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# Stepwise Deprotonation of a Thiol-Functionalized Bis(1,2,4-triazolium) Salt as a Selective Route to Heterometallic NHC Complexes

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Supporting Information


**ABSTRACT:** Heterometallic NHC complexes have been selectively prepared at room temperature directly from an azolium salt in a two-step procedure. In the unsymmetrically substituted bis(1,2,4-triazolium) ligand precursor, one of the *m*-xylylene-bridged triazolium units features an unprotected *o*-thiophenol substituent. This renders possible a selective deprotonation and in situ monopalladation at the NHC−thiolato unit. The obtained palladium(II) complex possesses two pendant triazolium units as vacant binding sites. After a second deprotonation/metalation step, a heterodinuclear palladium(II) gold(I) complex and a heterotrinuclear palladium(II) dicopper(I) complex were obtained. In the latter, two metal centers are connected via a thiolato bridge.

## INTRODUCTION

Since the discovery of transition-metal complexes with N-heterocyclic carbenes (NHCs) by Wanzlick[1] and Öfele[2] in 1968, they became established ligands in organometallic chemistry and homogeneous catalysis.[3] NHCs can be easily modified by attaching functional groups at their nitrogen atoms which can act as additional donor ligands. While NHC ligands with nitrogen, oxygen, or phosphorus as donor atoms are commonly used,[4] those with sulfur donors remain comparatively unexplored. Sulfur can occur in oxidation states from −II to +VI, and so NHC ligands with different sulfur functionalities such as thioether, thiolate, sulfoxide, sulfonate, and thiophene exist.[5] In this area thioether-functionalized NHCs are most commonly used,[6] whereas just a few NHC−thiolato ligands are known so far.[7] Herein, we present a thiol-functionalized bis(1,2,4-triazolium) salt as an NHC ligand precursor for heteronuclear complexes.

In the literature, only a limited number of heterobimetallic transition-metal complexes with NHC ligands have been reported. In the majority of the cases, an NHC binding site is mixed with an ancillary ligand, e.g. a phosphine,[8] a phenanthroline,[9] a cyclopentadienyl,[10] or a salen-type[11] ligand, to achieve binding of two different metal centers. Peris et al. used a dicarbene ligand to connect two different metal centers by stepwise deprotonation of the 1,2,4-trimethyl-1,2,4-triazolium precursor salt.[12] In this way, it was possible to bind at first iridium to one binding site of the ligand and then rhodium, palladium, or platinum to the other site of the triazolediylidene (Figure 1, left). These mixed-metal complexes were successfully employed in tandem reactions in which each metal carries out one catalytic transformation in a one-pot procedure.

The use of a bis-NHC as ligand, in which two NHC groups are linked by a variable spacer, is rare, due to the difficulty in prohibiting a chelating instead of the desired bridging coordination mode and in deprotonating the usually equal carbene precursors selectively to introduce stepwise the desired metals. Braunstein et al. prepared a stable free dicarbene by deprotonation of the bis(imidazolium) precursor salt, which was reacted with $[IrCl(cod)]_2$ in ethanol to obtain a mixture of the dinuclear Ir(I) complex and the mononuclear Ir(I) complex with its second NHC unit reprotonated.[13] After isolation of the monometalated species, it was reacted with $[RhCl(cod)]_2$ and $Cs_2CO_3$ to generate a heterodinuclear Ir(I)−Rh(I) complex (Figure 1, middle). Cowie et al. also used mono-NHC metal complexes with a pendant imidazolium unit as precursors for bis-NHC bridged mixed-metal complexes of Ir(I)−Rh(I), Pd(II)−Ir(I), and Pd(II)−Rh(I) (Figure 1, right).[14] Monometallic precursors were obtained in good yields when the bis(imidazolium) ligand precursor was reacted with (sub)-

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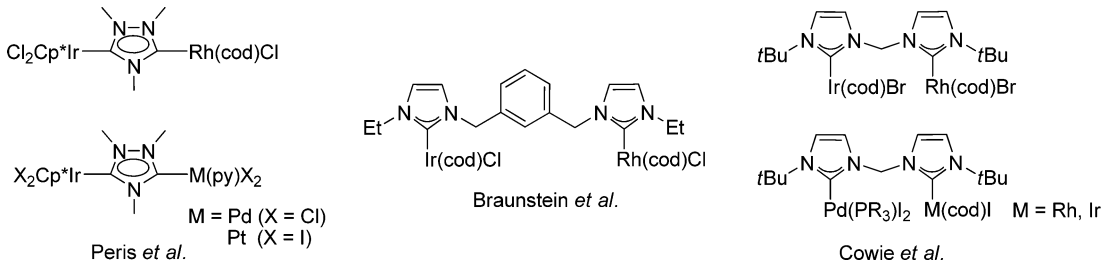
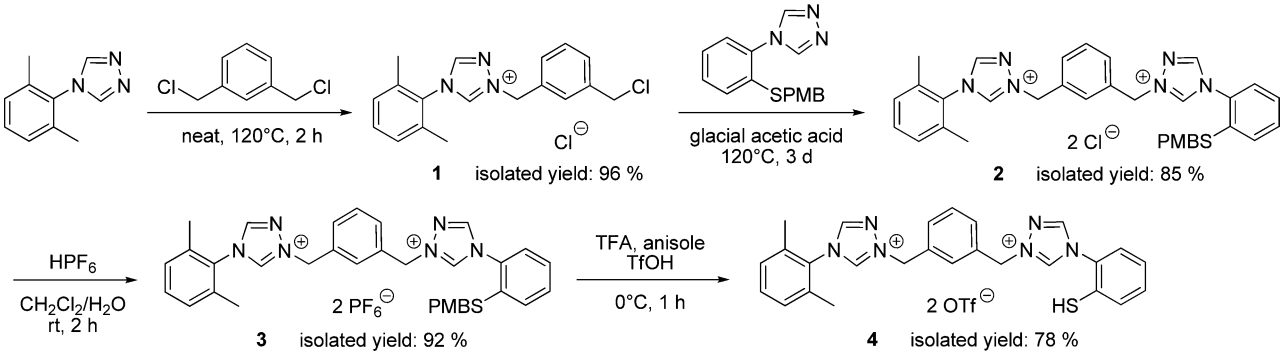


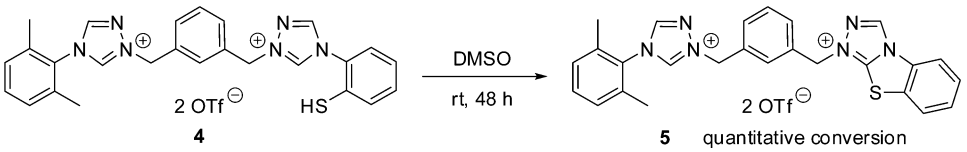

**Figure 1.** Mixed-metal complexes with triazolediylidene or a bis(imidazolylidene) as bridging ligand.

**Scheme 1. Synthesis of the Thiol-Functionalized Unsymmetrically Substituted Bis(1,2,4-triazolium) Salt 4**[a]




[a]PMB = *p*-methoxybenzyl as protecting group.

**Scheme 2. Oxidation of Thiophenol 4 in DMSO with Formation of Benzothiazole 5**




stoichiometric metal acetates, e.g. $Pd(OAc)_2$[15] and $[Rh(cod)(OAc)]_2$,[16] without additional base. The steric demand of the employed *tert*-butyl substituents of the methylene-linked NHC units appears to prevent a chelating coordination mode of the bis-NHC ligand.[17]

In this paper, we describe the selective deprotonation and metalation of the herein presented bis(1,2,4-triazolium) ligand precursor at its thiol-substituted triazolium fragment by reaction with $K_2CO_3$ and $PdCl_2$. The vacant triazolium unit of the obtained palladium(II) complex was coordinated to gold(I) or copper(I) to give mixed-metal complexes.

