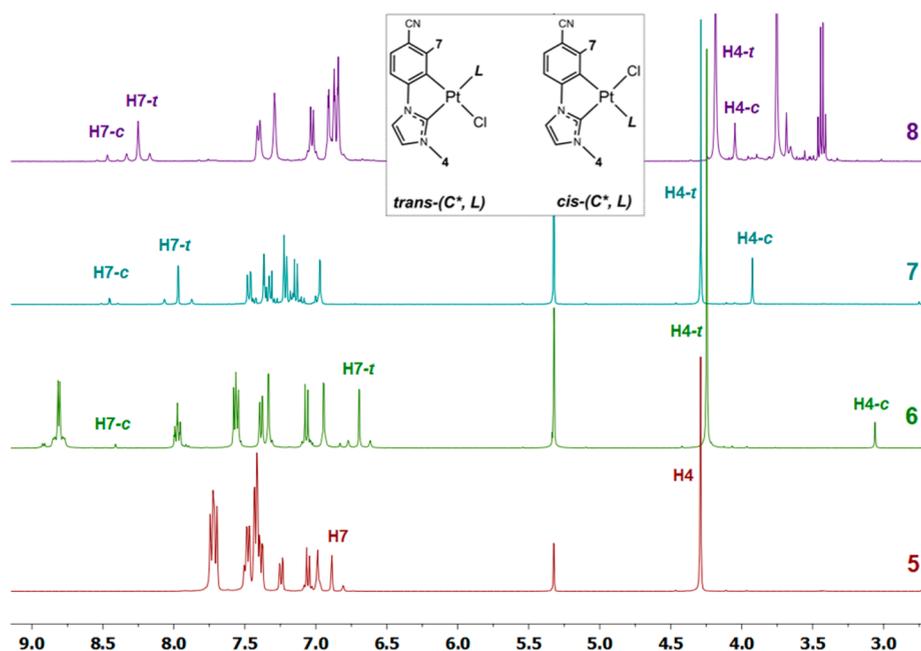
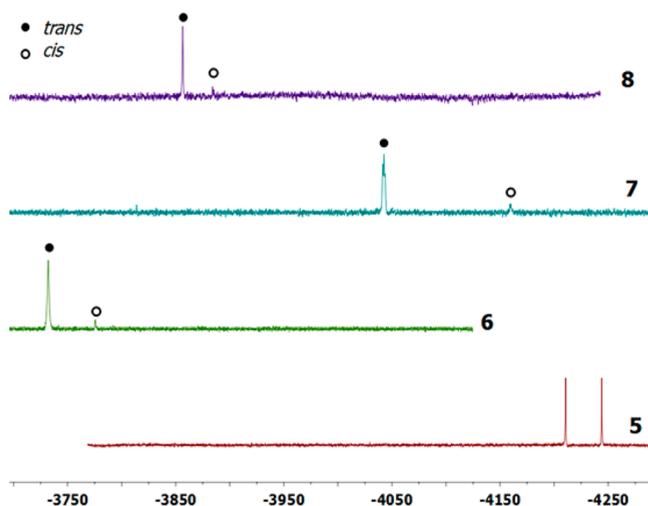
The molecular structure of **5** (see Figure 3), obtained by X-ray diffraction analysis of a single crystal of it, confirmed the complex to be the isomer *trans*-(C*,P)[PtCl(C* C*)(PPh₃)]. Data analysis is discussed below.

Synthesis and Characterization of the new Cationic “Pt(C* C*)” Complexes: *trans*-(C*,P)-[Pt(C* C*)(PPh₃)L’]PF₆ (L’ = py (9**), CNXyl (**10**), MMI (**11**)) and [Pt(C* C*)(dppe)]PF₆ (**12**).** With the aim of preparing new heteroleptic compounds with the N-heterocyclic carbene $\{\text{Pt}(\text{C}^*\text{C}^*)\text{LL}'\}$, 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 equimolar amounts of KPF₆ and L’ to a solution of **5** in acetone rendered 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 PPh₃ remains coordinated *trans* to the C*. Interestingly, compound **10** can also be prepared by adding

Table 1. Significant NMR Data for Compound Characterization^a

compd	δH ($J_{\text{Pt,H}}$)		δC ($J_{\text{Pt,C}}$)			δP ($J_{\text{Pt,P}}$)	δPt
	H7	H4	C1	C7	C3		
5 ^b	6.88 (64.0)	4.29	170.1	141.0 (57.0)	124.3 (26.0)	28.6 (2868.0)	-4227.0
6- <i>t</i>	6.69 (61.8)	4.24	152.7	135.2 (37.8)	123.1 (38.4)		-3731.9
6- <i>c</i>	8.41 (55.1)	3.06					-3775.4
7- <i>t</i>	7.97 (77.3)	4.28	167.7	140.8 (72.4)	123.9 (30.9)		-4042.7
7- <i>c</i>	8.45 (47.2)	3.92					-4160.2
8- <i>t</i>	8.27 (65.9)	4.19	159.3	135.4 (37.1)	123.6 (37.3)		-3856.5
8- <i>c</i>	8.47 (57.5)	4.04					-3884.2
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)	(<i>t</i> -C*): 50.2 (2673.8) (<i>c</i> -C*): 43.1 (2014.6)	-4996.0

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

Figure 1. ¹H NMR spectra of 5–8 in CD₂Cl₂.Figure 2. ¹⁹⁵Pt{¹H} spectra of 5–8 in CD₂Cl₂.

