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Synthesis and Electrical and Optical Properties of [PtTl$_{2-x}$Li$_x$(C$_6$F$_5$)$_2$(C≡CPh)$_2$] (x = 0, 1)

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The synthesis and properties of two novel platinum−thallium alkynyl complexes, [*trans,cis,cis*-PtTl$_2$(C$_6$F$_5$)$_2$(C≡CPh)$_2$], **1** (X-ray), with two Tl(I)−Pt(II) bonds, and [*cis*-PtTlLi(C$_6$F$_5$)$_2$(C≡CPh)$_2$], **2**, which is an ionic conductor in the solid state, are presented. Both complexes exhibit a strong yellow luminescence, which is attributed, on the basis of TD-DFT calculations, to charge transfer from Tl−Pt−Tl (**1**) or Tl−Pt (**2**) units to the platinum metal fragments.

Introduction

Transition metal alkynyl complexes have been thoroughly investigated in the last three decades because of their structural diversity as well as their chemical reactivity.[1] Interest in these systems has also been stimulated by their possible application in the field of materials science due to unique properties such as optical nonlinearity,[2a] electrical conductivity,[2b,c] and liquid crystallinity.[2d] Recent work includes luminescence studies and their implication in photochemical reactions and also their real or potential applications including molecular sensing and light-emitting diodes (LEDs).[3] Metal−metal bonding interactions are important in determining the formation and structure of many polynuclear complexes and also play an important role with respect to the photoluminescence of some of these species.[4]

On the other hand, it has long been recognized that ionic conductivity is a well-known phenomenon in the solid state.[5] Most studies on *solid electrolytes* have focused on rigid network matrixes as hosts such as oxides, lithium salts, glasses, or polymers. Interest in solids that conduct lithium ions has increased considerably in recent years because of the potential applications of such solids in rechargeable lithium batteries.[6] In most of these systems, high temperatures are usually necessary for good Li$^+$ conductivity due to the presence of relatively strong Li$^+$−O$^-$ bonds. As far as we know, no reports have appeared on Li$^+$ conductivity in organometallic systems.

Following our previous work on the synthesis, photophysics, and spectroscopic studies of heteropolynuclear platinum complexes[7] and in search of new properties, we envisaged that the preparation of a complex containing both Pt···M bonding interactions and Li$^+$ ions would promote both luminescence and ionic conductivity.

Here we report the synthesis and properties of two

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Table 1. Selected Bond Lengths [Å] and Angles [deg] for {[*trans,cis,cis*-$PtTl_2(C_6F_5)_2(C\equiv CPh)_2$]-(acetone)$_2$}$_2$ {1(acetone)$_2$}$_2$.

Pt(1)−C(1) 2.062(5)	Pt(1)−C(7) 2.058(5)
Pt(1)−C(13) 2.025(6)	Pt(1)−C(21) 2.015(6)
Pt(1)−Tl(1) 3.0274(6)	Pt(1)−Tl(2) 2.9921(5)
C(13)−C(14) 1.215(7)	C(21)−C(22) 1.215(7)
Tl(1)−C(13) 3.364	Tl(1)−C(21) 3.465
Tl(2)−C(13) 2.967	Tl(2)−C(21) 3.091
Tl(1)−F(1) 3.087	Tl(1)−F(10) 3.018
Tl(2)−F(5) 3.213	Tl(2)−F(6) 3.202
Tl(2)−O(1) 2.923	Tl(2)−O(2) 3.020
Tl(1)−C(21#) 3.039	Tl(1)−C(22#) 2.964
Tl(1#)−O(1) 2.963	
C(7)−Pt(1)−C(1) 86.6(2)	C(21)−Pt(1)−C(1) 89.7(2)
C(13)−Pt(1)−C(7) 92.3(2)	C(21)−Pt(1)−C(13) 91.3(2)
C(14)−C(13)−Pt(1) 176.0(5)	C(13)−C(14)−C(15) 179.2(6)
C(22)−C(21)−Pt(1) 176.3(4)	C(21)−C(22)−C(23) 177.6(5)
Tl(2)−Pt(1)−Tl(1) 141.867(14)	C(21)−Pt(1)−Tl(1) 84.25(13)
C(21)−Pt(1)−Tl(2) 73.34(13)	C(13)−Pt(1)−Tl(1) 80.85
C(13)−Pt(1)−Tl(2) 69.47	