## RESULTS AND DISCUSSION

**Synthesis of the Ligand Precursor.** The thiol-functionalized unsymmetrically substituted bis(triazolium) salt **4**, which can act as a carbene ligand precursor, was synthesized in a straightforward procedure. 4-(2,6-Dimethylphenyl)-1,2,4-4*H*-triazole[18] was reacted with an excess of $\alpha,\alpha'$-dichloro-*m*-xylene at 120 °C without solvent to give the mono(triazolium) salt **1** (Scheme 1). This compound did not react with 4-[2-(4-methoxybenzylthio)phenyl]-1,2,4-4*H*-triazole[7g] in a second nucleophilic substitution by melting the two substrates together accordingly in the first step. Thus, glacial acetic acid was used as a polar, high-boiling solvent which facilitates as protic media the disposal of the chloride anion.[19] The obtained bis(triazolium) salt **2** was objected to a counterion metathesis with hexafluorophosphoric acid to improve its solubility in organic solvents. In the last step, the *p*-methoxybenzyl protecting group was removed under strongly acidic conditions (trifluoromethanesulfonic acid/trifluoroacetic acid in a molar ratio of 1/10) to obtain the free thiophenol.[20] Thereby the anion was exchanged to obtain the bis(triazolium) bis(triflate) **4**.

Usually thiols are prone to oxidation by changing the oxidation state of the sulfur atom. For instance, mild oxidizing agents such as iodine[21] and dimethyl sulfoxide[22] convert thiols to disulfides. However, as described before,[7g] the thiol-functionalized triazolium salt **4** reacts with DMSO with ring closure, forming benzothiazole **5** instead of a disulfide (Scheme 2).

Formation of a benzothiazole was proved by slow oxidation of the precursor salt **4** by air, whereupon crystals suitable for single-crystal X-ray analysis were obtained (Figure 2). The three rings of the benzothiazole system are planar, in contrast to the observed torsion of the triazole and the phenyl ring of the second triazolium unit caused by the methyl substituents in ortho positions.

**Synthesis of Heterometallic Complexes.** The unsymmetrically substituted bis(triazolium) salt **4** was deprotonated selectively at the thiol-functionalized triazolium unit and bound two times to palladium in a neutral square-planar complex. This was achieved by reaction with palladium(II) chloride and potassium carbonate as a mild base in pyridine at room temperature over 3 days (Scheme 3). The second triazolium fragment of the ligand system was preserved in each case. This directed deprotonation of one triazolium unit is presumably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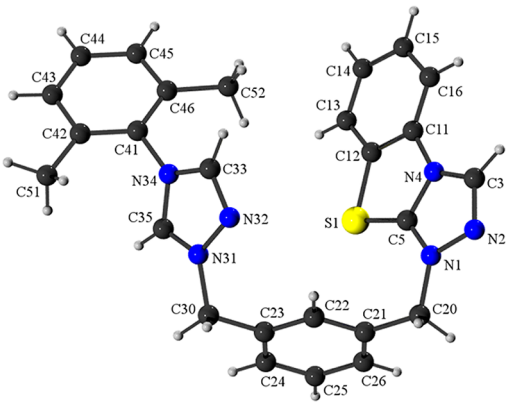


**Figure 2.** Ball-and-stick model of the X-ray structure of benzothiazole **5**. The counterions have been omitted for clarity. Both triflate anions are partially replaced by hexafluorophosphate anions, which originate from precursor salt **3**. The anions have been modeled as a superposition of both triflates using full local symmetry restraints. This means that chemically equivalent distances and angles within one anion as well as among the two independent copies were kept similar within a standard deviation of 0.02. Selected bond lengths (Å) and bond angles (deg): N(1)−N(2), 1.382(5); N(2)−C(3), 1.305(6); C(3)−N(4), 1.361(6); N(4)−C(5), 1.349(5); C(5)−N(1), 1.326(6); C(5)−S(1), 1.705(4); S(1)−C(12), 1.775(4); N(4)−C(11), 1.412(6); N(1)−N(2)−C(3), 104.7(4); N(2)−C(3)−N(4), 111.1(4); C(3)−N(4)−C(5), 106.9(4); N(4)−C(5)−N(1), 106.8(4); C(5)−N(1)−N(2), 110.5(3); S(1)−C(5)−N(4), 115.0(3); C(5)−N(4)−C(11), 113.6(3); N(4)−C(11)−C(12), 109.9(4); C(11)−C(12)−S(1), 112.9(3); C(12)−S(1)−C(5), 88.5(2); N(1)−C(5)−S(1)−C(12), 179.30; C(5)−N(1)−C(20)−C(21), 13.73; C(35)−N(31)−C(30)−C(23), 109.64; C(35)−N(34)−C(41)−C(42), 53.87.

based on the chelating effect of the adjacent sulfur atom. The precoordination of palladium to the thiolato donor facilitates coordination of the triazol-5-ylidene ligand. The free carbene is generated merely in small in situ concentrations through deprotonation by the mildly basic carbonate.

The $^{1}$H NMR spectrum shows palladium complex **6** as a mixture of its two diastereomers in a ratio of 2/1 (Figure 3). For each isomer two singlets of the protons at the C3 and C5 positions of the triazolium unit and one singlet of the remaining proton at the C3 position of the triazol-5-ylidene are observed. The absence of a signal of the proton at the C5 position indicates bonding to the metal center. In the case of the minor diastereomer, the proton signals of the two methylene groups of the *m*-xylylene linker split into two doublets. Each set can be observed, whereas in the case of the dominating diastereomer only two singlets are detected. The $^{13}$C NMR data exhibit two signals for Pd−$C_{carbene}$ at 172.4* and 175.5 ppm (* being the minor product). Since the signal of the carbene carbon of the *trans* isomer is generally shifted more downfield than that of the *cis* isomer at the same metal center,[23] we assume that the *trans* isomer is the dominating diastereomer due to steric hindrance. The ESI mass spectrum confirms the presence of palladium complex **6** as a dicationic species.

After monopalladation of the bis(carbene) precursor by selective deprotonation, gold(I) was incorporated as the second metal. The pendant triazolium unit of complex **6** was deprotonated with sodium methoxide in DMSO and reacted with gold(I) dimethyl sulfide chloride (Scheme 3). After extraction from the DMSO solution and purification by column chromatography the water- and air-stable palladium(II) gold(I) complex was objected to a salt metathesis with $KPF_6$ to obtain it as the hexafluorophosphate salt. Due to the small scale of preparation and the expensive workup procedure the compound was isolated in only moderate yields of 40%. Attempts to crystallize complex **7** failed. The purity of the obtained solid is sufficient, but small quantities of impurities remained. However, it represents a rare example of a heterobimetallic complex in which palladium is combined with a coinage metal.

The ESI mass spectrum contains only one peak, which corresponds to a monocationic complex containing one palladium and one gold atom. As indicated in Scheme 3, the gold(I) ion is presumably coordinated by two NHC ligands. The $^{1}$H NMR spectrum shows again two isomers in a ratio of 2/1 (Figure 3), which could not be separated by column chromatography or fractionated precipitation. For each isomer there are two singlets for the remaining protons at the C3 positions of the triazol-5-ylidenes. The nonequivalent protons of the methylene groups of the *m*-xylylene linker appear as four doublets (for each isomer), and the nonequivalent methyl groups of the dimethylphenyl substituent split into two singlets. The $^{13}$C NMR spectrum depicts four signals of the carbene carbons: at 172.1* and 176.0 ppm for the two Pd−$C_{carbene}$ groups as well as at 186.4* and 186.9 ppm for the two Au−$C_{carbene}$ groups. As the shifts of the carbon atoms bound to the palladium center are almost identical with those of the precursor complex **6**, the diastereomeric ratio was apparently conserved and the *trans* isomer dominates. Neither in the ESI mass spectrum nor in the NMR spectra were found any signs for the formation of a coordination polymer. The *m*-xylylene linker is presumably flexible enough to enable the coordination of a gold atom between the two NHC binding sites, even if palladium is coordinated in a *trans* geometry.