KPF₆ and PPh₃ 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, which is located *trans* to C* in 7-*t*, migrates to the *cis* position by the coordination of the PPh₃. When a suspension of 4 in acetone was treated with KPF₆ 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 ³¹P{¹H} NMR spectra of 9–11 show a singlet flanked by platinum satellites. The δP and ¹⁹⁵Pt–³¹P coupling constants are quite similar to those found in complex 5, indicating a *trans*-(C*,PPh₃) arrangement in these complexes. In the ³¹P 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

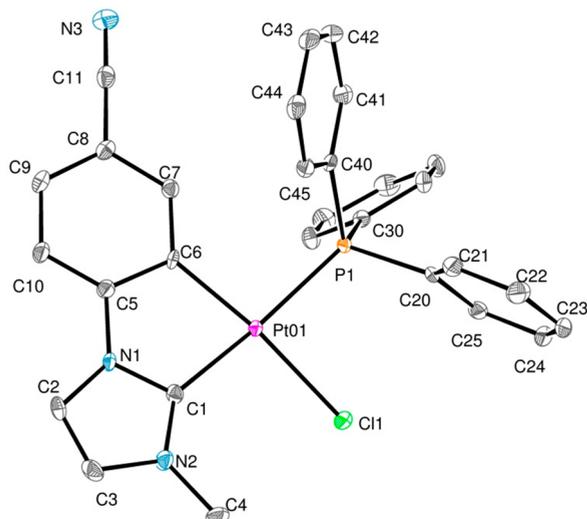
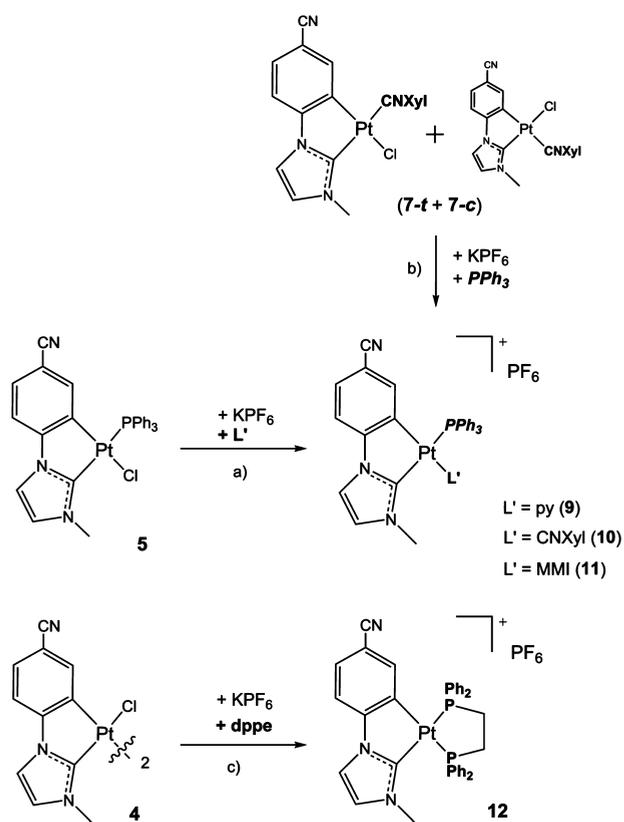


Figure 3. Molecular structure of complex **5·MeOH**. Thermal ellipsoids are drawn at the 50% probability level. Solvent molecules and hydrogen atoms have been omitted for clarity.

Scheme 3. Synthetic 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 from 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 $^{195}\text{Pt}\{^1\text{H}\}$ 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

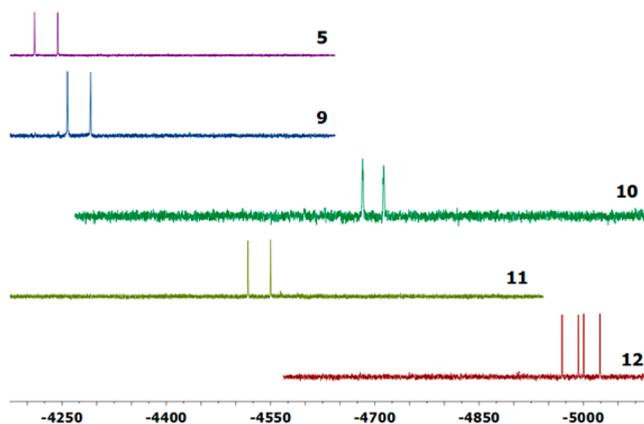


Figure 4. $^{195}\text{Pt}\{^1\text{H}\}$ spectra of **5** and **9**–**12** in CD_2Cl_2 .

of doublets for **12** due to the coupling with the ^{31}P nuclei; these chemical shifts are ranging from -4274 to -4996 ppm.

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 and S8 for complexes **9** and **11**).

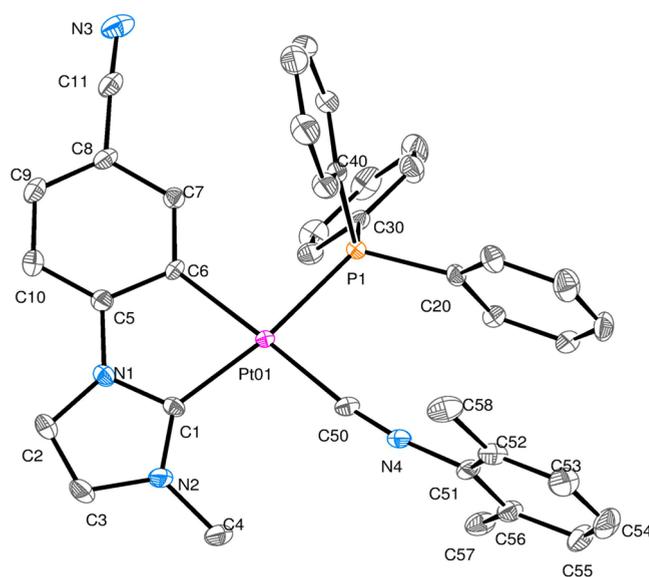


Figure 5. Molecular structure of the complex **10·0.5 OEt₂**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, PF_6^- , and solvent molecules have been omitted for clarity.

