A Cyclometalated N-Heterocyclic Carbene: The Wings of the First Pt₂(II,II) Butterfly Oxidized by CHI₃.

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Dedicated to Professor Ernesto Carmona on the occasion of his 70th birthday

Abstract: The X-ray study on a single crystal of the butterfly-like complex $[\{\text{Pt}(\text{C}^*\text{C})(\mu\text{-pz})\}_2]$ (**1**), containing a cyclometalated N-heterocyclic carbene ligand as wings ($\text{HC}^*\text{C}^* = 1$ -(4-(ethoxycarbonyl)phenyl)-3-methyl-1H-imidazol-2-ylidene), showed three molecules in the asymmetric unit with intermetallic separations (Å) of 3.2294(4) (**1A**), 3.2834(4) (**1B**), 3.1208(6) (**1C**). From the reaction of **1** with excess of CHI₃ in the air and the sunlight, complex $[\{\text{Pt}(\text{C}^*\text{C})(\mu\text{-pz})\}_2]$ (**2**) ($d_{\text{Pt-Pt}} = 2.6079(2)$ Å) was obtained as the major product, while $[\text{IPt}(\text{C}^*\text{C})(\mu\text{-pz})_2\text{Pt}(\text{C}^*\text{C})\text{CHI}_2]$ (**3**) ($d_{\text{Pt-Pt}} = 2.6324(3)$ Å) was under argon atmosphere in the dark. Experimental and theoretical investigations showed that an easily accessible radical-like mechanism operates under thermal conditions, with dioxygen acting as an efficient radical (R·) scavenger. The oxidation of a platinum “butterfly” by CHI₃ to give metal-metal bonded Pt₂(III,III) compounds is described now for the first time.

Introduction

The oxidative addition (OA) reaction is a fundamental process in organometallic chemistry with significant implications in many important catalytic reactions.^[1] The use of unsaturated dinuclear metal complexes can lead to reaction pathways and products unable from mononuclear ones because of the cooperative effects between the two adjacent metals.^[2] The mechanisms of OA of a range of halocarbons (RX) to d⁸ rhodium and iridium dinuclear bis-pyrazolate complexes have been proved to proceed through a bimetallic S_N2 pathway yielding metal-metal bonded M₂(II,II) compounds.^[3] Other times it follows a radical-like mechanism^[4] or a monometallic S_N2 pathways, in the latter resulting in the mixed valence M(I)-M(III) compounds.^[5] The mechanism of these reactions depends on many factors, such as the metal, the ligands or the nature of the added molecule,^[6] and sometimes requires visible or UV-light especially for chloroalkanes.^[7] In the case of pyrazolate-bridged dinuclear Pt(II) complexes, the chemistry has been focused on butterfly-like complexes such as $[\{\text{Pt}(\text{N}^*\text{N})(\mu\text{-Rpz})\}_2]$ (N^{*}N = diimines or pyridylpyrazolate),^[8] $[\{\text{Pt}(\text{C}^*\text{N})(\mu\text{-Rpz})\}_2]$ (C^{*}N: C,N-cyclometalated ligand)^[9] and $[\{\text{Pt}(\text{C}^*\text{C})(\mu\text{-Rpz})\}_2]$ ^[10] due to their

phosphorescent behavior. Many studies addressed the control of the bulkiness of the pyrazolate bridge (the butterfly body) and the bulk and electronic properties of the C^{*}N (the butterfly wings), as the way to control the Pt...Pt distance and then, the nature of the emissive state (³IL/³MLCT or ³MMLCT) and the color of the emission (from greenish-blue to orangish-red).^[9] To our knowledge [2c, 2e] oxidation processes of Pt₂(II,II) complexes by halocarbons (RX) to give the corresponding Pt₂(III,III)X₂ or Pt₂(III,III) RX had been described for lantern- or half-lantern complexes, such as $[\text{Pt}(\text{pop})_4]^{4-}$ (pop = pyrophosphite),^[11] $[\text{Pt}_2(\text{pyt})_4]$,^[12] $[\text{Pt}_2(\text{ppy})_2(\text{pyt})_2]$ ^[13] and $[\text{Pt}_2(\text{bzq})_2(\mu\text{-N}^*\text{S})_2]$,^[14] all of them with intermetallic distances of ca. 2.9 Å. However, for bis-pyrazolate complexes,^{[8],[9a-c, 15]} with intermetallic separations ranging from 3.4863(6) to 3.0457(7) Å (except in complex with C^{*}N = 2-(2,4-difluorophenyl)pyridyl and Rpz = 3,5-bis(tert-butyl)pyrazolate, $d_{\text{Pt-Pt}} = 2.8343(6)$ Å), this kind of reaction has been never reported. Herein we show compound $[\{\text{Pt}(\text{C}^*\text{C})(\mu\text{-pz})\}_2]$ (**1**) as the first “platinum-butterfly” ever oxidized by halocarbons, such as CHI₃. In the wings: a cyclometalated N-heterocyclic carbene ligand, C^{*}C*. The mechanism of the two-center two-electron [2c, 2e] oxidation of **1** has been elucidated experimentally and explained with the aid of theoretical calculations.

