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# Luminescent Platinum Complexes with $\pi$-Extended Aryl Acetylide Ligands Supported by Isocyanides or Acyclic Diaminocarbenes

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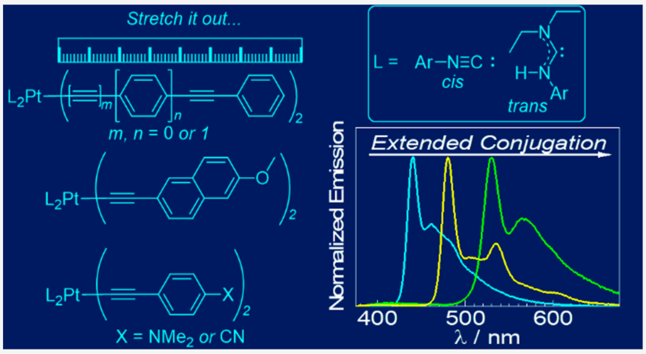

**ABSTRACT:** In this work, we present a series of luminescent platinum acetylide complexes with acetylides that are electronically modified and/or $\pi$-extended. Six isocyanide-supported complexes with the general formula *cis*-$[\mathrm{Pt(CNAr)_2(C{\equiv}CR)_2}]$ and six acyclic diaminocarbene (ADC) complexes of the form *trans*-$[\mathrm{Pt(ADC)_2(C{\equiv}CR)_2}]$, all using the same five acetylide ligands, are described. The compounds are characterized by multinuclear NMR, FT-IR, and single-crystal X-ray diffraction. In most cases, the phosphorescence arises from an acetylide-centered $^3(\pi \rightarrow \pi^*)$ excited state, although in one of the isocyanide compounds there is evidence for a charge-transfer excited state. The photoluminescence wavelength depends strongly on the substitution pattern and extent of the $\pi$ conjugation on the acetylide, with maxima spanning the range of ca. 460−540 nm. Most photoluminescence lifetimes are long, beyond 50 $\mu$s, and quantum yields are low to moderate, 0.043−0.27. The photoluminescence quantum yields and lifetimes in these compounds do not systematically improve in the ADC complexes compared to the isocyanide versions, suggesting the neutral ligand $\sigma$-donor character does not play a large role in the excited-state dynamics when the triplet excited state is delocalized over a large $\pi$ system.

## ■ INTRODUCTION

Several classes of organoplatinum compounds have intriguing photophysical properties, including cyclometalated platinum complexes[1−4] and platinum acetylide complexes;[5−14] sometimes those two motifs are combined in the same molecular platform.[15,16] Common structure types for platinum acetylide compounds are summarized in Figure 1, and they can exhibit a variety of excited states depending on the choice of ligands. In compounds where acetylides are paired with diimines or other highly conjugated chromophoric ligands (**A** and **B** in Figure 1), the low-energy triplet excited state is often a metal-to-ligand charge transfer ($^3$MLCT) state, and the acetylide ligands play a minor role in the excited-state frontier orbitals.[5,15] Compounds from class **B** in Figure 1 are also prone to aggregation through Pt···Pt and/or $\pi$-stacking interactions,[16] so in condensed phases, metal−metal interactions can play a role in the luminescent excited states. However, in many other classes of platinum acetylide complexes, e.g., **C** in Figure 1, a conjugated aryl acetylide is paired with a phosphine or *N*-heterocyclic carbene ligand that is not chromophoric, allowing the low-energy triplet state to be an acetylide-centered $^3(\pi \rightarrow \pi^*)$ excited state.[8−10,12−14] In this case, the substitution and conjugation of the aryl acetylide ligands are the primary determinants of the phosphorescence profile.

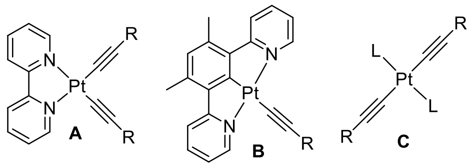

**Figure 1.** Structures of three common classes of platinum acetylide complexes.

When phenylacetylide is used, complexes from class **C** in Figure 1 typically have deep blue phosphorescence, making them appealing for optoelectronic applications relevant to color displays. In any blue-phosphorescent organometallic compound, a persistent challenge is presented by the ligand-field, d−d excited states that lie near or below the emissive triplet state ($T_1$), introducing nonradiative decay and photodissociation pathways.[17,18] As a result, some of the best-performing blue-phosphorescent compounds from the platinum bis-acetylide,[8−10,12−14] cyclometalated iridium,[17,19−22] and cyclometalated platinum[2,23−25] families feature strongly

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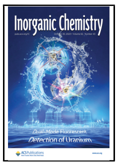

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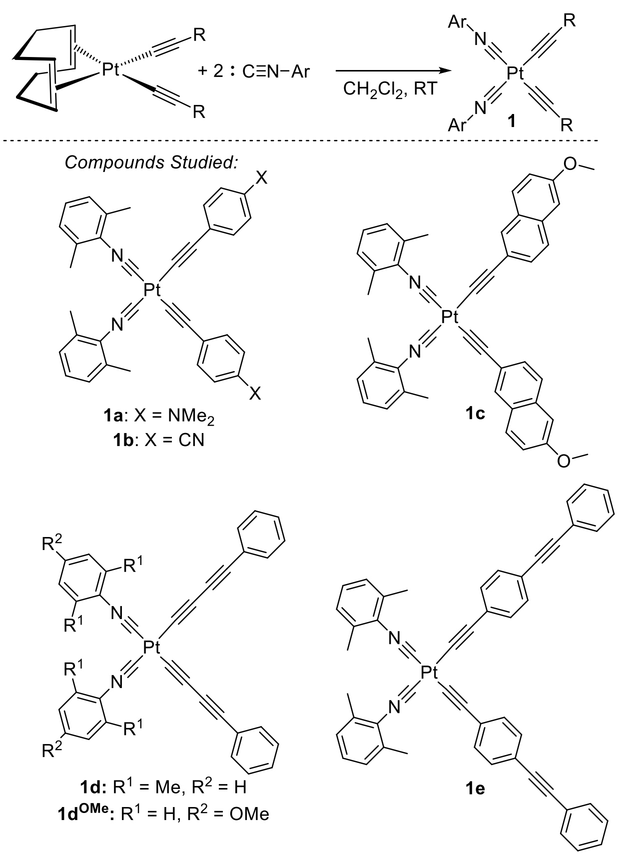
$\sigma$-donating *N*-heterocyclic carbene (NHC) ligands, capable of destabilizing the d−d excited states and improving both the efficiency and stability of blue phosphorescence. Wishing to enhance the neutral ligand $\sigma$-donor strength and improve blue phosphorescence to an even greater extent, our group has introduced luminescent platinum acetylide complexes supported by acyclic diaminocarbene (ADC) ligands, known to be stronger $\sigma$-donors than NHCs.[26] In our first effort we showed that the conversion of a single isocyanide ligand in blue-phosphorescent *cis*-[Pt(CNAr)$_2$(C≡CPh)$_2$] precursors to an ADC via amine nucleophilic addition results in a significant increase in photoluminescence quantum yield ($\Phi_{PL}$) and lifetime ($\tau$).[27] In a subsequent study on the same structure type, we showed that electronically modifying substituents on the phenylacetylide ligands engendered modest red shifts in the phosphorescence, while generalizing the outcome that the ADC complexes have higher quantum yields and longer lifetimes than the bis-isocyanide precursors.[28] In our most recent work, we introduced a complementary synthetic strategy that gives access to blue-phosphorescent compounds with two ADC ligands with the general formula *trans*-[Pt(ADC)$_2$(C≡CR)$_2$] and found a further increase in $\Phi_{PL}$ and $\tau$ in these compounds compared to those that have a single ADC.[29]