Crystal Structure 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 center lies in a distorted square planar coordination environment as a consequence of the small bite angle of the NHC-cyclometalated (C^*C^*) ligand [$79.83(11)$ – $78.54(13)^\circ$]. 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 carbene- $^{10a-h,13}$ 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.

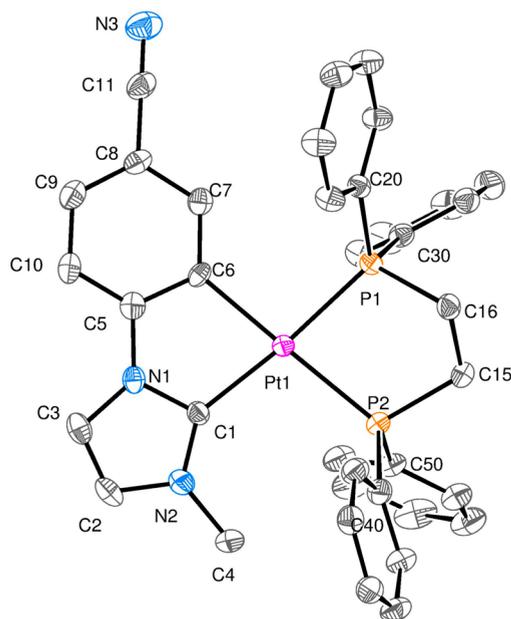


Figure 6. Molecular structure of complex **12**·CH₂Cl₂. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, PF₆⁻, and solvent molecules have been omitted for clarity.

The Pt–Cl,^{14b,c,22} Pt–N,²³ Pt–C,^{11c,f} 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 [from 2.015(3) (Cl, **5**) to 2.080(4) Å (P, **12**)], while 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[∧]C*)-L'L]^{0,+} heteroleptic complexes studied by X-ray diffraction. Thus far, all crystal structures of NHC-cycloplatinated compounds have been reported with diketonate derivative-^{10a–h}

The chelating dppe ligand adopts the gauche conformation with a P–CH₂–CH₂–P torsion angle of 46.7°. 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 (83.15°) are similar to those of related compounds.^{21c,26}

The cyclometalated 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)° (**5**), 6.42(9)° (**9**), 12.35(13)° (**10**), 5.79(8)° (**11**), and 5.81(14)° (**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)°

(**5**), 10.9(8)° (**9**), 8.83(8)° (**10**), 10.39(3)° (**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)° (N4, C12–C16, **9**), 82.48(12)° (N4, C50–C56, **10**), and 89.18(4)° (N4, N5, C50–C53, **11**).

Further inspection of the molecule packing within the crystal structures revealed the presence of weak intra- and intermolecular 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 the phenyl ring of the PPh₃ ligand, showing moderately short distances (C–H··· π ; C7···C_{ph} (PPh₃) = 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 PPh₃ 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)° (**9**), 5.42(16)° (**10**), 9.47(9)° (**11**)]. Additionally, compound **9** crystallizes with one water molecule, which is holding a hydrogen bond with the CN group of the cyclometalated 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 (**9**) and 3.32 Å (**12**)), see Figures S6 and S9).

DISCUSSION

As shown above, 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 PPh₃ (**5**). If L is py, CNXyl, and MMI, the bridge-splitting reaction gave mixtures of *cis*/*trans* isomers (**6**–**8**).

In an attempt to explain this behavior we 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 d⁸ 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 = PPh₃, tht, C \equiv NR (R = ^tBu, 2,6-dimethylphenyl)), and [Pt(C[∧]P)(C \equiv CPh)L] (C[∧]P = CH₂C₆H₄P(*o*-tolyl)₂- κ C,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,b} However, the steric requirements of the ligands involved can also play an important role in determining the geometries of these

Table 2. Selected Bond Lengths (Angstroms) and Angles (degrees) for **5** and **9**–**12**

	5 -MeOH (X = Cl(1))	9 -H ₂ O (X = N(4))	10 -0.5 Et ₂ O (X = C(50))	11 (X = S(1))	12 ·CH ₂ Cl 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)

complexes. In this sense, complex $[\text{Pt}(\text{C}^{\wedge}\text{P})(\text{C}\equiv\text{CPh})\text{PPh}_3]$, exhibits the *trans*-($\text{C},\text{C}\equiv\text{CPh}$) 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 $\text{P}(o\text{-tolyl})_2$ and PPh_3 groups.^{14a}

Therefore, we tried to explain the preferred geometry for complexes $[\text{PtCl}(\text{C}^{\wedge}\text{C}^*)\text{L}]$ (5–8) and $[\text{Pt}(\text{C}^{\wedge}\text{C}^*)(\text{PPh}_3)\text{L}]^+$ (9–11) on the basis of the transphobia effect (T). With this purpose we studied the relative trans influences of the two σ Pt–C bonds present in the $\text{Pt}(\text{C}^{\wedge}\text{C}^*)$ unit, both expected to have a great trans influence, and those of the auxiliary ligands (Cl, PPh_3 , py, CNXyl, MMI), comparing the $^1J_{\text{Pt,P}}$, $^2J_{\text{Pt,C}}$, and $^3J_{\text{Pt,H}}$ values affected by the ligands located at their trans positions.