Results and Discussion

Compound **1** was prepared by two paths, from $[\{\text{Pt}(\text{C}^*\text{C})(\mu\text{-Cl})\}_2]$ ^[16] or $[\text{Pt}(\text{C}^*\text{C})(\text{pzH})_2]\text{ClO}_4$ ^[17] as a mixture of *syn/anti* isomers with respect to the relative orientation of the two cyclometalating C^{*}C* ligands (see Scheme 1 paths a, b). The composition of **1**, with the *anti* isomer being the major one (¹H and ¹⁹⁵Pt{¹H} NMR spectra in Figures S1 and S2 in Supporting Information), is in agreement with the DFT ground-state (S₀) calculations, which showed the *anti* isomer to be 3.1 Kcal/mol lower in energy than the *syn* one (See Figure S3 in Supporting Information).^[9f] The synthesis of **1** was also performed at -10°C and in refluxing acetone following path b, getting always mixtures of isomers with little differences in the *syn/anti* ratio. Variable temperature NMR spectra of **1** in THF-*d*₈ (298 K, 318 K, 323 K and 323K) or benzene-*d*₆ (298K, 318 K, 338 K and 343K) showed no change in the *syn/anti* ratio (See Figures S4 and S5 in S.I.). Therefore, it seems that these two diastereoisomers (*syn/anti*), once formed, do not transform one into the other, even at 343 K. The X-ray study on a single crystal of **1** showed three butterfly-like molecules (A, B, C; see table 1 and Figure 1 and S6 in Supporting Information) in the asymmetric unit with intermetallic separations of 3.2294(4) Å (**1A**), 3.2834(4) Å (**1B**) and 3.1208(6) Å (**1C**), each of them shorter than those observed in other platinum “butterflies” with the same body (pz) but different wings (3.231-3.486 Å).^{[8],[9a-c, 15]} In each of them, **1A-1C**,

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the molecule shows a dinuclear structure comprised of two “Pt(EtO₂C-C[∧]C^{*})” metallocycles bridged by two pz ligands and displaying a *anti* arrangement of the C[∧]C^{*} groups. The six-membered ring Pt₂N₄ has the typical boat-like conformation with an angle between the Pt-N-N-Pt fragments of about 82° (82.27(13)° **1A**, 80.21(14)° **1B**, 83.64(14)° **1C**) and an angle between the best least-squares planes of the platinum environments [Pt1,C1,C6,N5,N7; Pt2,C14,C19,N6,N8] of ca. 70° (73.84(18)° **1A**, 78.96(15)° **1B**, 66.68(13)° **1C**). The angle between the Pt-Pt line and both metal coordination planes are close to 35° (36.55(13)° Pt(1) and 37.41(12)° Pt(2) **1A**, 35.95(9)° Pt(1) and 43.24(11)° Pt(2) **1B**, 33.40(10)° Pt(1) and 33.51(8)° Pt(2) **1C**). In the molecule, each Pt center lies in a distorted square planar coordination environment as a consequence of the small bite angle of the EtO₂C-C[∧]C^{*} cyclometalated ligand ca 80°. These angles and the Pt-C_{Ar} and Pt-C^{*} distances are similar to those found in other compounds containing five-membered cycloplatinated N-heterocyclic carbenes.^[16–18] The Pt-N bond distances are also similar to those found in dinuclear bis-pyrazolate-bridge complexes containing ligands with high *trans* influence.^[9a, 15, 19]

Figure 1. Molecular structure of complex **1A**. Ellipsoids are drawn at their 50% probability level; solvent molecules and hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for **1·0.5tol·0.16OEt₂**.