novel platinum alkynyl complexes: [*trans*,*cis*,*cis*-$PtTl_2(C_6F_5)_2(C\equiv CPh)_2$], **1**, which exhibits a strong yellow luminescence as do other well-known complexes containing Pt−Tl[7a] or M−Tl bonds,[4c] and [*cis*-$PtTlLi(C_6F_5)_2(C\equiv CPh)_2$], **2**. Complex **2** is, to our knowledge, the first example of an organometallic compound that is both luminescent and an ionic conductor in the solid state.

Results and Discussion

Complex [*trans*,*cis*,*cis*-$PtTl_2(C_6F_5)_2(C\equiv CPh)_2$], **1**, was prepared as a deep yellow solid (84% yield) by addition of 2.5 equiv of $TlNO_3$ in water to an aqueous solution of [*cis*-$Pt(C_6F_5)_2(C\equiv CPh)_2$]$^{2-}$, generated as previously reported.[8] Complex [*cis*-$PtTlLi(C_6F_5)_2(C\equiv CPh)_2$], **2**, was prepared in high yield (93%) by reacting [*trans*,*cis*,*cis*-$PtTl_2(C_6F_5)_2(C\equiv CPh)_2$], **1**, with LiCl (1:1 molar ratio) in an acetone/ethanol mixture (see Experimental Section for details). Treatment of **2** with 1 equiv of $TlPF_6$ in acetone regenerates almost quantitatively (96% yield) complex **1**. Both complexes were characterized by ^1H and ^{19}F NMR and IR spectroscopy and mass spectrometry and found to be analytically pure. Heteropolynuclear complexes containing alkynyl bridging ligands connecting metals and lithium centers have been previously reported.[9] In complex **2**, the presence of lithium was confirmed by ^7Li NMR spectroscopy, which shows a singlet without Pt satellites in the range −50 to +50 °C (δ at −50° 0.96). It should be noted that $^7Li-^{195}Pt$ coupling has been previously reported in [$Pt_2(C\equiv CPh)_4(PEt_3)_2(n\text{Bu})_2(\mu\text{-}Li)_2$].[9a] The observation of one [2089 cm^{-1}, **1**] or two [2087 and 2077 cm^{-1}, **2**] ν(C≡C) absorptions at a position similar to those observed in $(NBu_4)_2$[*cis*-$Pt(C_6F_5)_2(C\equiv CPh)_2$] (2095, 2082 cm^{-1})[8] suggests that the interaction of the Tl^+ or Li^+ ions with the acetylenic fragments is probably weak or very asymmetric.

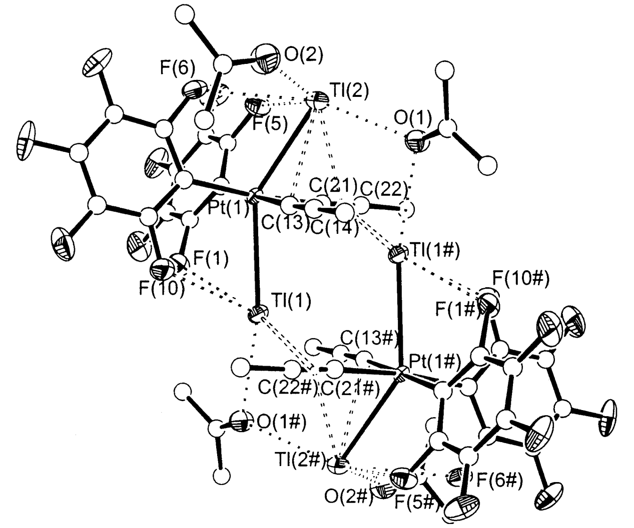

Figure 1. Molecular structure of {[*trans*,*cis*,*cis*-$PtTl_2(C_6F_5)_2(C\equiv CPh)_2$](acetone)$_2$}$_2$, **1**: view of the dimer species.

