Organometallics **2001,** *20,* 4847−4851 4847

Four Thallium(I) Ions Sandwiched by Two Tetraalkynylplatinate ($[Pt(C{\equiv}CR)_4]^{2-}$) Fragments: Synthesis and Luminescent Behavior of Pt_2Tl_4 Species

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Received June 25, 2001

Hexanuclear platinum−thallium complexes $[Pt_2Tl_4(C{\equiv}CR)_8]$ (R = ^tBu (**1**), Ph (**2**), $SiMe_3$ (**3**)) have been constructed by starting from the homoleptic species $[Pt(C{\equiv}CR)_4]^{2-}$ and $TlNO_3$. X-ray analysis of $[Pt_2Tl_4(C{\equiv}C^tBu)_8]$ (**1**) reveals that two eclipsed $[Pt(C{\equiv}C^tBu)_4]^{2-}$ fragments are connected by four bridging thallium(I) ions. Each Tl(I) is positioned away from the Pt fragments and interacts asymmetrically with four alkynyl ligands (μ_3-η^2:σ(Pt):η^2(Tl,Tl)), forming approximately the square-pyramidal geometry A_4Tl (A = midpoint of $C_\alpha{\equiv}C_\beta$) with the Tl at the apex. The optical properties of these complexes are presented.

Introduction

Since the initial report by Nagle et al.[1] showing that $[Pt(CN)_4]^{2-}$ interacts with Tl(I) to yields the luminescent six-coordinated platinum complex [*trans*-$PtTl_2(CN)_4$], instead of the expected Pt⋯Pt stacked columnar structure,[2] numerous examples of heteropolynuclear Tl(I) complexes have been reported.[3] Now it is clear that this structural chemistry is characterized by attractive metal−thallium interactions which on many occasions compete not only with d^8⋯d^8 or d^{10}⋯d^{10} metal−metal interactions but also with other Tl−X (X = N, π) bonds.[3] Attractive intermolecular contacts between Tl(I) metal atoms, which appear to arise from weak dispersion forces, also seem to play a significant role in the molecular aggregation of complexes of thallium(I).[4] While extensive studies have been focused[5] on cyclopentadienyl (or related ligands) and arene monovalent thallium complexes and although unstable and scarce alkyl or aryl Tl(I) derivatives have been also identified,[6] similar species involving acetylenic ligands have not been obtained so far. This lack of information on alkyne−Tl(I) interactions prompted our investigation into the reactivity of alkynylplatinate(II) complexes toward Tl(I) salts. We have previously reported[7] the results of the reaction between [*trans*-$Pt(C_6F_5)_2(C{\equiv}C^tBu)_2]^{2-}$ and $TlNO_3$. The solid-state structure of the $PtTl_2$ complex resulting from neutralization revealed the formation of a polymeric chain based on a six-coordinated platinum entity (*trans,trans,trans*-$PtTl_2(C_6F_5)_2(C{\equiv}C^tBu)_2$) linked by *secondary* Tl(I)−alkynyl short contacts between the thallium center and the C_α

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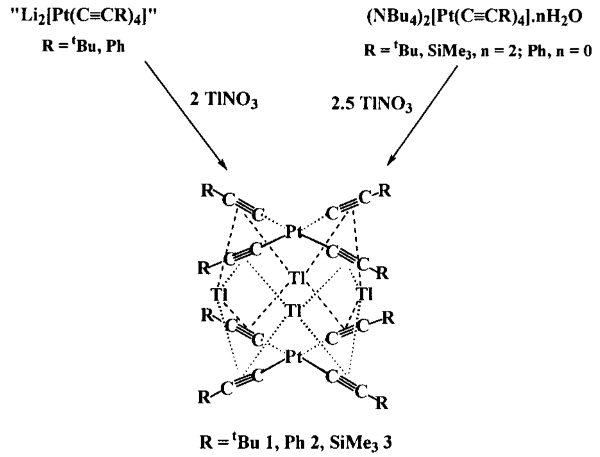
10.1021/om010554q CCC: $20.00
Publication on Web 10/02/2001

Scheme 1



of one of the alkynyl functions of the next unit. In this system the strength of the Pt(II)−Tl(I) bonds (Pt−Tl = 3.135 Å) clearly competes with the η^2-bonding capability of the C≡C^{t}Bu groups and, as expected, the complex exhibited a strong luminescence resembling that of other well-known complexes which have Pt−Tl [1,2,3g,l−n] or M-Tl[3f,o−q] bonds.