	1A	1B	1C
Pt(1)-C(1)	1.964(7)	1.964(6)	1.961(6)
Pt(1)-C(6)	2.003(6)	2.003(7)	2.007(6)
Pt(1)-N(5)	2.055(5)	2.043(5)	2.057(5)
Pt(1)-N(7)	2.092(5)	2.083(5)	2.089(5)
Pt...Pt	3.2294(4)	3.2834(4)	3.1210(3)
Pt(2)-C(14)	1.966(7)	1.956(6)	1.951(6)
Pt(2)-C(19)	2.013(6)	2.012(6)	2.020(6)
Pt(2)-N(6)	2.086(5)	2.082(5)	2.094(5)
Pt(2)-N(8)	2.043(5)	2.051(5)	2.064(5)
C(1)-Pt(1)-C(6)	80.0(3)	80.0(3)	80.3(3)
C(1)-Pt(1)-N(7)	100.5(3)	101.3(2)	100.2(2)
C(6)-Pt(1)-N(5)	94.8(2)	94.6(2)	94.8(2)
N(5)-Pt(1)-N(7)	84.8(2)	84.1(2)	84.4(2)
C(14)-Pt(2)-C(19)	80.0(3)	79.7(3)	80.5(3)
C(14)-Pt(2)-N(6)	100.8(3)	99.8(2)	98.6(2)
C(19)-Pt(2)-N(8)	95.1(2)	94.2(2)	95.5(2)
N(6)-Pt(2)-N(8)	84.2(2)	86.17(19)	85.3(2)

The reaction of **1** (*syn/anti* mixture) with an excess of CHI₃ (molar ratio 1:4, see Scheme 1 path c) in the air and in the sunlight rendered Pt₂(III,III)₂ as the major species, with complex [[Pt(C[∧]C^{*})(μ-pz)I]₂] (**2**), with an *anti* arrangement of the C[∧]C^{*} groups, being precipitated and separated from the mixture in a 41% yield. However, under Ar atmosphere the reaction was observed to render species “Pt₂(III,III)(CHI₂)” almost selectively. Compound [IPt(C[∧]C^{*})(μ-pz)₂Pt(C[∧]C^{*})(CHI₂)](**3**), with an *anti* arrangement of the C[∧]C^{*} groups, was in this case precipitated and separated from the mixture in a 43% yield. Compounds **2** and **3** were fully characterized (See Experimental Section, Figures 2-4 and Figures S7-S19 in Supporting Information). Their X-ray structures showed for both, **2** and **3** (See Figure 2) the expected boat-like shape of the molecule and also, the shortening of the intermetallic distance (*d*_{Pt-Pt}: 2.6079(2) Å **2**, 2.6324(3) Å **3**) with respect to **1** due to the formation of a Pt(III)-Pt(III) bond.^[12, 14, 20] These distances are shorter than the observed in the mixed-valent Pt^{III}Pt^{III}Pt^{II} complex [Pt₃Br₂(μ-pz)₆] (*d*_{Pt(III)-Pt(III)} = 2.7787(8) Å).^[21]

Scheme 1. Reaction pathways involving synthesis and reactivity of **1** including the Numerical scheme for NMR purposes.

Figure 2. Molecular structure of complex (a) **2·1.75 Me₂CO** and (b) **3**. Ellipsoids are drawn at their 50% probability level; solvent molecules and hydrogen atoms have been omitted for clarity.

In these complexes each Pt(III) center has a distorted octahedral environment with the axial positions occupied by an X fragment (I **2**, I and CHI₂ **3**) and the other Pt(III) center with the X-Pt-Pt

angles close to 165° . The Pt-Pt distance in **3** (2.6324(3) Å) is slightly longer than that in **2** (2.6079(2) Å), likely due to the larger *trans* influence of the CHI_2 fragment when compared to the I one. The Pt-I distances are also in the range of those found in other Pt(III) complexes.^[14, 20b, 20e, 20f] In the two complexes, **2** and **3**, the “Pt(EtO₂C-C^{*}AC^{*})” metalocycles display an *anti*-arrangement of the Pt-C* bonds (C1-Pt1-Pt2-C14 torsion angles are $82.25(17)^\circ$ **2** and $79.65(31)^\circ$ **3**), the six-membered ring Pt₂N₄ has the typical boat-like conformation (the angle between the Pt-N-N-Pt fragments being $89.25(6)^\circ$ for **2** and $89.32(9)^\circ$ for **3**). In each complex, the equatorial platinum coordination planes are non-parallel and form interplanar angles close to 40° ($37.58(9)^\circ$ **2**, $40.19(14)^\circ$ **3**) quite smaller than those observed for complexes 1A-1C ($66.68(13)^\circ$ - $78.96(15)^\circ$), which undoubtedly must be a consequence of the metal-metal bond formation. It also affects the angles between the Pt coordination planes and the Pt-Pt line [$18.03(7)^\circ$ Pt1, $19.59(6)^\circ$ Pt2 **2** and $21.30(11)^\circ$ Pt1, $18.89(10)^\circ$ Pt2 **3**] that became smaller than those in **1** (close to 36°).