Crystals of an acetone adduct of **1** ({**1**(acetone)$_2$}$_2$) were prepared by slow diffusion of *n*-hexane into an acetone solution of **1** at low temperature (−30 °C), and they have been structurally characterized by X-ray diffraction. Relevant bond distances and angles are shown in Table 1. The molecular structure reveals the presence of two donor−acceptor Pt−Tl bonds, giving a pseudooctahedral platinum center (Figure 1) which is dimerized by weak alkynyl−Tl interactions [Tl(1)−C(21#),C(22#) 3.039, 2.964 Å] and two bridging acetone ligands [Tl(2)−O(1) 2.923 Å, Tl(1#)−O(1) 2.963 Å]. Although the two Pt−Tl distances [Pt(1)−Tl(1),Tl(2) 3.0274(6) Å, 2.9921(5) Å] are similar and close to those reported for other Pt−Tl complexes,[7a,10] the interaction of the Tl centers with the platinate fragment is somewhat asymmetric. Thus, while the Tl(1) atom is located below the Pt atom, the Pt−Tl(1) vector being essentially perpendicular to the platinum coordination plane (angle with the normal 8.4°), the other thallium (Tl(2)) seems also to interact weakly with the C_α atoms of the alkynyl units [Tl(2)−C(13),C(21) 2.967, 3.091 Å]. As a consequence, this Pt−Tl(2) bond forms an angle of 27.1° with the normal to the square-planar coordination plane of the Pt atom and the resulting Tl−Pt−Tl angle is 141.867(14)°. In addition, and as it has been previously observed in other pentafluorophenyl platinate(II)−M complexes,[7a,11] the *ortho*-fluorine atoms of the C_6F_5 groups make close contacts with both Tl centers, which are shorter for Tl(1) [Tl(1)−F(1),F(10) 3.087, 3.018 Å vs Tl(2)−F(5),F(6) 3.213, 3.202 Å]. Finally, both Tl(1) and Tl(2) complete their coordination environment with acetone ligands: Tl(1) interacts with the oxygen atom of a bridging acetone (2.963 Å), adopting a distorted trigonal bipyramidal environment, while the stabiliza-

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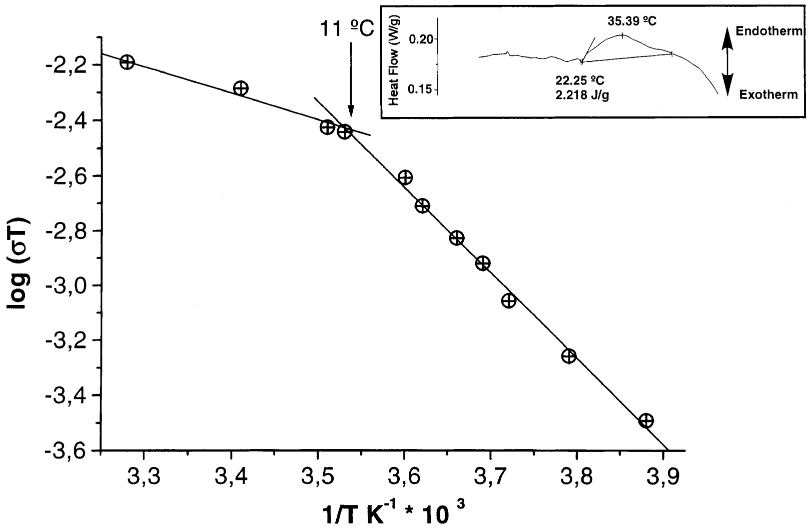

Figure 2. Temperature dependence of the conductivity and DSC data (in the inset) for [*cis*-PtTlLi(C_6F_5)$_2$(C≡CPh)$_2$], **2**.

tion of Tl(2) is achieved by interaction with terminal [Tl(2)−O(2) 3.020 Å] and bridging [Tl(2)−O(1) 2.923 Å] acetone ligands, giving a rather asymmetric heptacoordinated environment.