In addition to gold(I), it was also possible to incorporate copper(I) as the second metal into palladium(II) complex **6** by reaction with 2 equiv of copper(I) acetate (Scheme 3). The high acidity of 1,2,4-triazolium salts permits a facile deprotonation without the need for an additional base. The ESI mass spectra indicates the formation of a dicationic complex in which one copper(I) center is bound to each vacant NHC binding site. In contrast to palladium gold complex **7**, a heterotrinuclear palladium dicopper complex (**8**) was obtained. The anions were exchanged with hexafluorophosphate by reaction with $KPF_6$ in a two-phase system of dichloromethane/acetonitrile and water. Heteronuclear complex **8** crystallized from the dichloromethane/acetonitrile solution upon addition of diethyl ether. The single-crystal X-ray analysis confirms the presence of a dicationic palladium dicopper complex (Figure 4). Each copper ion binds to one triazol-5-ylidene ligand and to one sulfur atom of the NHC−thiolato unit attached to the palladium atom. Rotation at the methylene units of the *m*-xylylene linker enables this intramolecular coordination so that two metals are connected via a thiolato bridge. Additionally, acetonitrile is attached to each copper ion in a trigonal-planar geometry with an angle S(1)−Cu(1)−C(25) of 117°. The structure displays a square-planar coordination mode of two NHC−thiolato fragments to palladium with a C(5)−Pd(1)−S(1) angle of 88°. The planes of the triazole and the phenyl ring are distorted by 33° to facilitate ligation and to avoid steric hindrance induced by the substituents at the N1 position in the apparent *cis* configuration. The bond lengths Cu(1)−C(25) and Cu(1)−S(1) are, at 1.91 and 2.26 Å, slightly shorter than the bond lengths of Pd(1)−C(5) (1.99 Å) and Pd(1)−S(1)


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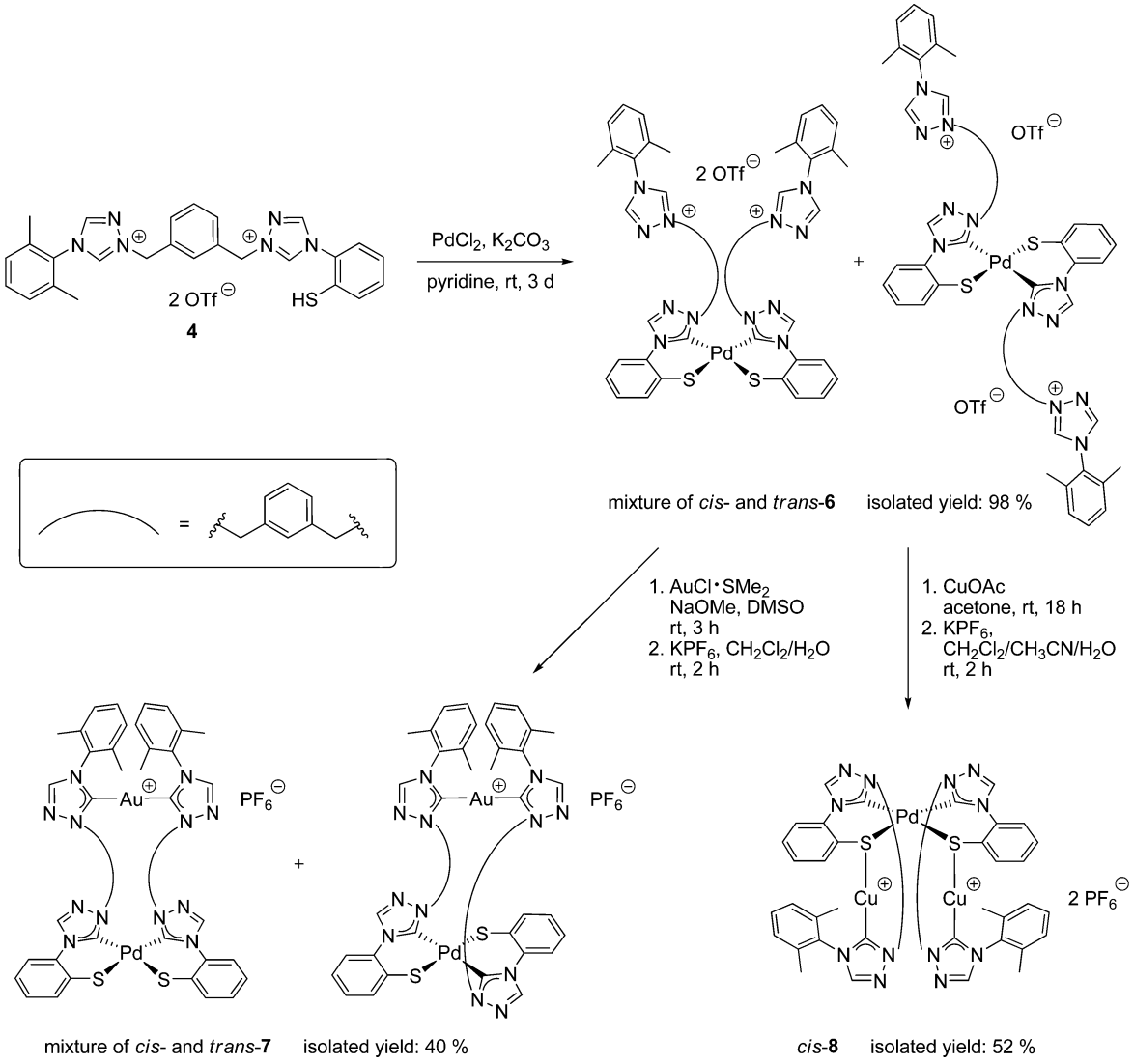
**Scheme 3. Stepwise Deprotonation and Metalation of Thiol-Functionalized Unsymmetrically Substituted Bis-NHC Precursor 4 with Palladium(II) and Gold(I) or Copper(I) to Obtain Heteronuclear Complexes 7 and 8, Respectively**




(2.33 Å). The Pd−Cu distance of 3.41 Å is too large for a direct metal−metal interaction.

The $^{1}$H NMR spectrum of palladium dicopper complex **8** represents only one species (Figure 3). The singlets of the remaining protons at the C3 position of the triazol-5-ylidenes coordinated to copper and palladium are visible at 8.19 and 8.82 ppm, respectively. The diastereotopic protons of the methylene groups of the *m*-xylylene linker split up into four doublets, and the methyl groups of the dimethylphenyl substituent split into two singlets. In the $^{13}$C NMR spectrum are depicted signals of Pd−$C_{carbene}$ at 168.9 ppm and Cu−$C_{carbene}$ at 182.3 ppm. The relatively small downfield shift of Pd−$C_{carbene}$ is consistent with the *cis* isomerism at the metal center. After drying of the solid product in vacuo, no acetonitrile was detected in the NMR spectra. The solvent molecules are apparently only loosely bound to the copper atoms. The elemental analysis is in agreement with a composition of two coppers per palladium without additional acetonitrile ligands in the isolated product.

## CONCLUSIONS

The high acidity of 1,2,4-triazolium salts leads to an in situ deprotonation and metalation under mild conditions. This synthetic advantage was successfully applied to the otherwise challenging selective preparation of heterometallic NHC complexes. The unsymmetrically substituted bis(1,2,4-triazolium) salt with one thiophenol substituent is a rare ligand precursor, because free thiol groups adjacent to azolium salts are prone to oxidation under C−S bond formation. This was structurally proven by a single-crystal X-ray analysis. Palladium(II) coordinated at the NHC−thiolato fragment, and then gold(I) or copper(I) reacted with the pendant triazolium ligand precursors in a second step to give water-stable heterodinuclear and heterotrinuclear complexes, respectively. To the best of our knowledge, these complexes are the first examples of bridged bis-NHC complexes containing palladium and coinage metals. In summary, we present a system that offers controlled metalation based on a directed stepwise deprotonation as a synthetic route to defined mixed-metal complexes.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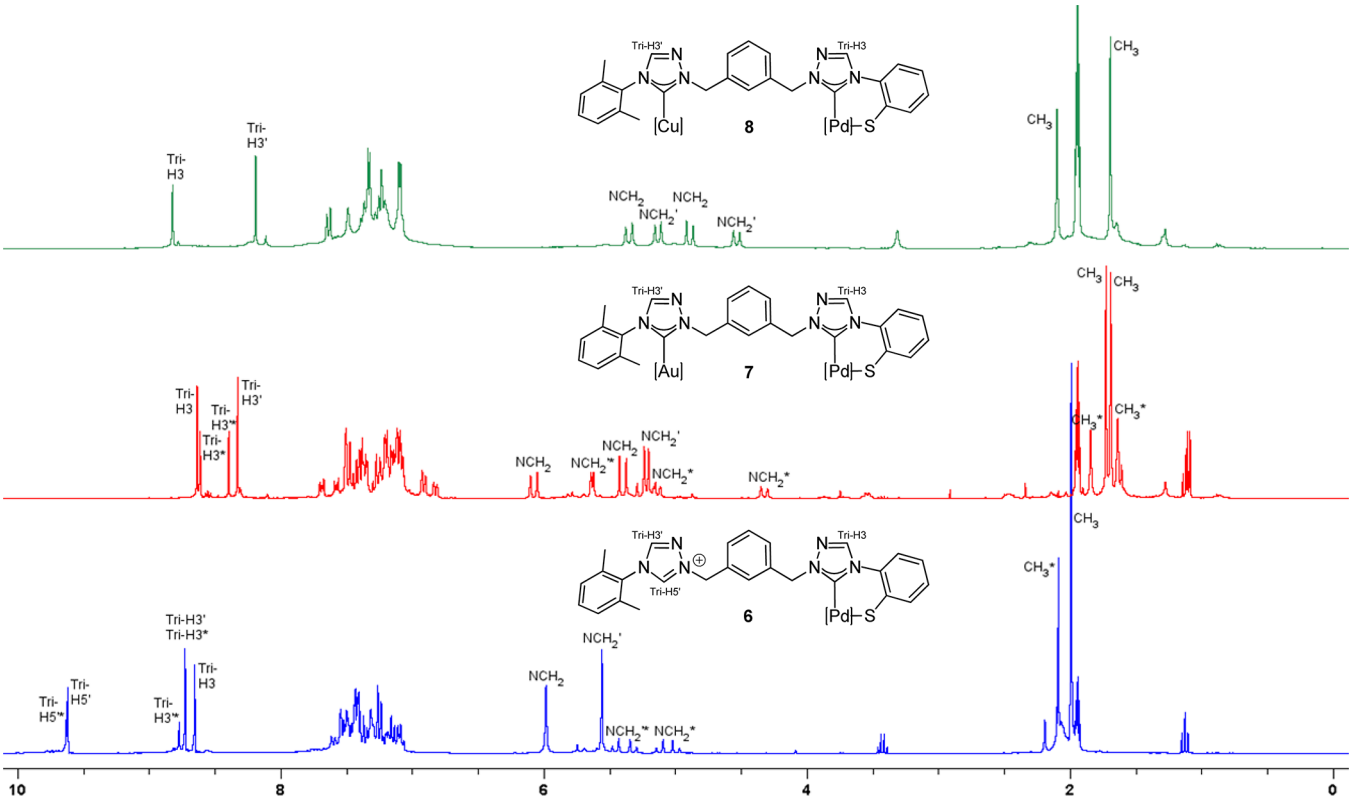