These latter efforts motivated us to pursue bis-ADC platinum acetylide complexes with electronically modified or $\pi$-extended acetylide ligands. In such complexes the acetylide-localized triplet state would be lower in energy than those of the previous blue-phosphorescent analogues, and it was not clear if the strongly $\sigma$-donating ADC ligands would have the same beneficial effect when the luminescence was outside the blue region and the $T_1$ excited state was delocalized over a larger $\pi$ system. In this work, we describe a series of such complexes with the general formula *trans*-[Pt(ADC)$_2$(C≡CR)$_2$], where the acetylide is either a substituted phenylacetylide with a strongly electron-donating dimethylamino or electron-withdrawing cyano group, a naphthyl acetylide with a polycyclic aromatic moiety, or one of two linearly conjugated diynes. These compounds are compared to isocyanide-ligated compounds of the type *cis*-[Pt(CNAr)$_2$(C≡CR)$_2$], which are constructed with the same set of conjugated acetylides. We find that the photoluminescence profiles are largely determined by the acetylide ligand and, in most cases, similar for the bis-isocyanide and bis-ADC analogues. Unlike previously studied blue-phosphorescent compounds from the same class, the quantum yields and lifetimes seem to not systematically depend on the neutral "L" ligand (ADC or isocyanide), suggesting that the ligand $\sigma$-donor strength plays less of a role in the photoluminescence dynamics when the $^3(\pi \rightarrow \pi^*)$ excited state is more delocalized and lower in energy.

## ■ RESULTS AND DISCUSSION

**Scheme 1. Synthesis of Bis-Isocyanide Complexes (1)**



**Synthesis and Characterization.** Two classes of platinum bis-acetylide complexes were prepared for this study using the same set of aryl acetylide ligands. Scheme 1 describes the synthesis of the bis-isocyanide complexes, which have the general formula *cis*-[Pt(CNAr)$_2$(C≡CR)$_2$] (**1**). The synthesis follows a general strategy that we had developed previously[27,28] and involves the initial installation of the acetylide ligands onto [Pt(COD)(C≡CR)$_2$] (COD = 1,5-cyclooctadiene) precursors, followed by substitution of the aryl isocyanide ligands. The acetylide ligands used are *para*-substituted phenyl acetylide ligands with electron-donating (**1a**, R = NMe$_2$) or electron-withdrawing (**1b**, R = CN) groups, a methoxy-substituted naphthyl acetylide (**1c**), a 4-phenyl-1,3-butadiynyl acetylide (**1d**), and a phenylene-spaced diynyl acetylide (**1e**). Aryl isocyanide ligands were exclusively used since they are required in the precursors that lead to the bis-ADC complexes (see below), and in most cases, 2,6-dimethylphenyl isocyanide was the choice. However, the poor solubility of the diynyl complex **1d** and its bis-ADC analogue (see below) motivated us to also prepare the complex **1d**$^{\mathbf{OMe}}$, which uses 4-methoxyphenyl isocyanide and is easier to characterize on account of higher solubility.

The identity and purity of bis-isocyanide complexes **1a**−**1e** were readily established by $^1$H and $^{13}$C{$^1$H} NMR spectroscopy (Figures S1 and S12) in combination with infrared spectroscopy (Figures S23−S28). The $^1$H NMR spectra clearly show peaks for both the aryl isocyanide and acetylide ligands and reveal that the two ligands are present in a 1:1 ratio on the complex. In the IR spectra, the C≡C (acetylide, $\tilde{\nu}_{C\equiv C}$ = 2078−2131 cm$^{-1}$) and C≡N (isocyanide, $\tilde{\nu}_{C\equiv N}$ = 2183−2221 cm$^{-1}$) stretches occur in a similar spectral region, and while only a single C≡C stretch is resolved, the observation of two distinct C≡N stretches from the isocyanide ligands is consistent with a *cis* geometry and approximate $C_{2v}$ symmetry. In the diynyl complex **1e**, a second C≡C stretch is observed, and 4-cyanophenylacetylide complex **1b** shows an additional C≡N stretch for the cyano substituent.

The molecular structures of two of the bis-isocyanide complexes, **1a** and **1c**, were determined by single-crystal X-ray diffraction. The structures are depicted in Figure 2, and the crystallographic data are summarized in Table S1. The *cis* geometry of the complexes is confirmed in the crystal

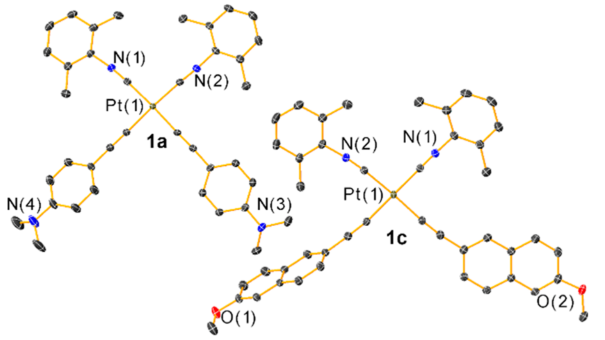
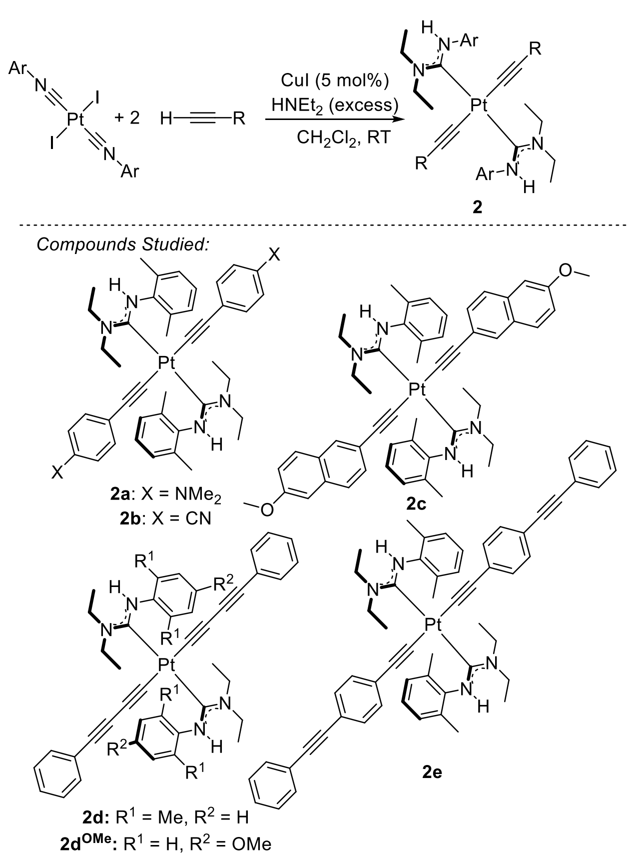


**Figure 2.** Molecular structures of **1a** and **1c**, determined by single-crystal X-ray diffraction. Ellipsoids are shown at the 50% probability level, with hydrogen atoms and solvent molecules omitted. In **1a**, only one of the two crystallographically independent molecules is shown.

structures, and in **1a** all four ligands are nearly coplanar, whereas in **1c** one of the naphthyl rings twists out of the coordination plane to accommodate a nearby $CH_2Cl_2$ solvent molecule. Despite their flat structures, **1a** and **1c** appear to be devoid of any obvious Pt···Pt and $\pi$-stacking packing interactions in the solid state. The nearly linear Pt−C≡C and Pt−C≡N bond angles, coupled with the short C≡C (1.207(3)−1.209(2) Å) and C≡N (1.152(3)−1.154(2) Å) distances, are consistent with little $\pi$ backbonding and formal triple bonds in the ligands.

