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Synthesis of Pd_3Tl and Pd_6Tl_2 Complexes Based on a Trinuclear Aryl−Palladium(II) Complex Acting as a Metallaligand Toward Thallium(I) Through Tl−Arene and Tl−I Bonds

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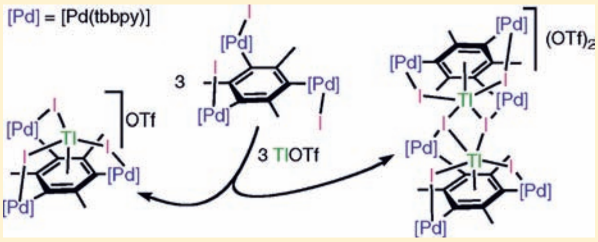
S *Supporting Information*

ABSTRACT: The metallaligand $[(PdIL_2)_3(C_6Me_3\text{-}1,3,5)]$ (L_2 = 4,4′-di-*tert*-butyl-2−2′-bipyridine = tbbpy) reacts with TlOTf to afford the complex $[\{(PdIL_2)_3C_6Me_3\text{-}1,3,5\}Tl]OTf$, which exists in the solid state as a 2:1 mixture of monomer and dimer, both showing Tl(I)−I and Tl(I)−η^6-mesitylene bonds. In solution, only the monomer is observed. Heating of toluene solutions of $[(PdIL_2)_3(C_6Me_3\text{-}1,3,5)]$ affords the dinuclear complex $[(PdIL_2)_2(C_6HMe_3\text{-}1,3,5)]$.



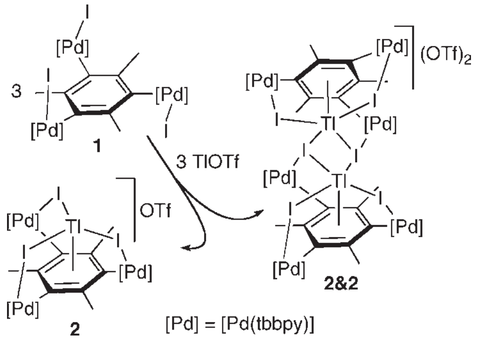
INTRODUCTION

Arylpalladium complexes have been extensively investigated because of their involvement in many important C−C and C−heteroatom bond-forming reactions.[1] Suitable substituents ortho to Pd(II) may influence the reactivity of these complexes[2,3] or participate in formation of organic compounds.[4,5] We are trying to extend this chemistry to 1,3,5-tripalladated benzene derivatives with substituents ortho to each Pd.[6,7] Such complexes could have a huge potential for the Pd-mediated synthesis of organic polycyclic compounds. This is an almost unexplored field, with only three publications on 1,3,5-tripalladated arenes, two of them by our research group.[6−8] Even with other transition metals there are only three examples of 1,3,5-trinuclear derivatives (one Mn and two Fe complexes).[9]

Tl(I) is known for its bewildering complexity of coordination numbers and geometries,[10] a nonstandard behavior often ascribed to relativistic effects arising from the $6s^2$ lone pair.[11] It is able to form π complexes with aromatic hydrocarbons, as first proposed for η^5-Cp ligands[12] and later for arenes.[13] Although not common, Tl(I) π-arene complexes are now well documented in the literature, with both inter- and intramolecular interactions reported.[14−16] However, there is no precedent for polynuclear heterobimetallic compounds based on Tl(I)−arene interactions, as reported here. The closest example is a $[Tl_2\{Fe(Cp_2)_3\}]$ complex with Tl−Cp interactions.[15]

In 2001 we published the synthesis of the trinuclear complex $[(PdIL_2)_3(\mu\text{-}C_6Me_3\text{-}1,3,5)]$ (L_2 = 4,4′-di-*tert*-butyl-2−2′-bipyridine, **1**) (Scheme 1),[6] prepared by oxidative addition of 1,3,5-triiodomesitylene to 3 equiv of $[Pd(dba)_2]$ (dba = dibenzylideneacetone) in the presence of L_2. Very frequently, Tl(I) salts of weakly coordinating anions are used as halide-abstracting agents toward organopalladium halocomplexes, creating a coordination vacancy and promoting reactions such as ligand exchange, cyclopalladation, insertion of unsaturated molecules, rearrangement processes, or decomposition reactions.[3,4] We report here a quite different behavior when trying to replace I by OTf in complex **1**.

Scheme 1



RESULTS AND DISCUSSION

Synthesis and Crystal Structures of 2 and 2&2. The reaction of complex **1** with 1 equiv of TlOTf in THF (Scheme 1) did not lead to a substitution product but to the unexpected formation of an adduct of stoichiometry **1**:TlOTf (89% yield). Its X-ray crystal structure shows two different molecules in the unit cell, the monomer $[\{(PdIL_2)_3(C_6Me_3\text{-}1,3,5)\}Tl]OTf$ (**2**, Scheme 1 and

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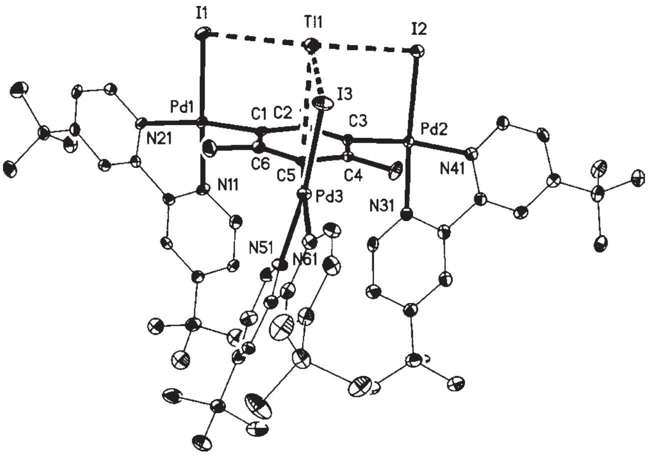