Although we have not been able to obtain suitable crystals of complex **2** for an X-ray study, the presence of only one Pt−Tl bond in this complex may be clearly inferred from ^{19}F NMR spectroscopy at low temperature. Thus, in the *ortho*-fluorine region, the broad singlet observed at room temperature coalesces between −10 and −15 °C, being resolved in the slow regime (at −50 °C and more clearly at −80 °C) into two different signals: one broad singlet with ^{195}Pt satellites [δ −112.8 (2F)] and one extensive doublet by strong coupling to a thallium center [δ −111.2 (2F), $J^{203,205}$ Tl-*o*-F = 3760 Hz]. This pattern confirms the presence of one Tl center coordinated to the platinum atom interacting with only two *ortho*-fluorines, one from each static C_6F_5 ring. For **1**, despite different Tl-*o*-F contacts in the solid state, the four *ortho*-fluorine atoms are isochronous even at −90 °C and appear as a broad doublet [δ_{183K}, −111.5, $J^{203,205}$Tl-*o*-F ≈ 3860 Hz, coalescence ca. 238 K, δ_{323K}, −113.4 (d), J^{195}Pt-*o*-F = 283 Hz]. For both complexes, the loss of thallium−fluorine coupling at high temperatures could be tentatively attributed to partial Pt−Tl dissociation in acetone (Λ_M 33 and 72 Ω^{-1} cm^2 mol^{-1} for **1** and **2**, respectively).

Electrical characterization has been carried out by alternating current techniques using complex impedance (Z) plots. In contrast with the expected insulator behavior of **1**, the lithium derivative **2** is an ionic conductor. Ionic conductivity values for **2** were determined from the complex impedance plots, which show tilted semicircles with a short tail at low frequencies typical of studies of solid electrolytes with electrodes blocking the ionic charge carriers (see Figure 1S in the Supporting Information). Figure 2 shows the conductivity data[12] expressed in the form of an Arrhenius plot (log σT vs $1/T$). As can be observed, the data can be fitted to two different lines in the 258−305 K range. The activation energy, E_a, obtained from the corresponding slope is 0.75 eV at temperatures below 284 K but apparently just 0.2 eV at higher temperatures. This variation in the slope, accompanied by a change in the frequency response, may be tentatively assigned to a phase transition on the basis of the thermal analysis. Thus, the DSC spectrum for **2** (see inset in Figure 2) shows an endothermic peak at 295 K, which can be assigned to a solid−solid transition, with decomposition at ~323 K. The activation energies, pre-exponential factors, and conductivity values ($\sigma_{10°C} = 1.28 \times 10^{-5}$ S cm^{-1}; $\sigma_{-15°C} = 1.24 \times 10^{-6}$ S cm^{-1}) are comparable to those obtained with other classical systems ($Li_{3.7}Al_{0.1}$-GeO_4[13a] $\sigma_{25°C} = 10^{-5}$ S cm^{-1}; Li-doped P_{12}TFSA (0−5%)[13b] $\sigma_{25°C} = 10^{-8}$−10^{-5} S cm^{-1}) and together suggest that this compound is a good ionic conductor.

In addition, both complexes show a similar and very intense yellow luminescence in the solid state (KBr $\lambda_{max/nm}$ 547 **1**, 542 **2**; λ_{exc} 410 nm **1** and **2**) and in frozen (77 K) CH_2Cl_2 solution (λ_{max} 537 **1**, 532 nm **2**; λ_{exc} 346, 394 nm **1**; 390 **2**) when exposed to UV light. The relatively long lifetime of the emissive states (KBr pellets 0.5 μs **1**, 0.35 μs **2**) and the large Stokes shifts are probably suggestive of triplet origin. The complexes are also slightly emissive in CH_2Cl_2 solution at room temperature. However, while the emission and excitation maxima for the PtTlLi complex **2** (see Figure 3) are rather similar to those observed at 77 K (298 K, λ_{max} 535 nm, λ_{exc} 416 nm), a notable shift to lower energies occurs for the PtTl$_2$ derivative **1** (Figure 4). This complex displays a dramatic change in the excitation profile with maxima at very low energy (554, 520, 480, and 440 nm) overlapping with the emission band now appearing at 574 nm. In this case, the relatively small Stokes shift of only 629 cm^{-1} suggests less modification of the electronic distribution upon optical excitation. It is evident that the formation of dimers (see Figure 1) could have significant effect on the solid state and frozen solution emissions of this complex and is probably responsible for the observed displacement to higher

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[12] The sample resistance was calculated by extrapolation of the high-frequency arc to the real axis and also by simulation to a (RQ) circuit using the program Equivalent Circuit v4.51, over a wide range of temperatures, and the data were analyzed by an Arrhenius equation of the form $\sigma T = \sigma_0 \exp(-E_a/kT)$.