To synthesize the ADC-supported complexes of the *trans*-$[Pt(ADC)_2(C{\equiv}CR)_2]$ structure type (**2**), a complementary synthetic approach was used, as summarized in Scheme 2. We previously introduced this route to synthesize analogous blue-phosphorescent compounds with phenylacetylide ligands or substituted variants,[29] and we show here it can be adapted to a wide variety of acetylide ligands. The *trans*-$[Pt(CNAr)_2(I)_2]$ precursors are only obtainable with aryl isocyanides, but once in hand, they can be converted to the bis-ADC, bis-acetylide complexes via a one-pot procedure. Stirring the iodo precursors with excess diethylamine and 2.5 equiv of the alkyne proligand in the presence of 5 mol % CuI furnishes the desired compounds in moderate to good yields after purification. The base acts as a nucleophile to generate the ADCs from the isocyanide precursors while also promoting the copper-catalyzed transmetalation reaction that installs the acetylides. The same acetylides used to prepare the bis-isocyanide complexes (Scheme 1) were used in the bis-ADC analogues, giving a suite of complexes which differ only in respect to the "L" ligands (isocyanides or ADCs) and the stereochemistry (*cis* vs *trans*).

**Scheme 2. Synthesis of Bis-ADC Complexes**



The bis-ADC complexes were likewise characterized by $^1H$ and $^{13}C\{^1H\}$ NMR (Figures S13−S22), except for **2a** and **2d**, which were too insoluble to obtain satisfactory $^{13}C\{^1H\}$ NMR data. The NMR spectra clearly show the $NEt_2$ groups that were installed via nucleophilic addition with two distinct chemical environments on account of the hindered rotation of the ADCs. Moreover, the $^1H$ NMR spectra show N−H proton resonance, near 6.5 ppm in most cases, with well-defined $^{195}Pt$ satellite coupling. The IR spectra (Figures S29−S34) are also consistent with the *trans*-$[Pt(ADC)_2(C{\equiv}CR)_2]$ structure, with the C≡N isocyanide stretch no longer observed. In **2a**−**2c** and **2e**, a single C≡C IR stretch is observed, consistent with the *trans* orientation, and in diynyl complexes **2d** and **2d$^{OMe}$**, two such stretches are noted.

Single-crystal X-ray diffraction validates three of the bis-ADC structures: **2b**, **2c**, and **2d$^{OMe}$** (Figure 3). In addition to confirming the *trans* geometry and approximate $C_{2h}$ symmetry, the structures reveal many of the features we have seen in several other platinum acetylide complexes supported by ADCs.[27−29] The ADC ligands adopt an *anti* conformation relative to one another and rotate out of the coordination plane to avoid unfavorable steric interactions with the

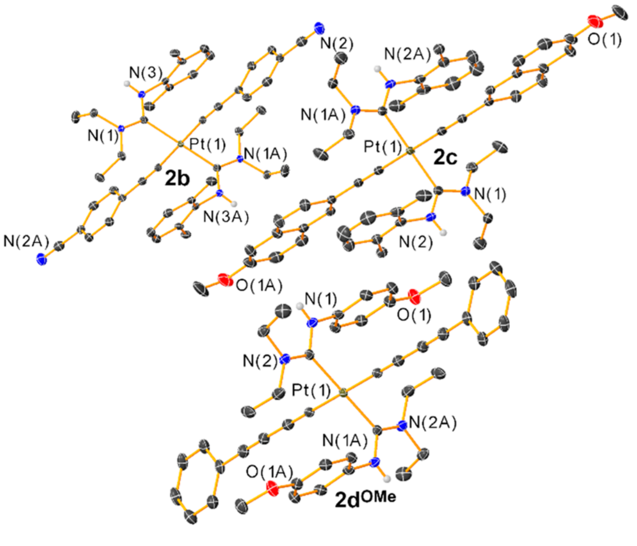


**Figure 3.** Molecular structures of **2b**, **2c**, and **2d$^{OMe}$**, determined by single-crystal X-ray diffraction. Ellipsoids are shown at a 50% probability level with carbon-bound hydrogen atoms omitted.

acetylides. This nearly perpendicular arrangement of the $PtC_4$ coordination plane and the ADC mean plane blocks the complexes from any notable stacking interactions in the solid state. The C≡C bond lengths proximal to the Pt center, 1.202(6)−1.214(4) Å, are not significantly different than those of the bis-isocyanide complexes (see above), and in **2d**$^{\mathbf{OMe}}$ the distal C≡C distance is 1.199(4) Å, only slightly shorter. The ADC N−C−N bond angles span the range of 116.2(2)−117.1(2)°, consistent with $sp^2$ hybridization and similar to many other ADC structures we have reported.[27−29]

**Photophysical Properties.** UV−vis absorption spectra in a $CH_2Cl_2$ solution and photoluminescence spectra in 2 wt % poly(methyl methacrylate) (PMMA) films were recorded for all complexes and are shown in Figure 4. Spectra for bis-isocyanide compounds (**1a**−**1e**) are in red, and those for bis-ADC compounds (**2a**−**2e**) are in blue. Absorption spectra are shown as dotted lines, and PL spectra are shown as solid lines in Figure 4. PL spectra for the bis-ADC complexes (**2**) were also recorded in a $CH_2Cl_2$ solution at room temperature, and they are collected in Figures S35−S40. In all cases, the spectra in the two media are nearly identical, and the discussion in this article will focus on the data recorded in PMMA.