Figure 1. Thermal ellipsoid plot (30% probability level) of **2**. Selected bond lengths (Å) and angles (deg): Tl(1)−C(1) = 3.099(7), Tl(1)−C(2) = 3.108(8), Tl(1)−C(3) = 3.153(8), Tl(1)−C(4) = 3.169(8), Tl(1)−C(5) = 3.174(7), Tl(1)−C(6) = 3.111(8), Tl(1)−I(1) = 3.5508(7), Tl(1)−I(2) = 3.6048(7), Tl(1)−I(3) = 3.6261(7), Pd(1)−C(1) = 2.002(8), Pd(1)−N(11) = 2.077(6), Pd(1)−N(21) = 2.137(6), Pd(1)−I(1) = 2.5714(8), Pd(2)−C(3) = 1.996(8), Pd(2)−N(31) = 2.079(7), Pd(2)−N(41) = 2.125(7), Pd(2)−I(2) = 2.5850(8), Pd(3)−C(5) = 2.010(8), Pd(3)−N(51) = 2.073(6), Pd(3)−N(61) = 2.140(6), Pd(3)−I(3) = 2.5625(8), Pd(1)−I(1)−Tl(1) = 93.05(2), Pd(2)−I(2)−Tl(1) = 92.91, Pd(3)−I(3)−Tl(1) = 93.80(2), C(1)−Pd(1)−N(11) = 94.0(3), C(1)−Pd(1)−I(1) = 87.9(2), N(11)−Pd(1)−N(21) = 77.8(2), N(21)−Pd(1)−I(1) = 100.45(17), C(3)−Pd(2)−N(31) =93.5(3), C(3)−Pd(2)−I(2) = 88.0(2), N(31)−Pd(2)−N(41) = 78.29(3), N(41)−Pd(2)−I(2) = 100.05(18), C(5)−Pd(3)−N(51) = 95.3(3), C(5)−Pd(3)−I(3) = 87.9(2), N(51)−Pd(3)−N(61) = 77.99(3), N(61)−Pd(3)−I(3) = 99.47(18).

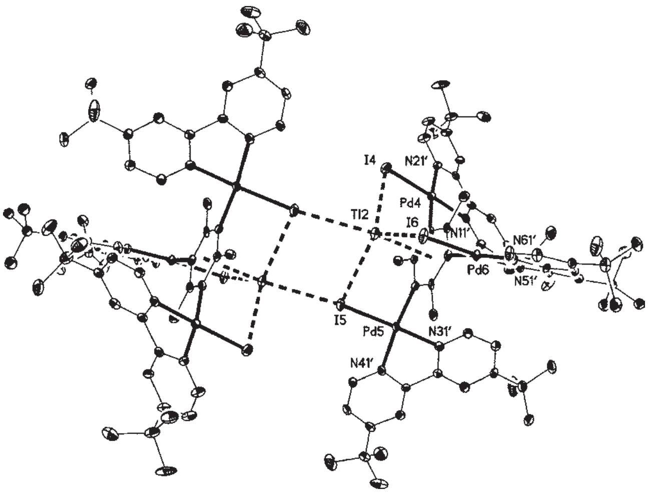
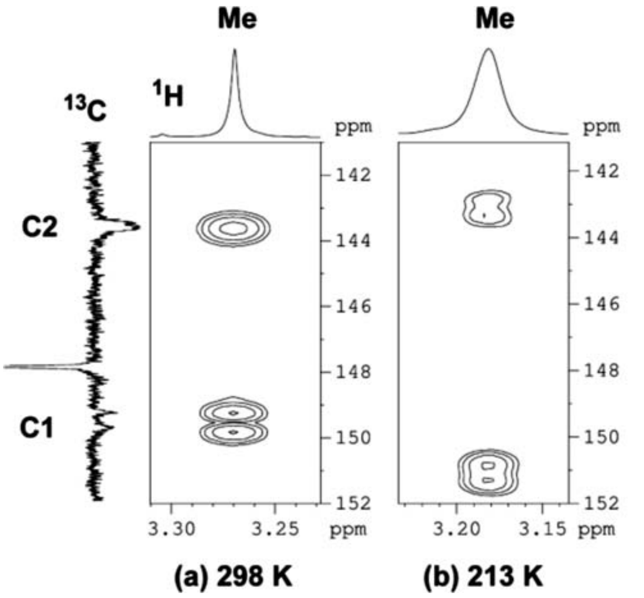


Figure 2. Thermal ellipsoid plot (30% probability level) of **2&2**. Selected bond lengths (Å) and angles (deg): Tl(2)−C(1′) = 3.047(8), Tl(2)−C(2′) = 3.101(8), Tl(2)−C(3′) 3.128(8), Tl(2)−C(4′) = 3.101(8), Tl(2)−C(5′) = 3.081(8), Tl(2)−C(6′) = 3.038(8), Tl(2)−I(4) = 3.4592(7), Tl(2)−I(5) = 3.6203(7), Tl(2)−I(6) = 3.5962(7), Pd(4)−C(1′) = 1.989(8), Pd(4)−N(11′) = 2.069(7), Pd(4)−N(21′) = 2.106(7), Pd(4)−I(4) = 2.5821(9), Pd(5)−C(3′) = 1.992(8), Pd(5)−N(31′) = 2.061(7), Pd(5)−N(41′) = 2.114(7), Pd(5)−I(5) = 2.5654(9), Pd(6)−C(5′) = 1.996(8), Pd(6)−N(51′) = 2.065(6), Pd(6)−N(61′) = 2.117(6), Pd(6)−I(6) = 2.5860(9), Pd(4)−I(4)−Tl(2) = 92.29(2), Pd(5)−I(5)−Tl(2) = 92.55, Pd(6)−I(6)−Tl(2) = 91.27(2), C(1′)−Pd(4)−N(11′) = 93.0(3), C(1′)−Pd(4)−I(4) = 88.1(2), N(11′)−Pd(4)−N(21′) = 78.4(3), N(21′)−Pd(4)−I(4) = 100.37(19), C(3′)−Pd(5)−N(31′) = 94.4(3), C(3′)−Pd(5)−I(5) = 87.7(2), N(31′)−Pd(5)−N(41′) = 78.7(3), N(41′)−Pd(5)−I(5) = 99.21(19), C(5′)−Pd(6)−N(51′) = 93.9(3), C(5′)−Pd(6)−I(6) = 89.0(2), N(51′)−Pd(6)−N(61′) = 79.3(2), N(61′)−Pd(6)−I(6) = 98.92(18).

Figure 1) and the centrosymmetric dimer $[\{(PdIL_2)_3(C_6Me_3\text{-}1,3,5)\}Tl]_2(OTf)_2$ (**2&2**, Scheme 1 and Figure 2). In both complexes, each Tl atom is η^6-bonded to one mesitylene ring. In addition, the Tl atom in **2** is bonded to the three iodo ligands in a distorted trigonal planar coordination and in **2&2** two Pd(μ^3-I)Tl$_2$ and four Pd(μ^2-I)Tl bridges are formed. Few examples have been reported in which a Tl(I) salt reacts with [M]−X complexes without precipitation of TlX, giving complexes containing Tl−X−M bonds. Most involve Ru[17] and for all X = F or Cl.[17−19] These species are formed when the halo ligands of mononuclear complexes form bridges with the Tl(I) ions. Only in one case an additional weak η^3−Tl−arene contact is observed.[19] Therefore, complexes **2** and **2&2** are unprecedented because (1) they involve the first example in which a trinuclear metal complex acts as a metallaligand, which, in addition, displays two different ways in which the metallaligand coordinates to Tl(I) in the solid state, the monomer **2** and the dimer **2&2**, and (2) Tl(I) coordinates in a fashion that establishes M−X−Tl and strong Tl(I)−arene bonds.

