ORGANOMETALLICS

New Trans-Configured Acetylide–Cyanide Platinum(II) Anions: Spectroscopic and Optical Studies

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Supporting Information

ABSTRACT: A novel series of phosphorescent stable mixed acetylide–cyanide anionic $(NBu_4)_2[trans-Pt(C \equiv CR)_2(CN)_2]$ (R = Tol (1), $C_6H_4CF_3$ -4 (2), C_5H_4N -4 (3), Np (4)) complexes were prepared by reactions of the neutral $[trans-Pt(C \equiv CR)_2(PPh_3)_2]$ precursors with excess $(NBu_4)CN$. The formation of 1–4 takes place through monoanionic $[trans-Pt(C \equiv CR)_2(CN)(PPh_3)]^-$ intermediate species, as confirmed by the isolation of the naphthyl derivative $(NBu_4)[trans-Pt(C \equiv CNp)_2(CN)(PPh_3)]$ (5). Further substitution of PPh₃ in 5 by $CN^{t}Bu$ gives $(NBu_4)[trans-Pt(C \equiv CNp)_2(CN)-$



(CN^tBu)], containing three different isoelectronic ligands. The complexes have been characterized (¹H, ¹³C, ¹⁹⁵Pt NMR, IR, MALDI-TOF), including X-ray crystallography for 2, 4, and 6, and their spectroscopic and optical properties compared to those of the related homoleptic $[Pt(C \equiv CR)_4]^{2^-}$ complexes. Time-dependent density functional theory (TD-DFT) calculations were performed for anions 1^{2^-} and 4^{2^-} and three different conformers of 6^- to provide further insight into the nature of the electronic transitions.

■ INTRODUCTION

The synthesis of transition-metal complexes with cyanide ligands has been a widely studied field for many years.¹ Their high stability and structural and bond characteristics, together with their interesting properties, have increased their attraction not only for chemistry but also for materials science.² In particular, cyanometalates have been extensively employed to prepare and study discrete or supramolecular heteronuclear cyanide-bridged arrays, exhibiting fascinating structures and tunable magnetic or photophysical properties facilitated by the presence of short bridges, which maximize the magnitude of magnetic exchange couplings and favor energy transfer processes.³ Furthermore, owing to the ability of the cyanide groups to act as hydrogen bond acceptors, these negatively charged cyanometalate units have been also successfully incorporated into hydrogen-bonded supramolecular assemblies.⁴ In platinum chemistry, particularly relevant are the widely studied tetracyanoplatinate ($[Pt(CN)_4]^{2-}$, TCP) based systems⁵ and some recent heteroleptic derivatives, such as the extended networks $[cis-Pt(CN)_2(CNR)_2]$, $K(H_2O)_x[Pt (C^{N})(CN)_{2}$ (C^N = bzq, ppy; x = 0, 1),⁷ Na₂[Pt- $(CN)_2(dcpy)] \cdot nH_2O$ (H₂dcpy = 4,4'-dicarboxy-2,2'-bypiridine; n = 2, 5,⁸ and [PtTl(L)(CN)₂] (L = bzq,⁹ C₄H₉N₄¹⁰) and {Tl[Tl{*cis*-Pt(C₆F₅)₂(CN)₂}](H₂O)]_n and [*trans,trans,trans*- $Tl_2Pt(C_6F_5)_2(CN)_2(acetone)_2]_{n'}^{n'}$ in which additional metallophillic interactions (Pt...Pt, Pt-Tl) play a remarkable role in their structures and associated optical properties.

On the other hand, transition-metal alkynyl complexes have been also attracting widespread interest for many years, largely due to their interesting reactivity, structural diversity, and photoluminescent properties, as well as their potential application in materials science. Several recent reviews cover different aspects of these compounds.¹²

In the realm of photophysics we^{12a,c,13} and others¹⁴ have been interested in using homoleptic and heteroleptic alkynyl platinates as precursors of clusters or supramolecular assemblies, which are stabilized by a synergistic combination of alkynyl σ/π bonding and metallophilic (Pt…Pt, Pt…M, M…M) interactions. This has allowed us to prepare fascinating high-nuclearity arrays having interesting properties, including luminescence,^{12a,c} thermochromism,⁹ mechanochromism,^{13f} and solvatochromism.^{12c,13e,15}

Following our interest in both cyanide and alkynyl luminescent platinum-based systems, we decided to explore the chemistry and properties of new platinum derivatives simultaneously containing these two kinds of ligands (alkynyl and cyanide), which have been essentially unexplored. Several years ago we reported (from $Pt(C \equiv CR)_2COD$ as precursors) the cis-configured mixed anionic complexes $[cis-Pt(C \equiv$ $(CR)_2(CN)_2^{2-}$ (R = Ph, ^tBu) as oily materials, which were combined with d⁸ (Pt^{II}, Rh^I, Ir^I) metal ions to construct multimetallic (triangle, square hexametallic) assemblies,¹⁶ and, more recently,¹⁷ the successful synthesis of the first novel transconfigured derivative $(NBu_4)_2[trans-Pt(C \equiv CTol)_2(CN)_2]$ (1), by using the neutral derivative $[trans-Pt(C \equiv CTol)_2(PPh_3)_2]$ as precursor. $(NBu_4)_2$ [trans-Pt(C=CTol)_2(CN)_2] (1) was found to be not only an interesting blue emitter but also an adequate tecton to construct two different $PtTl_2$ and $PtPb_2$ supramolecular heterometallic luminescent materials.¹ As a

Received: November 26, 2012 Published: January 31, 2013

continuation, in this report, we present the synthesis, structure, and photophysical properties of a family of dianionic bis(cyanide)bis(acetylide)platinum complexes $(NBu_4)_2[trans-Pt(C \equiv CR)_2(CN)_2]$ (R = C₆H₄CF₃-4 (2), C₅H₄N-4 (3), Np (4)). These complexes are generated through the monoanionic derivatives $[trans-Pt(C \equiv CR)_2(CN)(PPh_3)]^-$ as intermediate species, from which the complex $(NBu_4)[trans-Pt(C \equiv CNp)_2(CN)(PPh_3)]$ (5) has been isolated and fully characterized. We sought to probe that, in complex 5, PPh₃ can also be substituted by an isocyanide ligand, which has allowed us to prepare and structurally characterize the very unusual derivative $(NBu_4)[trans-Pt(C \equiv CNp)_2(CN)(CN^tBu)]$ (6) stabilized by three distinct isoelectronic ligands.

RESULTS AND DISCUSSION

Synthesis and Characterization. As detailed in the Experimental Section, complexes $(NBu_4)_2[trans-Pt(C \equiv CR)_2(CN)_2]$ (2-4) were conveniently synthesized following a strategy similar to that previously communicated for complex 1^{17} (eq 1), which has been also included in this work for comparative purposes.



In all cases, a suspension of the appropriate precursor [*trans*-Pt(C=CR)₂(PPh₃)₂] in acetone was treated with an excess of (NBu₄)CN (molar ratio 1:4), to drive the reaction to completion in ca. 15 min. The final solution was evaporated to dryness and the corresponding dianionic complex obtained as detailed in the Experimental Section. Thus, while the naphthyl derivative 4 precipitated as a pure pink solid by treating the residue with an *i*-PrOH/Et₂O mixture, complexes 2 and 3, which are more soluble, required a previous extraction in an equimolecular CH₂Cl₂/H₂O mixture to remove the excess (NBu₄)CN. They are isolated as white solids from solvent mixtures (CH₂Cl₂/MeOH/*n*-hexane, 2; *i*-PrOH/Et₂O, 3) only in a moderate yield (~40%).

Monitoring all reactions by ³¹P{¹H} NMR spectroscopy revealed that the substitution of PPh₃ by cyanide takes place rapidly through the initial formation of the monoanionic species [*trans*-Pt(C=CR)₂(CN)(PPh₃)]⁻, which exhibit the phosphorus resonance shifted to high field by ca. 5 ppm (δ (ppm)/¹J(³¹P-¹⁹⁵Pt) (Hz) = 13.4/2696 (R = Tol),¹⁸ 13.8/ 2682 (R = C₆H₄CF₃-4), 13.9/2668 (R = C₅H₄N-4), 13.7/2709 (R = Np)) in relation to the corresponding precursor [*trans*-Pt(C=CR)₂(PPh₃)₂] (δ (ppm)/¹J(³¹P-¹⁹⁵Pt) (Hz) = 18.6/ 2657 (R = Tol), 18.9/2620 (R = C₆H₄CF₃-4), 18.8/2598 (R = C₅H₄N-4), 18.8/2648 (R = Np)). This fact and the slight

Scheme 1

observed increase in the ${}^{31}P-{}^{195}Pt$ coupling constant are consistent with the excess of electronic density in the Pt atom and the lower trans influence of the incoming CN⁻ group in relation to the replaced PPh₃ ligand. We note that the displacement of the second PPh₃ occurs more slowly and, by using the stoichiometric amount of cyanide (2 equiv), is only complete in the case of complex 1 (R = Tol). For the other systems, mixtures of the monoanionic intermediates, PPh₃, and the final dianionic complexes 2–4 were always found, even after prolonged reaction times (1–2 days). However, in the presence of excess of CN⁻ the reactions go easily to completion (see the Experimental Section). We note that treatment of these dianionic complexes 2–4 with 2 equiv of PPh₃ does not evolve with substitution of cyanide by phosphine, even with long reaction times (3 days).