We now report that the reactions between the homoleptic dianionic $[Pt(C{\equiv}CR)_4]^{2-}$ species and Tl^+ ions generate the unexpected hexanuclear complexes $[Pt_2Tl_4(C{\equiv}CR)_8]$ (R = ^{t}Bu (**1**), Ph (**2**), $SiMe_3$ (**3**)), which are not stabilized by Pt···Tl(I) interactions but by Tl(I)−alkyne interactions.

Results and Discussion

As is shown in Scheme 1, treating a fresh aqueous solution of "$Li_2[Pt(C{\equiv}CR)_4]$" (R = ^{t}Bu, Ph), prepared as previously reported[8] from $[PtCl_2(tht)_2]$ and LiC≡CR, with 2 equiv of $TlNO_3$ results in the immediate precipitation of $[Pt_2Tl_4(C{\equiv}CR)_8]$ as yellow solids in high yields (R = ^{t}Bu (**1**; 83%), Ph (**2**; 78%)). Both compounds can also be prepared, but in lower yield (56% (**1**), 59% (**2**)), by reacting a solution of $(NBu_4)_2[Pt(C{\equiv}CR)_4]{\cdot}nH_2O$ (R = ^{t}Bu, $n = 2$; R = Ph, $n = 0$) in acetone with an aqueous solution of $TlNO_3$ (2.5 equiv) in water. The analogous complex $[Pt_2Tl_4(C{\equiv}CSiMe_3)_8]$ (**3**) can only be prepared as a white solid (71% yield) by reacting an acetonic solution of $(NBu_4)_2[Pt(C{\equiv}CSiMe_3)_4]{\cdot}2H_2O$ and 2.5 equiv of $TlNO_3$. The three complexes give a satisfactory elemental analysis but are rather insoluble in common organic solvents, with the exception of compound **1**, which is somewhat soluble in chloroform (δ(^{t}Bu) in $CDCl_3$ = 1.22). The IR spectra show ν(C≡C) absorptions (2092, 2081 cm^{-1}, **1**; 2094 cm^{-1}, **2**; 2013, 1988 cm^{-1}, **3**) only slightly shifted with respect to those observed in the homoleptic species $(NBu_4)_2[Pt(C{\equiv}CR)_4]$ (R = ^{t}Bu, 2081 cm^{-1}; R = Ph, 2075 cm^{-1}; R = SiMe, 2015, 1981 cm^{-1}),[9] suggesting that the interaction of the thallium centers with the acetylenic fragments is probably weak.