The Tl−I distances in **2** and **2&2** (range 3.4592(7)−3.6261(7) Å), are shorter than the sum of van der Waals radii (3.94 Å)[20] but significantly longer than the sum of covalent radii (2.84(10) Å).[21] One should however note that Tl(I) is usually ionic and thus resembles the largest alkali metal ion Cs$^+$. Tl(I)···I contacts are therefore long (cf. 3.782 and 3.802 Å for Tl(I)···ITlI$_3^-$ in a crown ether complex of Tl(I),[22] 3.470−3.696 Å for Tl(I)···IC$_6$F$_4$Au in a gold−thallium coordination polymer,[23] or 3.36 Å for the shortest Tl(I)−I distance in thallium(I) iodide).[24] An unusually short I−Tl(I) distance of 2.788(2) Å has been reported in a cluster in which thallium is bonded only to a triangular Ni$_3$ moiety and an iodide.[25] The Tl−centroid distances are 2.803 Å in **2** and 2.742 Å for **2&2**, significantly shorter than those found in other Tl(I) mesitylene complexes (Tl−Ct = 2.94−3.35 Å).[26] Indeed, 2.742 Å is the second shortest Tl−Ct distance for any Tl−arene complex, only surpassed by 2.723 Å in Tl(C$_6$Me$_6$).[16] The near identity (within 0.002 Å) of the Tl−plane and Tl−centroid distances means that the Tl atoms lie directly over the centers of the rings. The Pd−I lengths (2.5625(8)−2.5860(9) Å) are slightly shorter than those in **1** (2.5791(4)−2.5886(4) Å), possibly as a consequence of the strong Tl−mesitylene bond. The Tl−Tl distance in the dimer is 5.422 Å, which excludes any thallophillic interaction, and no Tl−O contacts are observed, neither in **2** nor in **2&2**.

Both **2** and **2&2** show somewhat distorted square planar coordination around the palladium atoms. Mean deviations from the best plane through Pd and the four donor atoms are in the range 0.014−0.097 Å (0.063 Å for Pd1, 0.029 Å for Pd2, and 0.097 Å for Pd3 in **2** and 0.014 Å for Pd4, 0.016 Å for Pd5, and 0.042 Å for Pd6 in **2&2**) The nine carbon atoms of the mesityl ring are coplanar, with mean deviations of only 0.020 (**2**) and 0.012 Å (**2&2**). The palladium substituents lie out of this plane by 0.29 (Pd1), 0.13 (Pd2), and 0.24 (Pd3) Å (**2**) and 0.16 (Pd4), 0.13 (Pd5), and 0.19 (Pd6) Å (**2&2**), always in the opposite direction from the relevant thallium atom. They are arranged with the Pd−I vectors approximately perpendicular to the mesityl plane (maximum deviation 10°). The Pd−C distances



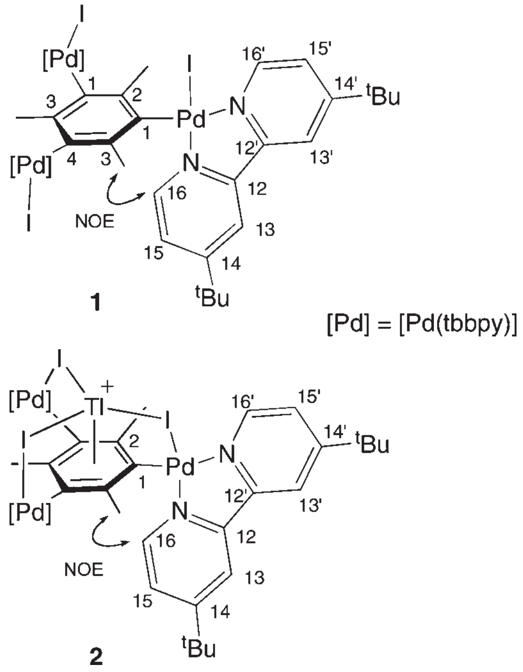
(a) 298 K (b) 213 K

Figure 3. Sections of the $^1H,^{13}C$ HMBC spectra of **2** at (a) 298 and (b) 213 K, both in $CDCl_3$, at 600.13 MHz. $^{13}C-^{205}Tl$ couplings are clearly appreciated in the shape of some of the $^1H,^{13}C$ cross-peaks. The vertical projection is the APT spectrum measured at 298 K.

for **2** and **2&2** are in the range 1.989(8)−2.010(8) Å, similar to those reported for **1** (1.989(4)−2.009(4) Å).[6]

Structure in Solution. *NMR Data of Complexes **1** and **2**.* When the solid mixture of **2** and **2&2** is dissolved in $CDCl_3$ or in d_6-acetone the ^1H NMR spectrum shows a single resonance for all the Me groups of the arene ligands, even at 193 K (in $CDCl_3$). Consequently, the Tl−I bridges of **2&2** break in solution to give complex **2** (which is stable even in a donor solvent such as d_6-acetone). The monomeric structure in solution is confirmed by ESI-MS (*m/z* 1827.0) and by PGSE diffusion measurements[27] in CD_2Cl_2 solutions of complex **1** (for which $D = 7.10 \times 10^{-10}$ m^2 s^{-1}) and the mixture of **2** and **2&2** (for which $D = 7.00 \times 10^{-10}$ m^2 s^{-1}). The coordination of Tl to the arene in solution is also reflected in the $^{205}Tl-^{13}C$ couplings observed in $CDCl_3$ for the aryl Pd−C carbons, C(1), at 298 K ($^2J_{TlC}$ = 89 Hz) and for both C(1) and C(2) at 213 K (both with $^2J_{TlC}$ = 69 Hz, Figure 3). Such $^{205}Tl-^{13}C$ couplings have been observed in other Tl−arene complexes.[28] Therefore, in complex **2** at room temperature the Tl atom is mainly bonded to the C−Pd carbons of the arene, while at low temperature all C−Tl interactions are similar but weaker than Tl−C(Pd) interactions at room temperature. Complex **2** in solution has a 3-fold symmetry axis along the Tl−arene bond, with the three [Pd] moieties being equivalent (as opposed to **1**, for which the NMR resonances appear in a 2:1 pattern because of the different orientation in the space of one of the [Pd] moieties). A full assignment of the ^1H and ^{13}C resonances of **1** and **2** has been achieved (see Experimental Section; the ^{13}C NMR data of **1** had not been previously reported). The assignment of the tbbpy protons H16 (δ 8.03−7.92 ppm) and H16′ (δ = 9.48−9.24 ppm) is based on the NOE cross-peaks found between H16 and the Me protons of the arene (Chart 1). The H16 protons in **1** and **2** are strongly shifted to lower frequencies with respect to H16′ and the model complex $[PdI_2(tbbpy)_2]$ [δ (H16) = 9.84 ppm], as a consequence of the anisotropic effect of the aryl ring.