Analytical and spectroscopic data (vide infra) confirm, in all cases, the retention of the trans geometry of the precursor, and, with the aim of confirming the monosubstitution step, we decided to isolate and characterize the monoanionic intermediate with the naphthylacetylide ligand.

Monitoring of this reaction (Scheme 1) by NMR spectroscopy at different stoichiometries showed that the formation of the monosubstituted anion $[trans-Pt(C \equiv CNp)_2(CN)]$ - (PPh_3)]⁻ (5⁻) takes place rapidly, but the disubstituted dianion 4^{2-} always appears before the neutral precursor [*trans*-Pt(C= $(CNp)_2(PPh_3)_2$ is consumed. The best conditions for the synthesis of 5⁻ were obtained by minimizing the formation of 4^{2-} , because their final separation is not an easy task. This was achieved by carrying out the reaction of $[trans-Pt(C \equiv$ $(CNp)_2(PPh_3)_2$ with 1 equiv of $(NBu_4)CN$ in acetone and using a short reaction time. As detailed in the Experimental Section, after 15 min, the reaction mixture is mainly formed by the desired monosubstituted anion $[trans-Pt(C \equiv CNp)_2(CN) (PPh_3)^{-}(5^{-})$ and free PPh₃, together with only small amounts of 4^{2-} and the neutral precursor [*trans*-Pt(C=CNp)₂(PPh₃)₂], which is still present. This starting material has very low solubility in acetone, allowing its elimination by filtration. Subsequent evaporation of the filtrate and treatment of the oily residue obtained with *i*-Pr₂O generates (NBu_4) [*trans*-Pt(C= $(CNp)_2(CN)(PPh_3)$ (5) as a white solid in moderate yield (46%). As is shown in Scheme 1, the PPh_3 ligand in complex 5 can be easily replaced by an isocyanide ligand. Thus, treatment of complex 5 with an excess of $C \equiv N^t Bu$ allows access to the unusual heteroleptic complex (NBu_4) [trans-Pt(C= $(CNp)_2(CN)(C \equiv N^tBu)$ (6), containing three isoelectronic ligands (acetylide, cyanide, and isocyanide) in the coordination sphere of the Pt^{II} center.

It is worth noting that these dianionic complexes are very stable both in the solid state and even in solution (at room temperature for several months). This fact is in contrast with the relatively low stability of the related homoleptic $(NBu_4)_2[Pt(C \equiv CR)_4]$ complexes.¹⁹



| Table | 1. Selected | IR (| (cm ⁻¹ | ', in Nujol |) and | d NMR Data | (δ | /ppm | $ J_{\rm Pt-C}/{\rm H} $ | z]) | of | Complexes 1– | -6 |
|-------|-------------|------|-------------------|-------------|-------|------------|----|------|--------------------------|-----|----|--------------|----|
|-------|-------------|------|-------------------|-------------|-------|------------|----|------|--------------------------|-----|----|--------------|----|

| | 1 | 2 | 3 | 4 | 5 | 6 |
|-------------------------------|---|--------------------------|--------------|--------------|------------|-------------|
| $\nu(C \equiv N)$ | 2114 | 2111 | 2111 | 2107 | 2129 | 2133 |
| $\nu(C \equiv C)$ | 2093 | 2088 | 2097 | 2079 | 2100, 2088 | 2105, 2092 |
| $\delta(C-CN)$ | 129.7 [1029] | 128.2 [1032] | 127.8 [1031] | 128.7 [1028] | а | b |
| $\delta(C^{lpha})$ | 111.9 [934] | 119.0 [934] | 122.4 [967] | 120.1 [970] | а | 108.2 [970] |
| $\delta(\mathrm{C}^{eta})$ | 104.0 [255] | 104.2 [279] | 103.5 [279] | 102.6 [278] | а | 102.8 [278] |
| $\delta(^{195}\mathrm{Pt})^c$ | -4437.6 | -4439.4 | -4427.1 | -4417.4 | а | -4469.1 |
| ^a Not soluble enou | gh ^b Not observed ^c S | Shifts are relative to N | [an[PtCL] | | | |

All complexes have been characterized by the usual spectroscopic and analytical techniques (see the Experimental Section and Table 1), and the crystal structures of complexes 2, 4 and 6 were determined by X-ray crystallography. The negative MALDI(-) mass spectra of 1-4 show the corresponding peaks due to the ions $[M - NBu_4]^-$ and [M- $2NBu_4$]⁻, respectively, and those of 5 and 6 show the expected $[M - NBu_4]^-$ peak (100% m/z 785.1 (5), 606.2 (6)) from the loss of the tetrabuthylammonium ion. The IR spectra of 1-4 confirm the presence of one strong $\nu(C \equiv N)$ (2107-2114 cm⁻¹) and one $\nu(C\equiv C)$ (2079–2097 cm⁻¹) stretching band in the expected regions,^{1,20} consistent with the trans geometry of the ligands (local D_{2h} symmetry). The $\nu(C \equiv C)$ bands appear slightly shifted to higher energies in relation to the corresponding homoleptic $(NBu_4)_2[Pt(C \equiv CR)_4]^{19a}$ complexes ($\Delta \nu = 12 \text{ cm}^{-1}$ (R = Tol), 13 cm⁻¹ (R = C₆H₄CF₃-4), 4 cm⁻¹ (C₅H₄N-4), 14 cm⁻¹ (Np)), whereas the ν (C \equiv N) stretches are found at low energies in relation to that for $[Pt(CN)_4]^{2-}$ (2122 cm⁻¹). This result is in accordance with the electronic perturbation in the Pt center, taking into account the better π^* -acceptor properties of cyanide groups. For the complexes $(NBu_4)[trans-Pt(C \equiv CNp)_2(CN)(PPh_3)]$ (5) and $(NBu_4)[trans-Pt(C \equiv CNp)_2(CN)(C \equiv N^tBu)]$ (6), in addition to the $\nu(C \equiv N)$ stretch (2129 cm⁻¹, 5; 2133 cm⁻¹, 6), two $\nu(C \equiv C)$ bands (2100, 2088 cm⁻¹, 5; 2105, 2092 cm⁻¹, 6) are observed, in accordance with the expected two active modes $(A_1 + B_1, C_{2\nu}$ symmetry). Complex 6 displays an additional high-energy $\nu(C \equiv N, C \equiv N^{t}Bu)$ absorption at 2209 cm^{-1.6,21} The small shifts to higher energies in the $\nu(C \equiv N)$ and $\nu(C \equiv$ C) bands in complex 6, in relation to complex 5, can be primarily attributed to the occurrence of a lesser electronic π back-donation from the Pt^{II} center to the cyanide and acetylide ligands, caused by the substitution of the PPh₃ by the C \equiv N^tBu (a better π -accepting ligand).

The most relevant data in the NMR spectra of 1-4 are the signals due to the CN groups and to the C^{α} and C^{β} acetylenic carbons compiled in Table 1. A comparison of the chemical shifts of the acetylenic carbons, which are easily assigned due to distinct couplings to the ¹⁹⁵Pt center (see Figure 1 as an illustration), with those of the homoleptic complexes $(NBu_4)_2[Pt(C \equiv CR)_4]^{19a}$ reveals that the signal due to the C^{α} atom is shifted upfield ($\Delta\delta(C^{\alpha})$ (ppm) = -6.5 (1), -6.0 (2), -0.9 (3)), whereas the signal due to C^{β} appears shifted slightly downfield $(\Delta\delta(C^{\beta}) \text{ (ppm)} = 1.9 \text{ (1)}, 1.2 \text{ (2)}, 0.9 \text{ (3)}).$ We attribute this, primarily, to the decrease in the net π backbonding component from platinum to $\pi^*(C \equiv CR)$ orbitals caused by the electron-withdrawing effect of CN ligands, which likely decreases the so-called paramagnetic contribution to the shift. This result is also in accordance with previous theoretical and experimental data,²² which suggest that a downfield ¹³C NMR shift of the C^{α} carbon in metal σ -acetylides might reflect



Figure 1. Carbon resonances of $[trans-Pt(C\equiv CNp)_2(CN)_2]^{2-}$ (4²⁻) extracted from the ${}^{13}C{}^{1}H$ NMR spectrum of complex 4 in CD₃COCD₃ at 293 K.

the cumulenic character associated with the resonant form II (Chart 1).