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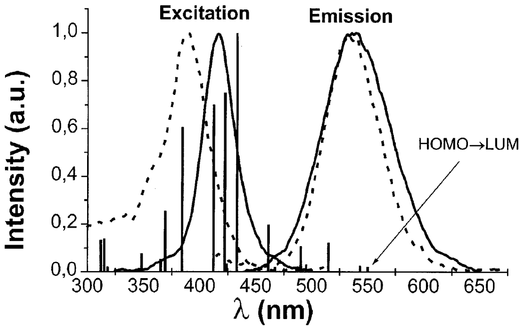

Figure 3. Excitation and emission spectra of **2** in CH_2Cl_2 at room temperature (—) and at 77 K (- - -) and theoretical excitations (columns) obtained from the TD-DFT calculations.

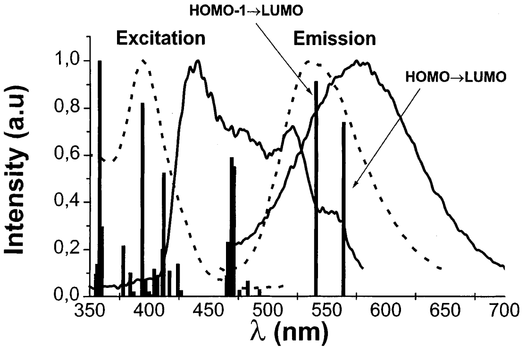

Figure 4. Excitation and emission spectra of **1** in CH_2Cl_2 at room temperature (—) and at 77 K (- - -) and theoretical excitations (columns) obtained from the TD-DFT calculations.

energies. To understand the nature of the emissions, the first singlet excitation energies of the [*trans,cis,cis*-$PtTl_2(C_6H_5)_2(C\equiv CPh)_2$] and [*cis*-$PtTlLi(C_6H_5)_2(C\equiv CPh)_2$] constructed from the X-ray results of **1** as model system were calculated at the TD-DFT level. The population analyses showing the contribution of metals and C_6H_5 and $C\equiv CPh$ fragments to the highest occupied and lowest unoccupied OMs as well as the contributions to the most important theoretical excitations are given in the Supporting Information (Tables 6S–9S and Figure 2S). As can be seen in Figures 3 and 4, which show the computed excitations taking into account the oscillator strengths, the agreement with the experimental excitation spectra is rather good. For model complex **1** the two low-energy bands predicted to arise from HOMO → LUMO (564 nm) and HOMO-1 → LUMO (541 nm) transitions match the experimentally observed emission maxima for complex **1**. The emissions in both **1** and **2** are believed to be due to a partial charge transference from the Tl–Pt–Tl (**1**) or Pt–Tl (**2**) units to the [*cis*-Pt($C\equiv CPh)_2(C_6H_5)_2$] fragments because of the notable contribution of Tl centers to the lowest unoccupied orbitals (LUMO to LUMO+4) and its negligible participation in the highest occupied orbitals (HOMO to HOMO-7) in both model systems.

All these results imply the existence of a new type of materials with potential for both luminescence and ionic conductivity. Therefore, the synthesis and properties of suitable novel alkynyl Pt–Tl–Li as well as Pt–Cd systems are under continuing study.

Experimental Section

General Considerations. The reactions were carried out under nitrogen atmosphere and the solvents were dried by standard methods prior to use. Complex [*cis*-$Pt(C_6F_5)_2(tht)_2$][14] was prepared as we described elsewhere. ^1H and ^{19}F NMR spectra were recorded on a Bruker ARX-300 spectrometer with the chemical shifts reported in ppm relative to external standards ($SiMe_4$ ^1H, $CFCl_3$ ^{19}F, and LiCl in H_2O ^7Li). Infrared spectra were recorded on 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 or Carlo Erba EA1110 CHNS-O microanalyzers. Mass spectra were obtained on a VG Autospec double-focusing mass spectrometer operating in the FAB mode. Molar conductivities were measured in acetone solutions (ca. 5×10^{-1} mol L^{-1}) using a Crison GLP 31 conductimeter. The optical absorption spectra have been registered in a U-3400 Hitachi spectrophotometer in the visible and near-UV ranges. Luminescence as well excitation spectra were registered using a standard calibrated tungsten–halogen lamp (the spectra have been corrected) and on a Perkin-Elmer luminescence spectrometer LS50B with a red-sensitive photomultiplier type R928. The lifetime was measured using a pulsed EG&G dye laser. Electrical conductivities on a pressed pellet were measured in the temperature range 258–305 K. Blocking electrodes were deposited on both sides of the pellet by silver paint. The pellet was stored at 233 K for two weeks. The conductivities were obtained by ac impedance measurements with a frequency response analyzer (Solartron 1260) over a frequency range 1 Hz to 1 MHz. Thermal analysis was measured in the temperature range 243–353 K with a DSC 2910 Modulated DSC, TA instruments, Thermal Analysis & Reology.