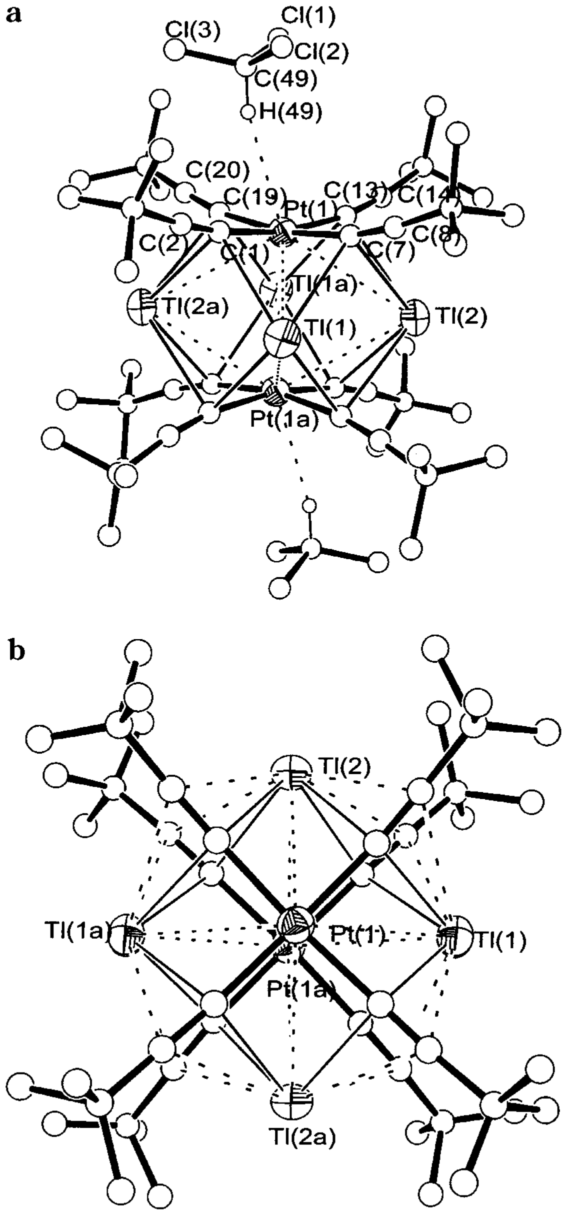


Figure 1. (a, top) Molecular structure of $[Pt_2Tl_4(C{\equiv}C^tBu)_8]$ (**1**, molecule A), showing the interaction between the Pt atom and the hydrogen of a molecule of $CHCl_3$. The interactions between Tl atoms and the C_β acetylenic carbons are omitted for clarity. (b, bottom) Perspective view of $[Pt_2Tl_4(C{\equiv}C^tBu)_8]$ (**1**).

Suitable crystals for an X-ray diffraction study (293 K) were obtained by slow diffusion of acetone at room temperature into a saturated solution of **1** in $CHCl_3$. Complex **1** crystallizes with two independent but very similar half molecules per asymmetric unit. However, for simplicity, selected results of only one (A) are discussed and given (Figure 1, Table 1). To our surprise this study revealed a highly symmetric Pt_2Tl_4 structure containing an octahedron of metal atoms with the thallium centers in the equatorial plane and the platinum atoms mutually trans. The molecule is formed by two identical and eclipsed (torsional angle C(1)−Pt(1)−Pt(1a)−C(13a) = 2.5°) tetraalkynyl platinate fragments connected by four thallium centers in a sandwich fashion. Although the sandwich type coordination of a *single* Tl(I) center by clusters or polynuclear units has been recently reported,[10,11] to date, the intercalation of four naked Tl^+ by two metal entities is unprecedented.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[Pt_2Tl_4(C\equiv C^tBu)_8]$ (1, Molecule A, 293 K)

Pt(1)−C(1)	2.038(12)	Pt(1)−C(7)	1.997(15)
Pt(1)−C(13)	2.025(13)	Pt(1)−C(19)	2.002(16)
Pt(1)−Tl(1)	3.4846(7)	Pt(1)−Tl(1a)	3.5033(6)
Pt(1)−Tl(2)	3.514	Pt(1)−Tl(2a)	3.4911(7)
Tl(1)−C(1)	2.852(13)	Tl(1)−C(7)	2.895(12)
Tl(1)−C(13a)	2.948	Tl(1)−C(19a)	2.901(12)
C(1)−C(2)	1.173(14)	C(7)−C(8)	1.195(17)
C(13)−C(14)	1.200(15)	C(19)−C(20)	1.223(18)
Tl(2)−C(1a)	2.919	Tl(2)−C(7)	2.926
Tl(2)−C(13)	2.893(13)	Tl(2)−C(19a)	2.906(12)
Pt(1)−Pt(1a)	3.573	Tl(1)−Tl(2)	4.270
Tl(1)−Tl(2a)	4.238		
C(1)−Pt(1)−C(7)	88.3(5)	C(1)−Pt(1)−C(19)	91.3(5)
C(13)−Pt(1)−C(7)	88.2(5)	C(13)−Pt(1)−C(19)	90.2(5)
Tl(1a)−Pt(1)−Tl(1)	118.508(16)	Tl(2)−Pt(1)−Tl(2a)	118.68
C(2)−C(1)−Pt(1)	173.0(11)	C(1)−C(2)−C(3)	174.5(14)
C(8)−C(7)−Pt(1)	168.8(12)	C(7)−C(8)−C(9)	173.4(16)
C(14)−C(13)−Pt(1)	168.9(12)	C(13)−C(14)−C(15)	171.9(14)
C(20)−C(19)−Pt(1)	170.8(12)	C(19)−C(20)−C(21)	176.4(15)