Chart 1. Numbering Schemes for Complexes 1 and 2; for 3 the numbering is as for 1, with H instead of [Pd] in position 4



The NMR spectra and X-ray crystal structure previously reported for **1**[6] reveal a C_s symmetry (Scheme 1), suggesting hindered rotation of the $PdIL_2$ moieties around the C−Pd bonds, as only this isomer was detected.[6] However, this rotation is necessary for the formation of **2**, which has C_{3v} symmetry. We hypothesized that the formation of **2** could occur through undetectable traces of the C_{3v} isomer of **1** in equilibrium with the C_s isomer. In an attempt to displace such an equilibrium to the C_s isomer, we heated d_8-toluene solutions of **1** up to 90 °C. What we found instead was the partial decomposition of **1** to give the dinuclear complex $[(PdIL_2)_2(C_6HMe_3\text{-}1,3,5)]$ (**3**). In addition, no exchange peaks between **1** and any other species were found in an EXSY experiment at 90 °C in d^8-toluene, which rules out the supposed $C_{3v} \leftrightarrows C_s$ equilibrium. Finally, we decided to check if removal of Tl from **2** (by reaction with NaI) would afford the C_{3v} isomer of **1**. Surprisingly, we obtained again the C_s isomer. Consequently, the rotation of the $PdIL_2$ group around the C−Pd bond in the $\mathbf{1}(C_{3v}) \rightarrow \mathbf{1}(C_s)$ sense is indeed possible which indicates that the C_s isomer is, probably for steric reasons, at much higher energy than that of the C_{3v} isomer. To explain that the $\mathbf{1}(C_s) \rightarrow \mathbf{1}(C_{3v})$ isomerization occurs when TlOTf is added to **1**, we propose that the complex acts as a chelating ligand toward the Tl^+ ion using the arene π system and the two I ligands located at the same side; this could modify the environment around the third $PdIL_2$ group, allowing its rotation to give **2**.

Synthesis, NMR Data, and X-ray Structure of 3. Complex **3** has been conveniently prepared by heating a toluene solution of **1** for 2 days, followed by chromatographic purification (see Experimental Section). Its X-ray crystal structure is reproduced in Figure 4. The two palladium atoms also show slightly distorted square planar coordination, with mean deviations from the best plane through Pd and the four donor atoms of 0.024 (Pd1) and 0.017 Å (Pd2). The nine carbon atoms of the mesityl ring are again coplanar, with a mean deviation of only 0.023 Å, and the

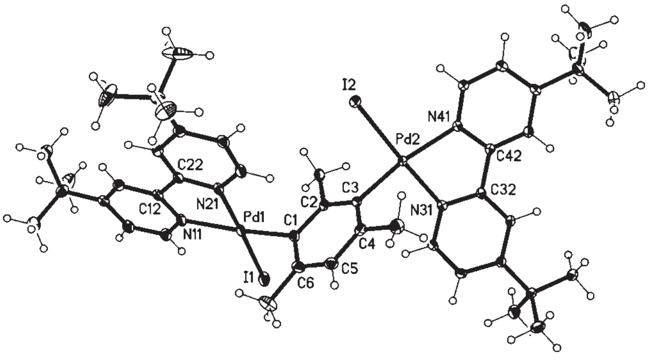


Figure 4. Thermal ellipsoid plot (30% probability level) of **3**. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 1.985(3), Pd(1)−N(11) = 2.133(3), Pd(1)−N(21) = 2.082(3), Pd(1)−I(1) = 2.5713(3), Pd(2)−C(3) = 1.995(3), Pd(2)−N(31) = 2.076(3), Pd(2)−N(41) = 2.132(3), Pd(2)−I(2) = 2.5907(3), C(1)−Pd(1)−N(21) = 91.64(12), C(1)−Pd(1)−I(1) = 90.77(10), N(11)−Pd(1)−N(21) = 77.87(11), (11)−Pd(1)−I(1) = 99.71(8), C(3)−Pd(2)−N(31) = 93.25(11), C(3)−Pd(2)−I(2) = 88.96(9), N(31)−Pd(2)−N(41) = 77.99(10), N(41)−Pd(2)−I(2) = 99.66(7).

palladium substituents lie out of this plane by 0.70 (Pd1) and 0.30 Å (Pd2), in opposite directions. The Pd−I vectors point to opposite sides of the central arene ring. While for Pd(2)−I(2) this vector is within 14° of perpendicular to the mesityl plane, for Pd(1)−I(1) the corresponding deviation is 21°. The Pd−C distances of 1.985(3) [Pd(1)−C(1)] and 1.995(3) Å [Pd(2)−C(3)] are similar to those found for **2**, **2&2** (see above), and **1**.[6] The NMR data of **3** in $CDCl_3$ show that in solution the two [PdI(tbbpy)] moieties are equivalent. Thus, replacement of the third [Pd] moiety in **1** by a H atom in **3** allows free rotation around the C−Pd bonds. Similarly to **1** and **2**, the H16 protons in **3** have been assigned by the NOE with the Me protons of the arene, and they are shifted to low frequency (δ 7.73 ppm) with respect to H16′ (δ 9.63 ppm) due to the anisotropic effect of the aryl ring.