Chart 1

$$[Pt] \stackrel{\Theta}{\longrightarrow} C \equiv C - R \xrightarrow{\leftarrow} [Pt] \equiv C \equiv C \stackrel{\Theta}{\searrow} I \qquad II \qquad R$$

The C(CN) resonance is observed in the narrow region from 127.8 to 129.7 ppm. The ¹⁹⁵Pt-C(cyanide) coupling constants (~1030 Hz) are higher than that reported by us in $[cis-Pt(C \equiv$ $C^{t}Bu_{2}(CN)_{2}]^{2-}$ (δ 132.5 ppm, J_{Pt-C} = 916 Hz),¹⁶ pointing to a greater trans influence for the C=CR ligand. Accordingly, these values are also higher than those observed for ${}^{1}I(Pt-C^{\alpha})$ bonds (see Table 1), suggesting a stronger Pt-C (Pt-C(CN)) > Pt- $C^{\alpha} \equiv C^{\beta}$) spin-spin interaction. The proton spectra of complexes 5 and 6 exhibit only one set of naphthyl resonances, which supports the proposed trans geometry. The ${}^{13}C{}^{1}H{}$ spectrum of 5 was not recorded due to its limited solubility. For complex 6, in addition to Np and ^tBu groups, the expected resonances due to acetylenic carbons with the corresponding ¹⁹⁵Pt satellites were observed, but despite prolonged accumulation, the quaternary C=N (CN, CN^tBu) carbons were not found. Interestingly, the C^{α} carbon is observed (δ 108.2 ppm) remarkably shifted to lower frequencies in relation to 4 (δ 120.1 ppm), reflecting again the lower electron density on the Pt center. We have also recorded the ¹⁹⁵Pt{¹H} NMR spectra of

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Figure 2. ORTEP views of the anions (a) $[trans-Pt(C \equiv CC_6H_4CF_3-4)_2(CN)_2]^{2^-}$ (2²⁻), (b, c) $[trans-Pt(C \equiv CNp)_2(CN)_2]^{2^-}$ (4²⁻), and (d, e) $[trans-Pt(C \equiv CNp)_2(CN)(C \equiv N^{t}Bu)]^{-}$ (6⁻). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

complexes 1–4 and 6. As can be seen in Table 1, all complexes exhibit a singlet resonance in the expected range (from –4427.1 to –4469.1 ppm).²³ For complex 1 this signal (δ CD₃COCD₃ –4437.6 ppm) is shifted upfield ($\Delta\delta$ 250 ppm) with respect to the homoleptic (NBu₄)₂[Pt(C=CTol)₄] complex (δ CD₂Cl₂ –4187 ppm), the only available reference.^{13a}

X-ray Crystal Structures. Suitable crystals for X-ray diffraction studies were obtained for (NBu₄)₂[trans-Pt(C≡ $CC_6H_4CF_3-4)_2(CN)_2$ (2), $(NBu_4)_2[trans-Pt(C \equiv$ $(Np)_2(CN)_2$ (4) and $(NBu_4)[trans-Pt(C \equiv CNp)_2(CN) (C \equiv N^{t}Bu)$] (6) (see the Experimental Section), which crystallize with solvent molecules as $2 \cdot \frac{3}{4} (CH_3)_2 CO_2$ $4 \cdot \frac{2}{3}$ EtOH· $\frac{1}{3}$ H₂O, and $6 \cdot \frac{3}{4}$ (CH₃)₂CO, respectively. Perspective drawings of anions 2^{2-} , 4^{2-} , and 6^- are depicted in Figure 2. Table S1 (Supporting Information) shows the most important crystallographic information, and selected lengths and angles are summarized in Table 2. To our knowledge, these are the first structurally characterized examples of Pt complexes simultaneously containing these types of isoelectronic ligands, which show the expected structural details. The Pt centers were found to adopt essentially a trans-square-planar geometry with the C^{α}-Pt-C(CN or CN^tBu) angles close to 90° (89.4(2)-90.7(2)°). The Pt- C^{α} (acetylide) (1.999(7)-2.007(6) Å), Pt-C(CN) (1.989(7)-2.006(11) Å), and $C \equiv C$ bond lengths (1.187(12)-1.219(9) Å) do not differ significantly for the three complexes, with values comparable to those found in other mononuclear platinum(II) σ -alkynyl^{19,20} or cyanide⁶ complexes. In complex 6, the $Pt-C(CN^{t}Bu)$ bond displays the shortest distance (1.946(7) Å), but also lies within the range of other Pt-isocyanide complexes.²¹

In the dianions, both aryl (2^{2-}) and naphtyl (4^{2-}) groups are nearly perpendicular to the platinum coordination plane (89.2° (2), 89.9° (4)) but essentially coplanar between them (deviation angles 9.44° (2) and 0° (4); see Figure 2c). Not unexpectedly, in both complexes, the supramolecular crystal packing is deeply influenced by the presence of the two tetrabuthylammonium counterions,²⁴ which interact with the cyanide ligands through weak C–H…N (C…N = 3.11–3.45 Å, H…N = 2.33–2.51 Å, C–H…N = 169.3–118.5°) and T-shaped C–H… π (CN) (C…C = 3.40–3.54 Å, H…C = 2.64–2.81 Å,

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2, 4, and 6

| $2\cdot^{3}/_{4}(CH_{3})_{2}CO$ and $4\cdot^{2}/_{3}EtOH\cdot^{1}/_{3}H_{2}O$ | | | | | | | |
|---|--------------|---------------|-----------------------------------|----------------------------------|--|--|--|
| | | $2 \cdot 3/4$ | CH ₃) ₂ CO | $4\cdot^2/_3 EtOH\cdot^1/_3H_2O$ | | | |
| $Pt-C^{\alpha}$ | | 2.004(8) | | 2.000(9) | | | |
| Pt-C(CN) | | 1.992(10) |), 2.006(11) | 1.993(9) | | | |
| $C^{\alpha}-C^{\beta}$ | | 1.199(9) | | 1.187(12) | | | |
| C-N | | 1.145(12) |), 1.149(11) | 1.147(11) | | | |
| $Pt-C^{\alpha}-C^{\beta}$ | | 178.8(7) | | 178.0(11) | | | |
| Pt-C-N | | 180.0(8), | 180.0(9) | 178.9(8) | | | |
| $C^{\alpha}-C^{\beta}-C^{\gamma}$ | | 177.0(8) | | 178.4(12) | | | |
| C^{α} -Pt-C(Cl | N) | 89.4(2), 9 | 90.6(2) | 89.9(3), 90.1(3) | | | |
| C^{α} -Pt- C^{α} | | 178.8(4) | | 180.0(4) | | | |
| C(CN)-Pt- | C(CN) | 180.0(3) | | 180.000(1) | | | |
| | | 6 · (CH | 3)2CO | | | | |
| $Pt-C^{\alpha}$ | 1.9997(7), 2 | 2.001(7) | $C^{\alpha}-C^{\beta}$ | 1.210(9), 1.219(9) | | | |
| Pt-C26 | 1.989(7) | | C26-N1 | 1.159(8) | | | |
| Pt-C27 | 1.946(7) | | C27-N2 | 1.161(8) | | | |
| | | | | | | | |
| $Pt-C^{\alpha}-C^{\beta}$ | 179.0(7), 1 | 79.1(7) | C^{α} -Pt-C26 | 89.8(3), 90.1(3) | | | |
| Pt-C26-N1 | 176.6(6) | | C^{α} -Pt-C27 | 90.4(3), 89.7(3) | | | |
| Pt-C27-N2 | 177.7(6) | | C1-Pt-C13 | 178.3(3) | | | |
| $C^{\alpha}-C^{\beta}-C^{\gamma}$ | 172.5(8), 17 | 75.6(7) | C26-Pt-C27 | 177.0(3) | | | |
| | | | | | | | |

C−H···C = 148.3−124.5°; C···N = 3.35−3.55 Å, H···N = 2.63−2.90 Å, C−H···N = 129.6−115.6°) hydrogen interactions. The NBu₄⁺ cations also show C−H···π(aromatic or C≡C) bonding interactions with the arylacetylide ligands (aromatic C···C = 3.58−3.85 Å, H···C = 2.82−2.95 Å, C−H···C = 169.04−134.4°; acetylide C···C = 3.57−3.62 Å, H···C = 2.69−2.82 Å, C−H···C = 175.0−117.9°), to give, in the case of 4, an extended 3D architecture with channels of ca. 6.4 Å diameter along the crystallographic *c* axis (Figure S1, Supporting Information), which connect voids of 429 Å³ containing the ethanol and water crystallization molecules.

Curiously, in contrast with the mutually anti parallel orientation of both Np substituents seen in complex 4, in the heteroleptic monoanion 6^- , both Np groups adopt a syn disposition, oriented to the side of the bulkiest ligand (CN^tBu). In addition, as can be seen in Figure 2e, while one of the Np

Table 3. Absorption of 1–6 in CH_2Cl_2 (5 × 10⁻⁵ M) and 1–4 in a 70/30 MeOH/H₂O Mixture (5 × 10⁻⁵ M)