The $^1J_{\text{Pt,P}}$ values observed for complexes *trans*-(C^*,P) $[\text{PtCl}(\text{C}^{\wedge}\text{C}^*)(\text{PPh}_3)]$ (5) and $[\text{Pt}(\text{C}^{\wedge}\text{C}^*)(\text{PPh}_3)\text{L}']\text{PF}_6$ ($\text{L}' = \text{py}$ (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 $[\text{Pt}(\text{CH}_2\text{-C}_6\text{H}_4\text{-P}(o\text{-tolyl})_2)(\text{C}\equiv\text{CPh})_2]$ ($\text{Q} = \text{Li}^+$ (2746 Hz), NBu_4^+ (2603 Hz)) with the Pt–P bond trans to a Pt–Cacetylide one.^{14a} In addition, the $J_{\text{Pt,P}}$ corresponding to the P trans to C^* (2673.8 Hz) in $[\text{Pt}(\text{C}^{\wedge}\text{C}^*)(\text{dppe})]\text{PF}_6$ (12) was found to be similar to that observed in complexes with phosphine ligands located in the trans position, such as $[\text{Pt}(\text{C}^{\wedge}\text{P})(\text{dppe})]^+$ [$\text{C}^{\wedge}\text{P} = \{(R)\text{-1-[1-diphenylphosphino]ethyl}]\text{naphthyl-C,P}$; $J_{\text{Pt,P}(\text{transP})} = 2770$ Hz,^{21c} or $[\text{Pt}(\text{dppe})(\text{PAn-H})]^+$ [$\text{PAn} = 9\text{-diphenylphosphinoanthracene}$; $J_{\text{Pt,P}(\text{transP})} = 2796$],^{26d} indicating that the C^* displays a great trans influence, similar to alkynyl or phosphine ligands.

Then we focused again on complex $[\text{Pt}(\text{C}^{\wedge}\text{C}^*)(\text{dppe})]\text{PF}_6$ (12), and we observed the $^1J_{\text{Pt,P}}$ values 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 $^3J_{\text{Pt,Ho}(\text{py})}$ 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)- $[\text{Pt}(\text{C}^{\wedge}\text{C}^*)(\text{PPh}_3)\text{L}]^{0,+}$ ($\text{L} = \text{Cl}$ (5), py (9), CNXyl (10), MMI (11)) or *cis*-(C^*,L)- $[\text{PtCl}(\text{C}^{\wedge}\text{C}^*)\text{L}]$ ($\text{L} = \text{py}$ (6-*c*), CNXyl (7-*c*), MMI (8-*c*)) (Table 1). On the basis of the observed $^3J_{\text{Pt,H7}}$ (64.0 (5), 58.8 (9), 50.7 (10), and 59.4 Hz (11)) and $^2J_{\text{Pt,C7}}$ (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 \approx 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 $^3J_{\text{Pt,C3}}$ (26.0 Hz (5), 38.4 (6-*t*), 30.9 (7-*t*), 37.3 (8-*t*)) in complexes *trans*-(C^*,L)- $[\text{PtCl}(\text{C}^{\wedge}\text{C}^*)\text{L}]$ ($\text{L} = \text{PPh}_3$ (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, X-ray data analysis of 5 and 9–12 (Table 2) indicates 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 $\text{PPh}_3/\text{dppe} > \text{CNXyl} > \text{py} \approx \text{MMI} > \text{Cl}$.

Taking into account all these assumptions $\text{T}[\text{C}_{\text{Ar}}/\text{L}] > \text{T}[\text{C}^*/\text{L}]$ and $\text{T}[\text{C}_{\text{Ar}}/\text{PPh}_3] > \text{T}[\text{C}_{\text{Ar}}/\text{CNXyl}] > \text{T}[\text{C}_{\text{Ar}}/\text{py}] \approx \text{T}[\text{C}_{\text{Ar}}/\text{MMI}] > \text{T}[\text{C}_{\text{Ar}}/\text{Cl}]$. Therefore, the $\text{T}[\text{C}_{\text{Ar}}/\text{PPh}_3]$ should be the greatest one, and the experimental results seem

to indicate that the difference between $\text{T}[\text{C}_{\text{Ar}}/\text{PPh}_3]$ and $\text{T}[\text{C}^*/\text{PPh}_3]$ is big enough to direct clean formation of *trans*-(C^*,PPh_3) complexes 5 and 9–11.

However, the difference between $\text{T}[\text{C}_{\text{Ar}}/\text{L}]$ and $\text{T}[\text{C}^*/\text{L}]$ ($\text{L} = \text{py}$, CNXyl, MMI, Cl) is, in each case, not big enough to avoid the formation of mixtures of isomers. On the basis of the order of $\text{T}[\text{C}_{\text{Ar}}/\text{L}]$ named above, the cleavage of the chlorine-bridge system in $[\{\text{Pt}(\mu\text{-Cl})(\text{C}^{\wedge}\text{C}^*)\}_2]$ (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 $\text{C}^{\wedge}\text{C}^*$ 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 $\cdots\pi$ (py) interactions to be involved in it. C–H $\cdots\pi$ interactions have been known to play a key role in the stereoselectivity of coordination compounds among other fields in chemistry.²⁸ It has been widely reported that intramolecular C–H $\cdots\pi$ hydrogen bonds can induce the formation of single linkage isomers.²⁹ In both isomers of 6, a C–H $\cdots\pi$ interaction could be possible: $\text{Csp}^3\text{-H4}(\text{Me})\cdots\pi(\text{py})$ in 6-*c* and a T-shaped $\text{Csp}^2\text{-H7}(\text{Ar})\cdots\pi(\text{py})$ 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} Thus, we would expect 6-*t* to be more stable than 6-*c*. DFT calculations for models of 6-*c*/-*t* in a solution of CH_2Cl_2 were carried out (see Figure 7). In effect, isomer 6-*t* with the C–H7 pointing at the

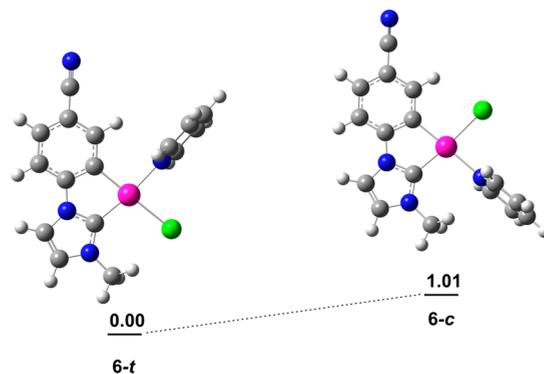


Figure 7. DFT-computed energies for the 6-*c*/-*t* isomers (ΔE , kcal mol⁻¹).

pyridine ring is 1.01 kcal mol⁻¹ more stable than 6-*c*. This subtle difference in energy added to the bigger $\text{T}[\text{C}_{\text{Ar}}/\text{py}]$ vs $\text{T}[\text{C}^*/\text{py}]$ results to be reasonably determining for the high stereoselectivity of isomers in 6.