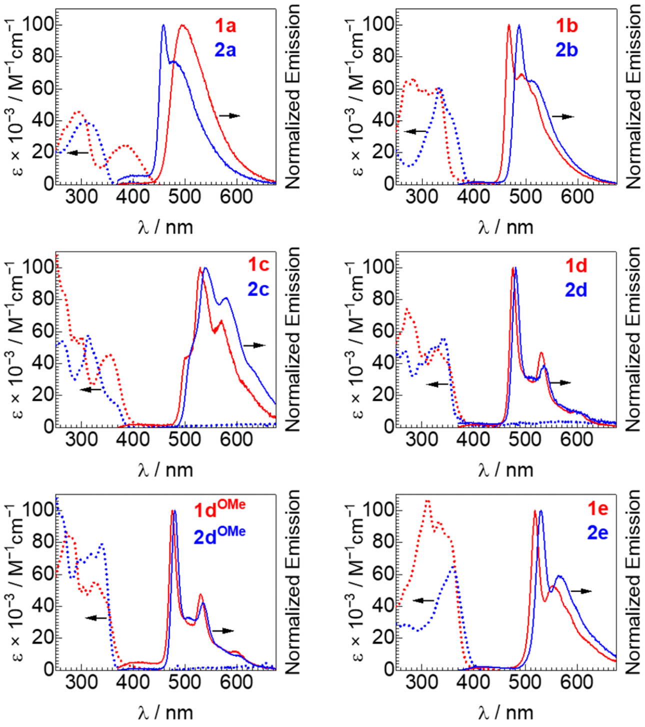
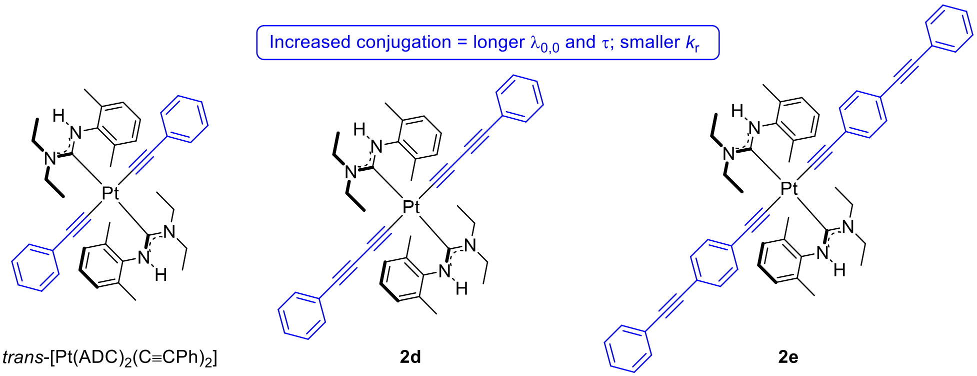


**Figure 4.** Overlaid UV−vis absorption (dotted lines) and normalized photoluminescence spectra (solid lines) of all platinum acetylide complexes. Spectra for bis-isocyanide (**1a**−**1e**, red) and bis-ADC (**2a**−**2e**, blue) are overlaid as a function of the acetylide ligand. Absorption spectra were recorded in $CH_2Cl_2$ at room temperature, and PL spectra were recorded in 2 wt % PMMA films at room temperature.

In most cases, except for **1a** and **2a**, for a given acetylide ligand the photoluminescence spectra for the bis-isocyanide compounds and bis-ADC compounds are very similar, with the respective peak maxima separated by 20 nm or less (880 $cm^{-1}$) and with nearly identical vibronic structure. These are all consistent with luminescence arising from an acetylide-centered $^3(\pi \rightarrow \pi^*)$ excited state, as is normally the case for platinum acetylide compounds with nonchromophoric ancillary ligands. However, in **1a** and **2a**, which use 4-dimethylaminophenylacetylide, the peak maxima differ by a larger amount (35 nm, 1550 $cm^{-1}$), and the bis-isocyanide complex **1a** is completely devoid of vibronic structure in its photoluminescence. We propose that in **1a**, the lowest-energy excited state is a charge-transfer state. Consistent with this supposition, the UV−vis absorption spectrum of **1a** (Figure 4) shows an additional featureless band near 400 nm, absent in all other complexes, and its lifetime ($\tau$ = 11 $\mu$s) and radiative rate constant ($k_r = 2.2 \times 10^4$ $s^{-1}$) are respectively a factor of 3 smaller and a factor of 5 larger than any other compound, consistent with PL that originates from a charge-transfer state rather than $^3(\pi \rightarrow \pi^*)$. Also worth noting is that the $\Phi_{PL}$ value in $NMe_2$-substituted **2a** is significantly lower than that of cyano-substituted **2b**, despite both having similar excited-state character, $^3(\pi \rightarrow \pi^*)$, and broadly similar peak wavelengths (458 nm in **2a** and 487 nm in **2b**). One of the origins of this difference is likely electron-transfer quenching by the dimethylamino group, which has been observed in other classes of platinum acetylide chromophores[30,31] and would be consistent with the much higher $k_{nr}$ value in **2a** vs **2b**.

The photoluminescence profiles for the compounds presented here are all in the blue-green to yellow regions, substantially red-shifted from those of related compounds with phenylacetylide ligands, which emit in the blue region.[27,29] There is one other key difference between the variants presented here and previous blue-phosphorescent analogues.[29] In most of the compounds presented here, the neutral donor ligand, isocyanide or ADC, has minimal impacts on the photoluminescence quantum yields and lifetimes. In contrast, the blue-phosphorescent analogues all show substantially higher $\Phi_{PL}$ and $\tau$ values when supported by stronger $\sigma$-donor ADCs instead of isocyanides. For example, $\Phi_{PL}$ is 7.4 times higher and $\tau$ is 12 times longer in *trans*-[Pt(ADC)$_2$(C≡CPh)$_2$] compared to *cis*-[Pt(CNAr$^{dmp}$)$_2$(C≡CPh)$_2$] (CNAr$^{dmp}$ = 2,6-dimethylphenylisocyanide, and the ADC is the same as all compounds here except **2d**$^{\mathbf{OMe}}$). Computational analysis attributed this large change to the destabilization of higher-lying, deleterious ligand-field ($d$−$d$) excited states by the strong $\sigma$-donor ADC.[29] In the compounds presented here, the ADCs seemingly have no beneficial effect on the photoluminescence. In some cases (**1a**/**2a**, **1c**/**2c**, and **1e**/**2e**), $\Phi_{PL}$ is noticeably lower in the bis-ADC complex, acknowledging the change in the nature of the excited state in **1a**/**2a**. In the rest, not only do the PL spectra change little between the bis-isocyanide and bis-ADC congeners but quantum yields and lifetimes are quite similar as well. This suggests that the nature of the L donor ligand and the relative energy of the higher-lying ligand-field excited states matter little when the emissive $^3(\pi \rightarrow \pi^*)$ state is more delocalized and lower in energy.

The three acetylides with extended $\pi$ conjugation used in this work (**c**−**e**, see Schemes 1 and 2), have been occasionally used in other platinum bis-acetylide complexes.[10,13,14] The greater $\pi$ conjugation on the acetylides has the effect of red-shifting the photoluminescence, as noted above, and leads to considerably longer lifetimes. To better visualize the effect of increasing $\pi$ conjugation, Figure 5 compares *trans*-[Pt(ADC)$_2$(C≡CPh)$_2$] with complexes **2d** and **2e**, which have increasingly longer conjugations on the acetylides. Unsurprisingly, the $\lambda_{0,0}$ value shifts to progressively longer wavelengths as the $\pi$ conjugation increases, shifting from 440 to 481 nm



*trans*-[Pt(ADC)$_2$(C≡CPh)$_2$]
$\lambda_{0,0}$ = 440 nm
$\Phi_{PL}$ = 0.43
$\tau$ = 35 μs
$k_r = 12 \times 10^3$ s$^{-1}$
$k_{nr} = 16 \times 10^3$ s$^{-1}$

**2d**
$\lambda_{0,0}$ = 481 nm
$\Phi_{PL}$ = 0.13
$\tau$ = 58 μs
$k_r = 2.2 \times 10^3$ s$^{-1}$
$k_{nr} = 15 \times 10^3$ s$^{-1}$

**2e**
$\lambda_{0,0}$ = 530 nm
$\Phi_{PL}$ = 0.13
$\tau$ = 101 μs
$k_r = 1.3 \times 10^3$ s$^{-1}$
$k_{nr} = 8.6 \times 10^3$ s$^{-1}$

**Figure 5.** Comparison of the key photoluminescence properties of a series of bis-ADC complexes with increasing $\pi$ conjugation on the acetylides.