Table 2. Selected bond lengths (Å) and angles ($^\circ$) for for **2**·1.75 Me₂CO and **3**·0.25 Me₂CO.

	2 ·1.75 Me ₂ CO	3 ·0.25 Me ₂ CO
Pt(1)-C(1)	1.983(4)	1.992(7)
Pt(1)-C(6)	2.031(4)	2.012(6)
Pt(1)-N(5)	2.086(3)	2.055(5)
Pt(1)-N(7)	2.117(3)	2.105(5)
Pt(1)-I(1)	2.7030(3)	2.8066(5)
Pt-Pt	2.6079(2)	2.6324(3)
Pt(2)-C(14)	1.991(4)	1.960(6)
Pt(2)-C(19)	2.025(4)	2.014(6)
Pt(2)-N(8)	2.075(3)	2.065(5)
Pt(2)-N(6)	2.115(3)	2.128(5)
Pt(2)-X'	2.7176(3) X'=I(2)	2.145(8) X'=CHI ₂
C(1)-Pt(1)-C(6)	79.64(16)	79.6(3)
C(1)-Pt(1)-N(7)	96.79(14)	98.6(3)
C(6)-Pt(1)-N(5)	96.45(14)	95.3(3)
N(5)-Pt(1)-N(7)	85.17(13)	84.91(18)
I(1)-Pt1-Pt2	163.328(10)	162.412(14)
C(14)-Pt(2)-C(19)	79.97(16)	80.4(3)
C(14)-Pt(2)-N(6)	98.38(15)	96.9(3)
C(19)-Pt(2)-N(8)	94.71(14)	94.7(2)
N(6)-Pt(2)-N(8)	85.71(13)	85.7(2)
X'-Pt2-Pt1	164.776(10) X'=I(2)	167.85(18) X'=CHI ₂

The increased oxidation state of Pt in **2** and **3** is evident from the significant downfield shift of the ^{195}Pt NMR signals with respect to that of **1** (see Figure 3). The presence of two widely separated ^{195}Pt signals at -2454 and -3107 ppm in the $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum of **3** in CD_2Cl_2 evidences the non-equivalence of the two Pt fragments within this diplatinum (III) complex. In spite of its low solubility, platinum satellites could be also detected with a $^1J_{\text{Pt},\text{Pt}}$ coupling constant of 1674 Hz, which is similar to the one observed for [Pt₂(pop)₄MeI] ($^1J_{\text{Pt},\text{Pt}}$ = 1550 Hz).^[11b] Structurally significant is also the singlet corresponding to the CHI_2 fragment at 5.11 ppm, which displays the expected ^{195}Pt satellite pattern ($^2J_{\text{Pt},\text{H}}$ = 30.2 Hz, $^3J_{\text{Pt},\text{H}}$ = 5.9 Hz) for its structure (see ^1H NMR spectrum in Figure 4).

Figure 3. $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra of **1** (acetone- d_6), **2** and **3** (CD_2Cl_2).

Figure 4. ^1H NMR spectrum of **3** in CD_2Cl_2 (sample prepared in the dark)

The mechanism of this unexpected [2c, 2e] oxidation process was studied. To do that **1** was reacted with CHI_3 in a 1:4 molar ratio in acetone- d_6 in NMR tubes in different conditions and the reactions followed by ^1H NMR spectroscopy (See Scheme 1). In the air, **1** was completely reacted in 15 min to give a mixture of **2** and **3**. However, while in the reaction performed in the dark the mixture remained unchanged for at least 24 h (see Figure S20), in that performed in the sunlight, after 24 h complex **3** was completely transformed into the dihalocomplex **2** and minor unknown species (see Figure S21).