EXPERIMENTAL SECTION

NMR Spectra were recorded on Bruker Avance 400 and 600 spectrometers. Chemical shifts are given in ppm (δ) relative to tetramethylsilane, $Si(CH_3)_4$ (^{1}H, ^{13}C). Assignment of the ^{1}H and ^{13}C resonances has been achieved with the help of 2D NMR experiments (see Chart 1 for atom numbering). Infrared spectra were recorded on a Perkin-Elmer 16F-PC-FT spectrometer with Nujol mulls between polyethylene sheets. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. The molar conductivity of **2** was measured for a ca. 5×10^{-4} M solution in acetone with a Crison MicroCM 2200 conductimeter. The mass spectrum was recorded on a Agilent HPLC/MS TOF 6220 mass spectrometer. TlOTf was prepared by reaction of Tl_2CO_3 and HO_3SCF_3 (1:2) in water and recrystallized from acetone/Et_2O. [1,3,5-μ^3-C_6Me_3{PdI(tbbpy)}$_3$] (**1**) was prepared as described in the literature.[6]

NMR data of [{PdI(tbbpy)}$_3$(μ_3-C_6Me_3-1,3,5)] (1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.48 (d, 2H, H16′ tbbpy, $^{3}J_{HH}$ = 6 Hz), 9.34 (d, 1H, H16′ tbbpy, $^{3}J_{HH}$ = 6 Hz), 8.03 (d, 2H, H16 tbbpy, $^{3}J_{HH}$ = 6 Hz), 7.93 (d, 1H, H13 tbbpy, $^{4}J_{HH}$ = 2 Hz), 7.92 (d, 1H, H16 tbbpy, $^{3}J_{HH}$ = 6 Hz), 7.901 and 7.896 (d, 2H each, H13 and 13′ tbbpy, $^{4}J_{HH}$ = 2 Hz), 7.88 (d, 1H, H13′ tbbpy, $^{4}J_{HH}$ = 2 Hz), 7.60 (dd, 1H, H15 tbbpy, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 2 Hz), 7.44 (dd, 2H, H15′ tbbpy, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 2 Hz), 7.42 (dd, 1H, H15′ tbbpy, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 2 Hz), 7.37 (dd, 2H, H15 tbbpy, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 2 Hz), 3.20 (s, 3H, Me2), 3.17 (s, 6H, Me3), 1.405 and 1.404 (s, 9H, tBu or tBu′), 1.400 and 1.388 (s, 18H, tBu or tBu′). $^{13}C\{^{1}H\}$ NMR (150.9 MHz, $CDCl_3$): δ 162.6 (1C, C14′ tbbpy), 162.5 (2C, C14′ tbbpy), 162.2 (1C, C14 tbbpy), 162.1 (2C, C14 tbbpy), 155.9 (2C, C12 tbbpy), 154.9 (1C, C12 tbbpy), 154.5 (1C, C12′ tbbpy), 153.9 (2C, C12′ tbbpy), 152.3 (2C, CH16′ tbbpy), 151.9 (1C, CH16 tbbpy), 151.7 (1C, CH16′ tbbpy), 150.4 (2C, CH16 tbbpy), 147.2 (2C, C1−Pd), 147.0 (1C, C4−Pd), 137.5 (1C, C2 aryl), 136.7 (2C, C3 aryl), 125.5 (1C, CH15 tbbpy), 123.8 (2C, CH15′ tbbpy), 123.43 (2C, CH15 tbbpy), 123.37 (1C, CH15′ tbbpy), 118.2 (2C, CH13 tbbpy), 117.8 (1C, CH13 tbbpy), 117.7 (3C, CH13′ tbbpy), 35.63 (1C), 35,56 (2C), 35.53 (1C) and 35.52 (2C) (CMe_3 and CMe_3′), 30.69 (2C, Me3), 30.66 (1C, Me2), 30.64 (9C), 30.63 (18C), 30.61 (18C), and 30.59 (9C) (C*Me*$_3$ and C*Me*$_3$′).

Synthesis of [{(PdI(tbbpy))$_3$$C_6Me_3$-1,3,5}Tl]OTf (2) and Its Dimer (2&2). TlOTf (13 mg, 0.036 mmol) was added to a solution of [1,3,5-μ^3-C_6Me_3{PdI(tbbpy)}$_3$] (**1**) (60 mg, 0.036 mmol) in dry degassed THF (15 mL) under N_2, and the resulting suspension was stirred overnight. The mixture was then filtered over Celite, and the resulting orange solution was evaporated to dryness. Et_2O (15 mL) was added to precipitate an orange solid, which was filtered off, washed with Et_2O (3 × 5 mL), and dried in vacuo to give a mixture of **2** and **2&2** as an orange solid. Yield: 63 mg (89%) Mp: 240−241 °C. Λ_M (acetone): 162 $\Omega^{-1}cm^2 mol^{-1}$. IR (cm^{-1}): ν(S=O), 1030, 1256. Anal. Calcd for $C_{64}H_{81}F_3I_3N_6O_3Pd_3STl$: C, 38.91; H 4.13; N 4.25; S, 1.62. Found: C, 38.45; H 3.85; N 4.18; S 1.61. ESI-MS: **2**-OTf *m/z* 1827.0. Single crystals were grown by slow diffusion of hexane into a $CHCl_3$ solution of **2**. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.24 (d, 3H, H16′ tbbpy, $^{3}J_{HH}$ = 6 Hz), 8.15 (d, 3H, H13 tbbpy, $^{4}J_{HH}$ = 2 Hz), 8.09 (d, 3H, H13′ tbbpy, $^{4}J_{HH}$ = 2 Hz), 7.94 (d, 3H, H16 tbbpy, $^{3}J_{HH}$ = 6 Hz), 7.52 (dd, 3H, H15′ tbbpy, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 2 Hz), 7.41 (dd, 3H, H15 tbbpy, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 2 Hz), 3.26 (s, 9H, Me2), 1.47 (s, 27 H, tBu), 1.42 (s, 27 H, tBu′). ^{1}H NMR (600 MHz, d^6-acetone): 9.21 (d, 3H, H16′ tbbpy, $^{3}J_{HH}$ = 6 Hz), 8.71 and 8.62 (d, 3H each, H13 and 13′ tbbpy, $^{4}J_{HH}$ = 2 Hz), 8.10 (d, 3H, H16 tbbpy, $^{3}J_{HH}$ = 6 Hz), 7.81 and 7.62 (dd, 3H each, H15 and 15′ tbbpy, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 2 Hz), 3.27 (s, 9H, Me2), 1.48 and 1.43 (s, 27H each, ^{t}Bu and ^{t}Bu′). $^{13}C\{^{1}H\}$ NMR (150.9 MHz, $CDCl_3$): δ 164.6 (3C, C14 tbbpy), 164.1, (3C, C14′ tbbpy), 156.9 (3C, C12 tbbpy), 153.7 (3C, C12′ tbbpy), 152.4 (br, 3C, CH16′ tbbpy), 149.4 (v br, d, $^{1}J_{TlC}$ = 87 Hz, 3C, C1 aryl), 147.9 (3C, CH16 tbbpy), 143.6 (v br, 3C, C2 aryl), 124.4 (3C, CH15′ tbbpy), 122.9 (3C, CH15 tbbpy), 121.1 (q, $^{1}J_{CF}$ = 332 Hz, 1C, CF_3SO_3), 120.2 (3C, CH13 tbbpy), 119.1 (3C, CH13′ tbbpy), 36.0 (3C, CMe_3), 35.8 (3C, CMe_3′), 30.8 (3C, Me2), 30.59 (9C, C*Me*$_3$′), 30.56 (9C, C*Me*$_3$).