**Table 1. Summary of Photoluminescence Data, Recorded at Room Temperature in 2 wt % PMMA Films**

| compound | $\lambda$ (nm) | $\Phi_{PL}$ | $\tau$ (μs) | $k_r \times 10^3$ (s$^{-1}$) | $k_{nr} \times 10^3$ (s$^{-1}$) |
|---|---|---|---|---|---|
| | Substituted Phenyl Acetylide [C≡C(4-X-$C_6H_4$)] | | | | |
| *cis*-[Pt(CNAr$^{dmp}$)$_2$(C≡CPh)$_2$][27] (X = H) | 435 | 0.058 | 2.8 | 21 | 330 |
| **1a** (X = NMe$_2$) | 493 | 0.24 | 11 | 22 | 69 |
| **1b** (X = CN) | 467, 492 | 0.27 | 58 | 4.7 | 13 |
| *trans*-[Pt(ADC)$_2$(C≡CPh)$_2$][29] (X = H) | 440 | 0.43 | 35 | 12 | 16 |
| **2a** (X = NMe$_2$) | 458, 476 | 0.087 | 58 | 1.5 | 16 |
| **2b** (X = CN) | 487, 511 | 0.26 | 89 | 2.9 | 8.3 |
| | 6-Methoxy-2-naphthyl Acetylide | | | | |
| **1c** | 499, 529, 570 | 0.14 | 96 | 1.5 | 9.0 |
| **2c** | 538, 578 | 0.043 | 104 | 0.41 | 9.2 |
| | 4-Phenyl-1,3-butadiynyl Acetylide | | | | |
| **1d** | 476, 530 | 0.13 | 34 | 3.8 | 26 |
| **2d** | 481, 536 | 0.13 | 58 | 2.2 | 15 |
| **1d$^{OMe}$** | 475, 530, 593 | 0.14 | 35 | 4.0 | 25 |
| **2d$^{OMe}$** | 480, 534 | 0.17 | 48 | 3.5 | 17 |
| | Phenylene-Spaced Diynyl Acetylide | | | | |
| **1e** | 518, 552 | 0.21 | 85 | 2.5 | 9.3 |
| **2e** | 530, 563 | 0.13 | 101 | 1.3 | 8.6 |

moving from the phenylacetylide complex to **2d**, and another 49 nm (to 530 nm) going from **2d** to **2e** with the introduction of a phenyl spacer into the diyne. The most notable change in the excited-state dynamics is in $k_r$, which decreases across the series, spanning almost an order of magnitude between the extremes. The nonradiative rate constant $k_{nr}$ is less affected, and the net result is an increasing lifetime across the series, going from 35 μs in the phenylacetylide analogue to 58 μs in **2d** and to 101 μs in **2e**. The extended conjugation in **2b** and **2c** also leads to substantially longer lifetimes than the parent phenylacetylide complex (see Table 1), showing that the exceptionally long lifetimes we obtain with longer $\pi$-conjugated acetylide ligands are a generalizable phenomenon.

## ■ CONCLUSIONS

In this work, we introduced isocyanide and ADC-supported platinum bis-acetylide complexes with substituted and $\pi$-extended acetylide ligands. The two classes of compounds are prepared via complementary routes, with the isocyanide compounds adopting a *cis* geometry and the ADC compounds a *trans* geometry. All compounds are photoluminescent, occurring in almost every case via phosphorescence from an acetylide-centered $^3(\pi \rightarrow \pi^*)$ excited state. That said, in one case, the dimethylamino-substituted bis-isocyanide complex **1a**, the appearance of the absorption and PL spectra suggest the presence of a low-lying charge-transfer state. Nevertheless, the electronically modifying substituents or extended $\pi$ conjugation in the acetylide ligands used here result in significant bathochromic shifts in PL relative to analogous compounds crafted from phenylacetylide ligands. Unlike those of these previous blue-phosphorescent analogues, the PL quantum yield and lifetime in the compounds described here are not systematically increased in the ADC complexes relative to the isocyanide analogues. In most cases, the values are very similar for a given acetylide, and in a couple of cases, $\Phi_{PL}$ is noticeably lower in the ADC versions. We propose that this is mainly a reflection of the lower-energy $^3(\pi \rightarrow \pi^*)$ excited states in these compounds lying further below the deleterious ligand-field states such that the destabilization of the latter states by the ADC ligands does not result in measurable improvements. This work does show that compounds of this type can have exceptionally long PL lifetimes, up to $10^{-4}$ s, with the substitution pattern and $\pi$ conjugation of the acetylide offering a convenient means of tuning the spectral profile.

## EXPERIMENTAL SECTION

**Materials.** The precursors $[Pt(COD)(C{\equiv}CR)_2]$ (COD = 1,5-cyclooctadiene)[28] were prepared analogously to our previous report, and the *trans*-$[Pt(CNAr)_2(I)_2]$ precursors are also available from a previously disclosed synthesis.[32] All alkynes are commercially available except buta-1,3-diynylbenzene, which was prepared as previously described.[14] The solvents for the reactions and photophysical experiments were sparged with argon and dried by passing through dual alumina columns on a Grubbs-type solvent purification system, and the NMR solvents were dried by storage over molecular sieves.

**Physical Methods.** $^1H$ and $^{13}C\{^1H\}$NMR spectra were recorded at room temperature using a JEOL ECA-400 or JEOL ECA-500 spectrometer. Infrared (IR) spectra were obtained by using a Thermo Nicolet Avatar FT-IR spectrometer with a diamond ATR. UV−vis absorption spectra were recorded in dichloromethane in screw-capped 1 cm quartz cuvettes using an Agilent Cary 8454 UV−vis spectrophotometer. Steady-state emission spectra were recorded using a Horiba FluoroMax-4 spectrofluorometer. Air-free solution samples for emission spectra were prepared in a nitrogen-filled glovebox by using dry, deoxygenated solvents. Measurements in solution were housed in 1 cm quartz cuvettes with septum-sealed screw caps. To prepare doped PMMA films for PL measurements, a solution of PMMA (98 mg, 35 kDa) in dichloromethane (1.0 mL) was prepared at room temperature inside a nitrogen-filled glovebox. Then, the respective platinum complex (2 mg, 2 wt %) was added to the solution and stirred until the solution became clear. The solution was then drop-coated onto a quartz substrate and dried at room temperature overnight prior to use. The quantum yields of the complexes doped into the poly(methyl methacrylate) (PMMA) thin films were recorded using a Spectralon-coated integrating sphere (3.2 in., Horiba). Phosphorescence lifetimes were measured on a Horiba DeltaFlex Lifetime System using 330 nm excitation.

**X-ray Crystallography Details.** Crystals were mounted on a Bruker Apex II three-circle diffractometer using MoK$\alpha$ radiation ($\lambda$ = 0.71073 Å). The data were collected at 123(2) K and were processed and refined within the APEXII software. Structures were solved by intrinsic phasing in SHELXT and refined by standard difference Fourier techniques in OLEX-2. Hydrogen atoms bonded to carbon were placed in calculated positions using the standard riding model and refined isotropically; all non-hydrogen atoms were refined anisotropically. N−H hydrogen atoms were located in the difference map and refined isotropically, restraining the N−H bond distance to 0.88 Å and constraining the isotropic displacement parameter to be 1.2 times that of the N atom it is bonded to.