Under Ar atmosphere in the dark, compound **1** was completely reacted in 1 h to render **3** in about a 93% but, the formation of **2** is also evident (see Figure S22). The mixture also remains unchanged for at least 24 h. So, the simultaneous formation of **2** and **3** in this reaction suggests a radical pathway for the thermal addition process.^[11b]

Comparative experiments were performed under Ar atmosphere in the dark with and without the trapping alkyl reagent galvinoxyl (Gal·). They showed that the reaction of **1** with CHI_3 in the presence of Gal· resulted to be slower than in the absence of it (in 1 h, most amount of **1** remains unreacted) After 24 h, **1** is completely reacted, being the ratio **2**:**3** bigger with Gal·, than without it (Figure S22). In spite of the fact that in the air the formation of quite small quantities of iodine (generated by O_2) and its subsequent addition to **1** can be not absolutely ruled out, the experimental results are in agreement with a radical pathway (Eq. 1-4) in which O_2 (or Gal·) acts as an efficient radical trap ($\text{R}\cdot$), increasing the ratio **2**:**3**.

To gain more in-depth knowledge about the thermal reaction of the dimer **1** and CHI_3 , we carried out theoretical calculations (see computational details in SI). Thus we have considered four conceptually different metal oxidation pathways: *i*) a classical $\text{S}_\text{N}2$ addition of iodoform to the $\text{Pt}(\text{II})$ - $\text{Pt}(\text{II})$ dimer; *ii*) an iodine-transfer from iodoform to the $\text{Pt}(\text{II})$ - $\text{Pt}(\text{II})$ dimer; *iii*) an electron-transfer from the $\text{Pt}(\text{II})$ - $\text{Pt}(\text{II})$ dimer to iodoform and; *iv*) an OA via singlet-triplet crossover processes (see Scheme 2 and Scheme S1 in SI. DFT calculations indicate that the pathways involving spin crossover processes and triplet state (T1) Pt-Pt species (paths *iva* and *ivb* in Scheme S1) can be ruled out under thermal conditions, so they will not be further discussed here. Oppositely, the formation of either the $\text{Pt-Pt}\cdots\text{CHI}_3$ or the $\text{Pt-Pt}\cdots\text{I}^\bullet\text{CHI}_2$ adducts as reaction intermediates is energetically feasible (Scheme 2). Interestingly, even though the $\text{S}_\text{N}2$ addition pathway (*i*) appears energetically accessible ($\Delta G^\ddagger = 23.6$ kcal/mol), iodine-atom transfer to the platinum dimer (*ii*a) is clearly favored ($\Delta G^0 = 17.0$ kcal/mol) and therefore emerges as the most likely reaction mechanism. Other variants as iodide transfer (*ii*b), iodine-cation transfer (*ii*c) and electron transfer from the platinum dimer to the iodoform (*iii*) are energetically disfavored processes.

DFT calculations show that pathway *ii*a is energetically compatible with the experimental results, that is, with a fast reaction which is completed in minutes. This means that the formation of the Pt^III - Pt^III compound **3** proceeds via a homolytic breakage of the I-C bond^[22] in a S_0 [$\text{Pt-Pt}\cdots\text{I}^\bullet\text{CHI}_2$] adduct. Furthermore, the concomitant generation of radicals in the reaction media is consistent with the observed formation of the diiodide derivative **2** and also with the variable outcomes observed in the reactions carried out under argon atmosphere or in the presence of O_2 or galvinoxyl.

Scheme 2. Single-state DFT-calculated pathways and energy barriers (Kcal/mol in blue) for the conversion of **1** to **3**.

Conclusions

In summary this paper shows the first reported “platinum butterfly” ever oxidized by halocarbons (CHI_3) to give metal-metal bonded platinum (III) complexes, $\text{Pt}_2(\text{III,III})\text{I}_2$ and $\text{Pt}_2(\text{III,III})\text{I}(\text{CHI}_2)$. In the wings: a cyclometalated N-heterocyclic carbene ligand, C^*C^* . The thermal addition seems to follow a radical-like pathway, with O_2 acting as an efficient radical trap ($\text{R}^\bullet$), likely due to the easily accessible Pt_2 -promoted homolytic I-C bond breakage of iodoform. By controlling the reaction conditions it was possible to get $\text{Pt}_2(\text{III,III})\text{I}_2$ and $\text{Pt}_2(\text{III,III})\text{I}(\text{CHI}_2)$ species almost selectively. Preliminary studies on the mechanism and reactivity of **1** towards other halocarbons, such as CHBr_3 , CHCl_3 or CH_2Cl_2 indicate that under ambient conditions the behavior is quite similar, which indicate the inconvenience of this kind of compounds to be treated with halogenated solvents.

