ORGANOMETALLICS

ARTICLE

Remarkable Influence of the Cyclometalating Ligand on the Nuclearity and Properties of Heterobridged $(\mu$ -X) $(\mu$ -C=CR) Platinum(II) Complexes

Jesús R. Berenguer, Álvaro Díez, Ana García, Elena Lalinde,* M. Teresa Moreno, Sergio Sánchez, and Javier Torroba

Departamento de Química, Grupo de Síntesis Química de La Rioja, UA-CSIC, Universidad de La Rioja, 26006, Logroño, Spain

Supporting Information

ABSTRACT: Partial dehalogenation reaction of $[Pt(C^N)(\mu-Cl)]_2 [C^N = 2,6$ -diphenylpyridinate (dppyH), 7,8-benzoquinolate (bzq)] with NaC=C^tBu (or HC=C^tBu/NEt₃/CuI) proceeds with formation of binuclear ($[\{Pt(dppyH)\}_2(\mu-Cl)(\mu-C=C^tBu)]$, 1) or tetranuclear ($[Pt_2(bzq)_2(\mu-Cl)(\mu-C=C^tBu)]_2$, 4) complexes, depending on the nature of the cyclometalated ligand. Similar halide-bridged complexes 2, 3, 5, and 6 have also been prepared. The X-ray structures of 1, 4, and 5 reveal the selective formation in all cases of the isomer having the bridging chlorine atom located in a *trans* position to the metalated carbon atoms of two Pt(C^N) units. In 4 and 5, the tetrahedral Pt₄ core is additionally stabilized by short Pt···Pt and $\pi \cdots \pi$ *intramolecular* bonding interactions, which have influence on their photophysical properties. The lower lying absorption bands are ascribed to mixed ¹MLCT [Pt→dppyH]/¹LL/CT [C=CR/X→dppyH] (complexes 1-3) or to ¹MMLL/CT transitions (L = C=CR, L' = bzq) (complexes 4-6, TD-DFT). Complexes



1−3 are nonemissive. By contrast, the tetranuclear clusters are brightly emissive at 77 K (solid state, frozen CH₂Cl₂), exhibiting an unstructured orange emission (560–580 nm). This emission has been attributed, according to computational studies of the frontier orbitals in the optimized T₁ state of 5, to an excited state of large [Pt(d)/ π (C≡CR)/Pt(d)→bzq/bzq] character, with the LUMO delocalized on the adjacent Pt(bzq) fragments. In frozen CH₂Cl₂, an additional low-energy shoulder (~640–675 nm) is also detected, probably due to the presence of close distinct emissive states originating in small modifications in the ground-state structure in frozen solution.

■ INTRODUCTION

Square-planar Pt(II) complexes combining strong ligand field cyclometalating groups and ancillary ligands such as acetylides have drawn great attention in the past decade, mainly because of their impressive and versatile photophysical properties.¹⁻⁶ Apart from the fundamental interest in their intrinsic emissive states, these compounds have shown potential in a variety of applications such as light-emitting materials,7-10 photocatalysts and hydrogen production,¹¹ dye-sensitized solar cells, biosensors, photoswitches,¹²⁻¹⁵ and singlet O_2 sensitization.¹⁶ To date, there have been considerable efforts devoted to mononuclear complexes in which excited-state properties can be easily tuned through structural modification of either the cyclometalated group and/or the electronic nature of the alkynyl substituent ligand. As reported in the literature for most of the alkynylcycloplatinate complexes, the luminescence origins are usually from excited states of metal-to-ligand (cyclometalated) charge transfer (³MLCT) mixed with some ligand-to-ligand charge transfer (³LLCT) character. In addition, some of these complexes show rich polymorphism in the solid state and also intriguing spectroscopic and photophysical properties associated

with their propensity to engage in interplanar stacking through the occurrence of Pt···Pt and/or $\pi \cdot \cdot \cdot \pi$ interactions.^{11,17–20}

In this area, the employment of diethynyls of type HC C-R-C=CH or polypyridyl-substituted acetylide groups has also allowed the study of bi- and polymetallic systems with interesting photophysical properties.^{21–24} However, despite the well-established ability of alkynyl groups to act as bridging ligands leading to bi- and multinuclear complexes^{25–43} and the numerous studies on their optical properties,^{34–43} the chemistry of cycloplatinated fragments connected by μ -C=CR groups remains to be fully explored. To our knowledge, only the C^N bimetallic complexes [*anti*-{Pt($\kappa^2 C$, N-N^C^N)(μ -C=CSiMe₃)}₂] [N^C^N = 2,6-(C=NR)₂C₆H₃, R = C₆H₄OCH₃-4]⁴⁴ and C^P complexes [Pt(C^P)(μ -C=CPh)]₂ and [Pt(C^P)(μ -C=CPh)₂Pt(C₆F₅)₂]⁻ [C^P = $\kappa^2 C$, P-CH₂C₆H₄P(*o*-tolyl)₂]⁴⁵ have been reported, but with a focus on their structural characteristics and reactivity.

In this context, recent research has shown that the spectroscopic properties (absorption and luminescence) of binuclear cycloplatinated Pt(II) complexes containing different types of

Received:December 15, 2010Published:February 28, 2011



Scheme 1



single or double bridging groups such as pyrazolates,^{46–53} diphosphines^{20,48,54–60} or bidentate organic anions^{53,60–67} are very interesting, because the degree of *intramolecular* Pt···Pt and/or $\pi \cdot \cdot \cdot \pi$ interactions in these systems can control the nature of the excited state. For instance, Thompson and coworkers have reported the influence of the pyrazolate substituents on the Pt···Pt separation and on the photophysical properties in a series of doubly bridged complexes $[(C^{N})Pt(\mu-pz)]_2$ $[C^{N} = 2-(4,6-difluorophenyl)pyridine].^{49,52} Curiously, the$ *intramolecular*metal–metal-to-ligand charge transfer (MMLCT) excited state can be tuned through regulation of the Pt···Pt spacing, but due to the larger interplanar separation between the cyclometalated C^NN ligands, the*intramolecular* $<math>\pi \cdot \cdot \cdot \pi$ interaction between its C^NN ligands is negligible.

Our group has recently reported the first preparation of monoanionic luminescent cycloplatinated complexes Q[Pt- $(bzq)(C \equiv CR)_2]^{68}$ and $Q[Pt(dppy)(C \equiv CR)]^4$ $(Q = NBu_4, NBu_4)$ bzqH = 7,8-benzoquinoline, $dppyH_2 = 2,6$ -diphenylpyridine). These complexes are useful precursors for the synthesis of cluster complexes, and in previous works, we have demonstrated that the photophysical properties of $[Pt(bzq)(C \equiv CR)_2]^-$ are significantly modified by neutralization with Tl⁺⁶⁹ or Pb^{2+,70} Continuing our studies on polymetallic alkynyl-bridging cycloplatinate systems, in this contribution we report the synthesis and preparation of three diplatinum complexes $[{Pt(dppyH)}_2$ - $(\mu$ -X) $(\mu$ -C=C^tBu)] (X = Cl 1, Br 2, I 3) and three tetranuclear clusters $[Pt_2(bzq)_2(\mu-Cl)(\mu-C\equiv CR)]_2$ (R = ^tBu 4, Ph 5, $C_6H_4CF_3-4$ 6), the latter containing an unusual tetrahedral Pt_4 core generated by two alkynyl and two chloride bridging ligands and stabilized by two pairs of additional intramolecular Pt···Pt and $\pi \cdots \pi$ bonding interactions.

RESULTS AND DISCUSSION

As summarized in Scheme 1i, the synthesis of complex 1 takes place following a classical dehydrohalogenation reaction. Thus, the reaction of the insoluble chloride binuclear complex $[Pt(dppyH)(\mu-Cl)]_2$, in which dppyH⁻ is the monodeprotonated 2,6-diphenylpyridinate, with excess tert-butylacetylene in the presence of NaOMe (4 equiv of $HC \equiv C^{t}Bu/NaOMe$), in acetone at room temperature for 48 h, evolves through a monodehydrohalogenation process to give the diplatinum complex [{Pt(dppyH)}₂(μ -Cl)(μ -C=C^tBu)] (1) as a yellow microcrystalline solid in moderate yield (61%). A similar result was obtained by using Sonogashira's conditions [excess of HC≡ $C^{t}Bu$ in the presence of the catalytic mixture (CuI/NEt₃) in chloroform (see Experimental Section for details)]. Although the expected second chloride/acetylide exchange does not occur, subsequent metathesis of the chloride bridging ligand with excess KBr or KI yielded the corresponding bromide (2) and iodide (3)derivatives (Scheme 1ii).

Complexes 1–3 were fully characterized by IR and ¹H NMR spectroscopy, elemental analysis, and MALDI spectrometry, and, in the case of 1, its molecular structure has been confirmed by X-ray crystallography. The three complexes show a characteristic $v_{C=C}$ band (1956 1, 1955 2, 1963 3 cm⁻¹) in the typical range of η^2 -alkynyl C=C^tBu bridging groups.^{71–77} Due to their limited solubility, good ¹³C{¹H} and ¹⁹⁵Pt{¹H} NMR spectra could not be acquired; however, the well-resolved ¹H NMR spectra reveal the presence of only one set of dppyH signals and one resonance due to the ^tBu alkynyl substituent. This pattern is consistent with a *syn* orientation of the metalated dppyH ligands and a fast σ/π exchange of the C=C^tBu group between both Pt centers. The molecular



Figure 1. Molecular structure of $[{Pt(dppyH)}_2(\mu$ -Cl) $(\mu$ -C \equiv C^tBu)] \cdot 0.5CH₂Cl₂ (1 \cdot 0.5CH₂Cl₂).