As can be observed in Figure 1b, each thallium is located away from the Pt coordination planes and is bonded to four alkynyl fragments (two associated with each platinum unit), forming the square-pyramidal geometry A_4-Tl (A_4 midpoint of $C_\alpha\equiv C_\beta$) with the Tl at the apex.

It has been previously noted[5a] that Tl^+, as a soft acid,[12] can be expected to show properties similar to those of Ag^+; however, structures containing thallium(I) are usually strongly influenced by the stereochemical demands of the lone pair of electrons, resulting in potentially reactive open coordination sites at the metal atom. Recently, Burini, Fackler, et al.[11] have shown that some electron-rich trinuclear Au(I) units intercalate Ag^+ and Tl^+ ions, giving similar final chains formed by sandwich clusters $(B_3AB_3B_3AB_3)_8$ (A = Ag, Tl; B = Au), thus suggesting that the lone pair of electrons on the Tl^+ is stereochemically inactive. As a whole, the structure of **1** has also some resemblance to that previously found for $[Pt_2Ag_4(C\equiv C^tBu)_8]$.[9a] However, in this platinum−silver complex both $[Pt(C\equiv C^tBu)_4]^{2-}$ fragments were staggered and each Ag^+ was only associated with two η^2-acetylenic entities. Consequently, while the alkynyl groups display a μ-η^2 (σ-Pt, π-Ag) bonding mode in the Pt_2Ag_4 complex, they are bonded in a μ_3-η^2 (σ-Pt, π-Tl, π-Tl) fashion in complex **1**. Another remarkable feature in complex **1** is the very short Pt···Pt separation found between both platinum fragments (Pt(1)−Pt(1a) = 3.573 Å (A), Pt(2)−Pt(2a) = 3.622 Å (B) vs 4.184 Å (A) and 4.253 Å (B), respectively, in $[Pt_2Ag_4(C\equiv C^tBu)_8]$[9a]), which is comparable to those seen in linear-chain Pt(II) complexes (range 3.01−3.75 Å).[2,13] The Pt···Tl distances (range 3.4846(7)−3.514 Å (A), 3.4637(8)−3.550 Å (B)), while shorter than the sum of the van der Waals radii (3.68 Å), lie out of the usual range of Pt(II)−Tl bond distances,[1,3a−c,e,g,h,j−n,10] and the attractive interaction is thus thought to be rather weak. Intramolecular Tl···Tl interactions can be discarded, judging from the large nonbonding distances (Tl(1)−Tl(2) = 4.270 Å; Tl(1)−Tl(2a) = 4.238 Å), which are clearly larger than the sum of the van der Waals radii (3.92 Å).

The η^2-acetylenic interactions are asymmetric, the $Tl-C_\alpha$ distances being 2.852(13)−2.948 Å, which are notably shorter than the $Tl-C_\beta$ distances (3.193−3.381 Å). Even taking into account the larger size of Tl(I), these distances are significantly greater that those observed in $[Pt_2Ag_4(C\equiv C^tBu)_8]$ ($Ag-C_\alpha$ = 2.25 Å; $Ag-C_\beta$ = 2.397, 2.450 Å averages), thus suggesting low covalent contribution to the bonding interaction in this complex. The $Tl-C_\alpha$ distances are comparable to those found in cyclopentadienyl complexes, while the $Tl-C_\beta$ separations lie within the typical range of arene−thallium contacts (3.13−3.52 Å).[5] All these values are close to the sum of the van der Waals radii of carbon (1.7 Å)[14a] and the ionic radius of Tl^+ (1.4−1.5 Å),[14b] once again confirming a notable ionic contribution.