In complexes 5 and 9–11, their X-ray structures and NMR data also show the presence of $\text{Csp}^2\text{-H7}(\text{Ar})\cdots\pi$ interactions, which will contribute together with the difference of $\text{T}[\text{C}_{\text{Ar}}/\text{L}]$ vs $\text{T}[\text{C}^*/\text{L}]$ 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 cyclometalated to the Pt center, which endorse the generality and viability of this step-by-step synthetic pathway for cyclometalated NHCs complexes, $[\{\text{Pt}(\mu\text{-Cl})(\text{C}^{\wedge}\text{C}^*)\}_2]$. 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 was $T[C_{Ar}/L] > T[C^*/L]$ and $T[C_{Ar}/PPh_3] > T[C_{Ar}/CNXyl] > T[C_{Ar}/py] \approx T[C_{Ar}/MMI] > T[C_{Ar}/Cl]$. 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[⋯]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[⋯]π (Ph) interactions present in the *trans*-(C^{*},PPh₃)-[Pt(C[∧]C^{*})(PPh₃)L] complexes (L = Cl (**5**), py (**9**), CNXyl (**10**), MMI (**11**)) would account for the stereoselective formation of this isomer in each case, as experimentally observed.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01655.

General procedures and materials, computational, and crystallographic details; 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 (PDF)
Crystallographic data (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sicilia@unizar.es.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Spanish Ministerio de Economía y Competitividad (MINECO)/FEDER (Project CTQ2012-35251 led by Dr. Babil Menjón) and the Departamento de Industria e Innovación del Gobierno de Aragón and Fondo Social Europeo (Grupo Consolidado E21: Química Inorgánica y de los Compuestos Organometálicos led by Dr. José M. Casas). The authors thank the Centro de Supercomputación de Galicia (CESGA) for generous allocation of computational resources and Dr. Antonio Martín for his valuable help with some of the X-ray structure determinations.