Synthesis of [{PdI(tbbpy)}$_2$$C_6HMe_3$] (3). A solution of [1,3,5-μ^3-C_6Me_3{PdI(tbbpy)}$_3$] (**1**) (125 mg, 0.075 mmol) in CH_2Cl_2 (10 mL) was introduced in a Carius tube, and the solvent was evaporated to dryness. Dry degassed toluene (15 mL) was then added under N_2, and the resulting solution was heated at 90 °C for 2 days. The solution was then evaporated to dryness, and the residue was extracted with distilled CH_2Cl_2 and filtered over $MgSO_4$. The filterate was evaporated to dryness, and Et_2O (15 mL) was added to precipitate an orange yellow solid, which was filtered off and washed with Et_2O. Yield: 54 mg. Preparative TLC was done on silica gel using a mixture of CH_2Cl_2/hexane as eluent. The band with R_f = 0.56 was collected, and the product was extracted with acetone (30 mL). Evaporation of the acetone and addition of Et_2O (15 mL) rendered a solid, which was filtered off, thoroughly washed with Et_2O and dried in vacuo to give **3** as a yellow solid. Yield: 32 mg (37%) Mp: 235−237 °C. Anal. Calcd for $C_{45}H_{58}I_2N_4Pd_2$: C, 48.19; H 5.21; N 5.00. Found: C, 48.08; H 5.54; N 4.63. Single crystals were grown by slow evaporation of a toluene solution of **3**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.41 (d, 2H, H16′ tbbpy, $^{3}J_{HH}$ = 6 Hz), 7.94 (d, 2H, $^{3}J_{HH}$ = 2 Hz, H13′ tbbpy), 7.91 (d, 2H, $^{3}J_{HH}$ = 2 Hz, H13 tbbpy), 7.73 (d, 2H, H16 tbbpy, $^{3}J_{HH}$ = 6 Hz), 7.46 (dd, 2H, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 2 Hz, H15), 7.44 (dd, 2H, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 2 Hz, H15′ tbbpy), 6.47 (s, 1H, aryl CH), 3.11 (s, 3H, Me2), 2.64 (s, 6H, Me3), 1.41 (s, 18H,

Table 1. Crystallographic Data for **2** + **2&2** and **3**

complex	$(\mathbf{2} + \mathbf{2\&2})\cdot 11/2CH_2Cl_2\cdot 1/2C_6H_{14}$	$\mathbf{3}\cdot 2C_7H_8$
formula	$C_{68.5}H_{91}Cl_3F_3I_3N_6O_3Pd_3STl$	$C_{59}H_{74}I_2N_4Pd$
fw	2146.15 (based on the monomer)	1305.82
temperature (K)	133(2)	100(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
cell constants		
a (Å)	21.7626(10)	22.5064(4)
b (Å)	38.8459(18)	12.0857(2)
c (Å)	20.8292(9)	22.0979(5)
α (deg)	90	90
β (deg)	117.2280	109.857(3)
γ (deg)	90	90
volume (Å^3)	15657.6(12)	5653.4
Z	8	4
ρ_{calcd} (Mg m^{-3})	1.821	1.534
μ (Mo Kα) (mm^{-1})	4.095	1.768
$F(000)$	8320	2616
cryst size (mm)	0.40 × 0.10 × 0.03	0.2 × 0.2 × 0.1
θ range (deg)	1.49−26.38	2.23−28.28
no. of reflns coll	237 161	220 676
no. of indep reflns/R_{int}	31 978/0.1046	14 013/0.0589
transmissions	0.8870 and 0.6004	1.00000 and 0.91015
restraints/parameters	1512/1622	0/621
goodness-of-fit on F^2	1.014	1.079
$R1$ ($I > 2\sigma(I)$)	0.0490	0.0371
$wR2$ (all reflns)	0.1264	0.0869
Largest diff. peak/hole (e·Å^{-3})	1.956/−1.575	2.890/−1.399

tBu′), 1.38 (s, 18H, tBu). ^{1}H NMR (400 MHz, d_8-toluene): δ 9.63 (d, 2H, H16′ tbbpy, $^3J_{HH}$ = 6 Hz), 8.10 (d, 2H, H16 tbbpy, $^3J_{HH}$ = 6 Hz), 7.48 and 7.45 (d, 2H each, $^3J_{HH}$ = 2 Hz, H13 and 13′ tbbpy), 7.05 (s, 1H, aryl CH), 6.80 and 6.58 (dd, 2H each, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, H15 and 15′ tbbpy), 3.88 (s, 3H, Me2), 3.27 (s, 6H, Me3), 1.01 and 0.91 (s, 18H each, tBu and tBu′). ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): δ 162.8 (2C, C14′ tbbpy), 162.6, (2C, C14 tbbpy), 155.5 (2C, C12 tbbpy), 154.2 (2C, C12′ tbbpy), 152.1 (2C, CH16′ tbbpy), 150.6 (2C, CH16 tbbpy), 145.2 (2C, C1−Pd), 141.9 (1C, C2 aryl), 136.3 (2C, C3 aryl), 127.2 (1C, CH4 aryl), 124.7 (2C, CH15 tbbpy), 123.7 (2C, CH15′ tbbpy), 118.1 (2C, CH13 tbbpy), 117.8 (2C, CH13′ tbbpy), 35.64 (2C, CMe_3), 35.58 (2C, CMe_3′), 32.0 (1C, Me2), 30.6 (6C, C*Me*$_3$′), 30.5 (6C, C*Me*$_3$), 26.2 (2C, Me3).

Diffusion Measurements. PGSE diffusion measurements on complexes **1** and **2** were performed on a Bruker AVANCE 600 MHz spectrometer equipped with a HR Z-gradient BBO probe and using the standard *ledbpgp2s* pulse program from Bruker Topspin software (using a stimulated echo and longitudinal eddy current delay, with bipolar gradient pulses and two spoiling gradients). Sine-shaped gradients were used, and measurements were recorded with 16 K time domain data points in t_2 dimension and 16 t_1 increments, 24 transients for each t_1 increment, and a relaxation delay of 5 s. The gradient length (δ = 2*P30) was 1.6 ms, and two different measurements with diffusion times Δ (D20) = 150 and 100 ms were performed to check reproducibility. The D values were measured following the integral decay of the Me and ^{t}Bu resonances. Thus, six D values were obtained for each complex from which the average is given in the text. The differences between these six D values were always below 2%.