Table 1.	Selected	Bond	Lengths	and	Bond	Angles	for
1.0.5CH	$_2Cl_2$						

Distances [Å]					
$\begin{array}{l} Pt-N_{dppyH}\\ Pt-C_{orth}\\ Pt(1)-Cl(1)\\ Pt(2)-Cl(1)\\ Pt(1)-C(1) \end{array}$	2.058(4), 2.097(4 1.980(4)-1.985(5 2.4728(11) 2.5017(12) 1.960(5)	$\begin{array}{llllllllllllllllllllllllllllllllllll$	2.191(4) 2.198(5) 1.236(6) 1.477(7) 3.1542(3)		
Angles [deg]					
N _{dppyH} -Pt-C _{orth}	81.15(18), 81.47(18)	C(1) - Pt(2) - C(2)	32.71(16)		
C(1) - Pt(1) - C(2)	7) 96.36(19)	Pt(1)-Cl(1)-Pt(2)	78.70(3)		
N(1)-Pt(1)-Cl(1) 103.48(10)	Pt(1)-C(1)-Pt(2)	98.74(18)		
C(1)-Pt(1)-Cl(1) 78.19(13)	C(1) - Pt(2) - C(24)	101.9(18)		
N(1)-Pt(1)-Pt(1)	2) 134.11(10)	N(2)-Pt(2)-Cl(1)	99.46(11)		
Pt(1) - C(1) - C(2)	2) 167.3(4)	C(1)-Pt(2)-Cl(1)	73.64(12)		
C(1)-C(2)-C(3)) 159.7(5)	N(2)-Pt(2)-Pt(1)	130.55(10)		

structure of complex 1 (Figure 1, Table 1) confirmed the *syn* orientation of the orthometalated groups and allowed to establish that of the two possible *syn* isomers (**B**, **D**, Chart 1); the one formed has the chlorine atom *trans* to both metalated carbon atoms (**B**). The selective formation of isomer **B** is in accordance with that which would be expected, taking into account the known greater *trans* influence of the $C \equiv C^t$ Bu relative to the chlorine. In addition, as can be seen in Figure S1 (in the Supporting Information), the expected larger steric interactions between the bulky *tert*-butyl group and the hanging phenyl groups are also probably disfavoring the other *syn* isomer (**D**) and the *anti* configuration **A**.

It is worth noting that although numerous examples of double $(\mu\text{-}C\equiv\text{CR})_2^{34,44,45,71-80}$ and mixed $(\mu\text{-}C\equiv\text{CR})(\mu\text{-}X)$ (X = hydride, ⁸¹⁻⁸⁴ PPh₂C≡CR^{72,78}) diplatinum complexes have been reported, as far as we know, complexes 1-3 are the first representative examples in platinum chemistry of homobimetal-lic complexes stabilized by a rare heterobridged mixed $(\mu\text{-}X)$ - $(\mu\text{-}C\equiv\text{CR})$ system. As is shown in Figure 1, due to the σ/π coordination of the acetylide ligand, the coordination environment of both Pt atoms is different. Thus, Pt(1) completes a distorted square-planar coordination with a σ -bonded alkynyl carbon (Pt(1)-C(1) 1.960(5) Å), while Pt(2) is side-on bonded to both alkynyl carbon atoms. The Pt(1)-C(1) bond distance is comparable to those found in the *anti* binuclear cyclometalated complex [*anti*-{Pt(κ^2C_n N-N^C^N)(μ -C≡CSiMe_3)}] (1.945(3), 1.935(4) Å) reported by Elsevier et al.⁴⁴ and in many other

Chart 1



complexes containing the $Pt(\mu-C \equiv CR)_2Pt$ core.^{34,44,45,71-80} However, the symmetrical Pt(2)-C(acetylide) side-on distances of 2.191(4) and 2.198(5) Å are relatively shorter when compared with values previously found in related anionic $([{Pt(C_6F_5)_2(\mu-C=CPh)}_2]^2 [2.263(12)-2.369(15) Å]^{71})$ or neutral ([anti-Pt(C₆F₅)L(μ -C \equiv CR)]₂ [L = PPh₃; R = Ph, C(OH)Ph₂, C(OMe)MeEt] [2.261(6)-2.362(6) Å],^{74,75} [anti- $C(OH)Ph_2$, C(OMe)MeEt] [2.261(6)-2.362(6) Å],^{74,75} [anti-Pt(C^P)(μ -C=CPh)]₂ [2.311(3), 2.368(3) Å]⁴⁵) doubly bridged bis(alkynyl) complexes. These short distances, which can be attributed to the small *trans* influence of the N(2) pyridine atom, suggest a very strong interaction of the Pt(2) center with the alkynyl unit $[C(1)\equiv C(2)]$. The distortion form linearity of the $Pt(1)-C(1)\equiv C(2)$ unit (angles at C(1) 167.3(4)° and C(2) $159.7(5)^{\circ}$ and the C(1)=C(2) distance (1.236(6) Å) are, however, within the range found in previous μ -(1 κC^{α} : η^2) alkynyl bridging complexes.^{34,44,45,71–80} The Pt–Cl bridging distances (2.4728(11), 2.5017(12) Å) are slightly longer than those found in [trans-Pt- $(C^N)(\mu$ -Cl)]₂ (C^NH = 2-(4-fluorophenyl)-6-propylpyridine; $Pt-Cl = 2.3100(6) Å (trans to N), 2.4620(6) Å (trans to C))^{85}$ and in the long end-range of chloride-bridged Pt(II) complexes.⁸⁶ The angle at the chlorine atom is very acute $(78.70(3)^{\circ})$, forcing a rather short $Pt \cdot \cdot \cdot Pt$ distance of 3.1542(3) Å, and, probably due to the steric demands of the hanging phenyl groups, the central diplatinacycle is quite puckered with a dihedral angle of 71.94° between the best platinum coordination planes. Curiously, these values are comparable to those found in $[anti-{Pt(\kappa^2C_iN-N^{\wedge}C^{\wedge}N)-}$ $(\mu$ -C=CSiMe₃)₂ (3.15573(13) Å and 75.07(12)°),⁴⁴ which also contains a bulky substituent attached to the cyclometalated ligand. However, remarkably less puckered (~45-49.6°) or even planar structures with longer Pt···Pt separations (3.22–3.65 Å) have been observed in other bis(alkynyl) bridging complexes,⁷⁵ thus reflecting the role played by the steric demands of co-ligands in the final geometry. The hanging Ph rings adopt a face-to-face configuration (C(20)-C(39) 4.16(3) Å), forming a dihedral angle of about 51.05° (see also Figure S1). This allows the chlorine atom to form two close intramolecular contacts with both electrophilic ipso-C atoms, with $Cl \cdots C$ distances (3.22(1) and 3.234(9) Å) shorter than the sum of the corresponding van der Waals radii (3.45 Å).⁸⁷



Figure 2. (a) View of the dimers formed for $1 \cdot 0.5$ CH₂Cl₂ by intermolecular $\pi \cdot \cdot \cdot \pi$ (black, dotted lines) and T-shaped (light blue, dotted lines) noncovalent interactions. (b) Space-filling diagram of the extended crystal lattice of $1 \cdot 0.5$ CH₂Cl₂ showing the formation of channels along the *c* axis.



Figure 3. Molecular structure of $[Pt_2(bzq)_2(\mu-Cl)(\mu-C\equiv C^tBu)]_2$. 1.6CHCl₃·1.5CH₃CH₂OH (4·1.6CHCl₃·1.5CH₃CH₂OH, A molecule).

As shown in Figure 2a, the molecules associate in dimers in a head-to-tail manner through intermolecular $\pi \cdots \pi$ interactions, which involve the central pyridine ring and the metalated phenyl group of two distinct dppyH ligands (interplanar distance 3.46 Å, dihedral angle between planes 0°), assisted by two secondary T-shaped C-H··· π interactions (C···C 3.53 Å, H···C 2.78 Å, C-H···C 139.1°). In the extended crystal lattice, these dimers arrange to yield circular void channels along the *c* axis (Figures 2b and S2), in which the dichloromethane solvent molecules are located.

The photoluminescence properties of all binuclear complexes 1-3 were investigated in solution (CH₂Cl₂, NCMe) and in the solid state, both at room and low temperature (77 K). To our surprise, despite the presence of cyclometalating and alkynyl groups (strong field ligands), which could raise the energy of deactivating metal-centered $d-d^*$ states, or even the relatively short Pt···Pt separation found in 1, complexes 1-3 were nonemissive. At present, it is not straightforward to explain the lack of emissive properties in these bimetallic complexes. The nature of the possible quenching process is not clear, although it could be attributed to easy deactivation due to the simultaneous presence of a hanging phenyl group and weak field chloride bridging ligand. However, the insoluble precursor [Pt(ddpyH)- $(\mu$ -Cl)]₂ exhibits in the solid state a bright orange emission [λ_{max} 585 nm (λ_{exc} 430 nm)].

Therefore, looking for better emissive properties, and also to further investigate the influence of the steric constraints of the cyclometalated group on the structure of these complexes, we



Figure 4. Molecular structure of $[Pt_2(bzq)_2(\mu-Cl)(\mu-C\equiv CPh)]_2$ · $3CH_3COCH_3$ (5· $3CH_3COCH_3$).

examined similar reactions using the 7,8-benzoquinolate diplatinum complex $[Pt(bzq)(\mu-Cl)]_2$ as starting precursor. Interestingly, this change afforded the synthesis of related chloride/ alkynyl bridging complexes, which form unprecedented tetranuclear photoluminescent $[Pt_4(bzq)_4(\mu-Cl)_2(\mu-C=CR)_2]$ compounds. As is shown in Scheme 1iii, the reactions of [Pt(bzq)- $(\mu$ -Cl)]₂ in acetone with 2 equiv of HC=CR (R = ^tBu, Ph, $C_6H_4CF_3-4$) and NaOMe at low temperature (0 °C) for 3 h allowed the compounds $[Pt_2(bzq)_2(\mu-Cl)(\mu-C \equiv CR)]_2$ (R = ^tBu 4, Ph 5, $C_6H_4CF_3-4$ 6) to be obtained in low yield (14–28%), as yellow (4) or pale orange (5, 6) microcrystalline solids. Similar yields were obtained using different stoichiometries. Their spectroscopic (1 H NMR, IR), high-resolution MALDI(+), and elemental analyses results were consistent with the formulation given in Scheme 1, and the molecular structures of 4 and 5 were unambiguously confirmed by single-crystal X-ray diffraction (see Figures 3, 4, S3 and Tables 2, 3, S1). Distinctive $\nu_{C \equiv C}$ stretching frequencies in the typical range of alkynyl bridging (1906–1922 cm^{-1}) groups were observed in the IR spectra, and their ¹H NMR spectra showed the expected two sets of proton resonances for the two nonequivalent types of benzoquinolate groups. Worth noting are the two proton H² resonances at very low field (δ 9.44, 8.67 4; 9.39, 8.67 5; 9.40, 8.73 6), as illustrated in Figure S4 for complex 5. Complex 4 shows a singlet resonance at δ 1.34, proving the chemical equivalence of both $C \equiv C^t Bu$ groups. The tetranuclear