| | solvent | $abs/nm (10^3 \varepsilon/M^{-1} cm^{-1})$ |
|---|--|---|
| 1 | $CH_2Cl_2 (5 \times 10^{-5} M)$ | 235 (23.3), 264 sh (30.6), 276 (37.2), 318 (38.5), 327 sh (36.0) |
| | MeOH/H ₂ O (5 × 10 ⁻⁵ M) | 250 (39.4), 262 sh (29.5), 274 sh (23.5), 310 (22.8), 322 sh (19.3) |
| $[Pt(C \equiv CTol)_4]^{2-a}$ | CH ₂ Cl ₂ | 285 (49.5), 334 (38.6), 345 sh (34.8) |
| 2 | $CH_2Cl_2 (5 \times 10^{-5} M)$ | 231 (19.1), 266 (28.5), 286 (36.9), 327 (30.2), 344 sh (21.8) |
| | MeOH/H ₂ O (5 × 10 ⁻⁵ M) | 222 (18.0), 233 sh (14.6), 262 sh (20.4), 279 (25.0), 315 (23.2) |
| $[Pt(C \equiv CC_6H_4CF_3-4)_4]^{2-a}$ | CH_2Cl_2 | 309 (48.5), 350 (44.7), 365 sh (35.5) |
| 3 | $CH_2Cl_2 (5 \times 10^{-5} M)$ | 231 (22.5), 264 (25.4), 290 (38.7), 325 (30.0) |
| | $MeOH/H_2O~(5 \times 10^{-5} M)$ | 223 (15.6), 234 (13.3), 260 sh (13.7), 285 (21.6), 321 (22.7) |
| $[Pt(C \equiv CC_5H_4N-4)_4]^{2-a}$ | CH_2Cl_2 | 345 (48.4), 398 (34.0) |
| 4 | $CH_2Cl_2 (5 \times 10^{-5} M)$ | 233 (42.5), 252 (25.4), 285 (15.0), 366 (32.3) |
| | $MeOH/H_2O~(5 \times 10^{-5} M)$ | 225 (46.4), 243 sh (26.9), 275 (14.5), 293 sh (11.4), 340 (19.5), 350 (19.4) |
| $[Pt(C \equiv CNp)_4]^{2-b}$ | CH_2Cl_2 | 240 (54.96), 260 (38.91), 282 sh (25.49), 340 sh (26.32), 360 sh (35.72), 378 sh (43.32), 398 (51.47) |
| 5 | $CH_2Cl_2 (5 \times 10^{-5} M)$ | 232 (34.6), 247 (22.5), 272 (7.7), 311 (6.9), 359 (18.7) |
| 6 | $CH_2Cl_2 (5 \times 10^{-5} M)$ | 231 (26.6), 246 (18.7), 303 (5.2), 358 (17.4) |
| ^{<i>a</i>} See ref 19a. ^{<i>b</i>} See ref 13f. | | |

groups forms a small angle with the Pt coordination plane (deviation 33.5°), the second is nearly coplanar (deviation 7.4°). Inspection of the extended crystal structure (Figure S2, Supporting Information) reveals that, in contrast to the structures of the dianionic complexes 2 and 4, the presence of only one NBu₄⁺ counterion lets the monoanionic platinates get closer to each other. As a consequence, one aromatic hydrogen atom of the Np groups of different platinate units is involved in C–H···N hydrogen interactions (C···N = 3.38, 3.42Å; H…N = 2.53, 2.65 Å; C–H…N = 136.1, 158.4°) with the N of the cyanide ligand, which also supports a third C-H…N interaction (C···N = 3.59 Å, H···N = 2.63 Å, C-H···N = 169.7°) with the NBu₄⁺ cation. As can be seen in Figure S2 (Supporting Information), other types of noncovalent interactions, including C–H··· π (aromatic or C=C) and C–H···O, are observed. The sum of all these interactions could favor the distinct disposition in the solid state of the Np groups in 6 with respect to that observed for 2 and 4.

Photophysical Properties. The photophysical properties of the dianionic complexes $(NBu_4)_2[trans-Pt(C \equiv CR)_2(CN)_2]$ (1-4) are summarized in Tables 3 and 4. For comparison, the absorption data of the homoleptic derivatives $(NBu_4)_2$ Pt(C= $(CR)_4$ ^{19a} are also included in Table 3. Complexes 1–4 (Figure 3) display in CH₂Cl₂ intense high-energy absorptions (230-290 nm), which are likely of mixed configuration, including intraligand (¹IL C=CR), metal to ligand (C=CR, CN), and ligand to ligand (CN \rightarrow C \equiv CR) character. The broad absorption band located in the near-UV region, which lies out of the absorption range seen for $(NBu_4)_2[Pt(CN)_4]^{25}$ and is sensitive to the alkynyl substituent, is ascribed to transitions associated with the *trans*-Pt($C \equiv CR$)₂ fragment. On the basis of theoretical calculations (see below) and previous assignments in related complexes, ^{14a,19a,22b,26} this low-energy band is assigned to a mixed ¹IL/¹MLCT (π (C=CR)/d π (Pt) \rightarrow $\pi^*(C \equiv CR)$) transition, having a predominant intraligand character. This assignment is consistent with the trend found in its maximum (318 nm (1) > 325 nm (3) \approx 327 nm (2) > 366 nm (4)), which correlates with the energy of the $\pi^*(C \equiv CR)$ orbitals $(C_6H_4CH_3-4 > C_6H_4CF_3-4 \approx C_5H_4N-4 > Np).^{22}$ As detailed in Table 3 and illustrated in Figure S3 (Supporting Information), this band appears blue-shifted with respect to the related band in the corresponding homoleptic $(NBu_4)[Pt(C \equiv$ CR)₄] derivatives,^{13f,19a} most likely because of the stabilization of the Pt d(π) orbitals due to the coordination of the π - accepting CN ligands. This would lower the energy of the mixed alkynyl/Pt based HOMO and significantly raise the transition energy. Along the same lines, the lower negative charge in the naphthylacetylide derivatives **5** and **6** is reflected in the slight hypsochromic shift of ca. ~10 nm, observed in the low-energy band in comparison to **4**. However, in both complexes the profiles are essentially identical, indicating that the change of PPh₃ by CN^tBu has no significant effect on the transition energy. In these complexes, because of the presence of the extended aromatic naphthyl groups, the low-energy band would be predominantly located on the C≡C−Np chromophores.²⁷

Previous studies in polypyridyl cyano metalate complexes have shown that intermolecular $O-H(solvent) \cdots N \equiv C$ interactions exert a remarkable effect on the ¹MLCT absorption and ³MLCT emission bands.²⁸ These interactions increase the π acceptor ability of the CN groups and the ligand field strength at the metal center, giving rise to larger HOMO-LUMO gaps and inducing significant hypsochromic shifts in comparison to the case where such interactions are absent. Accordingly, we investigated the absorption spectra of complexes 1-4 in a MeOH/H₂O (70/30) mixture, and the data are given in Table 3. In all complexes there is a blue shift of the lowest energy manifold. The observed effect is relatively small in complexes 1 (475 cm^{-1}) and 3 (383 cm^{-1}) but significant in 2 (2676 cm^{-1}) and 4 (1249 cm^{-1}) (see Figure 4), which can be compared to that observed in $[Ir(ppy)_2(CN)_2]^-$ (1829 cm⁻¹).^{28e,f} These hypsochromic shifts are consistent with the decrease in the electron density around the Pt^{II} caused by the formation of cyanide-hydrogen bonding interactions, which could likely lower the energy of the mixed alkynyl/Pt HOMO and, hence, increase the transition energy.

The luminescence data, including emission wavelengths in rigid and fluid media (CH₂Cl₂, MeOH), lifetimes, and quantum yields in the solid state, are summarized in Table 4. All complexes exhibit luminescence in the solid state and in solution, at room and at low temperature, which is enhanced and is brighter at 77 K. As an illustration, the emission spectra for 1–4 in glassy media are shown in Figure 5 (CH₂Cl₂, 77 K) and Figure S4 (MeOH, 77 K; Supporting Information). The spectra display typical vibronically structured alkynyl based profiles, which in all cases are blue-shifted and better resolved at 77 K. With reference to previous works^{14a,19a,22b,26} and the long lifetimes observed, indicative of phosphorescence, the origin of

| complex | medium | T/K | $\lambda_{\rm em}/{ m nm}~(\lambda_{\rm ex}/{ m nm})~\{\phi/\%\}$ | $\tau/\mu s \ (\lambda_{em}/mm)$ |
|---------|--|-----|---|----------------------------------|
| 1 | solid | 298 | 452 max (137), 473 sh (348) {12} | 137 ± 1 (452) |
| | | 77 | 446 max, 467, 481, 493, 518 sh (341) | 296 ± 1 (467) |
| | $CH_2Cl_2 (10^{-3} M)$ | 298 | 445 max, 462 sh (345) | a |
| | | 77 | 437 max, 459, 469, 481, 501 sh (333) | 460 ± 1 (437) |
| | MeOH (10 ⁻³ M) | 298 | 440 max, 457, 479 sh (330) | |
| | | 77 | 434 max, 455, 476 sh (330) | |
| 2^b | $\begin{array}{c} {\rm CH_2Cl_2} \\ {\rm (10^{-3}~M)} \end{array}$ | 298 | 460 max, 470 sh (327) | 12.1 ± 0.7 (460) |
| | | 77 | 441 max, 467, 477, 491, 514 sh (330) | 16.2 ± 0.8 (447) |
| | MeOH (10 ⁻³ M) | 298 | 452 max, 471 (330) | |
| | | 77 | 446 max, 467, 488 (330) | |
| 3 | solid | 298 | 441 max, 458, 480, 504 sh (300–430) {21} | 13.3 ± 0.6 (441) |
| | | 77 | 439 max, 456, 465, 476, 501 (295–400) | 18.4 ± 1.2 (439) |
| | $\begin{array}{c} CH_2 Cl_2 \ (10^{-3} \ M) \end{array}$ | 298 | 440, 467 max (330) ^c | 15.1 ± 0.5 (440) |
| | | 77 | 431 max, 446 sh, 470 sh (330) | 17.5 ± 1.1 (431) |
| | MeOH (10 ⁻³ M) | 298 | 439 max, 460 sh (330) | |
| | | 77 | 434 max, 456, 471, 500 sh (330) | |
| 4 | solid | 298 | 552 max, 605, 662 (387) {4} | 8.6 ± 0.5 (552) |
| | | 77 | 557 max, 605, 654 (300–420) | 120 ± 1 (557) |
| | $\begin{array}{c} {\rm CH_2Cl_2} \\ {\rm (10^{-3}~M)} \end{array}$ | 298 | 552 max, 596, 640 sh (388) | 8.5 ± 0.7 (552) |
| | | 77 | 548 max, 560 sh, 596, 612 sh, 641 (375, 400–450) | 48.9 ± 1.1 (548) |
| | MeOH (10 ⁻³ M) | 298 | 543, 590 sh (365) | |
| | | 77 | 540 max, 551 sh, 584, 599 sh, 632 (365) | |
| 5 | solid | 298 | 545 max, 618 br (365) | а |
| | | 77 | 551, 588 max, 630 sh (400) | 175 ± 2 (585) |
| | $\begin{array}{c} CH_2 Cl_2 \ (10^{-3} \ M) \end{array}$ | 298 | 547 max, 591, 632 sh (386, 426) | 7.2 ± 0.9 (547) |
| | | 77 | 545 max, 558 sh, 591 (375) | 242 ± 1 (545) |
| 6 | solid | 298 | 545 max, 590, 650 (380) | а |
| | | 77 | 547, 576 br (380) | 83.0 ± 1.3 (547) |
| | $\begin{array}{c} CH_2Cl_2 \\ (10^{-3} \text{ M}) \end{array}$ | 298 | 545 max, 588, 627 (378) | 8.5 ± 0.3 (545) |
| | | 77 | 544 max, 558 sh, 592 (378) | 43.7 ± 0.8 (544) |
| | | | _ | |