X-ray Crystallographic Analysis of $(\mathbf{2}+\mathbf{2\&2})\cdot 3/2CH_2Cl_2\cdot 1/2C_6H_{14}$ and $\mathbf{3}\cdot 2C_7H_8$. Crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a solution of **2** in $CHCl_3$ or by slow evaporation of a toluene solution of **3**. Crystal data and refinement details are shown in Table 1. For $(\mathbf{2}+\mathbf{2\&2})\cdot 3/2CH_2Cl_2\cdot 1/2C_6H_{14}$ a total of 23 7161 reflections were registered to 2θ 52° using Mo Kα radiation (λ = 0.71073 Å) on a Bruker SMART 1000 CCD diffractometer. For $\mathbf{3}\cdot 2C_7H_8$ a total of 220 676 reflections were registered to 2θ 56.6° using the same radiation on an Oxford Diffraction Xcalibur E diffractometer. Both measurements were performed at low temperature. Absorption corrections were based on multiscans. Structures were refined anisotropically on F^2 using SHELXL-97.[29] For $(\mathbf{2}+\mathbf{2\&2})\cdot 11/2CH_2Cl_2\cdot 1/2C_6H_{14}$, because of the size, the structure refinement was split into two blocks. The solvent molecules (CH_2Cl_2 and hexane) display high U values; two dichloromethanes are disordered. To improve refinement stability a system of restraints (to disordered residues and light-atom displacement parameters) was employed. For $\mathbf{3}\cdot 2C_7H_8$ the two toluene molecules are well ordered.

CONCLUSION

We report a series of unprecedented results in the reaction between a trinuclear halo Pd(II) complex **1** and TlOTf, concerning the nuclearity and nature of the ligands and bonds involved in the product. The different nature of the species in the solid state (a mixture of Pd_3Tl (**2**) and Pd_6Tl_2 (**2&2**) complexes with both Tl−arene and Tl−I bonds) and in solution (where only the Pd_3Tl species is present) is derived from X-ray crystallography, NMR, ESI-MS, and PGSE diffusion measurements. Isomerization of the trinuclear Pd(II) complex **1** from C_s to C_{3v} symmetry in **2** or **2&2** has been investigated, and a dinuclear Pd(II) complex **3** resulting from thermal decomposition of **2** has been characterized in solution and in the solid state by X-ray crystallography.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** CIF files for the crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley: Chichester, U.K., 1995. Whitcombe, N. J.; Hii, K. K.; Gibson, S. E. *Tetrahedron* **2001**, *57*, 7449. Li, G. Y.; Zheng, G.; Noonan, A. F. *J. Org. Chem.* **2001**, *66*, 8677. Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176. Larock, R. C.; Zeni,

G. *Chem. Rev.* **2006**, *106*, 4644. Heck, R. F. *Synlett* **2006**, 2855. Buchwald, S. L.; Mauger, C.; Mignani, G.; Scholz, U. *Adv. Synth. Catal.* **2006**, *348*, 23. Corbet, J. P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651. Sergeev, A. G.; Spannenberg, A.; Beller, M. *J. Am. Chem. Soc.* **2008**, *130*, 15549. Eichman, C. C.; Stambuli, J. P. *J. Org. Chem.* **2009**, *74*, 4005. Hayashi, S.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2009**, *131*, 2052. Fernández-Rodríguez, M. A.; Hartwig, J. F. *J. Org. Chem.* **2009**, *74*, 1663. Alacid, E.; Nájera, C. *J. Org. Chem.* **2009**, *74*, 2321. Tan, Y.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 3676. Cho, E. J.; Senecal, T. D.; Kinzel, T.; Zhang, Y.; Watson, D. A.; Buchwald, S. L. *Science* **2010**, *328*, 1679.

(2) Spencer, J.; Pfeffer, M.; Kyritsakas, N.; Fischer, J. *Organometallics* **1995**, *14*, 2214. Valk, J. M.; Boersma, J.; van Koten, G. *Organometallics* **1996**, *15*, 4366. Bosque, R.; Benito, M.; Lopez, C. *New J. Chem.* **2001**, *25*, 827. Vicente, J.; Abad, J. A.; Hernandez-Mata, F. S.; Jones, P. G. *J. Am. Chem. Soc.* **2002**, *124*, 3848. Vicente, J.; Chicote, M. T.; Martínez-Martínez, A. J.; Jones, P. G.; Bautista, D. *Organometallics* **2008**, *27*, 3254. Vicente, J.; Arcas, A.; Gálvez-López, M. D.; Juliá-Hernández, F.; Bautista, D.; Jones, P. G. *Organometallics* **2008**, *27*, 1582.

(3) Vicente, J.; Abad, J. A.; Bergs, R.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **1996**, *15*, 1422. Vicente, J.; Abad, J. A.; Bergs, R.; Ramirez de Arellano, M. C.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2000**, *19*, 5597. Vicente, J.; Abad, J. A.; Rink, B.; Hernández, F.-S.; Ramírez de Arellano, M. C. *Organometallics* **1997**, *16*, 5269. Vicente, J.; Abad, J. A.; Förtsch, W.; Jones, P. G.; Fischer, A. *Organometallics* **2001**, *20*, 2704. Vicente, J.; Abad, J. A.; Hernández-Mata, F. S.; Rink, B.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **2004**, *23*, 1292. Vicente, J.; Saura-Llamas, I.; Turpín, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1999**, *18*, 2683. Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem.—Eur. J.* **1999**, *5*, 3066. Vicente, J.; Abad, J. A.; Frankland, A. D.; Lopez-Serrano, J.; Ramirez de Arellano, M. C.; Jones, P. G. *Organometallics* **2002**, *21*, 272. Vicente, J.; Abad, J. A.; López-Sáez, M. J.; Förtsch, W.; Jones, P. G. *Organometallics* **2004**, *23*, 4414. Vicente, J.; Abad, J. A.; López-Sáez, M. J.; Jones, P. G. *Organometallics* **2006**, *25*, 1851.

(4) Vicente, J.; Abad, J. A.; Gil-Rubio, J. *Organometallics* **1996**, *15*, 3509. Vicente, J.; Abad, J. A.; López-Serrano, J.; Jones, P. G. *Organometallics* **2004**, *23*, 4711. Vicente, J.; Abad, J. A.; Shaw, K. F.; Gil-Rubio, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1997**, *16*, 4557. Vicente, J.; Abad, J.-A.; López-Serrano, J.; Jones, P. G.; Nájera, C.; Botella-Segura, L. *Organometallics* **2005**, *24*, 5044. Vicente, J.; Saura-Llamas, I.; García-López, J.-A.; Calmuschi-Cula, B.; Bautista, D. *Organometallics* **2007**, *26*, 2768. Vicente, J.; Saura-Llamas, I.; García-López, J.-A.; Bautista, D. *Organometallics* **2009**, *28*, 448.