	Dista	ances [Å]	
Pt-N _{bzq}	2.080(7)-2.090(6)	Cl(2)-Pt(3,4)	2.491(2), 2.477(2)
Pt-C _{orth}	1.982(8)-1.988(8)	C(53)-C(54)	1.254(11)
Pt(1) - C(53)	1.954(8)	C(59) - C(60)	1.224(11)
Pt(2) - C(59)	1.956(8)	$Pt(1) \cdots Pt(3)$	3.2764(4)
Pt(3) - C(59)	2.241(8)	$Pt(2) \cdots Pt(4)$	3.3450(7)
Pt(3) - C(60)	2.129(8)	$Pt(2) \cdots Pt(3)$	3.7046(4)
Pt(4) - C(53)	2.187(7)	$Pt(2) \cdots Pt(1)$	4.3139(4)
Pt(4) - C(54)	2.135(8)	$Pt(1) \cdots Pt(4)$	3.6669(6)
Cl(1)-Pt(1,2)	2.424(2), 2.436(2)	$Pt(3)\cdots Pt(4)$	3.6633(5)
	Ang	les [deg]	
$N_{bza} - Pt - C_{orth}$	80.7(3)-82.8(4)	C _{orth} -Pt-Cl	170.8(3)-174.4(3)
N(1) - Pt(1) - C(53)	173.0(3)	N _{bzq} -Pt-Cl	89.6(2)-94.2(2)
N(2) - Pt(2) - C(59)	171.0(3)	Pt(1)-C(53)-C(54)	164.5(7)
Pt(3)-Cl(2)-Pt(4)	95.03(8)	Pt(2)-C(59)-C(60)	167.1(7)
Pt(1)-Cl(1)-Pt(2)	125.17(9)	C(53) - C(54) - C(55)	160.5(8)
Cl(1) - Pt(1) - C(53)	95.6(2)	C(59) - C(60) - C(61)	160.1(8)
Cl(1) - Pt(2) - C(59)	96.9(2)		

Table 2. Selected Bond Lengths and Bond Angles for 4 · 1.6CHCl₃ · 1.5CH₃CH₂OH (A molecule)

Table 3. Selected Bond Lengths and Bond Angles for 5.3CH₃COCH₃

	Distances [Å]				
Pt-N _{bza}	2.074(5) - 2.106(5)	Cl(2) - Pt(2,4)	2.4098(16), 2.4263(17)		
$Pt-C_{orth}$	1.985(6)-1.999(7)	C(27)-C(28)	1.253(9)		
Pt(2) - C(27)	1.945(7)	C(61) - C(62)	1.249(9)		
Pt(4)-C(61)	1.929(7)	$Pt(1)\cdots Pt(2)$	3.2342(4)		
Pt(1)-C(61)	2.218(6)	$Pt(3)\cdots Pt(4)$	3.3850(4)		
Pt(1)-C(62)	2.106(6)	$Pt(1)\cdots Pt(3)$	3.5550(3)		
Pt(3)-C(27)	2.262(6)	$Pt(2) \cdots Pt(4)$	4.2709(4)		
Pt(3)-C(28)	2.124(6)	$Pt(1)\cdots Pt(4)$	3.7210(4)		
Cl(1) - Pt(1,3)	2.4601(17), 2.4483(17)	$Pt(2)\cdots Pt(3)$	3.7448(4)		
Angles [deg]					
N _{bzq} -Pt-C _{orth}	81.4(3)-82.4(2)	C_{orth} -Pt-Cl	170.2(2)-175.0(2)		
N(2) - Pt(2) - C(27)	174.0(2)	N _{bzq} -Pt-Cl	89.15(17)-93.03(18)		
N(4) - Pt(4) - C(61)	171.9(2)	Pt(2)-C(27)-C(28)	166.8(5)		
Pt(1)-Cl(1)-Pt(3)	92.81(6)	Pt(4) - C(61) - C(62)	164.2(5)		
Pt(2)-Cl(2)-Pt(4)	124.04(8)	C(27) - C(28) - C(29)	160.6(7)		
Cl(2) - Pt(4) - C(61)	97.11(19)	C(61) - C(62) - C(63)	160.6(7)		
Cl(2) - Pt(2) - C(27)	94.61(19)				

nature of all complexes is further confirmed by their MALDI(+) spectra, which exhibited the expected cluster peak (m/z 1726 4, 1766 5, and 1902 for 6), corresponding to M⁺.

The X-ray structures of 4 and 5 reveal that they are formed by four Pt(bzq) units linked by two μ -chloride and two μ - κ C^{α}: η ²acetylide bridging groups. In 4, the asymmetric part of the crystal structure shows two formula units, but due to their similarity, only one of them will be discussed (Figure 3, Table 2; see Table S1 and Figure S3 for complete data). In both complexes, the resulting tetrahedral platinum core is additionally stabilized by two short *intramolecular* Pt···Pt (Pt(1)–Pt(3) 3.2764(4), Pt-(2)–Pt(4) 3.3450(7) Å 4; Pt(1)–Pt(2) 3.2342(4), Pt(3)– Pt(4) 3.3850(4) Å 5) and π ··· π (minimum distance between bzq ligands, 3.232(9), 3.296(9) Å 4; 3.294(9), 3.325(9) Å 5) bonding interactions, which are probably the driving force of the observed final dimerization. To the best of our knowledge, the tetrahedral Pt₄ motif is unknown in platinum(II) chemistry.⁸⁸ The remaining four single-bridged edges of the tetrahedral array exhibit Pt···Pt distances (3.6633(5)-4.3139(4) Å 4, 3.5550(3)-4.2709(4) Å 5; see Tables 2, 3 and S1) longer than the van der Waals limit (3.5 Å),⁸⁷ excluding bonding interactions. Due to the side-on coordination of the C≡CR groups, there are two types of Pt environments (Pt(1)/Pt(2) and Pt(3)/Pt(4) 4, Pt(2)/Pt(4) and Pt(1)/Pt(3) 5), which, following the transphobia effect, exhibit an analogous structural disposition to that seen in the binuclear complex 1. Thus, Pt(1) and Pt(2) in 4 and Pt(2) and Pt(4) in 5 are σ -bonded to the C_{α} alkynyl carbon (Pt-C_{α} 1.929(7)-1.956(8) Å), which is located *trans* to the cycloplatinate N atoms N(1), N(2) and N(2), N(4), respectively. The other two platinum atoms are asymmetrically π -bonded (2.129(8)-2.241(8) Å 4; 2.106(6) - 2.262(6) Å 5) to the triple bonds of the alkynyl units $(C(53)\equiv C(54), C(59)\equiv C(60)$ 4; $C(27)\equiv C(28), C(61)\equiv C$ (62) 5), which adopt a *trans* disposition to the cycloplatinate N atoms. As a consequence, the cyclometalated C of each Pt(bzq) unit is coordinated *trans* to the chlorine atom of the corresponding single-bridging μ -Cl group with Pt-Cl distances (2.424(2)) 2.491(2) Å 4; 2.4098(16)-2.4601(17) Å 5) that are comparable to those seen in 1. The Pt(3)-Cl(2)-Pt(4) (4) and Pt(1)-Cl(1) - Pt(3) (5) angles $(95.03(8)^{\circ} 4, 92.81(6)^{\circ} 5)$ are more optimal than Pt(1)-Cl(1)-Pt(2) (4, 125.17(9)°) and Pt(2)-Cl(2)-Pt(4) (5, 124.04(8)°), and all of them wider than that observed in complex 1 ($78.70(3)^{\circ}$).

As can be seen, the two pairs of unbridged Pt(bzq) units adopt an eclipsed configuration being nearly coplanar (dihedral angles of 4.50° and 6.13° 4; 5.37° and 7.75° 5), thus favoring the simultaneous presence of close Pt···Pt and π ··· π bonding interactions, whereas the angles between adjacent μ -bridging Pt(bzq) units range from 70.93° ([Pt(1)] vs [Pt(2)]) to 75.74° ([Pt(3)] vs [Pt(4)]) in 4 and 76.32° ([Pt(2)] vs [Pt(4)]) to 81.50° ([Pt(1)] vs [Pt(3)]) in 5. As noted in the Introduction, $\pi \cdots \pi$ stacking is an important structural feature in platinum chemistry with chelating N-donor ligands.^{11,17–20} In these systems offset, slipped, or parallel displaced configurations are usually preferred over eclipsed configurations to reduce the electrostatic repulsions. Platinum complexes exhibiting a faceto-face eclipsed $\pi \cdots \pi$ stacking disposition are far less common. Although the factors that influence the preference for an eclipsed configuration are still unclear, it is worth pointing out that in the cyclometalated complexes [(RCNN)₂Pt₂(μ -dppm)₂] reported by Che et al.^{10,20,55,58} the preference for an eclipsed configuration has been noted to increase with the extent of π conjugation in the cyclometalating ligand.

We expected that the structural characteristics of these cumules (4-6), containing η^2 -alkynyl bridging and both Pt···Pt and $\pi \cdot \cdot \cdot \pi$ intramolecular interactions, allow us to get more insight into their relationship with the photophysical properties.

PHOTOPHYSICAL PROPERTIES

Absorption Spectroscopy. The spectroscopic (1-6) and photophysical (4-6) data are listed in Tables 4 and 5, respectively. Room-temperature electronic spectra of complexes 1-3 and 4-6 in CH₂Cl₂ are given in the Supporting Information (Figure S5) and in Figure 5, respectively. With reference to previous Pt(II) cyclometalated acetylide complexes,³⁻⁶ the intense absorption bands at λ < 350 nm are attributed to intraligand $(\pi\pi^*)$ transitions located on the cyclometalated and alkynyl ligands. The broad low-energy absorptions (with a shoulder in 1-3) tailing to 475-500 nm are mainly ascribed to charge transfer (CT) transitions, composed of both metal-toligand ($Pt \rightarrow bzq$) and ligand-to-ligand (alkynyl/halide $\rightarrow bzq$) contributions. According to time-dependent TD-DFT calculations (vide infra) on complex 5, the low-energy bands in the tetranuclear derivatives (4-6) have a remarkable ¹MMLL'CT character (L = alkynyl, L' = bzq). These transitions involve transfer of electronic charge from the system formed by the Pt centers connected through the alkynyl group, $[Pt(\mu-C \equiv CR)Pt]$, to the bzq ligand bonded to the $\pi(C \equiv C)$ Pt atom. At the long-

Table 4. Absorption Data for 1–6

compound	absorption, $\lambda_{\rm max}/{\rm nm}~(10^3~\epsilon~{\rm M}^{-1}~{\rm cm}^{-1})^a$
1	237 (46.0), 273 (36.5), 307 (22.3), 325sh (17.8), 342 (14.8), 390 (9.6), 430sh (4.1)
2	236 (39.9), 270 (30.4), 306 (16.6), 340 (13.0), 395 (7.1), 435sh (3.6)
3	235 (34.7), 267 (26.6), 312 (12.9), 341 (10.9), 402 (4.7), 440sh (1.9)
4	225 (163.7), 252sh (110.5), 310 (52.0), 370 (24.6), 379 (23.7), 425 (12.9)
5	223 (263.2), 240sh (168.8), 305 (73.4), 380 (25.3), 420 (19.4)
6	215 (196.2), 241sh (145.4), 309 (66.4), 333sh (54.0), 400 (29.1)
^{<i>a</i>} Measureme	ents were made on samples in CH ₂ Cl ₂ , 5×10^{-5} M.