**General Method for the Preparation of the *cis*-$[Pt(CNAr)_2(C{\equiv}CR)_2]$ Complexes (1).** The bis-isocyanide complexes were prepared in a similar fashion as previously described by our group,[27,28] treating the respective $[Pt(COD)(C{\equiv}CAr)_2]$ precursor (COD = 1,5-cyclooctadiene) with 2.5 equiv of aryl isocyanide (2,6-dimethylphenyl isocyanide, $CNAr^{dmp}$; or 4-methoxyphenyl isocyanide, $CNAr^{OMe}$) in dichloromethane at room temperature. After the solution was concentrated, the product was precipitated by the addition of diethyl ether, and the collected solid was washed with diethyl ether before drying in vacuo.

*cis-*$[Pt(CNAr^{dmp})_2(C{\equiv}C(4\text{-}NMe_2\text{-}C_6H_4)_2]$ ***(1a)***. Prepared from $[Pt(COD)(C{\equiv}C(4\text{-}NMe_2\text{-}C_6H_4)_2]$ (60 mg, 0.10 mmol) and 2.5 equiv of $CNAr^{dmp}$. Yield: 78% (59 mg, 0.079 mmol). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.36 (d, $J$ = 8.8 Hz, 4H, $Ar\underline{H}$), 7.26 (t, $J$ = 7.6 Hz, 2H, $Ar\underline{H}$), 7.13 (d, $J$ = 7.6 Hz, 4H, $Ar\underline{H}$), 6.60 (d, $J$ = 8.8 Hz, 4H, $Ar\underline{H}$), 2.93 (s, 12H, $N(C\underline{H}_3)_2$), 2.52 (s, 12H, $Ar{-}C\underline{H}_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): $\delta$ 148.8, 136.0, 133.2, 129.8, 128.2, 126.5 (br, $\underline{C}{\equiv}NAr^{dmp}$), 115.5, 112.0, 108.1 (s, $Pt{-}C{\equiv}\underline{C}{-}Ar$), 88.6 (s, $Pt{-}\underline{C}{\equiv}C{-}Ar$), 40.6 ($N(\underline{C}H_3)_2$), 18.9 ($Ar{-}\underline{C}H_3$). FT-IR ($cm^{-1}$): 2205 ($\tilde{\nu}_{C\equiv N}$), 2183 ($\tilde{\nu}_{C\equiv N}$), 2127 ($\tilde{\nu}_{C\equiv C}$).

*cis-*$[Pt(CNAr^{dmp})_2(C{\equiv}C(4\text{-}CN\text{-}C_6H_4)_2]$ ***(1b)***. Prepared from $[Pt(COD)(C{\equiv}C(4\text{-}CN\text{-}C_6H_4)_2]$ (70 mg, 0.13 mmol) and 2.5 equiv of $CNAr^{dmp}$. Yield: 66% (60 mg, 0.083 mmol). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.54−7.45 (AA′BB′ multiplet, 8H, $Ar\underline{H}$), 7.31 (t, $J$ = 7.6 Hz, 2H, $Ar\underline{H}$), 7.16 (d, $J$ = 7.6 Hz, 4H, $Ar\underline{H}$), 2.49 (s, 12H, $Ar{-}C\underline{H}_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): $\delta$ 136.0, 132.4, 132.0, 131.8, 130.5, 128.5, 125.8 (br, $\underline{C}{\equiv}NAr^{dmp}$), 119.4, 109.1, 106.3 (s, $Pt{-}C{\equiv}\underline{C}{-}Ar$), 98.0 (s, $Pt{-}\underline{C}{\equiv}C{-}Ar$), 18.8 ($Ar{-}\underline{C}H_3$). FT-IR ($cm^{-1}$): 2223 ($\tilde{\nu}_{C\equiv N}$), 2211 ($\tilde{\nu}_{C\equiv N}$), 2193 ($\tilde{\nu}_{C\equiv N}$), 2131 ($\tilde{\nu}_{C\equiv C}$).

*cis-*$[Pt(CNAr^{dmp})_2(C{\equiv}C(6\text{-}OMe\text{-}C_{10}H_6)_2]$ ***(1c)***. Prepared from $[Pt(COD)(C{\equiv}C(6\text{-}OMe\text{-}C_{10}H_6)_2]$ (118 mg, 0.315 mmol) and 2.5 equiv of $CNAr^{dmp}$. Yield: 72% (150 mg, 0.226 mmol). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.89 (s, 2H, $Ar\underline{H}$), 7.66−7.53 (m, 6H, $Ar\underline{H}$), 7.28 (t, $J$ = 7.6 Hz, 2H, $Ar\underline{H}$), 7.18−7.05 (m, 8H, $Ar\underline{H}$), 3.90 (s, 6H, $O{-}C\underline{H}_3$), 2.54 (s, 12H, $Ar{-}C\underline{H}_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): $\delta$ 157.5, 136.0, 133.1, 130.84, 130.81, 130.1, 129.2, 128.8, 128.3, 126.3 (br, $\underline{C}{\equiv}NAr^{dmp}$), 126.1, 122.6, 118.7, 107.9 (s, $Pt{-}C{\equiv}\underline{C}{-}Ar$), 105.8, 91.3 (s, $Pt{-}\underline{C}{\equiv}C{-}Ar$), 55.4 ($O{-}\underline{C}H_3$), 18.9 ($Ar{-}\underline{C}H_3$). FT-IR ($cm^{-1}$): 2203 ($\tilde{\nu}_{C\equiv N}$), 2178 ($\tilde{\nu}_{C\equiv N}$), 2122 ($\tilde{\nu}_{C\equiv C}$).

*cis-*$[Pt(CNAr^{dmp})_2(C{\equiv}C{-}C{\equiv}CPh)_2]$ ***(1d)***. Prepared from $[Pt(COD)(C{\equiv}C{-}C{\equiv}CPh)_2]$ (60 mg, 0.11 mmol) and 2.5 equiv of $CNAr^{dmp}$. Yield: 54% (42 mg, 0.059 mmol). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.47−7.41 (m, 4H, $Ar\underline{H}$), 7.32−7.23 (m, 8H, $Ar\underline{H}$), 7.16 (d, $J$ = 7.6 Hz, 4H, $Ar\underline{H}$), 2.51 (s, 12H, $Ar{-}C\underline{H}_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): $\delta$ 136.3, 132.6, 130.4, 128.4, 128.2, 127.9, 125.8 (br, $\underline{C}{\equiv}NAr^{dmp}$), 123.7, 89.7, 89.6, 72.5, 18.8 ($Ar{-}\underline{C}H_3$). FT-IR ($cm^{-1}$): 2212 ($\tilde{\nu}_{C\equiv N}$), 2184 ($\tilde{\nu}_{C\equiv N}$), 2085 ($\tilde{\nu}_{C\equiv C}$).