Experimental Section

Information describing Instrumental methods used for characterization, details concerning DFT calculations and X-ray structure determination are provided in the Supporting Information. The starting materials [$\text{Pt}(\mu\text{-Cl})(\text{EtO}_2\text{C-C}^*\text{C}^*)_2$] (**A**)^[16] and [$\text{Pt}(\text{EtO}_2\text{C-C}^*\text{C}^*)(\text{pzH})_2$] ClO_4 (**B**)^[17] were prepared following the literature procedure. pzH was purchased from MERCK.

Synthesis of syn/anti-[[Pt(C^*C^*)($\mu\text{-pz}$)]₂] (**1**)

Method A: Compound **A** (100.0 mg, 0.11 mmol) was added to a solution containing KOH (13.6 mg, 0.22 mmol) and pzH (14.8 mg, 0.22 mmol) in acetone/ EtOH (16 mL/8 mL). After 24 h of reaction at r.t. the solvent was removed under reduced pressure, filtered and washed with 2 x 5 mL of H_2O to give **1-anti** (92 %)/ **1-syn** (8%) as a yellow solid. Yield: 66 mg, 62 %. **Method B:** NEt_3 (0.5 mL, 3.62 mmol) was added to a solution of **B** (120 mg, 0.18 mmol) in acetone (40 mL) at r.t. After 2 h of reaction the solvent was removed in vacuo. The residue was treated with MeOH (5 mL), filtered, and washed to give **1-anti** (86 %)/ **1-syn** (14%) as a yellow solid. Yield: 60 mg, 68 %. Anal. Calcd for $\text{C}_{32}\text{H}_{32}\text{N}_8\text{O}_4\text{Pt}_2$: C, 39.11; H, 3.28; N, 11.40. Found: C, 38.72; H, 3.34; N, 11.26. ^1H NMR data for **1-anti** (500 MHz, acetone- d_6): $\delta = 7.97$ (d, $^4J_{\text{H7, H9}} = 1.7$, $^3J_{\text{H7, Pt}} = 54.2$, 2H, H₇), 7.72 (d, $^3J_{\text{H, H}} = 1.7$, 2H, pz), 7.96 (d, $^3J_{\text{H2, H3}} = 2.1$, 2H, H₂), 7.68 (d, $^3J_{\text{H, H}} = 2.0$, 2H, pz), 7.65 (dd, $^3J_{\text{H9, H10}} = 8.1$, $^4J_{\text{H9, H7}} = 1.8$, 2H, H₉), 7.22 (d, $^3J_{\text{H10, H9}} = 8.1$, 2H, H₁₀), 7.11 (d, $^3J_{\text{H3, H2}} = 2.1$, 2H, H₃), 6.38 (t, $^3J_{\text{H, H}} = 2.0$, 2H, H₄, pz), 4.23 (q, $^3J_{\text{H, H}} = 7.1$, 4H, CH₂, CO₂Et), 3.32 (s, 6H, H₄), 1.29 (t, $^3J_{\text{H, H}} = 7.1$, 6H, CH₃, CO₂Et). ^1H NMR data for **1-syn**: $\delta = 7.92$ (d, $^4J_{\text{H7, H9}} = 1.7$, 2H, H₇), 7.60 (dd, $^3J_{\text{H9, H10}} = 8.1$, $^4J_{\text{H9, H7}} = 1.8$, 2H, H₉), 6.41 (t, 1H, $^3J_{\text{H, H}} = 1.7$) and 6.30 (t, $^3J_{\text{H, H}} = 1.7$, 1H) (H₄ and H_{4'}, pz); the rest of the signals appear overlapped with those of the **1-anti** isomer. $^{195}\text{Pt}\{^1\text{H}\}$ NMR (85.6 MHz, acetone- d_6): $\delta = -3778$ (s) **1-anti**; $\delta = -3789$ (s) **1-syn**. MS (MALDI+): m/z 981.1 [[Pt(C^*C^*)($\mu\text{-pz}$)]₂]

Synthesis of [[Pt(C^*C^*)($\mu\text{-pz}$)]₂] (**2**)