Finally, it should be also noted that the four alkynyl fragments on each Pt unit are tilted away from the thallium centers ($Pt-C_\alpha-C_\beta$ = 168.8(12)−173.0(11)°; $C_\alpha-C_\beta-C(^tBu)$ = 171.9(14)−176.4(15)°), producing a hollow. This hollow incorporates, in one of the two molecules (A), a molecule of $CHCl_3$ as a guest through a short Pt(1)···H (2.725 Å) contact. The formation of hydrogen bonds involving transition-metal centers acting as proton acceptors (M···H−X) has many precedents,[15] and in particular, an example of Pt···H−C intermolecular interaction between a neutral platinum complex and a molecule of chloroform has been found in the crystal structure of [*cis*-$PtPh_2$(N−N)] (N−N = 2,2′-bis(5,6-dihydro-4*H*-1,3-thiazine-*N,N′*) (Pt···H = 2.48 Å, Pt−H−C = 169°).[16] In complex **1** this contact seems to be favored by the electropositive character of the hydrogen atom in the $H-CCl_3$ molecule and the basicity of the platinum atom on the dianionic $[Pt(C\equiv C^tBu)_4]^{2-}$ fragment, which is barely diminished through bonding interactions with the Tl centers. The H−C vector of the $HCCl_3$ molecule is directed toward the Pt atom (angle Pt−H−C = 166.35°), and this allows some kind of Pt···H interaction. In fact, the Pt···H distance (2.725 Å) is in the range in which these types of M···H interactions have been reported in the literature.[15−17]

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The influence of the temperature on the Pt⋯Pt distance in linear chain Pt(II) compounds has been previously established.[2,13d,e] We have also examined the structure of complex **1** at low temperature (173 K), and the results have been included as Supporting Information. The molecular structure is essentially unchanged at 173 K, except for the expected stronger Pt⋯H contact with the solvent molecule (Pt(1)⋯H = 2.549 Å) and the expected slight decrease in the Pt⋯Pt distance (Pt(2)⋯Pt(2a) = 3.520 Å; Pt(1)⋯Pt(1a) = 3.597 Å). Similar variations in Pt⋯Pt distances were recently measured by Connick et al. in Pt(II) chain compounds.[13d,e] Interestingly, the shorter Pt⋯Pt distance is observed in both cases in the molecular unit, which shows the presence of two molecules of $HCCl_3$ acting as a Lewis acid toward the Pt atoms ($\Delta = 0.077$ Å at 173 K and 0.048 Å at 293 K). This structural fact is in accordance with previous theoretical studies, which show how the addition of a Lewis acid to one of the metal atoms in $d^8 \cdots d^8$ dimers reinforces the M⋯M contact.[18] Finally, the remaining structural data, including the Pt⋯Tl separations (Pt(2)−Tl = 3.476−3.512 Å (molecule B); Pt(1)−Tl = 3.469−3.540 Å (molecule A), are comparable, within experimental error, to those observed at room temperature.

Complex **1** is quite stable, showing no reactivity with ligands such as 2,2′-bipy and 4,4′-bipy. From mixtures of **1** with 2,2′-bipy or 4,4′-bipy in $CHCl_3$ only crystals of complex **1** separate. The inability of Tl centers to interact with these N−N bidentate ligands is surprising, in view of the fact that $[Pt_2Ag_4(C{\equiv}C^tBu)_8]$ was observed to form an unusual 1:1 cocrystallization adduct with 2,2′-bipy.[19] Despite the presence of stronger η^2-acetylene−silver interactions, the equatorial Ag(I) ions are able to increase their coordination environment by misdirected long-range Ag⋯N interactions with a bridging 2,2′-bipy ligand between two cluster units. The failure of **1** to react with 2,2′-bipy or 4,4′-bipy demonstrates the stability of these largely electrostatic species and could be tentatively attributed to the lone-pair effect on Tl(I) centers (directed away from the center of the cluster), which probably decreases their electrophilicity.