**Figure 3.** $^{1}$H NMR spectra of palladium dicopper complex **8** (green, top) and palladium gold complex **7** (red, middle) in comparison to that of palladium complex **6** (blue, bottom). A prime (′) in the assignment of the signals signifies the triazole unit of the ligand with the 2,6-dimethylphenyl substituent; an asterisk (*) denotes the minor diastereomer.

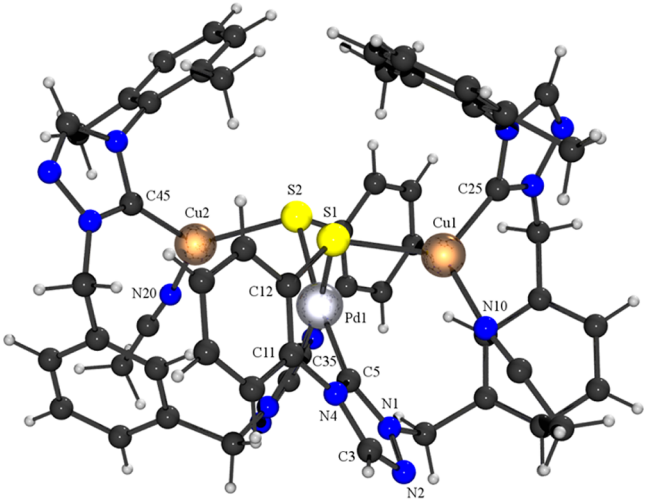


**Figure 4.** Ball-and-stick model of the X-ray structure of dicationic palladium dicopper complex **8**. The counterions have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pd(1)–C(5), 1.986(5); Pd(1)–C(35), 1.986(5); Pd(1)–S(1), 2.3265(14); Pd(1)–S(2), 2.3266(14); Cu(1)–S(1), 2.2639(17); Cu(1)–C(25), 1.913(6); Cu(1)–N(10), 1.937(6); C(5)–Pd(1)–S(1), 87.73(15); C(5)–Pd(1)–S(2), 170.13(15); S(1)–Cu(1)–C(25), 116.80(18); N(10)–Cu(1)–S(1), 120.36(15); C(25)–Cu(1)–N(10), 122.6(2); C(5)–N(4)–C(11)–C(12), 32.77.

## EXPERIMENTAL SECTION

**General Information.** All starting materials and solvents were obtained from commercial suppliers (Sigma-Aldrich, Fisher Scientific, Strem, Deutero, Eurisotop) and were used without further purification unless otherwise noted. Air- and moisture-sensitive reactions were carried out by using standard Schlenk or drybox techniques under an inert atmosphere (nitrogen or argon). NMR spectra were recorded by using Bruker Avance 300 and Bruker Avance 500 spectrometers at 25 °C. Chemical shifts ($\delta$) are reported in ppm relative to TMS and were determined by reference to the residual $^{1}$H or $^{13}$C solvent peaks.[24] ESI mass spectra were obtained on a Finnigan MAT LCQ and Bruker ICR Apex-Qe instruments. Melting points were determined using a Gallenkamp hot-stage microscope and are uncorrected.

**1-[1-(3-Chloromethyl)phenyl(methyl)]4-[2,6-dimethylphenyl]-1,2,4-4*H*-triazol-1-ium Chloride (1).** 4-(2,6-Dimethylphenyl)-1,2,4-4*H*-triazole[18] (2.89 mmol, 500 mg) and $\alpha,\alpha'$-dichloro-*m*-xylene (28.9 mmol, 5.05 g) were ground in a mortar and heated without solvent to 120 °C for 2 h. The resulting melt was minced and stirred in diethyl ether overnight. The colorless solid was filtered off, washed with diethyl ether, and dried in vacuo to give chloride **1** (970 mg, 96%).

$^{1}$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 2.15 (s, 6 H, $CH_3$), 4.80 (s, 2 H, $CH_2Cl$), 5.85 (s, 2 H, $NCH_2$), 7.37 (d, $^{3}J_{HH}$ = 7.5 Hz, 2 H, $H_{Xyl}$-3, $H_{Xyl}$-5), 7.44–7.49 (m, 2 H, $H_{Xyl}$-4, $H_{mXyl}$-5), 7.51–7.56 (m, 2 H, $H_{mXyl}$-4, $H_{mXyl}$-6), 7.64 (s, 1 H, $H_{mXyl}$-2), 9.69 (s, 1 H, N2CHN4), 11.39 (s, 1 H, N1CHN4). $^{13}$C{$^{1}$H} NMR (75 MHz, DMSO-$d_6$): $\delta$ 17.3 ($CH_3$), 45.6 ($CH_2Cl$), 54.7 ($NCH_2$), 128.7 ($C_{mXyl}$-6), 129.0 ($C_{Xyl}$-3, $C_{Xyl}$-5), 129.2 ($C_{mXyl}$-2), 129.2 ($C_{mXyl}$-5), 129.3 ($C_{mXyl}$-4), 130.4 ($C_{Xyl}$-1), 131.0 ($C_{Xyl}$-4), 133.6 ($C_{mXyl}$-1), 134.6 ($C_{Xyl}$-2, $C_{Xyl}$-6), 138.3 ($C_{mXyl}$-3), 144.0 (N1CHN4), 145.5 (N2CHN4). MS (ESI+): *m*/*z* (%) 312.13 (100) $[M - Cl]^+$, 659.22 (3) $[2M - Cl]^+$. HRMS (ESI+): *m*/*z* calculated for $[C_{18}H_{19}ClN_3]^+$ 312.1268, found 312.1262. Anal. Calcd for $C_{18}H_{19}Cl_2N_3$: C, 62.08; H, 5.50; N 12.07. Found: C, 61.85; H, 5.48; N, 11.96. Mp: 220 °C.