CHI_3 (83.4 mg, 0.21 mmol) was added to a solution of **1** (51.4 mg, 0.052 mmol) in acetone (15 mL) at r.t. and sunlight. After 8 h of reaction the resulting suspension was concentrated to a volume of ca. 5 mL, filtered and washed with *n*-hexane (20 mL) to give **2** as a dark orange solid. Yield: 26 mg, 41 %. Anal. Calcd for $\text{C}_{32}\text{H}_{32}\text{I}_2\text{N}_8\text{O}_4\text{Pt}_2$: C, 31.08; H, 2.61; N, 9.06. Found: C, 30.76; H, 2.57; N, 8.76. ^1H NMR data (400 MHz, CD_2Cl_2): $\delta = 7.98$ (d, $^3J_{\text{H, H}} = 1.9$, $^4J_{\text{H, Pt}} = 12.3$, 2H), 7.82 (d, $^3J_{\text{H, H}} = 1.9$, $^4J_{\text{H, Pt}} = 10.4$, 2H) [H₃ and H₅, pz], 7.54 (dd, $^3J_{\text{H9, H10}} = 8.3$, $^4J_{\text{H9, H7}} = 1.6$, 2H, H₉), 7.47 (d, $^4J_{\text{H9, H7}} = 1.6$, $^4J_{\text{H7, Pt}} = 40.4$, 2H, H₇), 6.97 (d, $^3J_{\text{H3, H2}} = 1.8$, 2H, H₂), 6.89 (d, $^3J_{\text{H10, H9}} = 8.3$, 2H, H₁₀), 6.37 (d, $^3J_{\text{H3, H2}} = 1.8$, 2H, H₃), 6.35 (t, $^3J_{\text{H, H}} = 1.9$, 2H, H₄, pz), 4.37–4.22 (m, 4H, CH₂, CO₂Et), 3.22

(s, 6H, H₄), 1.33 (t, ³J_{H, H} = 6.9, 6H, CH₃ (CO₂Et)). ¹³C{¹H} NMR plus HMBC and HSQC (101 MHz, CD₂Cl₂): δ = 166.4 (s, 2C, CO₂Et), 147.0 (s, 2C, C₅), 146.7 (s, 2C, C₁), 139.4 (s, 2C) and 138.3 (s, 2C) [C₃ and C₆, pz], 134.0 (s, 2C, C₇), 127.3 (s, 2C, C₉), 127.3 (s, 2C) and 124.2 (s, 2C) [C₆ and C₈, pz], 123.4 (s, 2C, C₂), 114.9 (s, 2C, C₃), 111.2 (s, 2C, C₁₀), 106.5 (s, 2C, C₄), 61.5 (s, 2C, CH₂, CO₂Et), 37.5 (s, 2C, C₄), 14.6 (s, 2C, CH₃ (CO₂Et)). ¹⁹⁵Pt{¹H} NMR (85.6 MHz, CD₂Cl₂): δ = -3092.1 (s). MS (MALDI+): m/z 1109.1 [(Pt(C^{AC}*)(μ-pz)₂)]⁺

Synthesis of [Pt(C^{AC}*)(μ-pz)₂Pt(C^{AC}*)CHL₂] (3)