Table 5. Emission Data for 4-6 at 77 K^a

compound	media	$\lambda_{ m em}/ m nm$	$ au/\mu { m s} \left(\lambda_{ m max} ight)$
4	solid	575 (λ _{exc} 360–490)	23.5 (575)
	$\begin{array}{c} CH_2Cl_2~5\times\\ 10^{-5}~M \end{array}$	580 _{max} , 675sh (λ _{exc} 360–480)	20.1 (580)
5	solid	580 ($\lambda_{\rm exc}$ 365–485)	10.9 (580)
	$\begin{array}{c} CH_2Cl_2 \ 5 \times \\ 10^{-5} \ M \end{array}$	575 (λ _{exc} 360–460)	18.8 (575)
		575, 640 _{max} (λ _{exc} 490)	14.2 (640)
6	solid	570 (λ_{exc} 360–500)	28.3 (570)
	$CH_2Cl_2 \ 5 \ \times$	560 _{max} , 660sh	27.5 (560),
	$10^{-5} { m M}$	$(\lambda_{\rm exc} \ 360-480)$	11.0 (660)
			- / .

^a In the solid state, at 298 K, a weak emission was detected (600 nm 4; 630 nm 5; 560 nm 6).

wavelength tail of each complex, the absorption, in part, could be attributed to a triplet charge transfer transition, which becomes partially allowed due to the enhancement of spin—orbit coupling via the heavy metal center,^{4,89–91} though some contribution of transitions due to ground-state intramolecular $\pi \cdots \pi/Pt \cdots Pt$ interactions could not be excluded. This suggestion is in line with the presence of short $Pt \cdots Pt [3.1542(3) Å]$ in 1 and close Pt···Pt [3.2342(4)-3.3850(4) Å] and $\pi \cdots \pi$ [3.23(9)-3.296(9) Å interactions in 4 and 5, as revealed from X-ray diffraction studies. It is worth noting that, in both series, the maximum of the low-energy broad band is affected by the nature of the bridging ligands. Thus, the band bathochromically shifts to lower energies (402, 440sh 3 < 395, 435sh 2 < 390, 430sh nm 1; 425 4 < 420 5 < 400 nm 6) as the electron donor ability of the co-ligand halide (I > Br > Cl 3-1) and acetylide (C=C^tBu > C=CPh > $C \equiv CC_6H_4CF_3-4$ increases, supporting the ligand (X/C $\equiv CR$) to ligand (cyclometalating) charge transfer contribution.

Emission Spectroscopy. As commented before, the binuclear halide–acetylide bridged complexes 1-3 are nonemissive. By contrast the tetranuclear complexes are brightly emissive at low temperatures, in both the solid state (77 K) and solution (CH₂Cl₂, 77 K). At room temperature, no emission was detected in solution, and in the solid state all three complexes exhibit only very weak orange emissions (560–630 nm). Upon cooling the solids at 77 K, complexes 4-6 produce brightly slightly blueshifted orange unstructured photoluminescence in the range

570-580 nm (Figure 6). The relatively long lifetimes (10.9-28.3 μ s) suggest that the emissive states are triplet in nature. In frozen CH₂Cl₂ solution, the emission profile for complexes 4 and 6 is not dependent on the wavelength. Upon exciting in the range 360-480 nm, both complexes show an asymmetrical band with the peak maximum slightly red-shifted in the case of 4 (λ_{em} 580 nm) or blue-shifted for 6 (560 nm) from that observed in the solid state (77 K). A low-energy shoulder better resolved in compound 6 (660 nm) is also detected (Figure S6). This fact suggests the contribution of two close emissive states to the emission profile, further confirmed by the measurement of different lifetimes monitoring at 560 (27.5 μ s) and 660 nm (11.0 μ s) for this complex. Dual phosphorescence is more evident in the phenylacetylide derivative 5. As can be seen in Figure 7, complex 5 shows a structureless symmetrical band, slightly blue-shifted (575 nm) from that of the solid, upon exciting in the range 360-460 nm. However, by increasing the excitation wavelength the intensity of the emission profile decreases and is resolved into two bands with different lifetimes (575 nm (18.8 μ s) and 640 nm (14.2 μ s)), the relative intensity of which depends on the excitation wavelength. The excitation spectra monitoring both maxima are different, excluding excimer-type emission formation and suggesting the presence of close distinct emissive states, which may be attributed to a small modification in the ground-state structure in the frozen glass. It is



Figure 5. Normalized absorption spectra of 4-6 in CH₂Cl₂, 5×10^{-5} M.

likely that the freezing process causes the formation of slightly different entities, having small intramolecular differences in the separation of the Pt(bzq) fragments, although the presence of intermolecular aggregates cannot be completely excluded. It is not straightforward to assign the nature of the emissive state in these clusters. However, the observed emissions are largely red-shifted in relation to typical monomeric benzoquinolate complexes, such as the anionic bis(chloride) (NBu₄)[Pt(bzq)Cl₂]⁴⁶ (CH₂Cl₂, 77 K, 494 nm) or bis(alkynyl) (NBu₄)[Pt(bzq)(C=CR)₂]⁵ (CH₂Cl₂) 77 K, $\lambda_{\text{max}} R = {}^{t}Bu$ 512, Ph 505, C₆H₄CF₃-4 492 nm) derivatives, and appear in the range of aggregate and/or excimeric induced emissions ascribed to ligand-ligand $(\pi \cdots \pi)/Pt \cdots Pt$ interactions $({}^{3}\pi\pi^{*}/{}^{3}MMLCT \text{ manifolds}), {}^{11,17-20,46-52,54-60}$ suggesting that they are likely involved in the emissive state. As shown in Table 5, although the influence of the alkynyl group is small, the energy maxima follow the same trend (580 nm 4 < 575 nm 5 < 560 nm 6) as that observed in the absorption maxima, which is consistent with its contribution to the metal-alkynyl-based HOMO $[Pt(5d)/\pi(C \equiv CR)]$. Taking into account these observations, and the salient features of the frontier orbitals in the optimized T₁ state on complex 5 (see below), we suggest that the emission comes from an excited state of largely $[Pt(d)/\pi(C \equiv CR)/Pt(d) \rightarrow bzq/bzq]$ character, with the LUMO widely delocalized onto the adjacent



Figure 7. Emission spectra of **5** in CH_2Cl_2 (5 × 10⁻⁵ M) at 77 K.



Figure 6. (a) Normalized emission spectra of 4-6 in the solid state at 77 K. (b) Normalized emission spectra of 4 at 298 (weak) and 77 K.



Figure 8. Frontier orbital plot for $[Pt_2(bzq)_2(\mu-Cl)(\mu-C=CPh)]_2$. 3CH₃COCH₃ (**5**·3CH₃COCH₃) for the ground state and excited state.

Pt(bzq) fragments. The intramolecular stacking of the planar "Pt-(bzq)" units is enhanced in the excited state, playing a key role in the emissive manifold.

DFT Calculations. The photophysics of lumophores can be better understood by revealing the electronic structures of the excited states. In this work, density functional theory (DFT) calculations were performed on one of the tetranuclear complexes (5), in order to get some insight into the electronic character of this type of cluster. The geometry of complex 5 in the ground state (S_0) and excited state (T_1) was optimized without any symmetry constraints, including the phenyl groups of the acetylide ligands. The most important geometrical parameters are given in Table S2, together with the corresponding experimental values for comparison. In the optimized ground-state geometry, the σ Pt-C (bzq, alkynyl) and Pt-N bond lengths are in very good agreement with those found in the structure, and the Pt-Cl and η^2 -Pt-C(alkynyl) bridging bond lengths are only slightly elongated (0.5-11%). However, the two observed Pt···Pt contacts in the crystal structure are clearly overestimated (3.6934; 3.6929 Å calculated vs 3.2342(4) and 3.3850(4) Å experimental). We note that this result is not unexpected, as dispersion and correlation effects have an important role in noncovalent $M \cdots M$ interactions, $^{92-94}$ and they are not currently accurately accounted for in commercial DFT programs.95 Some selected frontier molecular orbitals (HOMO-3 to LUMO+3), together with their composition in terms of ligands and metals, are collected in the Supporting Information (Figure S7, Table S3). As an illustration, the HOMO and LUMO are shown in Figure 8. As can be seen, the HOMO is mainly delocalized over the four platinum centers (32%) and the two phenylacetylide groups (60%), with a negligible contribution of chloride (3%), and the LUMO is essentially localized on the π^* orbitals of the two benzoquinolate groups located in trans disposition to the η^2 -alkynyl bonds.

To examine the UV—vis absorption spectrum, the lowest lying vertical singlet excitation (50) energies and the first triplet manifold were calculated by TD-DFT calculations based on the optimized structure, together with the consideration of the solvation effect (CH_2Cl_2). Data including energy gaps calculated and corresponding assignments of the transitions with strong oscillator strengths are listed in Table S4 of the Supporting Information, and, as an illustration, Figure 9 depicts the selected transitions as bars with the experimental spectrum of 5 in



Figure 9. Selected transitions and bars with the experimental spectrum of 5 in CH_2Cl_2 .