■ REFERENCES

- (1) (a) Murphy, L.; Williams, J. A. G. *Top. Organomet. Chem.* **2010**, *28*, 75–111. (b) Williams, J. A. G. *Top. Curr. Chem.* **2007**, *281*, 205–268. (c) Zhou, G.; Wang, Q.; Wang, X.; Ho, C.-L.; Wong, W.-Y.; Ma, D.; Wang, L.; Lin, Z. *J. Mater. Chem.* **2010**, *20*, 7472–7484.
- (2) (a) Zhao, Q.; Li, F.; Huang, C. *Chem. Soc. Rev.* **2010**, *39*, 3007–3030. (b) Wong, K. M.-C.; Chan, M. M.-Y.; Yam, V. W.-W. *Adv. Mater.* **2014**, *26*, 5558–5568. (c) Taylor, S. D.; Howard, W.; Kaval, N.; Hart, R.; Krause, J. A.; Connick, W. B. *Chem. Commun.* **2010**, *46*, 1070–1072.
- (3) (a) Wang, P.; Leung, C. H.; Ma, D. L.; Sun, R. W. Y.; Yan, S. C.; Chen, Q. S.; Che, C. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 2554–2558.
- (b) Wang, P.; Leung, C. H.; Ma, D. L.; Lu, W.; Che, C. M. *Chem. - Asian J.* **2010**, *5*, 2271–2280. (c) Koo, C. K.; Wong, K. L.; Man, C. W. Y.; Lam, Y. W.; So, K. Y.; Tam, H. L.; Tsao, S. W.; Cheah, K. W.; Lau, K. C.; Yang, Y. Y.; Chen, J. C.; Lam, M. H. W. *Inorg. Chem.* **2009**, *48*, 872–878.
- (4) (a) Williams, J. A. G.; Develay, S.; Rochester, D. L.; Murphy, L. *Coord. Chem. Rev.* **2008**, *252*, 2596–2611. (b) Williams, J. A. G. In *Topics in Organometallic Chemistry*; Bozec, H., Guerschais, V., Eds.; Springer: New York, 2009; Vol. 28.
- (5) Sajoto, T.; Djurovich, P. I.; Tamayo, A.; Yousufuddin, M.; Bau, R.; Thompson, M. E.; Holmes, R. J.; Forrest, S. R. *Inorg. Chem.* **2005**, *44*, 7992–8003.
- (6) (a) Bugaut, X.; Glorius, F. *Chem. Soc. Rev.* **2012**, *41*, 3511–3522. (b) Fortman, G. C.; Nolan, S. P. *Chem. Soc. Rev.* **2011**, *40*, 5151–5169. (c) Liddle, S. T.; Edworthy, I. S.; Arnold, P. L. *Chem. Soc. Rev.* **2007**, *36*, 1732–1744. (d) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309. (e) Köhl, O. *Chem. Soc. Rev.* **2007**, *36*, 592–607. (f) Wang, F. J.; Liu, L. J.; Wang, W. F.; Li, S. K.; Shi, M. *Coord. Chem. Rev.* **2012**, *256*, 804–853. (g) Nelson, D. J. *Eur. J. Inorg. Chem.* **2015**, *2015*, 2012–2027. (h) Levin, E.; Ivry, E.; Diesendruck, C. E.; Lemcoff, N. G. *Chem. Rev.* **2015**, *115*, 4607–4692. (i) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612–3676.
- (7) (a) Lin, I. J. B.; Vasam, C. S. *J. Organomet. Chem.* **2005**, *690*, 3498–3512. (b) Huang, R. T. W.; Wang, W. C.; Yang, R. Y.; Lu, J. T.; Lin, I. J. B. *Dalton Trans.* **2009**, 7121–7131. (c) Lee, C. K.; Vasam, C. S.; Huang, T. W.; Wang, H. M. J.; Yang, R. Y.; Lee, C. S.; Lin, I. J. B. *Organometallics* **2006**, *25*, 3768–3775.
- (8) (a) Melaiye, A.; Sun, Z. H.; Hindi, K.; Milsted, A.; Ely, D.; Reneker, D. H.; Tessier, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **2005**, *127*, 2285–2291. (b) Hindi, K. M.; Panzner, M. J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J. *Chem. Rev.* **2009**, *109*, 3859–3884. (c) Raubenheimer, H. G.; Cronje, S. *Chem. Soc. Rev.* **2008**, *37*, 1998–2011. (d) Mercks, L.; Albrecht, M. *Chem. Soc. Rev.* **2010**, *39*, 1903–1912.
- (9) (a) Yam, V. W. W.; Cheng, E. C. C. In *Photochemistry and Photophysics of Coordination Compounds II*; Balzani, V., Campagna, S., Eds.; Springer-Verlag: Berlin, 2007; Vol. 281, pp 269–309. (b) Hock, S. J.; Schaper, L.-A.; Herrmann, W. A.; Kuhn, F. E. *Chem. Soc. Rev.* **2013**, *42*, 5073–5089. (c) Son, S. U.; Park, K. H.; Lee, Y. S.; Kim, B. Y.; Choi, C. H.; Lah, M. S.; Jang, Y. H.; Jang, D. J.; Chung, Y. K. *Inorg. Chem.* **2004**, *43*, 6896–6898. (d) Unger, Y.; Zeller, A.; Ahrens, S.; Strassner, T. *Chem. Commun.* **2008**, 3263–3265. (e) Holmes, R. J.; Forrest, S. R.; Sajoto, T.; Tamayo, A.; Djurovich, P. I.; Thompson, M. E.; Brooks, J.; Tung, Y. J.; D’Andrade, B. W.; Weaver, M. S.; Kwong, R. C.; Brown, J. J. *Appl. Phys. Lett.* **2005**, *87*, 243507. (f) Chang, C. F.; Cheng, Y. M.; Chi, Y.; Chiu, Y. C.; Lin, C. C.; Lee, G. H.; Chou, P. T.; Chen, C. C.; Chang, C. H.; Wu, C. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 4542–4545. (g) Hsieh, C. H.; Wu, F. I.; Fan, C. H.; Huang, M. J.; Lu, K. Y.; Chou, P. Y.; Yang, Y. H. O.; Wu, S. H.; Chen, I. C.; Chou, S. H.; Wong, K. T.; Cheng, C. H. *Chem. - Eur. J.* **2011**, *17*, 9180–9187. (h) Sasabe, H.; Takamatsu, J.; Motoyama, T.; Watanabe, S.; Wagenblast, G.; Langer, N.; Molt, O.; Fuchs, E.; Lennartz, C.; Kido, J. *Adv. Mater.* **2010**, *22*, 5003. (i) Lu, K. Y.; Chou, H. H.; Hsieh, C. H.; Yang, Y. H. O.; Tsai, H. R.; Tsai, H. Y.; Hsu, L. C.; Chen, C. Y.; Chen, I. C.; Cheng, C. H. *Adv. Mater.* **2011**, *23*, 4933–4937. (j) Visbal, R.; Ospino, I.; Lopez-de-Luzuriaga, J. M.; Laguna, A.; Gimeno, M. C. *J. Am. Chem. Soc.* **2013**, *135*, 4712–4715. (k) Haneder, S.; Da Como, E.; Feldmann, J.; Lupton, J. M.; Lennartz, C.; Erk, P.; Fuchs, E.; Molt, O.; Munster, I.; Schildknecht, C.; Wagenblast, G. *Adv. Mater.* **2008**, *20*, 3325–3330.
- (10) (a) Tronnier, A.; Nischan, N.; Metz, S.; Wagenblast, G.; Münster, I.; Strassner, T. *Eur. J. Inorg. Chem.* **2014**, *2014*, 256–264. (b) Tronnier, A.; Pöthig, A.; Herdtweck, E.; Strassner, T. *Organometallics* **2014**, *33*, 898–908. (c) Tronnier, A.; Metz, S.; Wagenblast, G.; Münster, I.; Strassner, T. *Dalton Trans.* **2014**, *43*, 3297–3305. (d) Tronnier, A.; Nischan, N.; Strassner, T. *J. Organomet. Chem.* **2013**, *730*, 37–43. (e) Tronnier, A.; Risler, A.; Langer, N.; Wagenblast, G.; Münster, I.; Strassner, T. *Organometallics* **2012**, *31*, 7447–7452. (f) Hudson, Z. M.; Sun, C.; Helander, M. G.; Chang, Y. L.; Lu, Z. H.;