**1,1′-[1,3-Phenylenedi(methylene)][4-[2-(4-methoxybenzylthio)phenyl]-1,2,4-4*H*-triazol-1-ium][4-(2,6-dimethylphenyl)-1,2,4-4*H*-triazol-1-ium] Dichloride (2).** 4-[2-(4-Methoxybenzylthio)phenyl]-1,2,4-4*H*-triazole[7g] (2.34 mmol, 695 mg) and chloride **1** (1.56 mmol, 543 mg) were dissolved in glacial acetic


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acid (15 mL) and heated to 120 °C for 3 days. The solvent was removed under reduced pressure, and the obtained brown oil was dissolved in dichloromethane. On addition of diethyl ether, a light brown oil separated from the solution, which was washed with diethyl ether and dried in vacuo to give a light brown foam. The foam was dissolved again in dichloromethane, and on addition of diethyl ether the product precipitated as a light brown solid. The precipitate was filtered off, washed with diethyl ether, and dried in vacuo to give dichloride **2** (860 mg, 85%).

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 2.15 (s, 6 H, $CH_3$), 3.72 (s, 3 H, $OCH_3$), 4.18 (s, 2 H, $SCH_2$), 5.87 (s, 2 H, $NCH_2$), 5.88 (s, 2 H, $NCH_2$), 6.79 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, $H_{PMB}$-3, $H_{PMB}$-5), 7.10 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, $H_{PMB}$-2, $H_{PMB}$-6), 7.36 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, $H_{Xyl}$-3, $H_{Xyl}$-5), 7.46−7.51 (m, 1 H, $H_{Xyl}$-4), 7.50−7.63 (m, 4 H, $H_{mXyl}$-5, H-5, $H_{mXyl}$-4, $H_{mXyl}$-6), 7.65−7.70 (m, 1 H, H-4), 7.81 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.0 Hz, 1 H, H-3), 7.86−7.89 (m, 2 H, H-6, $H_{mXyl}$-2), 9.55 (s, 1 H, N2CHN4-$Tri_{PMB}$), 9.73 (s, 1 H, N2CHN4-$Tri_{Xyl}$), 11.40 (s, 1 H, N1CHN4-$Tri_{PMB}$), 11.57 (s, 1 H, N1CHN4-$Tri_{Xyl}$). $^{13}$C{$^1$H} NMR (75 MHz, DMSO-$d_6$): $\delta$ 17.4 ($CH_3$), 38.1 ($SCH_2$), 54.5 ($NCH_2$), 54.7 ($NCH_2$), 55.1 ($OCH_3$), 113.9 ($C_{PMB}$-3, $C_{PMB}$-5), 127.5 (C-6), 128.0 ($C_{PMB}$-1), 128.5 (C-5), 129.1 ($C_{Xyl}$-3, $C_{Xyl}$-5), 129.5 ($C_{mXyl}$-4, $C_{mXyl}$-5, $C_{mXyl}$-6), 129.7 ($C_{mXyl}$-2), 130.0 ($C_{PMB}$-2, $C_{PMB}$-6), 130.5 ($C_{Xyl}$-1), 131.1 ($C_{Xyl}$-4), 131.9 (C-4), 132.0 (C-1), 132.3 (C-2), 133.1 (C-3), 133.9 ($C_{mXyl}$-1, $C_{mXyl}$-3), 134.7 ($C_{Xyl}$-2, $C_{Xyl}$-6), 143.8 (N1CHN4-$Tri_{PMB}$), 144.3 (N1CHN4-$Tri_{Xyl}$), 145.4 (N2CHN4-$Tri_{PMB}$), 145.5 (N2CHN4-$Tri_{Xyl}$), 158.5 ($C_{PMB}$-4). MS (ESI+): $m/z$ (%) 287.13 (96) $[M - 2Cl]^{2+}$, 453.19 (91) $[M - C_8H_9O - 2Cl]^+$, 573.24 (100) $[M - H - 2Cl]^+$, 609.22 (46) $[M - Cl]^+$. HRMS (ESI+): $m/z$ calculated for $[C_{34}H_{33}N_6OS]^+$ 573.2431, found 573.2441; $m/z$ calculated for $[C_{34}H_{34}ClN_6OS]^+$ 609.2198, found 609.2208. Mp: 197 °C.

**1,1′-[1,3-Phenylenedi(methylene)][4-[2-(4-methoxybenzylthio)phenyl]-1,2,4-*4H*-triazol-1-ium][4-(2,6-dimethylphenyl)-1,2,4-*4H*-triazol-1-ium] Bis(hexafluorophosphate) (3).** To exchange the anions, dichloride **2** (1.26 mmol, 815 mg) was dissolved in dichloromethane and water was added. Hexafluorophosphoric acid (3.8 mmol, 0.56 mL (60% aqueous solution)) was added, and the two-phase system was vigorously stirred for 2 h. Then the phases were separated and the aqueous phase was extracted once with dichloromethane. The combined organic phases were washed three times with water, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure, and the obtained residue was dissolved in dichloromethane. On addition of diethyl ether, a light yellow oil separated from the solution, which was washed with diethyl ether and dried in vacuo to give bish(exafluorophosphate) **3** as a light yellow solid (1.00 g, 92%).

$^1$H NMR (300 MHz, acetone-$d_6$): $\delta$ 2.19 (s, 6 H, $CH_3$), 3.76 (s, 3 H, $OCH_3$), 4.11 (s, 2 H, $SCH_2$), 5.90 (s, 2 H, $N_{TriPMB}CH_2$), 5.98 (s, 2 H, $N_{TriXyl}CH_2$), 6.76 (d, $^3J_{HH}$ = 8.7 Hz, 2 H, $H_{PMB}$-3, $H_{PMB}$-5), 7.00 (d, $^3J_{HH}$ = 8.7 Hz, 2 H, $H_{PMB}$-2, $H_{PMB}$-6), 7.37 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, $H_{Xyl}$-3, $H_{Xyl}$-5), 7.47−7.52 (m, 1 H, $H_{Xyl}$-4), 7.59−7.66 (m, 2 H, H-5, $H_{mXyl}$-5), 7.70−7.76 (m, 4 H, $H_{mXyl}$-4, $H_{mXyl}$-6, H-4, H-6), 7.90−7.94 (m, 2 H, $H_{mXyl}$-2, H-3), 9.02 (s, 1 H, N2CHN4-$Tri_{PMB}$), 9.36 (s, 1 H, N2CHN4-$Tri_{Xyl}$), 10.15 (s, 1 H, N1CHN4-$Tri_{PMB}$), 10.34 (s, 1 H, N1CHN4-$Tri_{Xyl}$). $^{13}$C{$^1$H} NMR (75 MHz, acetone-$d_6$): $\delta$ 17.6 ($CH_3$), 40.3 ($SCH_2$), 55.6 ($OCH_3$), 56.6 ($N_{TriPMB}CH_2$), 56.9 ($N_{TriXyl}CH_2$), 114.9 ($C_{PMB}$-3, $C_{PMB}$-5), 127.9 (C-6), 129.4 ($C_{PMB}$-1), 130.1 ($C_{Xyl}$-3, $C_{Xyl}$-5), 130.1 (C-5), 130.7 ($C_{PMB}$-2, $C_{PMB}$-6), 131.0 ($C_{mXyl}$-5), 131.1, 131.2 ($C_{mXyl}$-4, $C_{mXyl}$-6), 131.3 ($C_{mXyl}$-2), 131.4 ($C_{Xyl}$-1), 132.5 ($C_{Xyl}$-4), 133.1 (C-2), 133.2 (C-4), 133.7 (C-1), 134.4 ($C_{mXyl}$-1, $C_{mXyl}$-3), 135.5 (C-3), 136.0 ($C_{Xyl}$-2, $C_{Xyl}$-6), 143.8 (N1CHN4-$Tri_{PMB}$), 144.3 (N1CHN4-$Tri_{Xyl}$), 146.1 (N2CHN4-$Tri_{PMB}$), 146.5 (N2CHN4-$Tri_{Xyl}$), 160.1 ($C_{PMB}$-4). $^{31}$P{$^1$H} NMR (121 MHz, acetone-$d_6$): −144.2 (sept, $^1J_{PF}$ = 709 Hz, $PF_6$). MS (ESI+): $m/z$ (%) 287.13 (97) $[M - 2PF_6]^{2+}$, 453.19 (81) $[M - C_8H_9O - 2PF_6]^+$, 573.24 (8) $[M - H - 2PF_6]^+$, 719.22 (100) $[M - PF_6]^+$. HRMS (ESI+): $m/z$ calculated for $[C_{34}H_{34}N_6OS]^{2+}$ 287.1252, found 287.1252; $m/z$ calculated for $[C_{34}H_{34}F_6N_6OPS]^+$ 719.2151, found 719.2150. Anal. Calcd for $C_{34}H_{34}F_{12}N_6OP_2S$: C, 47.23; H, 3.96; N, 9.72. Found: C, 47.38; H, 4.21; N, 10.01. Mp: 129 °C.