CH₂Cl₂. The calculated energy gap of the S₀→S₁ transition at 432 nm is close to the observed maximum found at 420 nm, and the triplet S₀→T₁ centered at 472 nm lies within the visible extended tail of the band. The S₁ state is mainly characterized by the HOMO→LUMO transition (88%), and therefore, the lowest lying absorption can be assigned as a charge transfer from the Pt(μ -C=CPh)Pt system to the benzoquinolate ligand located *trans* to the η^2 -alkynyl bond (MMLL'CT). The triplet is more complex, being attributed to the sum of several transitions (including the HOMO→LUMO) with contribution mainly from occupied orbitals located on the bzq groups. Other excited states such as S₃−S₅ (395–393 nm) also have additional contribution from intraligand transitions between opposite bzq groups.

The nature of the phosphorescent emission was addressed by optimization of the first triplet state. For comparison with the optimized ground state S₀ (and the X-ray diffraction structure), their geometric details are also included in Table S2. In the T₁ optimized geometry, which exhibits a C_2 symmetry, the Pt-C (σ and π) bond distances and the Pt · · · Pt separation between the stacked fragments are slightly shortened. These decreases could be the result of transferring one electron from the antibonding platinumalkynyl bridging based HOMO toward the two stacking Pt(bzq) fragments. The calculated emission energy as the difference between the energy of the T1 and the energy of the singlet state with the triplet state optimized is 538 nm, which is only qualitatively close to the experimental value (5 580 nm solid; 575 nm glass). As can be seen in Figure 8, the SOMO-1 is essentially analogous to the HOMO in the ground state, being located on the *four* platinum centers (33%) and the two C=CPh groups (58%). The highest singly occupied molecular orbital SOMO resembles the LUMO in S_0 , but now is more uniformly localized on the four π^* orbitals of the bzq (22% bzq *trans* to σ -alkynyl and 52% bzq *trans* to η^2 -C=C) and exhibits slightly higher Pt (15%) and alkynyl contribution (11%). From these results it can be suggested that due to the close proximity of the adjacent Pt(bzq) fragments, the two pairs of stacked bzq/bzq ligands participate in the excited state. The T₁ to S₀ de-excitation in the gas phase corresponds to ligand-ligand (bzq/bzq) to metal—ligand (alkynyl) charge transfer transition.

CONCLUSIONS

In summary, we present here two different types of heterobridged $(\mu$ -X) $(\mu$ -C \equiv CR) assemblies based on chromophoric cycloplatinated " $Pt(C^N)$ " units and the study of their photophysical properties.

It has been shown that typical dehalogenation reactions of $[Pt(C^N)(\mu-Cl)]_2$ with excess NaC=CR evolve with partial substitution, leading to selective (Cl trans to C_{metalate}) heterobridged $(\mu$ -Cl) $(\mu$ -C \equiv CR) complexes, whose nuclearity strongly depends on the steric and electronic characteristics of the cyclometalating group. Thus, the presence of sterically demanding phenyl substituents in the monoanionic dppyH ligand generates the strongly bent diplatinum complex $[{Pt(dppyH)}_2$ - $(\mu$ -Cl) $(\mu$ -C=C^tBu)] (1), which displays a short Pt···Pt distance (3.15 Å). Further $\pi \cdots \pi$ and T-shaped C-H $\cdots \pi$ intermolecular interactions, in a head-to-tail manner, form dimers, which additionally arrange through weak secondary hydrogen bonds, affording a final supramolecular network having circular channels. Similar bromide (2) and iodide (3) complexes were accessible by simple halide-exchange reactions. Surprisingly, the presence of the planar and more delocalized benzoquinolate ligand leads to discrete tetranuclear aggregates $[Pt_2(bzq)_2]$ $(\mu$ -C=CR) $(\mu$ -Cl)]₂ (4-6), as confirmed by X-ray studies, having an original and new tetrahedral platinum core. The formation of 4-6 implies a formal dimerization of the expected monomer, which may be associated with a more favorable orientation of the two monomers driven by the occurrence of two pairs of simultaneous strong Pt···Pt and π ··· π stacking interactions, leading to the final Pt₄ core.

Both series display different photophysical properties. Thus, while the diplatinum complexes 1-3 are nonemissive, the tetranuclear aggregates 4-6 exhibit an interesting luminescence behavior. The role of the alkynyl bridging group in the electronic properties of these clusters (4-6) is supported by TD-DFT calculations on complex 5, allowing us to assign the lowest lying absorption mainly to a charge transfer from the $Pt(\mu-C \equiv CR)Pt$ system to the bzq ligand *trans*-disposed to the η^2 -alkynyl bond (¹MMLL'CT). On the other hand, the computational studies suggest that the intramolecular stacking of the eclipsed Pt(bzq) fragments is enhanced in the excited state, playing a key role in the emissive manifold. The phosphorescent emission observed in rigid media $(560-580 \text{ nm}, \text{ solid}, \text{CH}_2\text{Cl}_2 \text{ glassy}, 77 \text{ K})$ has been attributed, according to the frontier orbitals in the optimized T₁ state of 5, to an excited state of large $[Pt(d)/\pi(C \equiv CR)/$ $Pt(d) \rightarrow bzq/bzq$ character, with the LUMO delocalized on the adjacent stacked Pt(bzq) fragments. The intriguing structures and properties of complexes 1-6 invite further investigation to examine related systems by simple modifications of bridging and cyclometalating groups.

EXPERIMENTAL SECTION

General Comments. All reactions were carried out under an atmosphere of dry argon, using standard Schlenk techniques and solvents from a solvent purification system (MBraun MB SPS-800). NMR spectra were recorded at 293 K on Bruker ARX 300 or ARX 400 spectrometers. Chemical shifts are reported in ppm relative to external standards (SiMe₄, CFCl₃), and all coupling constants are given in Hz. IR spectra were obtained on a Nicolet Nexus FT-IR spectrometer, using Nujol mulls between polyethylene sheets. Elemental analyses were carried out with Perkin-Elmer 2400 CHNS/O or Carlo Erba EA1110 CHNS-O microanalyzers. Mass spectra were recorded on a Microflex MALDI-TOF Bruker (MALDI) spectrometer operating in the linear and reflector modes using dithranol as matrix. The optical absorption spectra were recorded using a Hewlett-Packard 8453 (solution) spectrophotometer in the visible

and near-UV ranges. Emission and excitation spectra were obtained on a Jobin-Yvon Horiba Fluorolog 3-11 Tau-3 spectrofluorimeter, with the lifetime measured in phosphorimeter mode. The starting materials $[Pt(bzq)(\mu-Cl)]_2^{96}$ and $[Pt(dppyH)(\mu-Cl)]_2^{97}$ were prepared according to reported procedures with slight modifications.

Preparation of $[{Pt(dppyH)}_2(\mu-CI)(\mu-C=C^rBu)]$ (1). Method A: Complex $[Pt(dppyH)(\mu-Cl)]_2$ (0.15 g, 0.16 mmol) in acetone (25 mL) was treated with excess HC \equiv C^tBu (80 μ L, 0.65 mmol) and NaOMe (0.035 g, 0.65 mmol) for 48 h under anhydrous conditions at room temperature. The resulting crude was evaporated to dryness, 50 mL of dichloromethane was added, and the mixture was filtered through Celite. The yellow solution obtained was evaporated to \sim 2 mL and treated with 15 mL of cooled ⁱPrOH, yielding complex 1 as a yellow microcrystalline solid (0.096 g, 61%). *Method B*: 80 μ L of HC=C^tBu (0.65 mmol), 5 mg of CuI (0.03 mmol), and 1 mL of distilled NEt₃ were added to a $[Pt(dppyH)(\mu-Cl)]_2$ suspension (0.15 g, 0.16 mmol) in 40 mL of anhydrous CHCl₃. After 24 h of stirring, the resulting suspension was filtered under Ar and the clear yellow solution evaporated to dryness. The treatment of the residue with 5 mL of cooled ⁱPrOH yielded complex 1 as a yellow microcrystalline product (0.093 g, 59%). Anal. Found: C, 49.43; H, 3.35; N, 2.66. C40H33ClN2Pt2 requires: C, 49.67; H, 3.44; N, 2.90. MS MALDI(+): m/z (%) 931 $[M - Cl]^+$ (100). MS MALDI(-): m/z (%) 35 Cl⁻ (100). IR (cm⁻¹, Nujol): ν (C=C) 1956(w). ¹H NMR (δ , 300.13 MHz, CDCl₃): 7.85 (t, $J \approx 8, 2H, dppyH$), 7.69 (m, 6H, dppyH), 7.45 (m, 2H, dppyH), 7.27 (m, 6H, dppyH), 7.15 (m, 4H, dppyH), 7.03 (m, 4H, dppyH), 1.54 (s, 9H, ^tBu).

Preparation of $[\{Pt(dppyH)\}_2(\mu-Br)(\mu-C \equiv C^tBu)]$ (2). A 25 mg amount of KBr (0.20 mmol) was added to an acetone (20 mL) suspension of $[\{Pt(dppyH)\}_2(\mu-Cl)(\mu-C \equiv C^tBu)]$ (1) (0.10 g, 0.10 mmol). After stirring for 5 h, the crude was evaporated to dryness and treated with 50 mL of dichloromethane. The mixture was filtered through Celite and evaporated to dryness again. Complex 2 was obtained as a yellow solid by adding 10 mL of diethyl ether (0.066 g, 65%). Anal. Found: C, 47.63; H, 3.22; N, 2.68. C₄₀H₃₃BrN₂Pt₂ requires: C, 47.48; H, 3.29; N, 2.77. MS MALDI(+): m/z (%) 931 [M - Br]⁺ (100). MS MALDI(-): m/z (%) 79 Br⁻ (100). IR (cm⁻¹, Nujol): $\nu(C \equiv C)$ 1955(w). ¹H NMR (δ , 300.13 MHz, CDCl₃): 7.84 (t, $J \approx 8$, 2H, dppyH), 7.67 (m, 6H, dppyH), 7.03 (m, 4H, dppyH), 1.54 (s, 9H, ^tBu).