Synthesis of [*trans,cis,cis*-$PtTl_2(C_6F_5)_2(C\equiv CPh)_2$] (1). [*cis*-$Pt(C_6F_5)_2(tht)_2$] (0.800 g, 1.134 mmol) was added under nitrogen to a fresh solution of $LiC\equiv CPh$ (5.68 mmol) (1:5 molar ratio) in distilled diethyl ether/hexane (25 mL) at low temperature (−10 °C). The mixture was allowed to warm to room temperature, stirred for 30 min, and then removed in a vacuum. The solid residue containing "Li_2[*cis*-$Pt(C_6F_5)_2(C\equiv CPh)_2$]"[8] (1.134 mmol) was treated under nitrogen with deoxygenated water (50 mL). The resulting colorless aqueous solution was filtered and added dropwise to a solution of $TlNO_3$ (0.755 g, 2.835 mmol) in H_2O (15 mL), causing the precipitation of **1** as a yellow solid. After 2 h of stirring, the resulting solid was filtered, washed with deoxygenated water, and air-dried. Yield: 1.091 g (84%). Anal. Calcd for $C_{28}H_{10}F_{10}PtTl_2$: C, 29.50; H, 0.88. Found: C, 29.85; H, 0.88. MS FAB(+): *m/z* 1345 [M + Tl]$^+$ 17%, 973 [$PtTl_2(C_6F_5)(C\equiv CPh)_2$]$^+$ 4%, 872 [$PtTl_2(C_6F_5)(C\equiv CPh)$]$^+$ 6%, 705 [$PtTl_2(C\equiv CPh)$]$^+$ 6%. IR (cm^{-1}): $\nu(C\equiv C)$ 2089 (m); $\nu(C_6F_5)_{X-sens}$ 797 (m), 776 (m). Λ_M: 33 Ω^{-1} cm^2 mol^{-1}. λ_{abs} (KBr pellets): 262, 391 nm. ^1H NMR (CD_3COCD_3, 20 °C): δ 7.36 (m, 4H); 7.11 (m, 6H). ^{19}F NMR (CD_3COCD_3): at +50 °C, δ −113.4 (d, J_{Pt-o-F} = 283 Hz, *o*-F); −165.7 (m, *m*-F, *p*-F); at + 20 °C, δ −112.9 (s, br, J_{Pt-o-F} = 256 Hz, *o*-F); −165.3 (m, *m*-F, *p*-F); at −90 °C, δ −111.5 (dm, br, J_{Tl-o-F} = 3860 Hz, *o*-F), −163.8 (s, *p*-F), −164.4 (s, *m*-F).

Synthesis of [*cis*-$PtTlLi(C_6F_5)_2(C\equiv CPh)_2$] (2). LiCl (0.022 g, 0.526 mmol) in ethanol (10 mL) was added to a solution of [*trans,cis,cis*-$PtTl_2(C_6F_5)_2(C\equiv CPh)_2$], **1** (0.600 g, 0.526 mmol), in acetone (30 mL) at room temperature. The mixture was stirred for 6 h, and then the precipitate (TlCl) was removed, giving rise to a yellow solution. Evaporation to dryness and addition of *n*-hexane (10 mL) afforded the precipitation of a yellow solid, **2**. Yield: 0.463 g (93%). Anal. Calcd for $C_{28}H_{10}F_{10}LiPtTl$: C, 35.67; H, 1.07. Found: C, 35.49; H, 1.17. MS ES(−): *m/z* 1775 [$Pt_2TlLi(C_6F_5)_4(C\equiv CPh)_5$]$^-$ 12%; 1465 [$Pt_2Tl(C_6F_5)_4(C\equiv CPh)_2$]$^-$ 25%; 1262 [$Pt_2Tl(C_6F_5)_4$]$^-$ 20%; 696