(5) Catellani, M.; Motti, E.; Ghelli, S. *Chem. Commun.* **2000**, 2003. Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **2000**, *19*, 752. Vicente, J.; Saura-Llamas, I.; Grünwald, C.; Alcaraz, C.; Jones, P. G.; Bautista, D. *Organometallics* **2002**, *21*, 3587. Vicente, J.; Abad, J. A.; López-Peláez, B.; Martínez-Viviente, E. *Organometallics* **2002**, *21*, 58. Vicente, J.; Saura-Llamas, I. *Comments Inorg. Chem.* **2007**, *28*, 39. Sirlin, C.; Chengebroyen, J.; Konrath, R.; Ebeling, G.; Raad, I.; Dupont, J.; Paschaki, M.; Kotzyba-Hibert, F.; Harf-Monteil, C.; Pfeffer, M. *Eur. J. Org. Chem.* **2004**, 1724.

(6) Vicente, J.; Lyakhovych, M.; Bautista, D.; Jones, P. G. *Organometallics* **2001**, *20*, 4695.

(7) Vicente, J.; Shenoy, R. V.; Martínez-Viviente, E.; Jones, P. G. *Organometallics* **2009**, *28*, 6101.

(8) Sumby, C. J.; Steel, P. J. *Organometallics* **2003**, *22*, 2358.

(9) Hunter, D. J. B.; Szigety, A. B. *Organometallics* **1989**, *8*, 2670. Hunter, A. D. *Organometallics* **1989**, *8*, 1118. Hunter, A. D.; McLernon, J. L. *Organometallics* **1989**, *8*, 2679. Artamkina, G. A.; Beletskaya, I. P. *Mendeleev Commun.* **2003**, *13*, 43. Artamkina, G. A.; Shilova, E. A.; Shtern, M. M.; Beletskaya, I. P. *Russ. J. Org. Chem.* **2003**, *39*, 1282.

(10) Akhbari, K.; Morsali, A. *Coord. Chem. Rev.* **2010**, *254*, 1977.

(11) Wiesbrock, F.; Schmidbaur, H. *J. Am. Chem. Soc.* **2003**, *125*, 3622.

(12) Meister, H. *Angew. Chem.* **1957**, *69*, 533.

(13) Auel, T.; Amma, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 5941.

(14) Janiak, C. *Coord. Chem. Rev.* **1997**, *163*, 107. Gade, L. H. *Dalton Trans.* **2003**, 267. Fernández, E. J.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Montiel, M.; Olmos, M. E. *Inorg. Chem.* **2007**, *46*, 2953. Schmidbaur, H.; Schier, A. *Organometallics* **2008**, *27*, 2361. Welsch, S.; Lescop, C.; Réau, R.; Scheer, M. *Dalton Trans.* **2009**, 2683. Zhu, Z.; Wright, R. J.; Brown, Z. D.; Fox, A. R.; Phillips, A. D.; Richards, A. F.; Olmstead, M. M.; Power, P. P. *Organometallics* **2009**, *28*, 2512.

(15) Sarazin, Y.; Hughes, D. L.; Kaltsoyannis, N.; Wright, J. A.; Bochmann, M. *J. Am. Chem. Soc.* **2007**, *129*, 881.

(16) Sarazin, Y.; Kaltsoyannis, N.; Wright, J. A.; Bochmann, M. *Organometallics* **2007**, *26*, 1811.

(17) Barthazy, P.; Togni, A.; Mezzetti, A. *Organometallics* **2001**, *20*, 3472. Becker, C.; Kieltsch, I.; Broggini, D.; Mezzetti, A. *Inorg. Chem.* **2003**, *42*, 8417. Drouin, S. D.; Foucault, H. M.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2004**, *23*, 2583. Szymczak, N. K.; Han, F.; Tyler, D. R. *Dalton Trans.* **2004**, 3941. Blake, A. J.; Christie, R. M.; Roberts, Y. V.; Sullivan, M. J.; Schroder, M.; Yellowlees, L. J. *J. Chem. Soc., Chem. Commun.* **1992**, 848.

(18) Devic, T.; Batail, P.; Fourmigue, M.; Avarvari, N. *Inorg. Chem.* **2004**, *43*, 3136. Davis, K. B.; Harris, T. D.; Castellani, M. P.; Golen, J. A.; Rheingold, A. L. *Organometallics* **2007**, *26*, 4843. Paredes, P.; Diez, J.; Gamasa, M. P. *Organometallics* **2008**, *27*, 2597.

(19) Kunrath, F. A.; Casagrande, O. L.; Toupet, L.; Carpentier, J.-F. *Eur. J. Inorg. Chem.* **2004**, *2004*, 4803.

(20) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(21) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832.

(22) Mudring, A.-V.; Rieger, F. *Inorg. Chem.* **2005**, *44*, 6240.

(23) Fernández, E. J.; Laguna, A.; Lasanta, T.; López-de-Luzuriaga, J. M.; Montiel, M.; Olmos, M. E. *Organometallics* **2008**, *27*, 2971.

(24) Quoted in A. F. Wells, *Structural Inorganic Chemistry*; Clarendon Press: Oxford, U.K., 1984.

(25) Johnson, M. J. A.; Gantzel, P. K.; Kubiak, C. P. *Organometallics* **2002**, *21*, 3831.

(26) Noirot, M. D.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1987**, *26*, 2216. Strauss, S. H.; Noirot, M. D.; Anderson, O. P. *Inorg. Chem.* **1986**, *25*, 3850. Schmidbaur, H.; Bublak, W.; Riede, J.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 414. Frank, W.; Korrell, G.; Reiss, G. J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 765. Frank, W.; Korrell, G.; Reiss, G. J. *J. Organomet. Chem.* **1996**, *506*, 293. Wright, R. J.; Brynda, M.; Power, P. P. *Inorg. Chem.* **2005**, *44*, 3368.

(27) Price, W. S. *Annu. Rep. NMR Spectrosc.* **1996**, *32*, 51. Pregosin, P.; Kumar, P. G. A.; Fernandez, I. *Chem. Rev.* **2005**, *105*, 2977.

(28) Schumann, H.; Kucht, H.; Dietrich, A.; Esser, L. *Chem. Ber.* **1990**, *123*, 1811. Kunze, A.; Gleiter, R.; Bethke, S.; Rominger, F. *Organometallics* **2006**, *25*, 4787.

(29) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.