**1,1′-[1,3-Phenylenedi(methylene)][4-(2-thiophenyl)-1,2,4-*4H*-triazol-1-ium][4-(2,6-dimethylphenyl)-1,2,4-*4H*-triazol-1-ium] Bis(triflate) (4).** The bis(hexafluorophosphate) **3** (0.400 mmol, 346 mg) was dissolved at 0 °C under an argon atmosphere in trifluoroacetic acid (20.0 mmol, 1.54 mL). Anisole (2.0 mmol, 0.22 mL) and then trifluoromethanesulfonic acid (2.0 mmol, 0.18 mL) were added. The mixture was stirred for 1 h at 0 °C before the solvent was evaporated under reduced pressure. The obtained red oil was suspended in diethyl ether/water. A yellow oil separated between the two phases. The organic phase was pipetted off, and the aqueous phase with the oil was washed two times with diethyl ether in this way. To the aqueous phase were added dichloromethane and a small amount of acetonitrile until the oil was dissolved. The organic phase was washed twice with water and then dried over $MgSO_4$ and filtered. The volume of the solution was decreased under reduced pressure. On addition of diethyl ether, the product precipitated, which was filtered off, washed with diethyl ether, and dried in vacuo to give bis(triflate) **4** as a light yellow solid (234 mg, 78%).

$^1$H NMR (300 MHz, $CD_3CN$): $\delta$ 2.09 (s, 6 H, $CH_3$), 5.71 (s, 2 H, $N_{TriSH}CH_2$), 5.73 (s, 2 H, $N_{TriXyl}CH_2$), 7.32 (d, $^3J_{HH}$ = 7.4 Hz, 2 H, $H_{Xyl}$-3, $H_{Xyl}$-5), 7.45−7.51 (m, 2 H, $H_{Xyl}$-4, H-4), 7.52−7.57 (m, 2 H, $H_{mXyl}$-5, H-5), 7.59−7.63 (m, 3 H, $H_{mXyl}$-4, $H_{mXyl}$-6, H-3), 7.69−7.73 (m, 1 H, H-6), 7.74 (br. s, 1 H, $H_{mXyl}$-2), 8.80 (s, 1 H, N2CHN4-$Tri_{Xyl}$), 8.89 (s, 1 H, N2CHN4-$Tri_{SH}$), 9.71 (s, 1 H, N1CHN4-$Tri_{Xyl}$), 9.79 (s, 1 H, N1CHN4-$Tri_{SH}$). $^{13}$C{$^1$H} NMR (75 MHz, $CD_3CN$): $\delta$ 17.9 ($CH_3$), 56.9 ($N_{TriSH}CH_2$), 57.0 ($N_{TriXyl}CH_2$), 122.0 ($C_{OTf}$, $^1J_{CF}$ = 321 Hz), 128.6 (C-5), 129.1 (C-4), 129.7 (C-1), 130.3 ($C_{Xyl}$-3, $C_{Xyl}$-5), 131.2 ($C_{mXyl}$-5), 131.6 ($C_{mXyl}$-4, $C_{mXyl}$-6), 131.7 ($C_{mXyl}$-2), 131.8 (C-2), 132.8 ($C_{Xyl}$-4), 133.2 (C-3), 134.0 ($C_{Xyl}$-1), 134.1 ($C_{mXyl}$-1, $C_{mXyl}$-3), 134.4 (C-6), 136.1 ($C_{Xyl}$-2, $C_{Xyl}$-6), 143.7 (N1CHN4-$Tri_{SH}$), 143.8 (N1CHN4-$Tri_{Xyl}$), 146.0 (N2CHN4-$Tri_{SH}$), 146.3 (N2CHN4-$Tri_{Xyl}$). MS (ESI+): $m/z$ (%) 453.19 (100) $[M - H - 2OTf]^+$, 603.15 (15) $[M - OTf]^+$. HRMS (ESI+): $m/z$ calculated for $[C_{26}H_{25}N_6S]^+$ 453.1856, found 453.1857; $m/z$ calculated for $[C_{27}H_{26}F_3N_6O_3S_2]^+$ 603.1454, found 603.1459. Anal. Calcd for $C_{28}H_{26}F_6N_6O_6S_3$: C, 44.68; H, 3.48; N, 11.16. Found: C, 44.41; H, 3.66; N, 11.15. Mp: 160 °C.

**1,1′-[1,3-Phenylenedi(methylene)](1,2,4-triazol-1-ium[2,1-*b*]benzothiazole)[4-(2,6-dimethylphenyl)-1,2,4-*4H*-triazol-1-ium] Bis(triflate) (5).** Under a nitrogen atmosphere, the bis(triflate) **4** (0.05 mmol, 38 mg) was dissolved in dry DMSO-$d_6$ (0.5 mL) and stirred at room temperature. After 48 h the conversion to benzothiazole **5** was completed.

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 2.08 (s, 6 H, $CH_3$), 5.79 (s, 2 H, $N_{TriXyl}CH_2$), 5.90 (s, 2 H, $N_{TriS}CH_2$), 7.37 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, $H_{Xyl}$-3, $H_{Xyl}$-5), 7.48−7.53 (m, 1 H, $H_{Xyl}$-4), 7.64 (br. s, 3 H, $H_{mXyl}$-4, $H_{mXyl}$-5, $H_{mXyl}$-6), 7.71−7.76 (m, 2 H, $H_{mXyl}$-2, H-4), 7.81−7.87 (m, 1 H, H-5), 8.27 (d, $^3J_{HH}$ = 8.3 Hz, 1 H, H-3), 8.40 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, H-6), 9.56 (s, 1 H, N2CHN4-$Tri_{Xyl}$), 10.25 (s, 1 H, N2CHN4-$Tri_S$), 10.60 (s, 1 H, N1CHN4-$Tri_{Xyl}$). $^{13}$C{$^1$H} NMR (75 MHz, DMSO-$d_6$): $\delta$ 17.2 ($CH_3$), 54.8 ($N_{TriS}CH_2$), 55.1 ($N_{TriXyl}CH_2$), 115.9 (C-6), 120.7 ($C_{OTf}$, $^1J_{CF}$ = 323 Hz), 126.2 (C-3), 128.6 (C-1, C-5), 128.8 (C-4), 129.1 ($C_{Xyl}$-3, $C_{Xyl}$-5), 129.9 ($C_{Xyl}$-1), 130.1 ($C_{mXyl}$-5), 130.2 ($C_{mXyl}$-2), 130.5 ($C_{mXyl}$-4, $C_{mXyl}$-6), 131.3 ($C_{Xyl}$-4), 131.7 (C-2), 132.5 ($C_{mXyl}$-1), 133.8 ($C_{mXyl}$-3), 134.8 ($C_{Xyl}$-2, $C_{Xyl}$-6), 137.3 (N2CHN4-$Tri_S$), 143.8 (N1CHN4-$Tri_{Xyl}$), 145.7 (N2CHN4-$Tri_{Xyl}$), 154.3 (N1CN4-$Tri_S$). MS (ESI+): $m/z$ (%) 226.09 (23) $[M - 2OTf]^{2+}$, 451.17 (4) $[M - H - 2OTf]^+$, 601.13 (100) $[M - OTf]^+$. HRMS (ESI+): $m/z$ calculated for $[C_{26}H_{24}N_6S]^{2+}$ 226.0886, found 226.0887; $m/z$ calculated for $[C_{27}H_{24}F_3N_6O_3S_2]^+$ 601.1298, found 601.1295.

***cis*-/*trans*-Bis[1,1′-[1,3-phenylenedi(methylene)][4-(2,6-dimethylphenyl)-1,2,4-*4H*-triazol-1-ium][4-(2-thiophenyl)-1,2,4-*4H*-triazol-5-ylidene]]palladium(II) Bis(triflate) (6).** Under an argon atmosphere, pyridine (2 mL) was added to **4** (0.217 mmol, 163 mg), palladium(II) chloride (0.106 mmol, 18.7 mg), and potassium carbonate (0.53 mmol, 73 mg). The mixture was stirred at room temperature for 3 days until all palladium(II) chloride was dissolved. The mixture was diluted with dichloromethane, the yellow solution was filtered off, and the residue was washed with dichloromethane. The solvent was removed under reduced pressure.