*cis-*$[Pt(CNAr^{OMe})_2(C{\equiv}C{-}C{\equiv}CPh)_2]$ ***(1d$^{OMe}$)***. Prepared from $[Pt(COD)(C{\equiv}C{-}C{\equiv}CPh)_2]$ (60 mg, 0.11 mmol) and 2.5 equiv of $CNAr^{OMe}$. Yield: 62% (42 mg, 0.067 mmol). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.51 (d, $J$ = 8.4 Hz, 4H, $Ar\underline{H}$), 7.46−7.37 (br, m, 4H, $Ar\underline{H}$), 7.30−7.20 (m, overlapped with residual solvent peak, 6H, $Ar\underline{H}$), 6.91 (d, $J$ = 8.4 Hz, 4H, $Ar\underline{H}$), 3.80 (s, 6H, $O{-}C\underline{H}_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): $\delta$ 161.1, 132.6, 128.8, 128.2, 127.9, 123.7, 115.0, 102.9, 93.5, 90.2, 88.9, 55.8 ($O{-}\underline{C}H_3$). FT-IR ($cm^{-1}$): 2221 ($\tilde{\nu}_{C\equiv N}$), 2188 ($\tilde{\nu}_{C\equiv N}$), 2078 ($\tilde{\nu}_{C\equiv C}$).

*cis-*$[Pt(CNAr^{dmp})_2(C{\equiv}CC_6H_4C{\equiv}CPh)_2]$ ***(1e)***. Prepared from $[Pt(COD)(C{\equiv}CC_6H_4C{\equiv}CPh)_2]$ (70 mg, 0.10 mmol) and 2.5 equiv of $CNAr^{dmp}$. Yield: 79% (68 mg, 0.079 mmol). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.54−7.49 (m, 4H, $Ar\underline{H}$), 7.54−7.37 (m, 8H, $Ar\underline{H}$), 7.37−7.25 (m, 8H, $Ar\underline{H}$), 7.15 (d, $J$ = 8.0 Hz, 4H, $Ar\underline{H}$), 2.51 (s, 12H, $Ar{-}C\underline{H}_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): $\delta$ 136.0, 132.0, 131.7, 131.2, 130.2, 128.44, 128.38, 128.2, 127.4, 126.1 (br, $\underline{C}{\equiv}NAr^{dmp}$), 123.6, 120.6, 118.7, 107.4 (s, $Pt{-}C{\equiv}\underline{C}{-}Ar$), 94.3 (s, $Pt{-}\underline{C}{\equiv}C{-}Ar$), 90.2, 90.0, 18.8 ($Ar{-}\underline{C}H_3$). FT-IR ($cm^{-1}$): 2208 ($\tilde{\nu}_{C\equiv N}$), 2191 ($\tilde{\nu}_{C\equiv N}$), 2158 ($\tilde{\nu}_{C\equiv C}$), 2126 ($\tilde{\nu}_{C\equiv C}$).

**General Method for the Preparation of the *trans*-$[Pt(ADC)_2(C{\equiv}CR)_2]$ Complexes (2).** The bis-ADC complexes were prepared in a similar fashion as previously described by our group.[29] They were obtained from the reaction of the respective *trans*-$[Pt(CNAr)_2(I)_2]$ complex with the corresponding acetylene (2.5 equiv) in the presence of CuI (5% mol) and 3 mL of diethylamine, using $CH_2Cl_2$ (5 mL) as the solvent. The mixture was prepared and stirred for 24 h inside of the glovebox. After that, $CH_2Cl_2$ was added to the mixture until complete dissolution of the precipitated solid was achieved, and the solution was extracted with deionized water four times, collecting the organic layer and drying it over $MgSO_4$. The solvent was evaporated, and a solid was precipitated by the addition of $Et_2O$/pentane. This solid was recrystallized from $CH_2Cl_2/Et_2O$, collected by filtration, and vacuum-dried to obtain the desired product.

*trans-*$[Pt(ADC^{dmp})_2(C{\equiv}C(4\text{-}NMe_2\text{-}C_6H_4)_2]$ ***(2a)***. Prepared from *trans*-$[Pt(CNAr^{dmp})_2I_2]$ (100 mg, 0.141 mmol) and 2.5 equiv of $HC{\equiv}C(4\text{-}NMe_2\text{-}C_6H_4)$. As a slight modification, the product was recrystallized an additional time from $CH_2Cl_2$ at ca. −20 °C. Yield: 60% (70 mg, 0.078 mmol). $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.11−6.98 (m, 10H, $Ar\underline{H}$), 6.61 (d, $J$ = 8.5 Hz, 4H, $Ar\underline{H}$), 6.48 (br, s with $^{195}Pt$ satellites, $^3J_{Pt-H}$ = 60 Hz, 2H, $N\underline{H}$), 3.56 (br, s, 4H, $NC\underline{H}_2CH_3$), 3.27 (br, m, 4H, $NC\underline{H}_2CH_3$), 2.89 (s, 12H, $N(C\underline{H}_3)_2$), 2.56 (s, 12H, $Ar{-}C\underline{H}_3$), 1.20 (br, m, 6H, $NCH_2C\underline{H}_3$), 0.98 (br, s, 6H, $NCH_2C\underline{H}_3$).

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This compound was too insoluble for $^{13}$C{$^{1}$H} NMR analysis. FT-IR (cm$^{-1}$): 2090 ($\tilde{\nu}_{C\equiv C}$).

*trans-[Pt(ADC$^{dmp}$)$_2$(C≡C(4-CN-C$_6$H$_4$)$_2$]* ***(2b)***. Prepared from *trans*-[Pt(CNAr$^{dmp}$)$_2$I$_2$] (100 mg, 0.141 mmol) and 2.5 equiv of HC≡C(4-CN-C$_6$H$_4$). Yield: 60% (72 mg, 0.088 mmol). $^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.43 (d, $J$ = 8.0 Hz, 4H, Ar$\underline{H}$), 7.17 (d, $J$ = 8.5 Hz, 4H, Ar$\underline{H}$), 7.12 (t, $J$ = 7.5 Hz, 2H, Ar$\underline{H}$), 7.03 (d, $J$ = 7.5 Hz, 4H, Ar$\underline{H}$), 6.54 (br, s with $^{195}$Pt satellites, $^{3}J_{\text{Pt-H}}$ = 66 Hz, 2H, N$\underline{H}$), 3.52 (br, q, $J$ = 7.5 Hz, 4H, NC$\underline{H}_2$CH$_3$), 3.32 (br, q, $J$ = 6.5 Hz, 4H, NC$\underline{H}_2$CH$_3$), 2.44 (s, 12H, Ar−C$\underline{H}_3$), 1.21 (br, t, $J$ = 7.2 Hz, 6H, NCH$_2$C$\underline{H}_3$), 0.97 (br, t, $J$ = 7.0 Hz, 6H, NCH$_2$C$\underline{H}_3$). $^{13}$C{$^{1}$H} NMR (125.7 MHz, CDCl$_3$): $\delta$ 194.5, 138.4, 138.0, 135.2, 131.7, 131.1, 127.9, 127.4, 120.2, 106.2, 106.1, 51.7, 40.3, 19.9, 13.5, 12.7. FT-IR (cm$^{-1}$): 2222 ($\tilde{\nu}_{C\equiv N}$), 2216 ($\tilde{\nu}_{C\equiv N}$), 2083 ($\tilde{\nu}_{C\equiv C}$).