CHL₃ (25.0 mg, 0.06 mmol) was added in the dark to a solution of **1** (50. mg, 0.05 mmol) in degassed acetone (5 mL) at r.t under an argon atmosphere. After 30 min of reaction, an orange precipitate was filtered off and washed with n-hexane (5 mL) to give **3** as an orange solid. Yield: 30 mg, 43 %. Anal. Calcd for C₃₃H₃₃N₃O₄Pt₂: C, 28.79; H, 2.42; N, 8.14. Found: C, 28.56; H, 2.47; N, 7.82. ¹H NMR data (400 MHz, CD₂Cl₂): δ = 8.60 (d, ³J_{H, H} = 2.3, ³J_{H, Pt} = 5.0, 1H, pz), 8.24 (d, ³J_{H, H} = 2.2, ³J_{H, Pt} = 6.6, 1H, pz), 8.12 (d, ³J_{H, H} = 1.9, ³J_{H, Pt} = 11.1, 1H, pz), 7.96 (d, ³J_{H, H} = 2.1, ³J_{H, Pt} = 9.2, 1H, pz), 7.73 (dd, ³J_{H9, H10} = 8.1, ⁴J_{H9, H7} = 1.7, 1H, H₉ (Pt-CHL₂)), 7.55 (dd, ³J_{H9, H10} = 7.5, ⁴J_{H9, H7} = 1.8, 1H, H₉ (Pt-I)), 7.54 (m, partially overlapped with H₉, ³J_{H, Pt} = 44.9, 1H, H₇ (Pt-I)), 7.46 (d, ³J_{H, H} = 2.3, ³J_{H, Pt} = 44.8, 1H, H₇ (Pt-CHL₂)), 7.02 (d, ³J_{H3, H2} = 2.2, ⁴J_{H, Pt} = 5.0, 1H, H₂ (Pt-CHL₂)), 6.97 (d, ³J_{H3, H2} = 2.2, 1H, H₂ (Pt-I)), 6.94 (d, ³J_{H10, H9} = 8.2, 1H, H₁₀ (Pt-I)), 6.87 (d, ³J_{H10, H9} = 8.8, 1H, H₁₀ (Pt-CHL₂)), 6.47 (t, ³J_{H, H} = 2.2, 1H, H₄, pz), 6.43 (t, ³J_{H, H} = 2.1, 1H, H₄, pz), 6.40 (d, ³J_{H3, H2} = 2.1, ⁴J_{H, Pt} = 6.8, 1H, H₃ (Pt-CHL₂)), 6.35 (d, ³J_{H3, H2} = 2.2, ⁴J_{H, Pt} = 6.9, 1H, H₃ (Pt-I)), 5.11 (s, ²J_{Pt, H} = 30.4, ³J_{Pt, H} = 5.9, 1H, CHL₂), 4.25-4.41 (m, 4H, CH₂, CO₂Et), 3.31 (s, ⁴J_{Pt, H} = 4.3, 3H, H₄ (Pt-CHL₂)), 3.11 (s, 3H, H₄ (Pt-I)), 1.36 (t, 6H, CH₃ (CO₂Et)). ¹³C{¹H} NMR plus HMBC and HSQC (101 MHz, CD₂Cl₂): δ = 141.4, 140.1, 133.8 and 131.6 (s, 4C, CH, pz), 132.8 (s, 1C, C₇), 128.1 (s, 1C, C₉), 126.2 (s, 2C, C₇ and C₉), 123.7 (s, 1C, C₃ (Pt-CHL₂)), 121.9 (s, 1C, C₃ (Pt-I)), 111.8 (s, 1C, C₁₀), 110.5 (s, 1C, C₁₀), 105.9 (m, 2C, C₄), 61.6 (s, 2C, CH₂, CO₂Et), 61.3 (s, 2C, CH₂, CO₂Et), 37.4 and 37.2 (s, 2C, C₄), 14.6 (s, 6C, CH₃ (CO₂Et)). The rest of signals are not detected due to solubility issues. ¹⁹⁵Pt{¹H} NMR (85.6 MHz, CD₂Cl₂): δ = -2454 (s, ¹J_{Pt, Pt} = 1674 Hz, Pt-CHL₂) and -3107 ppm (s, Pt-I). MS (MALDI+): m/z 1109.1 [(Pt(EtO₂C-C^{AC}*)(μ-pz)₂)], 1249.0 [(Pt(EtO₂C-C^{AC}*)(μ-pz)₂CHL₂)]

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Keywords: Cyclometalated NHC • Molecular Butterfly • oxidative addition • dinuclear Pt(III) • bridging pyrazolate

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Entry for the Table of Contents

FULL PAPER

$[\{\text{Pt}(\text{C}^*\text{C}^*)(\mu\text{-pz})\}_2]$ is the first “platinum-butterfly” with a cyclometalated N-heterocyclic carbene (C^*C^*) acting as wings, that has ever been oxidized by halocarbons. The control of the reaction conditions allowed to get almost selectively $[\{\text{Pt}(\text{C}^*\text{C}^*)(\mu\text{-pz})\}_2\text{Pt}(\text{C}^*\text{C}^*)\text{CHI}_2]$ or $[\text{IPt}(\text{C}^*\text{C}^*)(\mu\text{-pz})_2\text{Pt}(\text{C}^*\text{C}^*)\text{CHI}_2]$ which were fully characterized. Experimental and theoretical investigations showed that an easily accessible radical-like mechanism operates under thermal conditions.

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**A Cyclometalated N-Heterocyclic
Carbene: The Wings of The First
 $\text{Pt}_2(\text{II},\text{II})$ Butterfly Oxidized by CHI_3**