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The obtained solid was dissolved in dichloromethane and the solution filtered off again. The product precipitated on addition of diethyl ether, which was filtered off, washed with diethyl ether, and dried in vacuo. Palladium complex **6** was obtained as a yellow solid which is a mixture of the two isomers in a 2/1 ratio (136 mg, 98%).

$^1$H NMR (500 MHz, $CD_3CN$): $\delta$ 1.98 (s, 6 H, $CH_3$), 2.08 (s, 6 H, $CH_3$*), 5.00 (d, $^2J_{HH}$ = 15.5 Hz, 1 H, $CH_2N_{Pd}$*), 5.12 (d, $^2J_{HH}$ = 15.5 Hz, 1 H, $CH_2N_{Pd}$*), 5.31 (d, $^2J_{HH}$ = 14.6 Hz, 1 H, $CH_2N_{Tri}$*), 5.44 (d, $^2J_{HH}$ = 14.6 Hz, 1 H, $CH_2N_{Tri}$*), 5.55 (s, 2 H, $CH_2N_{Tri}$), 5.98 (s, 2 H, $CH_2N_{Pd}$), 7.07–7.11 (m, 2 H, $H_{Ar}$), 7.13–7.25 (m, 6 H, $H_{Ar}$), 7.29–7.31 (m, 4 H, $H_{Ar}$), 7.35–7.38 (m, 1 H, $H_{Ar}$), 7.41–7.53 (m, 8 H, $H_{Ar}$), 7.58–7.60 (m, 1 H, $H_{Ar}$), 8.65 (s, 1 H, N2CHN4$_{Pd}$), 8.71 (s, 1 H, N2CHN4$_{Tri}$), 8.72 (s, 1 H, N2CHN4$_{Pd}$*), 8.76 (s, 1 H, N2CHN4$_{Tri}$*), 9.63 (s, 1 H, N1CHN4$_{Tri}$), 9.65 (s, 1 H, N1CHN4$_{Tri}$*) (* denotes the minor product). $^{13}$C{$^1$H} NMR (125 MHz, $CD_3CN$): $\delta$ 17.9 ($CH_3$), 18.1 ($CH_3$*), 56.4 ($CH_2N_{Pd}$), 57.2 ($CH_2N_{Tri}$), 57.3 ($CH_2N_{Pd}$*/$CH_2N_{Tri}$*), 122.1 ($C_{OTf}$, $^1J_{CF}$ = 321 Hz), 122.9 ($C_{Ar}$), 123.2 ($C_{Ar}$), 124.8 ($C_{Ar}$), 125.3 ($C_{Ar}$), 129.0 ($C_{Ar}$), 129.1 ($C_{Ar}$), 129.4 ($C_{Ar}$), 129.7 ($C_{Ar}$), 129.7 ($C_{Ar}$), 130.1 ($C_{Ar}$), 130.2 ($C_{Ar}$), 130.2 ($C_{Ar}$), 130.3 ($C_{Ar}$), 130.5 ($C_{Ar}$), 130.6 ($C_{Ar}$), 131.1 ($C_{Ar}$), 131.2 ($C_{Ar}$), 132.7 ($C_{Ar}$), 133.0 ($C_{Ar}$), 133.1 ($C_{Ar}$), 133.3 ($C_{Ar}$), 133.4 ($C_{Ar}$), 136.0 ($C_{Ar}$), 136.0 ($C_{Ar}$), 137.4 ($C_{Ar}$), 137.8 ($C_{Ar}$), 138.5 ($C_{Ar}$), 138.8 ($C_{Ar}$), 139.5 ($C_{Ar}$), 142.7 (N2CHN4$_{Pd}$), 143.1 (N2CHN4$_{Pd}$*), 143.4 (N1CHN4$_{Tri}$*), 143.5 (N1CHN4$_{Tri}$), 146.2 (N2CHN4$_{Tri}$), 146.2 (N2CHN4$_{Tri}$*), 172.4 (N1CN4$_{Pd}$*), 175.5 (N1CN4$_{Pd}$) (* denotes the minor product). MS (ESI+): $m/z$ (%) 505.3 (100) $[M - 2OTf]^{2+}$, 1159.1 (47) $[M - OTf]^+$. HRMS (ESI+): $m/z$ calculated for $[C_{52}H_{48}N_{12}PdS_2]^{2+}$ 505.1303, found 505.1292; $m/z$ calculated for $[C_{53}H_{48}F_3N_{12}O_3PdS_3]^+$ 1159.2121, found 1159.2127. Anal. Calcd for $C_{54}H_{48}F_6N_{12}O_6PdS_4$: C, 49.52; H, 3.69; N, 12.83. Found: C, 49.73; H, 3.93; N, 12.61. Mp: 196 °C.

***cis*-/*trans*-Bis[1,1′-[1,3-phenylenedi(methylene)][4-(2,6-dimethylphenyl)-1,2,4-4*H*-triazol-5-ylidene][4-(2-thiophenyl)-1,2,4-4*H*-triazol-5-ylidene]]gold(I)palladium(II) Hexafluorophosphate (7).** Under an argon atmosphere, palladium(II) complex **6** (0.145 mmol, 190 mg), (dimethyl sulfide)gold(I) chloride (0.145 mmol, 42.7 mg), and sodium methoxide (0.29 mmol, 16 mg) were dissolved in dry DMSO (3 mL). After it was stirred for 3 h at room temperature, the brown solution was extracted with dichloromethane/water. The organic phase was washed three times with water, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, dichloromethane/2-propanol 30/1). The obtained yellow solid was subjected to a salt metathesis. An excess of potassium hexafluorophosphate (0.725 mmol, 133 mg) was dissolved in water (5 mL) and added to a solution of the product in dichloromethane (5 mL). The two-phase system was stirred vigorously for 2 h. The phases were separated, and the aqueous phase was extracted once with dichloromethane. The combined organic phases were washed three times with water, dried over $MgSO_4$, and filtered. The volume of the solution was decreased under reduced pressure, and on addition of diethyl ether the product precipitated. The yellow solid was filtered off, washed with diethyl ether, and dried in vacuo. The obtained palladium gold complex **7** is a mixture of the two isomers in a ratio of 2/1 (78 mg, 40%).