*trans-[Pt(ADC$^{dmp}$)$_2$(C≡C(6-OMe-C$_{10}$H$_6$)$_2$]* ***(2c)***. Prepared from *trans*-[Pt(CNAr$^{dmp}$)$_2$I$_2$] (100 mg, 0.141 mmol) and 2.5 equiv of HC≡C(6-OMe-C$_{10}$H$_6$). Yield: 63% (85 mg, 0.088 mmol). $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 (d, $J$ = 8.4 Hz, 2H, Ar$\underline{H}$), 7.57−7.50 (m, 4H, Ar$\underline{H}$), 7.28 (dd, $J$ = 8.4 Hz, 1.6 Hz, 2H, Ar$\underline{H}$), 7.16−7.10 (m, 2H, Ar$\underline{H}$), 7.09−7.03 (m, 8H, Ar$\underline{H}$), 6.55 (br, s with $^{195}$Pt satellites, $^{3}J_{\text{Pt-H}}$ = 66 Hz, 2H, N$\underline{H}$), 3.90 (s, 6H, O−C$\underline{H}_3$) 3.62 (br, s, 4H, NC$\underline{H}_2$CH$_3$), 3.32 (br, q, $J$ = 7.6 Hz, 4H, NC$\underline{H}_2$CH$_3$), 2.58 (s, 12H, Ar−C$\underline{H}_3$), 1.24 (br, t, $J$ = 6.8 Hz, 6H, NCH$_2$C$\underline{H}_3$), 1.05 (br, s, 6H, NCH$_2$C$\underline{H}_3$). $^{13}$C{$^{1}$H} NMR (125.7 MHz, CDCl$_3$): $\delta$ 195.9, 156.7, 138.8, 138.4, 131.8, 130.7, 129.3, 128.7, 128.2, 127.8, 127.1, 126.1, 125.9, 118.4, 105.9, 55.4, 51.9, 40.3, 20.2, 13.6, 12.8. FT-IR (cm$^{-1}$): 2085 ($\tilde{\nu}_{C\equiv C}$).

*trans-[Pt(ADC$^{dmp}$)$_2$(C≡C−C≡CPh)$_2$]* ***(2d)***. Prepared from *trans*-[Pt(CNAr$^{dmp}$)$_2$I$_2$] (100 mg, 0.141 mmol) and 2.5 equiv of HC≡C−C≡CPh. In a slight modification of the general procedure, the product precipitated during the reaction was collected by filtration and washed several times with CH$_2$Cl$_2$. Yield: 67% (80 mg, 0.088 mmol). $^{1}$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.46−7.36 (m, 4H, Ar$\underline{H}$), 7.30−7.20 (m, 6H, Ar$\underline{H}$), 7.15−7.06 (m, 6H, Ar$\underline{H}$), 6.70 (br, s with $^{195}$Pt satellites, $^{3}J_{\text{Pt-H}}$ = 66 Hz, 2H, N$\underline{H}$), 3.46 (q, $J$ = 7.0 Hz, 4H, NC$\underline{H}_2$CH$_3$), 3.37 (q, $J$ = 7.2 Hz, 4H, NC$\underline{H}_2$CH$_3$), 2.48 (s, 12H, Ar−C$\underline{H}_3$), 1.26 (t, $J$ = 7.2 Hz, 6H, NCH$_2$C$\underline{H}_3$), 1.01 (t, $J$ = 7.2 Hz, 6H, NCH$_2$C$\underline{H}_3$). This compound was too insoluble for $^{13}$C{$^{1}$H} NMR analysis. FT-IR (cm$^{-1}$): 2167 ($\tilde{\nu}_{C\equiv C}$), 2049 ($\tilde{\nu}_{C\equiv C}$).

*trans-[Pt(ADC$^{OMe}$)$_2$(C≡C−C≡CPh)$_2$]* ***(2d$^{OMe}$)***. Prepared from *trans*-[Pt(CNAr$^{OMe}$)$_2$I$_2$] (100 mg, 0.141 mmol) and 2.5 equiv of HC≡C−C≡CPh. In a slight modification of the general procedure, after workup the crude product was purified by column chromatography using silica gel as the stationary phase and eluting with CH$_2$Cl$_2$/hexane (2:1). Yield: 29% (35 mg, 0.041 mmol). $^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.48−7.41 (m, 4H, Ar$\underline{H}$), 7.26−7.18 (m, 6H, Ar$\underline{H}$), 7.05 (br, s with $^{195}$Pt satellites, $^{3}J_{\text{Pt-H}}$ = 56 Hz, 2H, N$\underline{H}$), 6.88 (d, $J$ = 9.0 Hz, 4H, Ar$\underline{H}$), 3.82 (s, 6H, O−C$\underline{H}_3$), 3.50 (br, q, $J$ = 7.5 Hz, 4H, NC$\underline{H}_2$CH$_3$), 3.31 (q, $J$ = 7.2 Hz, 4H, NC$\underline{H}_2$CH$_3$), 1.25 (t, $J$ = 7.2 Hz, 6H, NCH$_2$C$\underline{H}_3$), 1.00 (t, $J$ = 7.2 Hz, 6H, NCH$_2$C$\underline{H}_3$). $^{13}$C{$^{1}$H} NMR (127.7 MHz, CDCl$_3$): $\delta$ 193.0, 158.0, 133.9, 132.4, 130.2, 128.1, 126.9, 125.1, 113.6, 109.5, 85.2, 80.1, 66.7, 55.6, 51.4, 40.4, 13.7, 12.5. FT-IR (cm$^{-1}$): 2164 ($\tilde{\nu}_{C\equiv C}$), 2044 ($\tilde{\nu}_{C\equiv C}$).

*trans-[Pt(ADC$^{dmp}$)$_2$(C≡CC$_6$H$_4$C≡CPh)$_2$]* ***(2e)***. Prepared from *trans*-[Pt(CNAr$^{dmp}$)$_2$I$_2$] (95 mg, 0.13 mmol) and 2.5 equiv of HC≡CC$_6$H$_4$C≡CPh. Yield: 67% (90 mg, 0.088 mmol). $^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.51 (d, $J$ = 6.5 Hz, 4H, Ar$\underline{H}$), 7.36−7.29 (m, 10H, Ar$\underline{H}$), 7.16−7.09 (m, 6H, Ar$\underline{H}$), 7.04 (d, $J$ = 7.5 Hz, 4H, Ar$\underline{H}$), 6.53 (br, s, $^{195}$Pt satellites poorly resolved, 2H, N$\underline{H}$), 3.56 (br, s, 4H, NC$\underline{H}_2$CH$_3$), 3.31 (br, s, 4H, NC$\underline{H}_2$CH$_3$), 2.51 (s, 12H, Ar−C$\underline{H}_3$), 1.22 (br, s, 6H, NCH$_2$C$\underline{H}_3$), 0.99 (br, s, 6H, NCH$_2$C$\underline{H}_3$). $^{13}$C{$^{1}$H} NMR (127.7 MHz, CDCl$_3$): 195.4, 138.7, 138.3, 131.6, 131.2, 130.8, 130.7, 028.4, 128.0, 127.8, 127.2, 123.9, 117.9, 117.1, 90.6, 89.4, 51.8, 40.3, 20.1, 13.5, 12.7. FT-IR (cm$^{-1}$): 2089 ($\tilde{\nu}_{C\equiv C}$).

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c02641.

X-ray crystallography summary tables, NMR spectra, IR spectra, and additional photoluminescence data (PDF)

### Accession Codes

CCDC 2234160−2234164 contain the supplemental crystallographic data for this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, 583 Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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