Preparation of [{**Pt(dppyH)**}₂(*μ*-1)(*μ*-**C**≡**C**^t**Bu**]] (3). Complex [{Pt(dppyH)}₂(*μ*-I)(*μ*-**C**≡**C**^tBu)] (3) was obtained (0.074 g, 70%) as a microcrystalline yellow product using an identical procedure to that for **2**, treating the precursor material [{Pt(dppyH)}₂(*μ*-Cl)(*μ*-C≡C^tBu)] (0.10 g, 0.10 mmol) with excess KI (33 mg, 0.20 mmol). Anal. Found: C, 45.10; H, 3.10; N, 2.71. C₄₀H₃₃IN₂Pt₂ requires: C, 45.38; H, 3.14; N, 2.65. MS MALDI(+): *m/z* (%) 931 [M − I]⁺ (100). MS MALDI(−): *m/z* (%) 127 I[−] (100). IR (cm^{−1}, Nujol): *ν*(C≡C) 1963(w). ¹H NMR (δ, 300.13 MHz, CDCl₃): 7.82 (t, *J* ≈ 8, 2H, dppyH), 7.69 (m, 4H, dppyH), 7.56 (m, 2H, dppyH), 7.43 (m, 2H, dppyH), 7.33−7.18 (m, 10H, dppyH), 7.05 (m, 4H, dppyH), 1.54 (s, 9H, ^tBu).

Preparation of [Pt₂(bzq)₂(μ-Cl)(μ-C≡C^tBu)]₂ (4). HC≡C^tBu (54 μL, 0.367 mmol) and NaOCH₃ (0.020 g, 0.367 mmol) were added over a yellow suspension of [Pt(bzq)(μ-Cl)]₂ (0.150 g, 0.183 mmol) in acetone (25 mL) at 0 °C. After 5 h of stirring, the suspension was evaporated to dryness and the residue was treated with CH₂Cl₂ (25 mL). The mixture was stirred for 30 min and filtered through Celite. The resultant yellow solution was evaporated to ca. 2 mL, and 1 mL of EtOH was added. After 10 h at −30 °C, 4 was obtained as a yellow solid (0.022 g, 14%). Anal. Found: C, 44.40; H, 3.01; N, 3.00. C₆₄H₅₀Cl₂N₄Pt₄ requires: C, 44.53; H, 2.92; N, 3.25. MS MALDI(+): m/z (%) 1236 [M − Pt(bzq)Cl(C≡C^{-t}Bu)]⁺ (31), 1282 [M − Pt(bzq)Cl₂]⁺ (100), 1690 [M − Cl]⁺ (1), 1726 [M]⁺ (0.5). IR (cm⁻¹, Nujol): ν(C≡C) 1922(m). ¹H NMR (δ, 400.17 MHz, CDCl₃, 223 K): 9.44 (d, ³J_{H−H} = 5.2, 2H², bzq), 8.67 (d, ³J_{H−H} = 5.2, 2H², bzq), 8.29 (d, ³J_{H−H} = 7.2, 2H⁹, bzq), 8.08

(d, ${}^{3}J_{H-H} = 7.6, 2H^{4}, bzq$), 7.85 (d, ${}^{3}J_{H-H} = 7.2, 2H^{9}, bzq$), 7.49 (AB, ${}^{3}J_{H-H} = 8.8, 2H^{5/6}, bzq$), 7.40 (pt, 2H⁴, 2H⁷, bzq), 7.28 (d, 2H^{5/6}, bzq) (only one of the signals is seen, the other one is overlapped with the CHCl₃ signal), 7.19 (t, ${}^{3}J_{H-H} = 9.6, 2H^{8}, bzq$), 7.00 (m, 2H⁸, 2H³, bzq), 6.88 (t, ${}^{3}J_{H-H} = 5.6, 2H^{3}, bzq$), 6.74 (m, 2H^{5/6}, 2H⁷, bzq), 6.57 (AB, ${}^{3}J_{H-H} = 8.8, 2H^{5/6}, bzq$), 1.34 (s, 18H, ^tBu).

Preparation of [Pt₂(bzq)₂(µ-Cl)(µ-C≡CPh)]₂ (5). HC≡CPh $(27\,\mu\text{L}, 0.245\,\text{mmol})$ and NaOMe $(0.013\,\text{g}, 0.245\,\text{mmol})$ were added to a suspension of $[Pt(bzq)(\mu-Cl)]_2$ (0.100 g, 0.122 mmol) in 20 mL of acetone at 0 °C. The resulting suspension was stirred for 3 h, the volatiles were removed in vacuo, and CH₂Cl₂ (20 mL) was added. After 30 min of vigorous stirring, the mixture was filtered through Celite and the yellow solution was evaporated to ca. 3 mL to yield 5 as a pale orange solid (0.028 g, 26%). Anal. Found: C, 46.49; H, 2.68; N, 2.98. C₆₈H₄₂- $Cl_2N_4Pt_4$ requires: C, 46.24; H, 2.40; N, 3.17. MS MALDI(+): m/z (%) 847 $[Pt_2(bzq)_2(C \equiv CPh)]^+$ (100), 1256 $[M - Pt(bzq)Cl(C \equiv CPh)]^+$ (68), 1321 $[M - Pt(bzq)Cl_2]^+$ (89), 1358 $[M - Pt(bzq)Cl + H^+]^+$ (10), 1730 $[M - Cl]^+$ (10), 1766 $[M]^+$ (2). IR (cm⁻¹, Nujol): ν (C=C) 1937sh, 1916(m). ¹H NMR (δ , 400.17 MHz, CDCl₃): 9.39 (d, ${}^{3}J_{H-H} = 5.2, 2H^{2}, bzq$), 8.67 (d, ${}^{3}J_{H-H} = 5.2, 2H^{2}, bzq$), 7.99 (d, ${}^{3}J_{H-H}$ = 7.2, 2H⁹, bzq), 7.89 (m, 4H, Ph), 7.83 (d, ${}^{3}J_{H-H}$ = 8.0, 2H³, bzq), 7.58 (d, ${}^{3}J_{H-H}$ = 7.4, 2H⁹, bzq), 7.51 (AB, ${}^{3}J_{H-H}$ = 8.8, 2H^{5/6}, bzq), 7.41 (d, ${}^{3}J_{H-H} = 7.8, 2H^{7}, bzq$), 7.35 (d, ${}^{3}J_{H-H} = 7.8, 2H^{4}, bzq$), 7.27 (d, $2H^{5/6}$, bzq) (only one of the signals is seen, the other one is overlapped with the CHCl₃ signal), 7.11 (m, 2H⁸ bzq + Ph), 6.92 (t, ${}^{3}J_{H-H} = 7.6, 2H^{8}, bzq), 6.83 (m, 4H^{3}, 2H^{5/6}, bzq), 6.76 (d, {}^{3}J_{H-H} = 7.8,$ $2H^7$, bzq), 6.63 (AB, ${}^3J_{H-H} = 8.8$, $2H^{5/6}$, bzq).

Preparation of $[Pt_2(bzq)_2(\mu-CI)(\mu-C \equiv CC_6H_4CF_3-4)]_2$ (6). Complex 6 was prepared as a pale orange solid in a similar way to complex 4 starting from $[Pt(bzq)(\mu-Cl)]_2$ (0.150 g, 0.183 mmol), HC≡CC₆H₄CF₃-4 (60 µL, 0.367 mmol), and NaOMe (0.020 g, 0.367 mmol), but in this case it was stirred for 3 h (0.049 g, 28%). Anal. Found: C, 44.39; H, 2.33; N, 2.63. C₇₀H₄₀Cl₂F₆N₄Pt₄ requires: C, 44.20; H, 2.12; N, 2.95. MS MALDI(+): m/z (%) 1324 [M - $Pt(bzq)Cl(C \equiv CC_6H_4CF_3-4)]^+$ (100), 1457 $[M - Pt(bzq)Cl_2]^+$ (60), 1866 $[M - Cl]^+$ (22), 1902 $[M]^+$ (5). IR (cm⁻¹, Nujol): ν (C=C) 1914sh, 1906(s). ¹H NMR (δ , 300.13 MHz, CDCl₃): 9.40 (d, ³ J_{H-H} = 5.0, ${}^{3}J_{Pt-H} = 30.9, 2H^{2}, bzq), 8.73 (d, {}^{3}J_{H-H} = 5.1, {}^{3}J_{Pt-H} = 28.8, 2H^{2},$ bzq), 7.95 (m, 4H, bzq/C₆H₄CF₃-4), 7.83 (d, ${}^{3}J_{H-H} = 7.8, 2H, bzq)$, 7.53 (m, 4H bzq/C₆H₄CF₃-4), 7.41 (pd, 4H, bzq/C₆H₄CF₃-4), 7.32 (pt, 4H, bzq/C₆H₄CF₃-4), 7.12 (t, ${}^{3}J_{H-H}$ = 7.8, 4H, bzq), 6.86 (m, 12H, bzq/C₆H₄CF₃-4), 6.67 (d, ${}^{3}J_{H-H} = 8.7, 2H^{5/6}, bzq)$. ¹⁹F NMR (δ, 282.41 MHz, CDCl₃): -136.3 (s, C₆H₄CF₃-4).

X-ray Crystallography. Details of the structural analyses for all complexes are summarized in Table S7 (in the Supporting Information). Yellow crystals of 1, 4, and 5 were obtained by slow diffusion at -30 °C of *n*-hexane (1, 5) or ethanol (4) into the respective solutions of the complexes in CH_2Cl_2 (1), $CHCl_3$ (4), or acetone (5). Three molecules of acetone were found in the asymmetric unit of complex 5. For complexes 1 and 4, disordered solvent crystallization molecules (CH₂Cl₂ 1, CHCl₃ and EtOH 4) were observed. In spite of many attempts, we could not resolve the disorders adequately, and both of the situations were modeled using the program SQUEEZE.^{98,99} For 1, the program found three clear voids of 747 Å³ containing 134 electrons in the unit cell, which fits well with the presence of 0.5 molecule of dichloromethane in each asymmetric unit, which has been, thus, included in the empirical formula $(1 \cdot 0.5 CH_2 Cl_2)$. In the case of 4, the program found four voids of 1127 Å³ with 375 electrons and another four voids of 394 Å³ with 148 electrons (which fit well with 3.2 molecules of CHCl₃ and 3 molecules of CH₃CH₂OH in each asymmetric unit). Thus, we have assigned 4.1.6CHCl₃.1.5CH₃CH₂OH as the empirical formula.