| Table 4. E | Emission | Properties o | f 1–6 i | n the | Solid | State | and in |
|------------|--------------|---------------------|-----------------------------|-------|-------|--------|--------|
| Solution | (CH_2Cl_2) | and MeOH, | , 10 ⁻³] | M) at | 298 | and 7' | 7 K |

^{*a*}Too weak for an accurate measurement. ^{*b*}Oily sample, not measured in the solid state. ^{*c*}A weak fluorescence band at 409 nm is also observed.

the emission is ascribed to a mixed ${}^{3}\text{IL}(\pi \rightarrow \pi^{*}(C \equiv CR))/{}^{3}\text{MLCT}(d\pi(Pt) \rightarrow \pi^{*}(C \equiv CR))$ excited state, having a predominant intraligand character. Accordingly, the emission energies were found to be sensitive to the alkynyl substituent. The aryl (1, 2) and pyridyl (3) derivatives emit in the blue region, following the energy order 3 > 1 > 2 in CH₂Cl₂ at 77 K



Figure 3. Absorption spectra of complexes 1 (black), 2 (green), 3 (blue), and 4 (orange) in CH_2Cl_2 (5 × 10⁻⁵ M).



Figure 4. Absorption spectra of complexes 2 (green) and 4 (orange) in CH₂Cl₂ (5 × 10⁻⁵ M) (solid line) vs MeOH/H₂O (70:30, 5 × 10⁻⁵) (dashed line), highlighting the energetic difference between the lowest energy absorptions in each solvent.



Figure 5. Normalized emission spectra of 1 (black), 2 (green), 3 (blue), and 4 (orange) in $\rm CH_2Cl_2$ (10 $^{-3}$ M) at 77 K.

(431 nm (3), 437 nm (1), 441 nm (2)) and $3 \approx 1 > 2$ in MeOH at 77 K (434 nm (1, 3) > 446 nm (2)). The observed lower energy emission in the *p*-trifluoromethylphenyl derivative 2 related to those of 1 and 3 is consistent with the involvement of the $\pi^*(C \equiv CR)$ character in the LUMO. Obviously, the presence of the two low-lying extended polyaromatic napthyl groups in complexes 4-6 lowers the energy of the transition, thus inducing a remarkable red shift of the emission. The nearly

identical yellow-orange emission bands found for complexes 4-6 (Figure 6) are suggestive of an emissive state of mainly ³IL



Figure 6. Normalized emission spectra of 4 (orange), 5 (violet), and 6 (pink) in CH_2Cl_2 (10⁻³ M) at 77 K.

character. However, the slight bathochromic shift in the dianionic complex 4 in relation to 5 and 6 (see Table 4) reflects the increase of electronic density on the Pt^{II} atom, which is generally involved in the π system of the HOMO; thus, the emission of 4-6 has also some ³MLCT character, as has been further supported by TD-DFT calculations (vide infra). It is worth noting that, in comparison with the emission observed for the homoleptic complexes $(NBu_4)_2[Pt(C \equiv CR)_4]$ $(\lambda_{\text{max}}/\text{nm CH}_2\text{Cl}_2, 77 \text{ K}: 447 \text{ (R = Tol)}, 463 \text{ (R = C_6H_4CF_3-4)},$ 471 (R = C₅H₄N-4), 565 (R = Np)), the emissions of 1-4 are significantly blue-shifted to higher energies. The change of two electron-rich alkynyl fragments for cyanide ligands stabilizes the $d\pi(Pt^{II})$ orbitals, which, by orbital mixing, stabilizes the Ptalkynyl-based HOMO, thus increasing the gap of the transition. The measured lifetimes and quantum yields for 1-4 in the solid state are relatively longer than those reported for $[Pt(C \equiv$ $(CR)_4$ ²⁻, a result which is indicative of a greater intraligand contribution in the mixed ³IL/³MLCT manifold. We have also examined the emissions of 1-4 in MeOH as solvent. As can be

observed in Table 4, only slight blue shifts were observed for the bis(cyanide) derivatives 1–4 in fluid methanol relative to CH_2Cl_2 (5 nm (411 cm⁻¹), 1; 8 nm (385 cm⁻¹), 2; 1 nm (52 cm⁻¹), 3; 9 nm (300 cm⁻¹), 4). This fact is not unexpected and has been also previously observed in ³MLCT emissions of cyanopolypyridyl d⁶ systems.²⁸ The lesser solvent dependence in the emission relative to the absorption has been attributed to the fact that the electron density on the CN ligands is smaller in the triplet than in the singlet state and, hence, the direct donor–acceptor CN···H(solvent) interactions are weaker in the triplet state.

Theoretical Calculations. In order to get a further insight into the photophysics of these complexes, theoretical calculations were performed for 4 and 6. The absorption and emission spectra of both complexes were examined on the optimized geometries (for the S_0 and T_1 states) of the corresponding anions of both complexes at the B3LYP/ LanL2DZ(Pt)/6-31G**(ligand atoms) level. The equilibrium geometries, the coordinates, and the most important geometrical parameters, together with the experimental values for comparison, are given in the Supporting Information (Tables S2-S6). In the anion 4^{2-} , the optimized ground-state geometry is in fair agreement with the structural data, with both Np groups coplanar and orthogonal to the NC-Pt-CN axis (see Figure S5, Supporting Information). In the case of the monoanion 6^- , the X-ray analyses show that both Np groups adopt a syn disposition, with deviation angles of 33.5 and 7.40° to the Pt coordination plane. That disposition, with both Np groups oriented toward the most bulky ligand and the difference from the disposition observed in complex 4, incited us to perform geometry optimizations using as starting points three different geometries of 6^- . When the starting structure of 6^{-} had both Np groups oriented toward the CN ligands, the geometry optimization resulted in a transition state structure with both Np ligands almost coplanar with the Pt coordination plane. When the optimizations were performed starting from the X-ray data (Np groups oriented toward the CN^tBu ligand) or starting with both Np groups orthogonal to the Pt coordination plane (as observed in the X-ray structure of 4), two different energy minima were found (see Figure S6,



Figure 7. Experimental UV-vis spectra in CH_2Cl_2 (5 × 10⁻⁵ M) and calculated absorption spectra (blue bars) in CH_2Cl_2 together with frontier orbital plots obtained by DFT, for (a) 4 and (b) 6.

Organometallics

Supporting Information), as established by subsequent frequency calculations. As the two obtained minimum are close in energy ($\Delta E = 0.67$ kcal/mol), we carried out TD-DFT calculations with both geometries. The calculated absorption spectrum obtained using the geometry with both Np groups oriented orthogonal to the NC-Pt-CNC axis fits better with the experimental UV-vis spectrum, even though the interpretation of this is not straightforward. The distances and angles of the ground-state optimized structure compare well with the X-ray data obtained for complex 6 (see Table S6), the only remarkable difference being the angles between the Np groups and the Pt coordination plane (86.77, 73.86° in S_0 vs 7.4, 33.5° in the X-ray structure). Some selected frontier molecular orbitals of both anions are depicted in Figures S7 and S8 (Supporting Information), and the composition in terms of ligands and metals are collected in Table S7 (Supporting Information). For comparison, the recently reported data of the anion 1^{2-} have been also included. The HOMOs of all complexes are delocalized over the platinum and the acetylide ligands, with a higher contribution of the Pt center in both dianionic derivatives (41% (1), 43% (4)) than in the monoanionic derivative (9% (6)), thus reflecting the influence of the charge of the anion. The LUMOs are mainly centered on the alkynyl fragments (98% (1), 99% (4 and 6)). The next lowenergy unoccupied orbitals in 1 and 4 are also centered on the alkynyl fragments (from LUMO+1 to LUMO+3 in 1; from LUMO+1 to LUMO+5 in 4); whereas in 6 LUMO+1 is localized on the alkynyl moieties, but LUMO+2 is delocalized on the alkynyl (11%), isocyanide (49%), and Pt center (34%). To examine the UV-vis absorption spectra, the lowest lying vertical singlet excitation energies were calculated by TD-DFT calculations with the consideration of the solvation effect (CH₂Cl₂) using the PCM method. Data including energy gaps (nm) and corresponding assignments of the transitions with strong oscillator strengths are given in Table S8 (Supporting Information). As can be seen in Figure 7, the computed lowest energy transitions at 372 nm (4) and 354 nm (6) closely resemble the observed experimental bands (366 nm (4), 358 nm (6)). These transitions mainly arise from the HOMO \rightarrow LUMO excitation (89% (4), 72% (6)); therefore, the lowest lying absorption can be assigned as a mixture of ¹IL/¹MLCT transitions in both derivatives, with a stronger MLCT character in 4.