Luminescence Spectra. The emission spectra for all three complexes in the solid state (powder or KBr pellets for **1** and KBr pellets for **2** and **3**) and in $CHCl_3$ solution for complex **1** have been determined. Excitation of solid samples of **1**−**3** in KBr pellets with visible light at room temperature results in intense luminescence. The emission spectra are dominated by a broad, asymmetric, intense orange luminescence. The emission and excitation spectra of the three compounds are shown in Figure 2. It is interesting to note that **1** and **3** emit at similar energies ($\lambda_{\max}^{\mathrm{em}}$ 631 nm (**1**), 635 nm (**3**)), the most remarkable difference being the presence of an additional high-energy shoulder in complex **1** (located at ca. 538 nm) and the fact that the emission in the phenylacetylide derivative is slightly blue-shifted ($\lambda_{\max}^{\mathrm{em}}$ 594 nm). The large Stokes shifts (7848 cm^{-1} (**1**), 4857 cm^{-1} (**2**), 9697 cm^{-1} (**3**)) suggest that these emissions are probably phosphorescence, but measurements of the emission lifetimes may confirm this. It is also important to note that the emissions are notably shifted to lower energies in relation to those observed in related platinum−silver compounds $[Pt_2Ag_4(C{\equiv}CR)_8]$ (R = ^tBu, 476 nm; R = Ph (yellow form, monomer), 570 nm).[13c] This fact could be tentatively attributed to the structural differences commented on above, in particular the η^2-acetylenic interaction of each $C{\equiv}C^tBu$ fragment with two Tl centers (μ_3-η^2 in **1** vs μ-η^2 in $[Pt_2Ag_4(C{\equiv}C^tBu)_8]$) and the very short Pt⋯Pt separation between the platinum entities, and could also confirm the implication of the metal (Tl or Ag) orbitals in the optical transition. Complex **1** does not emit in $CHCl_3$ solution at room temperature but is strongly luminescent in frozen solution. As can be observed (Figure 3) the emission is clearly resolved in two bands, a lower energy one in the orange (ca. 590 nm) region similar to that observed in the solid state and a higher energy band in the green region (ca. 497 nm) which correlates with the shoulder seen in the solid state. Such dual emissive behavior suggests two closely lying emissive states of separate origins. Although temperature control is not accurate with our instrumentation, it was observed that the relative intensities of both bands are temperature-dependent, with the intensity of the orange band increasing at lower temperatures. Interestingly, the emission profile is also dependent on the excitation wavelength, with the intensity of the green band increasing by decreasing the λ value of the excitation.

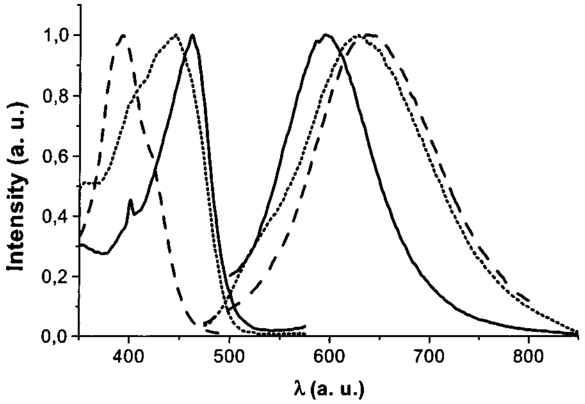

Figure 2. Excitation and emission spectra of complexes **1** (⋯), **2** (—), and **3** (- - -) in KBr pellets at room temperature.