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Table 2. Crystal Data and Structure Refinement for {1(acetone)$_2$}$_2$

empirical formula	$C_{68}F_{20}H_{44}O_4Pt_2Tl_4$
fw	2512.69
temperature (K)	173(2)
cryst syst, space group	triclinic, $P\bar{1}$
unit cell dimens, a (Å)	12.240(2)
b (Å)	12.527(2)
c (Å)	12.895(2)
α (deg)	115.550(9)
β (deg)	91.877(14)
γ (deg)	103.569(10)
volume (Å^3)	1713.7(5)
Z, D_{calcd} (Mg/m^3)	1, 2.435
abs coeff (mm^{-1})	13.536
$F(000)$	1144
cryst dimens (mm)	0.3 × 0.3 × 0.2
θ range for data collection (deg)	1.73 to 30.70
no. of data/restraints/params	7695/0/464
goodness-of-fit on F^2	0.872
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0258$, $wR_2 = 0.0513$
R indices (all data)	$R_1 = 0.0412$, $wR_2 = 0.0554$
largest diff peak and hole (e A^{-3})	1.061 and −1.327

$[Pt(C_6F_5)_3]^-$ 100%. IR (cm^{-1}): $\nu(C{\equiv}C)$ 2087 (m, br), 2077 (m, br); $\nu(C_6F_5)_{X-sens}$ 797 (w), 776 (w). Λ_M: 72 Ω^{-1} cm^2 mol^{-1}. λ_{abs} (KBr pellets): 261, 310, 402 nm. ^{1}H NMR (CD_3COCD_3, 20 °C): δ 7.40 (d, J = 6.7 Hz, 4H); 6.98 (m, 6H). ^{7}Li{^{1}H} NMR (CD_3COCD_3): at −50 °C, δ 0.96 (s); at 20 °C, 1.11 (s). ^{19}F NMR (CD_3COCD_3): at +20 °C, δ −112.7 (s, br, ^{195}Pt satellites are not observed, *o*-F); −167.2 (t, *p*-F); −166.6 (m, *m*-F); at −80 °C, δ −112.8 (s, br, J_{Pt-o-F} = 230 Hz, 2 *o*-F); −111.2 (dm, J_{Tl-o-F} = 3760 Hz, 2 *o*-F); −165.4 (m, *p*-F, *m*-F).

X-ray Crystal Structure Determination. Crystal data and other details of the structure analysis are presented in Table 2. All diffraction measurements were made at −100° C with a Siemens three-circle SMART area-detector diffractometer using graphite-monochromated Mo Kα radiation. The structure was solved by direct methods and refined using full-matrix least-squares refinement on F^2 with the SHELXTL[15] program. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the U_{iso} value of their attached carbon for the aromatic hydrogens and 1.5 that for the methyl hydrogens. Carbon atoms C27 and C28 are disordered over two different positions (half-occupancy).

Computational Details. In this work, the units [*trans,cis,cis*-$PtTl_2(C_6H_5)_2(C{\equiv}CPh)_2$] and [*cis*-$PtTl(C_6H_5)_2(C{\equiv}CPh)_2$] were used as computational models for **1** and **2** based on the crystal structure of **1**. The density functional calculations were carried out on isolated molecules using the Gaussian 98 program package.[16] The basis set for the platinum atom was LANL2DZ,[17] and Stuttgart RLC ECP for Tl,[18] using for the heavy atoms the corresponding ECPs, and 6-31G(d,p) for the C and H atoms. The excitation energies were obtained using the time-dependent theory (TD-DFT).

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Supporting Information Available: Further details of the structure determination of **1** including atomic coordinates, bond distances and angles, and thermal parameters. Impedance data at three selected temperatures for **2** (Figure 1S) and results of TD-DFT calculations (Tables 6S−9S and Figure 2S). This material is available free of charge via the Internet at http://pubs.acs.org.

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