The nature of the phosphorescent emission was addressed by optimization of the first triplet state of the anions of 4 and 6. For 4^{2-} , the geometrical parameters of the computed triplet state are similar to those found for the corresponding ground state (Table S6, Supporting Information). However, in the case of 6^- the anion adopts a more planar configuration in the optimized T1 state, pointing to a higher degree of conjugation in relation to the nonplanar S₀ ground state. The SOMO and SOMO-1 of both anions are depicted in Figure 8, together with their composition in terms of metal and ligands. The lowest energy emission calculated as ΔE_{T1-S0} at 515.2 nm (4) and 600.0 nm (6) are qualitatively close to the experimental values (552 nm (4), 545 nm (6)). The compositions of the singly occupied orbitals are mainly centered on the alkynyl fragments in both complexes (89–99%), suggesting an essentially ³IL character of the emission, although the participation of the Pt center in SOMO-1 (11% (4), 7% (6)) confirms some ³MLCT character. Therefore, the emission can be assigned as an ³IL/³MLCT mixture of transitions.



Figure 8. Frontier orbital plots obtained by DFT for the first triplet state of the anions of complexes 4 and 6.

CONCLUSIONS

In summary, a method of generating stable anionic transconfigured heteroleptic alkynyl platinate complexes [trans- $Pt(C \equiv CR)_2(CN)_2]^{2-}$ is reported. Neutral *trans*-bis(alkynyl)bis(triphenylphosphine) platinum(II) substrates were reacted with (NBu₄)CN, producing the disubstituted dianionic complexes with retention of the configuration, through the monoanionic $[trans-Pt(C \equiv CR)_2(CN)(PPh_3)]^-$ as intermediate species. As illustration, the naphthylacetylide derivative (5, R = Np) was isolated and has allowed us to access to (NBu_4) [*trans*-Pt(C=CNp)₂(CN)(CN^tBu)] (6) by subsequent displacement of the phosphine ligand. Their spectroscopic and photophysical properties were examined and compared to those found for the homoleptic $[Pt(C \equiv CR)_4]^{2-}$ derivatives, which has demonstrated that substitution of two alkynyl ligands for two π -acceptor groups produces a stabilization of the platinum-alkynyl-based HOMO $Pt(d\pi)/\pi(C \equiv CR)$, giving rise to a significant blue shift in both the absorption and emission. The arylacetylide compounds 1-3 display bright blue emissions and the naphthylacetylide compounds 4-6 orange emissions, originating mainly from a mixed ${}^{3}\text{IL}(\pi \rightarrow \pi^{*}\text{C})$ $CR)/^{3}MLCT(5d(Pt) \rightarrow \pi^{*}C \equiv CR)$ excited state with predominant intraligand character. According to TD-DFT calculations, the metal to ligand (acetylide) charge transfer contribution decreases with the charge of the anion on going from $[trans-Pt(C \equiv CR)_2(CN)_2]^{2-}$ (4²⁻) to $[trans-Pt(C \equiv CR)_2(CN)_2]^{2-}$ $CR)_2(CN)(CN^tBu)]$ (6⁻).

It is hoped that these new platinate systems, having three distinct basic sites (Pt, $C \equiv CR$, and CN), will behave as excellent building blocks for the design of novel high-dimensionality systems. The interaction of these modular chromophoric precursors with different cations or electrophilic fragments will stimulate future investigations aiming to generate or even harness new interesting and useful properties.

EXPERIMENTAL SECTION

Materials and Methods. All reactions were carried out under Ar using dried solvents purified by known procedures and distilled prior to use. IR spectra were recorded on a FT-IR Nicolet Nexus spectrometer as Nujol mulls between polyethylene sheets, and NMR spectra were recorded on Bruker ARX 300 and DRX 400 spectrometers. Chemical shifts are reported in ppm relative to external standards (SiMe₄, CFCl₃, and 85% H₃PO₄). Elemental analyses were carried out with a Perkin-Elmer 2400 CHNS/O microanalyzer, and MALDI-TOF spectra on a Microflex MALDI-TOF Bruker spec-

trometer operating in the linear and reflector modes using dithranol as matrix. Conductivities were measured in acetone solutions (ca. 5 × 10^{-4} mol L⁻¹) using a Crison GLP31 conductimeter. UV-vis absorption spectra were recorded on a Hewlet-Packard 8453 spectrometer. Excitation and emission spectra were obtained on a Jobin-Yvon Horiba Fluorolog 3-11 Tau-3 spectrofluorimeter. The lifetime measurements were performed operating in the phosphorimeter mode using a 450 W Xe lamp (with a F1-1029 lifetime emission photomultiplier tube assembly). Lifetime measurement errors, which correspond to deviation of the experimental data with respect to the theoretical decay function, are included in Table 4. Quantum yields in the solid state were measured using a F-3018 Integrating Sphere mounted on a Fluorolog 3-11 Tau-3 spectrofluorimeter. The estimated relative error of the quantum yields is about 10%. Emission data have been fitted using the Jobin Yvon software package and Origin 5. Literature methods were used to prepare the starting materials [trans- $Pt(C \equiv CR)_2(PPh_3)_2$, ^{18,29} and other reagents were obtained from commercial sources.

Data for the complex [*trans*-Pt(C=CC₆H₄CF₃-4)₂(PPh₃)₂] are as follows. ¹H NMR (δ , 300.13 MHz, CDCl₃, 293 K): 7.76 (m, 12H, H^{2.6}, PPh₃), 7.35 (m, 18H, PPh₃), 7.11 (d, J = 8.1 Hz, 4H, C₆H₄, C₆H₄CF₃-4), 6.28 (d, J = 8.1 Hz, 4H, C₆H₄, C₆H₄CF₃-4), 6.28 (d, J = 8.1 Hz, 4H, C₆H₄, C₆H₄CF₃-4). ³¹P{¹H} NMR (δ , 121.5 MHz, CDCl₃, 293 K): 18.9 (s, ¹ $J_{P-Pt} = 2620$ Hz, P, PPh₃). ¹⁹F{¹H} NMR (δ , 282.4 MHz, CDCl₃, 293 K): -136.2 (s, CF₃, C₆H₄CF₃-4).

Data for the complex $[trans-Pt(C \equiv CNp)_2(PPh_3)_2]$ are as follows. IR (cm⁻¹): ν (C \equiv C) 2098 (vs). ¹H NMR (δ , 300.13 MHz, CDCl₃, 293 K): 7.87 (d, J = 5.2 Hz, 12H, H^{2,6}, PPh₃), 7.58 (d, J = 8.0 Hz, 2H, H², Np), 7.41 (d, J = 8.1 Hz, 2H, Np), 7.29–7.20 (m, 2H, Np overlapped with 18H, PPh₃), 7.16 (d, J = 8.3 Hz, 2H, Np), 7.03 (m, 2H, Np), 6.93 (m, 2H, Np), 6.35 (d, J = 7.1 Hz, 2H, Np). ³¹P{¹H} NMR (δ , 121.5 MHz, CDCl₃, 293 K): 18.8 (s, ¹J_{P-Pt} = 2648 Hz, P, PPh₃).

X-ray Crystallography. Details of the structural analyses for all complexes are summarized in Table S1 (Supporting Information). Colorless crystals of complex 2 were obtained by slow evaporation of a saturated acetone solution of the complex. Pink (4) or white (6) crystals were obtained by slow diffusion of Et₂O into EtOH (4) or acetone (6) saturated solutions of the corresponding compound. X-ray intensity data were collected with a NONIUS-KCCD area-detector diffractometer, using graphite-monochromated Mo K α radiation. Images were processed using the DENZO and SCALEPACK suite of programs,³⁰ and the absorption corrections were performed with MULTI-SCAN³¹ (2 and 4) or XABS³² (6), using the program suite WINGX.33 The structures were solved by direct methods using SHELXS-97³⁴ and refined by full-matrix least squares on F^2 with SHELXL-97.³⁴ All non-hydrogen atoms were assigned anisotropic displacement parameters. All the hydrogen atoms were constrained to idealized geometries, fixing isotropic displacement parameters 1.2 times the U_{iso} value of their attached carbon for the aromatic and 1.5 times that value for the methyl groups. For complexes 2 and 4, disordered crystallization molecules of acetone (2) or ethanol and water (4) were observed. Despite many attempts, we could not resolve the disorders adequately.