- Wang, S. N. *J. Am. Chem. Soc.* **2012**, *134*, 13930–13933. (g) Hudson, Z. M.; Blight, B. A.; Wang, S. N. *Org. Lett.* **2012**, *14*, 1700–1703. (h) Unger, Y.; Meyer, D.; Molt, O.; Schildknecht, C.; Münster, I.; Wagenblast, G.; Strassner, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 10214–10216. (i) Tronnier, A.; Schleicher, D.; Strassner, T. *J. Organomet. Chem.* **2015**, *775*, 155–163. (j) Tronnier, A.; Pöthig, A.; Metz, S.; Wagenblast, G.; Münster, I.; Strassner, T. *Inorg. Chem.* **2014**, *53*, 6346–6356. (k) Tronnier, A.; Heinemeyer, U.; Metz, S.; Wagenblast, G.; Muenster, I.; Strassner, T. *J. Mater. Chem. C* **2015**, *3*, 1680–1693. (l) Ko, S.-B.; Park, H.-J.; Gong, S.; Wang, X. N.; Lu, Z.-H.; Wang, S. N. *Dalton Trans.* **2015**, *44*, 8433–8443. (m) Zhang, Y. X.; Jullien, H.; Brissy, D.; Retailleau, P.; Voituriez, A.; Marinetti, A. *ChemCatChem* **2013**, *5*, 2051–2057. (n) Jullien, H.; Brissy, D.; Sylvain, R.; Retailleau, P.; Naubron, J.-V.; Gladiali, S.; Marinetti, A. *Adv. Synth. Catal.* **2011**, *353*, 1109–1124. (o) Brissy, D.; Skander, M.; Jullien, H.; Retailleau, P.; Marinetti, A. *Org. Lett.* **2009**, *11*, 2137–2139.
- (11) (a) Fernández, S.; Fornies, J.; Gil, B.; Gómez, J.; Lalinde, E. *Dalton Trans.* **2003**, 822–830. (b) Fornies, J.; Fuertes, S.; Lopez, J. A.; Martin, A.; Sicilia, V. *Inorg. Chem.* **2008**, *47*, 7166–7176. (c) Diez, A.; Fornies, J.; Fuertes, S.; Lalinde, E.; Larraz, C.; Lopez, J. A.; Martin, A.; Moreno, M. T.; Sicilia, V. *Organometallics* **2009**, *28*, 1705–1718. (d) Fornies, J.; Fuertes, S.; Martin, A.; Sicilia, V.; Gil, B.; Lalinde, E. *Dalton Trans.* **2009**, 2224–2234. (e) Diez, A.; Fornies, J.; Larraz, C.; Lalinde, E.; López, J. A.; Martin, A.; Moreno, M. T.; Sicilia, V. *Inorg. Chem.* **2010**, *49*, 3239–3259. (f) Fornies, J.; Sicilia, V.; Borja, P.; Casas, J. M.; Diez, A.; Lalinde, E.; Larraz, C.; Martin, A.; Moreno, M. T. *Chem. - Asian J.* **2012**, *7*, 2813–2823.
- (12) Palacios, L.; Di Giuseppe, A.; Castarlenas, R.; Lahoz, F. J.; Perez-Torrente, J. J.; Oro, L. A. *Dalton Trans.* **2015**, *44*, 5777–5789 and references therein..
- (13) Fuertes, S.; Garcia, H.; Peralvarez, M.; Hertog, W.; Carreras, J.; Sicilia, V. *Chem. - Eur. J.* **2015**, *21*, 1620–1631.
- (14) (a) Casas, J. M.; Fornies, J.; Fuertes, S.; Martin, A.; Sicilia, V. *Organometallics* **2007**, *26*, 1674–1685. (b) Sicilia, V.; Fuertes, S.; Martin, A.; Palacios, A. *Organometallics* **2013**, *32*, 4092–4102. (c) Fornies, J.; Sicilia, V.; Larraz, C.; Camerano, J. A.; Martin, A.; Casas, J. M.; Tsipis, A. C. *Organometallics* **2010**, *29*, 1396–1405. (d) Slater, J. W.; Lydon, D. P.; Alcock, N. W.; Rourke, J. P. *Organometallics* **2001**, *20*, 4418–4423. (e) Vicente, J.; Abad, J. A.; Martinez-Viviente, E.; Jones, P. G. *Organometallics* **2002**, *21*, 4454–4467.
- (15) Mabbott, D. J.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 294–299.
- (16) (a) Huang, Y. Z.; Miao, H.; Zhang, Q. H.; Chen, C.; Xu, J. *Catal. Lett.* **2008**, *122*, 344–348. (b) Zhu, L. B.; Cheng, L.; Zhang, Y. X.; Xie, R. G.; You, J. S. *J. Org. Chem.* **2007**, *72*, 2737–2743. (c) Wang, H. F.; Li, Y. M.; Sun, F. F.; Feng, Y.; Jin, K.; Wang, X. N. *J. Org. Chem.* **2008**, *73*, 8639–8642.
- (17) Bernhammer, J. C.; Huynh, H. V. *Organometallics* **2014**, *33*, 172–180.
- (18) (a) Edwards, G. L.; Black, D. S. C.; Deacon, G. B.; Wakelin, L. P. G. *Can. J. Chem.* **2005**, *83*, 980–989. (b) Newman, C. P.; Casey-Green, K.; Clarkson, G. J.; Cave, G. W. V.; Errington, W.; Rourke, J. P. *Dalton Trans.* **2007**, 3170–3182. (c) Perez, S.; Lopez, C.; Caubet, A.; Solans, X.; Font-Bardia, M. *J. Organomet. Chem.* **2004**, *689*, 3184–3196.
- (19) Zucca, A.; Maidich, L.; Carta, V.; Petretto, G. L.; Stoccoro, S.; Agostina Cinellu, M.; Pilo, M. I.; Clarkson, G. J. *Eur. J. Inorg. Chem.* **2014**, *2014*, 2278–2287.
- (20) (a) Maidich, L.; Zuri, G.; Stoccoro, S.; Cinellu, M. A.; Zucca, A. *Dalton Trans.* **2014**, 43, 14806–14815. (b) Minghetti, G.; Zucca, A.; Stoccoro, S.; Cinellu, M. A.; Manassero, M.; Sansoni, M. *J. Organomet. Chem.* **1994**, *481*, 195–204.