X-ray intensity data were collected with a NONIUS- κ CCD areadetector diffractometer, using graphite-monochromated Mo K α radiation. Images were processed using the DENZO and SCALEPACK suite of programs,¹⁰⁰ carrying out the absorption correction at this point for complex 5. The other absorption corrections were performed using $SORTAV^{101}$ (1) or XABS2¹⁰² (4). The structures were solved by Patterson and Fourier methods using DIRDIF92 (1 and 5)¹⁰³ or direct methods using SHELXS-97 (4).¹⁰⁴ The structures were refined by fullmatrix least-squares on F^2 with SHELXL-97,¹⁰⁴ and all non-hydrogen atoms were assigned anisotropic displacement parameters. The hydrogen atoms were constrained to idealized geometries fixing isotropic displacement parameters 1.2 times the Uiso value of their attached carbon for the aromatic and 1.5 times for the methyl groups. For complex 4, inspection of the symmetry (using PLATON¹⁰⁵) suggests no obvious space group change. Also, for complexes 4 and 5, the correct assignment of the position of the orthometalated carbon atom of all the bzq ligands (always in a transoidal disposition to the bridging chlorine atoms) was confirmed by examination of the Δ MSDA values for bonds involving these atoms^{105,106} (after refining the structures with the identities of the C and N atoms of each benzoquinolate group in one position, reversed, and with 50/50 hybrid scattering factors at each of the affected atomic sites). Several restraints have been used to model one acetone molecule in 5. Finally, all the structures present some residual peaks greater than 1 e $Å^{-3}$ in the vicinity of the metal atoms (or the crystallization solvent for 5), but with no chemical meaning.

Computational Details for Theoretical Calculations. DFT and TD-DFT calculations were performed on complex **5** with Gaussian 03 (revision E.01).¹⁰⁷ Geometries in the S₀ ground state and T₁ excited state were optimized using the restricted B3LYP (S₀) or unrestricted U-B3LYP (T₁) Becke's three-parameter functional combined with Lee-Yang-Parr's correlation functional.¹⁰⁸⁻¹¹⁰ The basis set used for the platinum centers was the LanL2DZ effective core potential¹¹¹ and 6-31G(d,p) for the ligand atoms. The solvent effect of the dichloromethane in the TD-DFT calculation was taken into consideration by the polarizable continuum model (PCM),¹¹² using CPCM.¹¹³

ASSOCIATED CONTENT

S Supporting Information. Selected bond lengths and bond angles for 4.1.6CHCl₃.1.5CH₃CH₂OH (B molecule, Table S1). Complete reference for Gaussian 03 (revision E.01). Comparative geometrical parameters of the experimental and the DFT-calculated structures of 5.3CH3COCH3 (Table S2). Composition (%) of frontier MOs in the ground state for 5 in the gas phase (Table S3). Selected low-lying singlet excited states (S_n) and first triplet computed by TD-DFT/CPCM (CH_2Cl_2) with the orbitals involved, vertical excitation energies (nm), and assignments for 5 (Table S4). DFT-optimized coordinates of 5 in the ground state (S_0) (Table S5) and in the excited state (T_1) (Table S6). Crystallographic data for complexes 1, 4, and 5 (Table S7). View of the molecular structure of $[{Pt(dppyH)}_2(\mu$ -Cl)(μ -C \equiv C^tBu)] \cdot 0.5CH₂Cl₂ (1 \cdot 0.5CH₂Cl₂) along the *b* axis (Figure S1). View of the supramolecular organization of complex 1 along the *c* axis (Figure S2). Molecular structure of 4.1.6CHCl₃.1.5CH₃CH₂OH (B molecule, Figure S3). 2D correlation ${}^{1}H^{-1}H$ spectrum (COSY) of 5 in CDCl₃ (Figure S4). Normalized absorption spectra of 1, 2, and 3 in CH_2Cl_2 , 5×10^{-5} M (Figure S5). Normalized emission spectra of **6** in CH_2Cl_2 at 77 K (Figure S6). Representative frontier orbitals for 5.3CH₃COCH₃ (Figure S7). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Fax: (+34) 941 299 621. E-mail: elena.lalinde@unirioja.es.

ACKNOWLEDGMENT

This work was supported by the Spanish MICINN (Project CTQ2008-06669-C02-02/BQU and a grant for A.D.). S.S. thanks the CSIC for a grant. We also thank CESGA for computer support.

REFERENCES

(1) Muro, M. L.; Rachford, A. A.; Wang, X.; Castellano, F. N. Top. Organomet. Chem. 2010, 29, 159.

- (2) Lai, S. W.; Che, C. M. Top. Curr. Chem. 2004, 241, 27.
- (3) Clark, M. L.; Diring, S.; Retailleau, P.; McMillin, D. R.; Ziessel, R. *Chem.—Eur. J.* **2008**, *14*, 7168.
- (4) Berenguer, J. R.; Lalinde, E.; Torroba, J. Inorg. Chem. 2007, 46, 9919.
- (5) Fernández, S.; Forniés, J.; Gil, B.; Gómez, J.; Lalinde, E. Dalton Trans. 2003, 822.
- (6) Liu, R.; Chang, J.; Xiao, Q.; Li, Y.; Chen, H.; Zhu, H. Dyes Pigm. 2011, 88, 88.
 - (7) Yersin, H. Top. Curr. Chem. 2004, 241, 1.
- (8) Evans, R. C.; Douglas, P.; Wiscom, C. J. Coord. Chem. Rev. 2006, 250, 2093.
- (9) Lu, W.; Mi, B. X.; Chan, M. C. W.; Hui, Z.; Zhu, N.; Lee, S. T.; Che, C. M. *Chem. Commun.* **2002**, 206.
- (10) Lu, W.; Mi, B. X.; Chan, M. C. W.; Hui, Z.; Che, C. M.; Zhu, N.; Lee, S. T. J. Am. Chem. Soc. **2004**, *126*, 4958.
- (11) Schneider, J.; Du, P.; Jarosz, P.; Lazarides, T.; Wang, X.; Brennessel, W. W.; Eisenberg, R. *Inorg. Chem.* **2009**, *48*, 4306.
- (12) Yam, V. W. W.; Tang, R. P. L.; Wong, K. M. C.; Lu, X. X.; Cheung, K. K.; Zhu, N. *Chem.*—*Eur. J.* **2002**, *8*, 4066.
- (13) Yang, Q. Z.; Wu, L. Z.; Zhang, H.; Chen, B.; Wu, Z. X.; Zhang,
 L. P.; Tung, C. H. *Inorg. Chem.* 2004, 43, 5195.
- (14) Siu, P. K. M.; Lai, S. W.; Lu, W.; Zhu, N.; Che, C. M. Eur. J. Inorg. Chem. 2003, 2749.
- (15) Lanoë, P. H.; Le Bozec, H.; Williams, J. A. G.; Fillaut, J. L.; Guerchais, V. Dalton Trans. 2010, 39, 707.
- (16) Djurovich, P. I.; Murphy, D.; Thompson, M. E.; Hernandez, B.; Gao, R.; Hunt, P. L.; Selcke, M. *Dalton Trans.* **2007**, 3763.
- (17) Yuen, M. Y.; Roy, V. A. L.; Lu, W.; Kui, S. C. F.; Tong, G. S. M.; So, M. H.; Chui, S. S. Y.; Muccini, M.; Ning, J. Q.; Xu, S. J.; Che, C. M. *Angew. Chem., Int. Ed.* **2008**, 47, 9895.
- (18) Chen, Y.; Li, K.; Lu, W.; Chui, S. S. Y.; Ma, C. W.; Che, C. M. Angew. Chem., Int. Ed. **2009**, 48, 9909.
 - (19) Shao, P.; Li, Y.; Sun, W. J. Phys. Chem. A 2008, 112, 1172.
- (20) Lu, W.; Chan, M. C. W.; Cheung, K. K.; Che, C. M. Organometallics 2001, 20, 2477.
- (21) Bai, F. Q.; Zhou, X.; Xia, B. H.; Liu, T.; Zhang, J. P.; Zhang, H. X. J. Organomet. Chem. **2009**, 694, 1848.
- (22) Seneclanze, J. B.; Retailleau, P.; Ziessel, R. New J. Chem. 2007, 31, 1412.
- (23) Shao, P.; Li, Y.; Yi, J.; Pritchett, T. M.; Sun, W. Inorg. Chem. 2010, 49, 4507.
- (24) Shao, P.; Li, Y.; Azenkeng, A.; Hoffmann, M. R.; Sun, W. Inorg. Chem. 2009, 48, 2407.
- (25) Belluco, U.; Bertani, R.; Michelin, R. A.; Mozzon, M. J. Organomet. Chem. 2000, 600, 37.
- (26) Lang, H.; George, D. S. A.; Rheinwald, G. Coord. Chem. Rev. 2000, 206–207, 101.
 - (27) Lang, H.; Stein, T. J. Organomet. Chem. 2002, 641, 41.
- (28) Buschbeck, R.; Low, P. J.; Lang, H. Coord. Chem. Rev. 2011, 255, 241.
- (29) Long, N. J.; Williams, C. K. Angew. Chem., Int. Ed. 2003, 42, 2586.
 - (30) Bruce, M. I.; Low, P. J. Adv. Organomet. Chem. 2004, 50, 179.
 - (31) Rosenthal, V. Angew. Chem., Int. Ed. 2003, 42, 1794.
 - (32) Mak, T. C. W.; Zhao, L. Chem. Asian J. 2007, 2, 456.
- (33) Mathur, P.; Chatterjee, S.; Avasare, V. D. Adv. Organomet. Chem. 2008, 55, 201.