Thus, we have used the SQUEEZE program³⁵ as an alternative to the modeling of the solvent. For the structure of complex **2**, the use of SQUEEZE revealed the existence in the unit cell of four voids of 157 Å³ containing 23 e each, which fits well with the presence of 0.75 acetone molecules in each of them. In the case of **4**, the presence of three voids of 430 Å³ with 63 e (which fits well for two molecules of ethanol and one water in each void) were observed. Therefore, we have included them as crystallization solvents in the corresponding empirical formula, to give the final stoichiometries $2 \cdot 3/_4 (CH_3)_2 CO$ and $4 \cdot 2/_3 EtOH \cdot 1/_3 H_2 O$. Complex **6** also crystallizes with 0.75 molecules of acetone ($6 \cdot 3/_4 (CH_3)_2 CO$). In both cases, several restraints have been used to model the NBu₄ counteranion, and the three structures present some residual peaks greater than 1 e A⁻³, but without chemical meaning.

Computational Details for DFT Calculations. DFT calculations were performed on the anions of complexes **4** and **6** with Gaussian 09 (revision B.01).³⁶ Geometries in the S⁰ ground state were optimized using the B3LYP method and in the T¹ excited state using the unrestricted U-B3LYP (T¹) Becke three-parameter functional combined with the Lee–Yang–Parr correlation functional.³⁷ In the case of 6⁻, the geometry of the ground state was optimized starting from three different geometries. No negative frequency was found in the vibrational frequency analysis of the final equilibrium geometries. The basis set used for the platinum centers was the LanL2DZ effective core potential³⁸ and 6-31G(d,p) for the ligand atoms. The solvent effect of dichloromethane in the TD-DFT calculations was taken into consideration by the polarizable continuum model (PCM).³⁹

Preparation of (NBu₄)₂[trans-Pt(C=CTol)₂(CN)₂] (1). (NBu₄)-CN (0.268 g, 1 mmol) was added to a suspension of trans-Pt(C≡ $(CTol)_2(PPh_3)_2$ (0.475 g, 0.5 mmol) in acetone. After 1 h of stirring at room temperature, a yellow solution was obtained. The solvent was removed under vacuum and the yellow oily residue treated with ~ 30 mL of Et₂O. The mixture was stirred for 1 h, which dissolved free PPh₃ and caused the separation of 1 as a pale -yellow solid. The solid was filtered off and repeatedly washed with Et₂O (0.414 g, 86%). Anal. Calcd for C₅₂H₈₆N₄Pt (962.36): C, 64.90; H, 9.01; N, 5.82. Found: C, 64.85; H, 8.74; N, 6.02. MS MALDI(-): m/z 719.3 ([M - NBu₄]⁻, 49%), 477.0 ($[M - 2NBu_4]^-$, 100%). IR (cm⁻¹): ν (C \equiv N) 2114 (vs), ν (C \equiv C) 2093 (vs). ¹H NMR (δ , 300.13 MHz, CDCl₃, 293 K): 7.15 $(d, J = 7.8 Hz, 4H, C_6H_4, Tol), 6.90 (d, J = 7.8 Hz, 4H, C_6H_4, Tol),$ 3.43 (m, 16H, NCH₂, NBu₄), 2.23 (s, 6H, CH₃, Tol), 1.66 (m, 16H, CH₂, NBu₄), 1.50 (m, 16H, CH₂, NBu₄), 0.94 (t, 24H, CH₃, NBu₄). ¹³C{¹H} NMR (δ, 100.14 MHz, CD₃COCD₃, 293 K): 133.0 (s, C⁴, Tol), 131.8 (s, CH, ${}^{4}J_{C-Pt} \approx 9$ Hz, Tol), 129.7 (s, C¹, ${}^{3}J_{C-Pt} \approx 24$ Hz, Tol), 129.7 (s, C-CN, ${}^{1}J_{C-Pt} = 1029$ Hz, CN), 129.1 (s, CH, Tol), 111.9 (s, ${}^{1}J_{C-Pt} = 934$ Hz, C_a, C \equiv C), 104.0 (s, ${}^{2}J_{C-Pt} = 255$ Hz, C_b C=C), 59.6 (s, N-CH₂, NBu₄), 24.9 (s, $-CH_2$ -, NBu₄), 21.3 (s, -CH₃, Tol), 20.5 (s, -CH₂-, NBu₄), 14.2 (s, -CH₃, NBu₄). ¹⁹⁵Pt NMR (δ, 85.68 MHz, CDCl₃, 293 K): -4437.67. Λ_M ((CH₃)₂CO): 174.5 $\dot{\Omega}^{-1}$ cm² mol⁻¹

Preparation of $(NBu_4)_2[trans-Pt(C \equiv CC_6H_4CF_3-4)_2(CN)_2]$ (2). This complex was prepared in a way similar to that described for 1, starting from trans-Pt(C=CC₆H₄CF₃-4)₂(PPh₃)₂ (0.600 g, 0.57 mmol) and (NBu₄)CN (0.608 g, 2.28 mmol). In this case, the reaction mixture was stirred for 15 min. The solvent was removed under vacuum, and the complex was extracted with a CH₂Cl₂/H₂O mixture (20/20). The dichloromethane solution was dried with anhydrous MgSO4 and filtered through Celite. The filtrate was evaporated to dryness, and ~10 mL of a CH₂Cl₂/MeOH/hexane mixture ($\sim 1/19/80$) was added to the flask. The slow evaporation (up to 7 days) of this mixture at -30 °C caused the crystallization of 2 as an oily solid. This solid was filtered, washed with cold hexane, and dried (0.244 g, 40%). Anal. Calcd for $C_{52}H_{80}N_4F_6Pt$ (1070.30): C, 58.35; H, 7.53; N, 5.23. Found: C, 58.54; H, 7.91; N, 5.05. MS MALDI(–): m/z 827.3 ([M – NBu₄]⁻, 21%), 585.0 ([M – 2NBu₄]⁻, 51%). IR (cm⁻¹): ν (C \equiv N) 2111 (vs) ν (C \equiv C) 2088 (vs). ¹H NMR $(\delta, 300.13 \text{ MHz}, \text{CD}_3\text{COCD}_3, 293 \text{ K})$: 7.45 (d, J = 7.9 Hz, 4H, C₆H₄, $C_6H_4CF_{3}-4$), 7.34 (d, J = 7.9 Hz, 4H, C_6H_4 , $C_6H_4CF_{3}-4$), 3.51 (m, 16H, NCH₂, NBu₄), 1.81 (m, 16H, CH₂, NBu₄), 1.47 (m, 16H, CH₂, NBu₄), 0.96 (t, 24H, CH₃, NBu₄). ¹⁹F NMR (282.4 MHz, CD_3COCD_3 , 293 K): -145.6 (s, CF_3 , $C_6H_4CF_3$ -4). ¹³C{¹H} NMR (δ, 100.14 MHz, CD₃COCD₃, 293 K): 135.8 (s, C¹, C₆H₄CF₃-4), 131.8 (s, CH, C₆H₄CF₃·4), 128.2 (s, C-CN, ${}^{1}J_{C-Pt} = 1032$ Hz, CN), 125.7 (q, CF₃, ${}^{1}J_{C-F} = 271$ Hz, C₆H₄CF₃·4), 125.1 (s, CH, C₆H₄CF₃·4), 125.1 (q, ${}^{2}J_{C-F} = 32$ Hz, C⁴, C₆H₄CF₃·4), 119.0 (s, ${}^{1}J_{C-Pt} = 934$ Hz, C_a, C \equiv C), 104.2 (s, ${}^{2}J_{C-Pt} = 279$ Hz, C⁶, C \equiv C), 59.2 (s, N-CH₂) NBu₄), 24.5 (s, $-CH_2-$, NBu₄), 20.2 (s, $-CH_2-$, NBu₄), 13.9 (s, $-CH_3$, NBu₄). ¹⁹⁵Pt NMR (δ , 85.68 MHz, CDCl₃, 293 K): -4439.4. $\Lambda_{\rm M}$ ((CH₃)₂CO): 180.2 Ω^{-1} cm² mol⁻¹

Preparation of (NBu_4)_2[trans-Pt(C \equiv CC_5H_4N-4)_2(CN)_2] (3). This complex was prepared in a way similar to that for 2 starting from *trans-*Pt(C \equiv CC_5H_4N-4)_2(PPh_3)_2 (0.500 g, 0.52 mmol) and (NBu_4)CN (0.556 g, 2.08 mmol). In this case, after the extraction with CH_2Cl_2/H_2O, the white oily residue was treated with an *i*-PrOH/Et₂O mixture (5/95) to give 3 as a white solid (0.212 g, 42%). Anal. Calcd for C₄₈H₈₀N₆Pt (936.28): C, 61.58; H, 8.61; N, 8.98. Found: C, 61.95; H, 8.92; N, 9.12. MALDI(–): m/z 693.2 ([M – NBu₄]⁻, 80%), 451.0 ([M – 2NBu₄]⁻, 100%). IR (cm⁻¹): ν (C \equiv N) 2111 (vs), ν (C \equiv C) 2097 (vs). ¹H NMR (δ , 300.13 MHz, CDCl₃, 293 K): 8.30 (d, J = 5.5 Hz, 4H, C₅H₄, C₅H₄N-4), 7.08 (d, J = 5.5 Hz, 4H, C₅H₄, C₅H₄N-4), 3.39 (m, 16H, NCH₂, NBu₄), 1.67 (m, 16H, CH₂, NBu₄), 1.50 (m, 16H, CH₂, NBu₄), 0.94 (t, 24H, CH₃, NBu₄). ¹³C{¹H} NMR (δ , 100.14 MHz, CD₃COCD₃, 293 K): 149.6 (s, CH, C₅H₄N-4), 139.0 (s, C¹, ⁴ J_{C-Pt} = 24 Hz, C₅H₄N-4), 127.8 (s, C-CN, ¹ J_{C-Pt} = 1031 Hz, CN), 126.4 (s, CH, C₅H₄N-4), 122.4 (s, ¹ J_{C-Pt} = 967 Hz, C_a, C \equiv C), 103.5 (s, ² J_{C-Pt} = 279 Hz, C_β, C \equiv C), 59.5 (s, N–CH₂, NBu₄), 24.7 (s, -CH₂-, NBu₄), 20.3 (s, -CH₂-, NBu₄), 14.0 (s, -CH₃, NBu₄). ¹⁹⁵Pt NMR (δ , 85.68 MHz, CDCl₃, 293 K): -4427.1. Λ_M ((CH₃)₂CO): 169.7 Ω⁻¹ cm² mol⁻¹.