- (21) (a) Haghghi, M. G.; Rashidi, M.; Nabavizadeh, S. M.; Jamali, S.; Puddephatt, R. J. *Dalton Trans.* **2010**, 39, 11396–11402. (b) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229–266. (c) Jia, Y.-X.; Li, B.-B.; Li, Y.; Pullarkat, S. A.; Xu, K.; Hirao, H.; Leung, P.-H. *Organometallics* **2014**, *33*, 6053–6058.
- (22) (a) Meijer, M. D.; Kleij, A. W.; Williams, B. S.; Ellis, D.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2002**, *21*, 264–271. (b) Zucca, A.; Cinellu, M. A.; Minghetti, G.; Stoccoro, S.; Manassero, M. *Eur. J. Inorg. Chem.* **2004**, *2004*, 4484–4490. (c) Zucca, A.; Petretto, G. L.; Stoccoro, S.; Cinellu, M. A.; Manassero, M.; Manassero, C.; Minghetti, G. *Organometallics* **2009**, *28*, 2150–2159. (d) Martin, R.; Crespo, M.; Font-Bardia, M.; Calvet, T. *Organometallics* **2009**, *28*, 587–597.
- (23) (a) Rao, Y.-L.; Wang, S. N. *Inorg. Chem.* **2009**, *48*, 7698–7713. (b) Harris, C. F.; Vezzu, D. A. K.; Bartolotti, L.; Boyle, P. D.; Huo, S. Q. *Inorg. Chem.* **2013**, *52*, 11711–11722. (c) Karakostas, N.; Mavridis, I. M.; Seintis, K.; Fakis, M.; Koini, E. N.; Petsalakis, I. D.; Pistolis, G. *Chem. Commun.* **2014**, *50*, 1362–1365. (d) Jude, H.; Krause Bauer, J. A.; Connick, W. B. *Inorg. Chem.* **2004**, *43*, 725–733.
- (24) (a) Fornies, J.; Sicilia, V.; Casas, J. M.; Martin, A.; Lopez, J. A.; Larraz, C.; Borja, P.; Ovejero, C. *Dalton Trans.* **2011**, *40*, 2898–2912. (b) Jacquot-Rousseau, S.; Khatyr, A.; Schmitt, G.; Knorr, M.; Kubicki, M. M.; Blacque, O. *Inorg. Chem. Commun.* **2005**, *8*, 610–613. (c) Hudson, Z. M.; Zhao, S.-B.; Wang, R.-Y.; Wang, S. N. *Chem. - Eur. J.* **2009**, *15*, 6131–6137. (d) Chuchuryukin, A. V.; Chase, P. A.; Mills, A. M.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G. *Inorg. Chem.* **2006**, *45*, 2045–2054.
- (25) (a) Crespo, M.; Anderson, C. M.; Kfoury, N.; Font-Bardia, M.; Calvet, T. *Organometallics* **2012**, *31*, 4401–4404. (b) Alcarazo, M.; Radkowski, K.; Goddard, R.; Furstner, A. *Chem. Commun.* **2011**, *47*, 776–778. (c) Anderson, C.; Crespo, M.; Rochon, F. D. *J. Organomet. Chem.* **2001**, *631*, 164–174. (d) Rodríguez, J.; Zafrilla, J.; Albert, J.; Crespo, M.; Granell, J.; Calvet, T.; Font-Bardia, M. *J. Organomet. Chem.* **2009**, *694*, 2467–2475.
- (26) (a) DePriest, J.; Zheng, G. Y.; Woods, C.; Rillema, D. P.; Mikirova, N. A.; Zandler, M. E. *Inorg. Chim. Acta* **1997**, *264*, 287–296. (b) Haghghi, M. G.; Nabavizadeh, S. M.; Rashidi, M.; Kubicki, M. *Dalton Trans.* **2013**, *42*, 13369–13380. (c) Saha, R.; Abdul Qaium, M.; Debnath, D.; Younus, M.; Chawdhury, N.; Sultana, N.; Kociok-Köhne, G.; Ooi, L.; Raithby, P. R.; Kijima, M. *Dalton Trans.* **2005**, 2760–2765. (d) Hu, J.; Lin, R.; Yip, J. H. K.; Wong, K.-Y.; Ma, D.-L.; Vittal, J. J. *Organometallics* **2007**, *26*, 6533–6543.
- (27) Nardelli, M. *J. Appl. Crystallogr.* **1995**, *28*, 659–659.
- (28) (a) Nishio, M.; Umezawa, Y.; Honda, K.; Tsuboyama, S.; Suezawa, H. *CrystEngComm* **2009**, *11*, 1757–1788. (b) Saigo, K.; Kobayashi, Y. *Chem. Rec.* **2007**, *7*, 47–56. (c) Nishio, M.; Umezawa, Y. *Topics in Stereochemistry* **2006**, *25*, 255–302.
- (29) (a) Yamanari, K.; Nozaki, T.; Fuyuhiro, A.; Kushi, Y.; Kaizaki, S. *J. Chem. Soc., Dalton Trans.* **1996**, 2851–2856. (b) Yamanari, K.; Nozaki, T.; Fuyuhiro, A.; Kaizaki, S. *Chem. Lett.* **1996**, 35–36. (c) Nakamura, M.; Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3377–3378. (d) Onaka, S.; Furuta, H.; Takagi, S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 87–88. (e) Chowdhury, S. K.; Joshi, V. S.; Samuel, A. G.; Puranik, V. G.; Tavale, S. S.; Sarkar, A. *Organometallics* **1994**, *13*, 4092–4096.
- (30) Tsuzuki, S.; Honda, K.; Uchamaru, T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2002**, *124*, 104–112.

NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on October 8, 2015, with errors in Table 1. The corrected version was reposted on October 8, 2015.