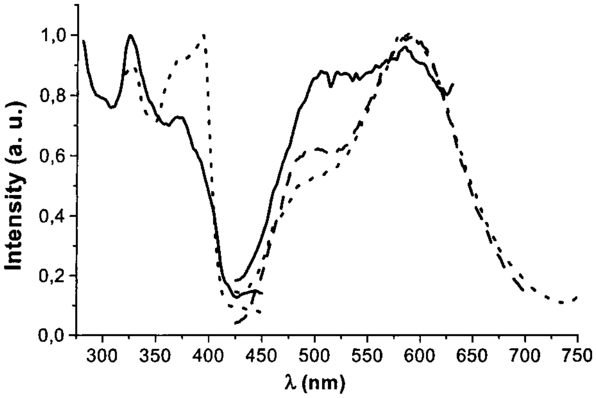

Figure 3. Photoexcitation spectra monitoring the emission at 500 nm (—) and at 590 nm (⋯) and emission spectra by exciting at 330 nm (—), at 370 nm (- - -), and at 390 nm (⋯) of complex **1** (in $CHCl_3$ at ~123 K).

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[18] Aullón, G.; Alvarez, S. *Inorg. Chem.* **1996**, *35*, 3137 and examples given therein.

[19] Ara, I.; Forniés, J.; Gómez, J.; Lalinde, E.; Moreno, M. T. *Organometallics* **2000**, *19*, 3737.

The excitation spectra obtained by monitoring both bands are also different (see Figure 3), suggesting again that the green and orange emission bands may not arise from a common center but rather that the emissive states could be coupled. Similar dual luminescence has many precedents in alkynylcopper or -gold complexes.[20]

Experimental Section

All reactions were carried out under a nitrogen atmosphere, and solvents were dried by standard procedures and distilled under dry N_2 before use. $(NBu_4)_2[Pt(C\equiv CR)_4]\cdot nH_2O$ was prepared as described elsewhere (R = ${}^tBu$, Ph,[9a] $SiMe_3$[9b]). Proton NMR spectra were recorded on a Bruker ARX-300 spectrometer. The chemical shifts were externally referenced to $SiMe_4$. Infrared spectra were recorded with a Perkin-Elmer 883 spectrometer as Nujol mulls between polyethylene sheets. C, H, and N analyses were carried out with Perkin-Elmer 2400 CHNS/O and Carlo Erba EA1110 CHNS-O microanalyzers. Mass spectra were obtained on a VG Autospec double-focusing instrument (FAB). Luminescence as well as excitation spectra have been recorded on a Perkin-Elmer luminescence spectrometer (LS 50B) with a red-sensitive photomultiplier (type R928).

Synthesis of $[Pt_2Tl_4(C\equiv CR)_8]$ (R = ${}^tBu$ (1), Ph (2)). Method a. $[PtCl_2(tht)_2]$ (0.400 g, 0.904 mmol) was added to a fresh solution of $LiC\equiv C{}^tBu$ (4.974 mmol) (1:5.5 molar ratio) in diethyl ether/hexane (25 mL) at low temperature (−10 °C). The mixture was warmed to room temperature, stirred for 30 min, and then vacuum-removed. The solid residue containing $Li_2[Pt(C\equiv C{}^tBu)_4]$ (0.904 mmol) was treated with 50 mL of deoxygenated water. The resulting colorless aqueous solution was filtered and added dropwise to a solution of $TlNO_3$ (0.482 g, 1.808 mmol) in 15 mL of H_2O, causing the precipitation of **1** as a yellow solid. After 1 h of stirring, the resulting solid was filtered, washed with deoxygenated water, and air-dried. Yield: 0.7 g (83%).

Method b. A solution of $TlNO_3$ (0.128 g, 0.480 mmol) in water (10 mL) was added to an acetone solution (5 mL) of $(NBu_4)_2[Pt(C\equiv C{}^tBu)_4]\cdot 2H_2O$ (0.200 g, 0.192 mmol), and a yellow solid immediately started to precipitate. After 2 h of stirring the solid was filtered off and washed successively with water and acetone (3 mL) (0.100 g, 56% yield).