- (34) Berenguer, J. R.; Lalinde, E.; Moreno, M. T. *Coord. Chem. Rev.* 2010, 254, 832.
 - (35) Wong, W. Y. Coord. Chem. Rev. 2007, 251, 2400.
 - (36) Yam, V. W. W. Acc. Chem. Res. 2002, 35, 555.
 - (37) Yam, V. W. W.; Lo, K. K. W. Chem. Soc. Rev. 1999, 28, 323.
- (38) Yam, V. W. W.; Lo, K. K. W.; Wong, K. M. C. J. Organomet. Chem. 1999, 578, 3.
- (39) Yam, V. W. W.; Lo, W. Y.; Lam, C. H.; Fung, W. K. M.; Wong, K. M. C.; Lau, V. C. Y.; Zhu, N. *Coord. Chem. Rev.* **2003**, 245, 39.
- (40) Yam, V. W. W. J. Organomet. Chem. 2004, 689, 1393.
 - (41) Wong, W. Y. Dalton Trans. 2007, 4495.
- (42) Chen, Z. N.; Zhao, N.; Fan, Y.; Ni, J. Coord. Chem. Rev. 2009, 253, 1.
 - (43) Chen, Z. N.; Fan, Y.; Ni, J. Dalton Trans. 2008, 573.
- (44) Hoogervorst, W. J.; Elsevier, C. J.; Lutz, M.; Spek, A. L. Organometallics 2001, 20, 4437.
- (45) Casas, J. M.; Forniés, J.; Fuertes, S.; Martín, A.; Sicilia, V. Organometallics 2007, 26, 1674.
- (46) Lai, S. W.; Chan, M. C. W.; Cheung, K. K.; Peng, S. M.; Che,
 C. M. Organometallics 1999, 18, 3991.
- (47) Koo, C. K.; Ho, Y. M.; Chow, C. F.; Lam, M. H. W.; Lau, T. C.; Wong, W. Y. Inorg. Chem. 2007, 46, 3603.
- (48) Lai, S. W.; Chan, M. C. W.; Cheung, T. C.; Peng, S. M.; Che, C. M. Inorg. Chem. **1999**, 38, 4046.
- (49) Ma, B.; Li, J.; Djurovich, P. I.; Yousufuddin, M.; Bau, R.; Thompson, M. E. J. Am. Chem. Soc. 2005, 127, 28.
- (50) Rachford, A. A.; Castellano, F. N. Inorg. Chem. 2009, 48, 10865.
- (51) Saito, K.; Nakao, Y.; Sakaki, S. Inorg. Chem. 2008, 47, 4329.
- (52) Ma, B.; Djurovich, P. I.; Garon, S.; Alleyne, B.; Thompson, M. E. *Adv. Funct. Mater.* **2006**, *16*, 2438.
- (53) Saito, K.; Nakao, Y.; Umakoshi, K.; Sakaki, S. Inorg. Chem. 2010, 49, 8977.
- (54) Koo, C. K.; Wong, K. L.; Lau, K. C.; Wong, W. Y.; Lam, M. H. W. Chem.—Eur. J. **2009**, 15, 7689.
- (55) Kui, S. C. F.; Chui, S. S. Y.; Che, C. M.; Zhu, N. J. Am. Chem. Soc. 2006, 128, 8297.
 - (56) Sun, W.; Zhu, H.; Barron, P. M. Chem. Matter 2006, 18, 2602.
- (57) Lu, W.; Chan, M. C. W.; Zhu, N.; Che, C. M.; Li, C.; Hui, Z. J. Am. Chem. Soc. 2004, 126, 7639.
- (58) Kui, S. C. F.; Sham, I. H. T.; Cheung, C. C. C.; Ma, C. W.; Yan, B.; Zhu, N.; Che, C. M.; Fu, W. F. *Chem.—Eur. J.* **2007**, *13*, 417.
- (59) Shao, P.; Sun, W. Inorg. Chem. **200**7, 46, 8603.
- (60) Ding, J.; Pan, D.; Tung, C. H.; Wu, L. Z. Inorg. Chem. 2008, 47, 5099.
- (61) Hu, J.; Lin, R.; Yip, J. H. K.; Wong, K. Y.; Ma, D. L.; Vittal, J. J. Organometallics **2007**, *26*, 6533.
- (62) Jude, H.; Bauer, J. A. K.; Connick, W. B. Inorg. Chem. 2005, 44, 1211.
- (63) Ma, B.; Djurovich, P. I.; Yousufuddin, M.; Bau, R.; Thompson, M. E. J. Phys. Chem. C 2008, 112, 8022.
 - (64) Develay, S.; Williams, J. A. G. Dalton Trans. 2008, 4562.
 - (65) Guo, Z.; Chan, M. C. W. Chem.-Eur. J. 2009, 15, 12585.
 - (66) Koshiyama, T.; Omura, A.; Kato, M. Chem. Lett. 2004, 33, 1386.
- (67) Tzeng, B. C.; Chiu, T. H.; Lin, S. Y.; Yang, C. M.; Chang, T. Y.;
- Huang, C. H.; Chang, A. H. H.; Lee, G. H. Cryst. Growth Des. 2009, 9, 5356.
- (68) Fernández, S.; Forniés, J.; Gil, B.; Gómez, J.; Lalinde, E. Dalton Trans. 2003, 822.
- (69) Forniés, J.; Fuertes, S.; Martín, A.; Sicilia, V.; Gil, B.; Lalinde, E. Dalton Trans. **2009**, 2224.
- (70) Berenguer, J. R.; Díez, A.; Fernández, J.; Forniés, J.; García, A.; Gil, B.; Lalinde, E.; Moreno, M. T. *Inorg. Chem.* **2008**, 47, 7703.
- (71) Forniés, J.; Gómez-Saso, M. A.; Lalinde, E.; Martínez, F.; Moreno, M. T. Organometallics **1992**, *11*, 2873.
- (72) Ara, I.; Falvello, L. R.; Fernández, S.; Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T. *Organometallics* **1997**, *16*, 5923.
- (73) Falvello, L. R.; Forniés, J.; Gómez, J.; Lalinde, E.; Martín, A.; Martínez, F.; Moreno, M. T. J. Chem. Soc., Dalton Trans. 2001, 2132.

(74) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martín, A.; Serrano, B. J. Chem. Soc., Dalton Trans. **2001**, 2926.

- (75) Berenguer, J. R.; Forniés, J.; Martínez, F.; Cubero, J. C.; Lalinde, E.; Moreno, M. T.; Welch, A. J. *Polyhedron* **1993**, *12*, 1797.
- (76) Falvello, L. R.; Forniés, J.; Martín, A.; Gómez, J.; Lalinde, E.; Moreno, M. T.; Sacristán, J. Inorg. Chem. **1999**, 38, 3116.
- (77) Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T. J. Chem. Soc., Dalton Trans. 1994, 135.
- (78) García, A.; Lalinde, E.; Moreno, M. T. Eur. J. Inorg. Chem. 2007, 3553.
 - (79) Aullón, G.; Alvarez, S. Organometallics 2002, 21, 2627.
- (80) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martínez, F. J. Organomet. Chem. 1994, 470, C15.
- (81) Ara, I.; Falvello, L. R.; Forniés, J.; Lalinde, E.; Martín, A.; Martínez, F.; Moreno, M. T. Organometallics **1997**, *16*, 5392.
- (82) Berenguer, J. R.; Bernechea, M.; Forniés, J.; Lalinde, E.; Torroba, J. *Organometallics* **2005**, *24*, 431.

(83) Berenguer, J. R.; Bernechea, M.; Lalinde, E. Organometallics 2007, 26, 1161.

(84) Berenguer, J. R.; Bernechea, M.; Lalinde, E. Dalton Trans. 2007, 2384.

(85) Crosby, S. H.; Clarkson, C. J.; Deeth, R. J.; Rourke, J. P. Organometallics **2010**, *29*, 1966.

- (86) Aullón, G.; Ujaque, G.; Lledós, A.; Alvarez, S.; Alemany, P. Inorg. Chem. **1998**, 37, 804.
- (87) Winter, M. In *WebElementsTM; The Periodic Table of the www;* http://www.webelements.com: University of Scheffield: UK, accesed Nov 2010.

(88) Jain, V. J.; Jain, L. Coord. Chem. Rev. 2010, 254, 2848.

- (89) Díez, A.; Forniés, J.; Fuertes, S.; Larraz, C.; Lalinde, E.; López,
- J. A.; Martín, A.; Moreno, M. T.; Sicilia, V. Organometallics 2009, 28, 1705.

(90) Díez, A.; Forniés, J.; Larraz, C.; Lalinde, E.; López, J. A.; Martín, A.; Moreno, M. T.; Sicilia, V. *Inorg. Chem.* **2010**, *49*, 3239.

(91) Develay, S.; Blackburn, O.; Thompson, A. L.; Williams, J. A. G. Inorg. Chem. **2008**, *47*, 11129.

- (92) Grimme, S.; Djukic, J. P. Inorg. Chem. 2010, 49, 2911.
- (93) Schwabe, T.; Grimme, S.; Djukic, J. P. J. Am. Chem. Soc. 2009, 131, 14156.
- (94) Hyla-Kryspin, I.; Grimme, S.; Djukic, J. P. Organometallics 2009, 28, 1001.
- (95) Phillips, V.; Willard, K. J.; Golen, J. A.; Moore, C. J.; Rheingold, A. L.; Doerrer, L. H. *Inorg. Chem.* **2010**, *49*, 9265.
- (96) Pregosin, P. S.; Wombacher, F.; Albinati, A.; Lianza, F. J. Organomet. Chem. **1991**, 418, 249.

(97) Cave, G. W. V.; Fanizzi, F. P.; Deeth, R. J.; Errington, W.; Rourke, J. P. Organometallics 2000, 19, 1355.

(98) Van der Sluis, P.; Spek, A. L. Acta Crystallogr. 1990, A46, 194.

(99) Spek, A. L. SQUEEZE, incorporated into *PLATON*: A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 2005.

(100) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. V., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276A, p 307.

(101) Blessing, R. H. Acta Crystallogr. 1995, A51, 33.

(102) Parkin, S.; Moezzi, B.; Hope, H. J. Appl. Crystallogr. 1995, 28, 53.

(103) Beursken, P. T.; Beursken, G.; Bosman, W. P.; de Gelser, R.; García-Granda, S.; Gould, R. O.; Smith, J. M. M.; Smykalla, C. *The DIRDIF92 Program System*; University of Nijmegen: The Netherlands, 1992.

(104) Sheldrick, G. M. SHELX-97 a Program for the Refinement of Crystal Structures; University of Göttingen: Germany, 1997.

- (105) Speck, A. L. Acta Crystallogr., Sect. A 1990, 46, c34.
- (106) Hirshfeld, F. L. Acta Crystallogr., Sect. A 1976, 32, 239.

(107) Frisch, M. J.; et al. *Gaussian 03*, Revision E.01; Gaussian, Inc.: Wallingford, CT, 2004 (see Supporting Information for complete citation).

- (108) Becke, A. D. Phys. Rev. A: At., Mol., Opt. Phys. 1988, 38, 3098.
- (109) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B: Condens. Matter Phys. **1988**, B37, 785.
 - (110) Becke, A. D. J. Chem. Phys. 1993, 98, 5648.
 - (111) Wadt, W. R.; Hay, P. J. J. Chem. Phys. 1985, 82, 284.
 - (112) Barone, V.; Cossi, M. J. Phys. Chem. A 1998, 102, 1995.
- (113) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. J. Comput. Chem. 2003, 24, 669.