Preparation of (NBu₄)₂[trans-Pt(C=CNp)₂(CN)₂] (4). This complex was prepared in a way similar to that for 2, starting from trans-Pt(C \equiv CNp)₂(PPh₃)₂ (1.250 g, 1.22 mmol) and (NBu₄)CN (1.5 g, 4.88 mmol). An oily pink residue was obtained, which was treated with *i*-PrOH (~10 mL) and Et_2O (~20 mL), giving rise to 4 as a pink solid (0.723 g, 57%). Anal. Calcd for C₅₈H₈₆N₄Pt (1034.43): C, 67.35; H, 8.38; N, 5.42. Found: C, 67.84; H, 8.40; N, 5.30. MALDI(-): m/z 791.4 ([M - NBu₄]⁻, 73%), 549.1 ([M - 2NBu₄]⁻, 100%). IR (cm⁻¹): ν (C \equiv N) 2107 (vs), ν (C \equiv C) 2079 (vs). ¹H NMR (δ, 300.13 MHz, CD₃COCD₃, 293 K): 8.99 (d, J = 7.9 Hz, 2H, H⁴, Np), 7.74 (d, J = 8.2 Hz, 2H, H², Np), 7.52 (d, J = 8.0 Hz, 2H, Np), 7.45-7.30 (m, 6H, Np), 7.28 (m, 2H, Np), 3.48 (m, 16H, Np), 7.43–7.30 (iii, 6H, 1P), 7.26 (iii, 21, Np), 3.46 (iii, 6H, 1P), NE4, NB4, 1.42 (m, 16H, CH₂, NB4), 1.74 (m, 16H, CH₂, NB4), 1.42 (m, 16H, CH₂, NB4), 0.88 (t, 24H, CH₃, NB4). $^{13}C{}^{1}H$ NMR (δ , 100.14 MHz, CD₃COCD₃, 293 K): 136.1 (s, C¹, $^{3}J_{C-P1} \approx 6$ Hz, Np), 134.7 (s, C, Np), 130.1 (s, C, Np), 129.9 (s, CH, Np), 128.7 (s, C-CN, ${}^{1}J_{C-Pt} =$ 1028 Hz, CN), 128.4 (s, CH, Np), 128.1 (s, CH, ${}^{4}J_{C-Pt} \approx 10$ Hz, Np), 126.4 (s, CH, Np), 126.3 (s, CH, Np), 125.8 (s, CH, Np), 124.2 (s, CH, Np), 120.1 (s, ${}^{1}J_{C-Pt} = 970$ Hz, $\hat{C}_{\alpha\nu}$ C=C), 102.6 (s, ${}^{2}J_{C-Pt} = 278$ Hz, C_{β} , $C \equiv C$), 59.6 (s, N-CH₂, NBu₄), 24.6 (s, -CH₂-, NBu₄), 20.5 (s, -CH₂-, NBu₄), 14.2 (s, -CH₃, NBu₄). ¹⁹⁵Pt{¹H} NMR (δ , 85.68 MHz, CDCl₃, 293 K): -4417.4. $\Lambda_{\rm M}$ ((CH₃)₂CO): 171.1 Ω^{-1} cm² mol⁻¹

Preparation of (NBu₄)[trans-Pt(C=CNp)₂(CN)(PPh₃)] (5). (NBu₄)CN (0.079 g, 0.294 mmol) was added to a suspension of trans-Pt(C \equiv CNp)₂(PPh₃)₂ (0.300 g, 0.294 mmol) in acetone and the mixture stirred for 15 min. The solution that was obtained was filtered through Celite and the solvent removed to dryness. The residue that was obtained was stirred with i-Pr₂O (~20 mL), which dissolves free PPh₃ and causes the precipitation of a white solid. This solid was filtered off, washed with i-PrOH and Et₂O, and labeled as 5 (0.140 g, 46%). Anal. Calcd for C₅₉H₆₅N₂PPt (1028.23): C, 68.92; H, 6.37; N, 2.72. Found: C, 69.10; H, 6.50; N, 2.95. MALDI(-): m/z 785.1 ([M − NBu₄]⁻, 100%). IR (cm⁻¹): ν (C≡N) 2129 (s), ν (C≡C) 2100 (s), 2088 (s). ¹H NMR (δ , 300.13 MHz, CD₃COCD₃, 293 K): 8.35 (d, *J* = 8.0 Hz, 2H, H⁴, Np), 7.89 (m, 6H, PPh₃), 7.70 (d, J = 7.9 Hz, 2H, H², Np), 7.51 (d, J = 8.2 Hz, 2H, Np), 7.45-7.25 (m, 4H, Np overlapped with 9H, PPh₃), 7.21 (m, 2H, Np), 7.03 (d, J = 7.0 Hz, 2H, Np), 3.49 (m, 8H, NCH₂, NBu₄), 1.74 (m, 8H, CH₂, NBu₄), 1.39 (m, 8H, OCH₂, NBu₄), 0.82 (t, 12H, CH₃, NBu₄). ³¹P{¹H} (δ , 121.5 MHz, CD₃COCD₃, 293 K): 14.4 (s, ¹J_{P-Pt} = 2686 Hz, P, PPh₃). ³¹P{¹H} NMR (δ , 300.13 MHz, CDCl₃, 293 K): 13.7 (s, ¹J_{P-Pt} = 2709 Hz, P, Ph₃). PPh₃). $\Lambda_{\rm M}$ ((CH₃)₂CO): 98.5 Ω^{-1} cm² mol⁻¹

Preparation of (NBu₄)[*trans*-Pt(C=CNp)₂(CN)(C=N^tBu)] (6). A high excess of CN^tBu (77 μ L, 0.68 mmol) was added to a solution of **5** (0.070 g, 0.068 mmol) in distillated acetone (10 mL). The mixture was stirred for 5 h at room temperature, and the solvent was removed under vacuum. Stirring in the presence of Et₂O (20 mL) dissolved free PPh₃ and caused the precipitation of **6** as a white solid (0.050 g, 86%). Anal. Calcd for C₄₆H₅₉N₃Pt (849.07): C, 65.07; H, 7.00; N, 4.95. Found: C, 65.51 H, 7.17; N, 5.12. MALDI(-): m/z606.2 ([M - NBu₄]⁻, 100%). IR (cm⁻¹): ν (C=N^tBu) 2209 (s), ν (C=N) 2133 (s), ν (C=C) 2105 (s), 2092 (s). ¹H NMR (δ , 400 MHz, CD₃COCD₃, 293 K): 8.79 (dd, J = 8.1 Hz, J = 0.7 Hz, 2H, H⁴, Np), 7.80 (d, J = 7.8 Hz, 2H, H², Np), 7.61 (d, J = 8.2 Hz, 2H, Np), 7.51–7.43 (m, 6H, Np), 7.34 (dd, J = 8.0 Hz, J = 7.3 Hz, 2H, Np), 3.46 (m, 8H, NCH₂, NBu₄), 1.82 (m, 8H, CH₂, NBu₄), 1.65 (s, 9H) ¹Bu), 1.43 (m, 8H, CH₂, NBu₄), 0.98 (t, 12H, CH₃, NBu₄). ¹³C{¹H} NMR (δ, 100.14 MHz, CD₃COCD₃, 293 K): 136.1 (s, C, Np), 135.1 (s, C, Np), 130.0 (s, C, Np), 129.4 (s, CH, Np), 129.2 (s, CH, Np), 128.2 (s, C, ³J_{Pt-C} = 24 Hz, Np), 127.3 (s, CH, Np), 127.1 (s, CH, Np), 126.6 (s, CH, Np), 108.2 (s, ¹J_{C-Pt} = 970 Hz, C_α, C≡C), 102.8 (s, ²J_{C-Pt} = 278 Hz, C_β, C≡C), 60.4 (s, N−CH₂, NBu₄), 58.5 (s, CH₃, ¹Bu, CN^tBu), 31.6 (C-CH₃, CN^tBu), 25.5 (s, −CH₂−, NBu₄), 21.2 (s, −CH₂−, NBu₄), 15.0 (s, −CH₃, NBu₄). Resonances due to the quaternary carbon atoms of CN and CN^tBu groups were not observed. ¹⁹⁵Pt NMR (δ, 85.68 MHz, CDCl₃, 293 K): −4469.1.

ASSOCIATED CONTENT

Supporting Information

Figures S1–S8, Tables S1–S7, and CIF files giving additional structural data, characterization data, details of the calculations, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Spanish MICINN (Project CTQ2008-06669-C02-02/BQU) and the CAR (COLABORA project 2009/05). S.S. thanks the CSIC for a grant.

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