Complex **2** (yellow solid) was similarly prepared by starting from the following: (a) $[PtCl_2(tht)_2]$ (0.500 g, 1.130 mmol), $LiC\equiv CPh$ (9.043 mmol), and $TlNO_3$ (0.602 g, 2.260 mmol); yield 0.89 g (78%); (b) $TlNO_3$ (0.123 g, 0.461 mmol) and $(NBu_4)_2[Pt(C\equiv CPh)_4]$ (0.200 g, 0.184 mmol), the mixture being stirred for 18 h; yield 0.11 g (59%).

1: Anal. Calcd for $C_{48}H_{72}Pt_2Tl_4$ (M_r 1856.82): C, 31.05; H, 3.91. Found: C, 31.20; H, 4.18. MS FAB(+): m/z 2062 ($[M^+ + Tl]$, 53); 1327 ($[Pt_2Tl_3(C\equiv C{}^tBu)_4{}^+]$, 30); 1133 ($[PtTl_3(C\equiv C{}^tBu)_4{}^+]$,100). IR (cm^{-1}): $\nu(C\equiv C)$ 2092 (m), 2081 (s). ^1H NMR ($CDCl_3$, δ): 1.22 (s, ${}^tBu$).

2: Anal. Calcd for $C_{64}H_{40}Pt_2Tl_4$ (M_r 2016.74): C, 38.12; H, 2.00. Found: C, 38.53; H, 1.63. MS FAB(+): m/z 2114 ($[M^+ + C\equiv CPh - 3]$, 9); 1711 ($[M^+ - Tl - C\equiv CPh]$, 25); 1311 ($[PtTl_3(C\equiv CPh)_5{}^+, - 3]$, 56); 1007 ($[PtTl_2(C\equiv CPh)_4{}^+ - 1]$, 31); 509 ($[Tl_2(C\equiv CPh)^+]$, 100). IR ($cm^{-1}$): $\nu(C\equiv C)$ 2094 (vs). Its low solubility prevented characterization by NMR spectroscopy.

Synthesis of $[Pt_2Tl_4(C\equiv CSiMe_3)_8]$ (3). Method b. A solution of $(NBu_4)_2[Pt(C\equiv CSiMe_3)_4]\cdot 2H_2O$ (0.250 g, 0.226 mmol) in acetone (15 mL) was treated with a solution of $TlNO_3$ (0.151 g, 0.566 mmol) in water (10 mL). The mixture was stirred for 5 h, causing the precipitation of **3**, which was filtered, washed with water, and air-dried. Yield: 0.160 g (71%). Anal. Calcd for $C_{40}H_{72}Pt_2Si_8Tl_4$ (M_r 1985.41): C, 24.20; H, 3.66. Found: C, 23.72; H, 3.42. MS FAB(+): m/z 2188 ($[M^+ + Tl]$, 11); 1499 ($[PtTl_4(C\equiv CSiMe_3)_5{}^+]$, 13); 1197 ($[PtTl_3(C\equiv CSiMe_3)_4{}^+]$, 100); 1003 ($[PtTl_3(C\equiv CSiMe_3)_2{}^+]$, 66). IR ($cm^{-1}$): $\nu(C\equiv C)$ 2013 (s), 1988 (br, s). Its low solubility prevented characterization by NMR spectroscopy.

Acknowledgment. We wish to thank the Dirección General de Enseñanza Superior (Spain Projects PB98-1595-C02-01, 02) and the University of La Rioja (Project API-00/B17) for their financial support.

Supporting Information Available: X-ray experimental data, including tables with selected bond lengths and angles for **1**, molecule B at 293 K (Table 1), molecule A at 173 K (Table 2), and molecule B at 173 K (Table 3), figures that show the molecular structure of these molecules, and tables of crystal data and structure refinement details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1** at 293 K and at 173 K. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010554Q

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