$^1$H NMR (300 MHz, $CD_3CN$): $\delta$ 1.64 (s, 3 H, $CH_3$*), 1.69 (s, 3 H, $CH_3$), 1.73 (s, 3 H, $CH_3$), 1.84 (s, 3 H, $CH_3$*), 4.33 (d, $^2J_{HH}$ = 14.8 Hz, 1 H, $CH_2N_{Pd}$*), 5.14 (d, $^2J_{HH}$ = 14.8 Hz, 1 H, $CH_2N_{Pd}$*), 5.18 (d, $^2J_{HH}$ = 15.5 Hz, 1 H, $CH_2N_{Au}$), 5.26 (d, $^2J_{HH}$ = 15.5 Hz, 1 H, $CH_2N_{Au}$), 5.40 (d, $^2J_{HH}$ = 15.5 Hz, 1 H, $CH_2N_{Pd}$), 5.60 (d, $^2J_{HH}$ = 15.3 Hz, 1 H, $CH_2N_{Au}$*), 5.66 (d, $^2J_{HH}$ = 15.3 Hz, 1 H, $CH_2N_{Au}$*), 6.08 (d, $^2J_{HH}$ = 15.5 Hz, 1 H, $CH_2N_{Pd}$), 6.85–6.88 (m, 1 H, $H_{Ar}$), 6.91–6.93 (m, 1 H, $H_{Ar}$), 7.07–7.32 (m, 11 H, $H_{Ar}$), 7.35–7.51 (m, 8 H, $H_{Ar}$), 7.56–7.59 (m, 1 H, $H_{Ar}$), 7.69–7.72 (m, 1 H, $H_{Ar}$), 8.33 (s, 1 H, N2CHN4$_{Au}$), 8.40 (s, 1 H, N2CHN4$_{Au}$*), 8.63 (s, 1 H, N2CHN4$_{Pd}$*), 8.64 (s, 1 H, N2CHN4$_{Pd}$) (* denotes the minor product). $^{13}$C{$^1$H} NMR (75 MHz, $CD_3CN$): $\delta$ 17.8 ($CH_3$*), 17.9 ($CH_3$), 18.0 ($CH_3$), 18.1 ($CH_3$*), 56.3 ($CH_2N_{Pd}$), 57.0 ($CH_2N_{Au}$), 57.1 ($CH_2N_{Au}$*), 57.4 ($CH_2N_{Pd}$*), 122.8 ($C_{Ar}$), 122.9 ($C_{Ar}$), 124.5 ($C_{Ar}$), 125.2 ($C_{Ar}$), 127.3 ($C_{Ar}$), 127.4 ($C_{Ar}$), 127.6 ($C_{Ar}$), 128.4 ($C_{Ar}$), 128.9 ($C_{Ar}$), 129.0 ($C_{Ar}$), 129.7 ($C_{Ar}$), 130.0 ($C_{Ar}$), 130.3 ($C_{Ar}$), 130.7 ($C_{Ar}$), 131.6 ($C_{Ar}$), 131.7 ($C_{Ar}$), 133.3 ($C_{Ar}$), 134.2 ($C_{Ar}$), 136.0 ($C_{Ar}$), 136.1 ($C_{Ar}$), 136.5 ($C_{Ar}$), 136.8 ($C_{Ar}$), 137.1 ($C_{Ar}$), 138.2 ($C_{Ar}$), 138.4 ($C_{Ar}$), 138.6 ($C_{Ar}$), 142.9 (N2CHN4$_{Pd}$), 143.0 (N2CHN4$_{Pd}$*), 145.1 (N2CHN4$_{Au}$), 145.5 (N2CHN4$_{Au}$*), 172.1 (N1CN4$_{Pd}$*), 176.0 (N1CN4$_{Pd}$), 186.4 (N1CN4$_{Au}$*), 186.9 (N1CN4$_{Au}$) (* denotes the minor product). $^{31}$P{$^1$H} NMR (121 MHz, $CD_3CN$): −144.5 (sept, $^1J_{PF}$ = 707 Hz, $PF_6$). $^{19}$F{$^1$H} NMR (282 MHz, $CD_3CN$): −72.7 (d, $^1J_{PF}$ = 707 Hz, $PF_6$). MS (ESI+): $m/z$ (%) 1205.21 (100) $[M - PF_6]^+$. HRMS (ESI+): $m/z$ calculated for $[C_{52}H_{46}AuN_{12}PdS_2]^+$ 1205.2121, found 1205.2125. Anal. Calcd for $C_{52}H_{46}AuF_6N_{12}PPdS_2$: C, 46.21; H, 3.43; N, 12.44; S, 4.75. Found: C, 45.67; H, 3.62; N, 11.91; S, 4.69. Mp: 285 °C dec.

***cis*-Bis[1,1′-[1,3-phenylenedi(methylene)][4-(2,6-dimethylphenyl)-1,2,4-4*H*-triazol-5-ylidene][4-(2-thiophenyl)-1,2,4-4*H*-triazol-5-ylidene]]dicopper(I)palladium(II) Bis(hexafluorophosphate) (8).** Under an argon atmosphere, palladium(II) complex **6** (0.076 mmol, 100 mg) and copper(I) acetate (0.16 mmol, 20 mg) were dissolved in dry acetone (2 mL). After it was stirred at room temperature overnight, the yellow solution was filtered off the gray precipitate and the solvent was removed under reduced pressure. The obtained yellow solid was subjected to a salt metathesis. The product was dissolved under an argon atmosphere in dry dichloromethane (2 mL) and a small amount of dry acetonitrile until all solid was dissolved. A solution of potassium hexafluorophosphate (1.52 mmol, 280 mg) in degassed water (2 mL) was added, and the two-phase system was stirred vigorously for 2 h. The phases were separated, and the aqueous phase was extracted three times with dichloromethane. The combined organic phases were dried over $MgSO_4$ and filtered. The volume of the solution was decreased under reduced pressure, and on addition of diethyl ether the product precipitated. The yellow solid was filtered off, washed with diethyl ether, and dried in vacuo to give the *cis* isomer of palladium dicopper complex **8** as a yellow solid (56 mg, 52%).

$^1$H NMR (300 MHz, $CD_3CN$): $\delta$ 1.70 (s, 3 H, $CH_3$), 2.10 (s, 3 H, $CH_3$), 4.55 (d, $^2J_{HH}$ = 14.2 Hz, 1 H, $CH_2N_{Cu}$), 4.89 (d, $^2J_{HH}$ = 15.1 Hz, 1 H, $CH_2N_{Pd}$), 5.14 (d, $^2J_{HH}$ = 14.2 Hz, 1 H, $CH_2N_{Cu}$), 5.35 (d, $^2J_{HH}$ = 15.1 Hz, 1 H, $CH_2N_{Pd}$), 7.07–7.12 (m, 2 H, $H_{Ar}$), 7.18–7.39 (m, 7 H, $H_{Ar}$), 7.48 (br.s, 1 H, $H_{Ar}$), 7.62–7.65 (m, 1 H, $H_{Ar}$), 8.19 (s, 1 H, N2CHN4$_{Cu}$), 8.82 (s, 1 H, N2CHN4$_{Pd}$). $^{13}$C{$^1$H} NMR (75 MHz, $CD_3CN$): $\delta$ 17.7 ($CH_3$), 18.8 ($CH_3$), 56.8 ($CH_2N_{Cu}$), 57.8 ($CH_2N_{Pd}$), 124.1 ($C_{Ar}$), 127.5 ($C_{Ar}$), 129.2 ($C_{Ar}$), 129.5 ($C_{Ar}$), 129.6 ($C_{Ar}$), 129.8 ($C_{Ar}$), 130.7 ($C_{Ar}$), 130.8 ($C_{Ar}$), 133.3 ($C_{Ar}$), 135.9 ($C_{Ar}$), 136.4 ($C_{Ar}$), 136.9 ($C_{Ar}$), 137.1 ($C_{Ar}$), 137.3 ($C_{Ar}$), 137.5 ($C_{Ar}$), 143.2 (N2CHN4$_{Cu}$), 143.7 (N2CHN4$_{Pd}$), 168.9 (N1CN4$_{Pd}$), 182.3 (N1CN4$_{Cu}$). $^{31}$P{$^1$H} NMR (121 MHz, $CD_3CN$): −144.6 (sept, $^1J_{PF}$ = 707 Hz, $PF_6$). $^{19}$F{$^1$H} NMR (282 MHz, $CD_3CN$): −72.7 (d, $^1J_{PF}$ = 707 Hz, $PF_6$). MS (ESI+): $m/z$ (%) 537.0 (15) $[M + H - Cu - 2PF_6]^{2+}$, 568.8 (60) $[M - 2PF_6]^{2+}$, 1073.0 (100) $[M - Cu - 2PF_6]^+$. HRMS (ESI+): $m/z$ calculated for $[C_{52}H_{46}Cu_2N_{12}PdS_2]^{2+}$ 567.0518, found 567.0512; $m/z$ calculated for $[C_{52}H_{46}CuN_{12}PdS_2]^+$ 1071.1748., found 1071.1751. Anal. Calcd for $C_{52}H_{46}Cu_2F_{12}N_{12}P_2PdS_2$: C, 43.78; H, 3.25; N, 11.78; S, 4.50. Found: C, 43.83; H, 3.68; N, 11.46; S, 4.66. Mp: >220 °C dec.

**X-ray Diffraction Studies.** The single-crystal X-ray diffraction data sets were collected at 200(2) K on a Bruker APEX diffractometer or a Bruker APEX II Quazar diffractometer equipped with a CCD area detector and a standard sealed-tube Mo K$\alpha$ ($\lambda$ = 0.71073 Å) radiation source. 0.3° $\omega$ scans covering a whole sphere in reciprocal space were taken in each case, and an empirical absorption correction was applied using SADABS[25] on the basis of the Laue symmetry of the reciprocal space. Structures were solved by direct methods and refined against $F^2$ with a full-matrix least-squares algorithm using the SHELXTL-PLUS (6.10) software package.[26] For analysis and graphic representation, the programs ORTEP[27] and POV-Ray[28] were used. CCDC 924413 (for **5**) and 924414 (for **8**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## ■ ASSOCIATED CONTENT

### Supporting Information

Figures, tables, and CIF files giving $^{1}H$ and $^{13}C$ NMR spectra and crystal data for structures **5** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES


(1) Wanzlick, H.-W.; Schönherr, H.-J. *Angew. Chem., Int. Ed.* **1968**, *7*, 141.

(2) Öfele, K. *J. Organomet. Chem.* **1968**, *12*, P42.

(3) (a) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (b) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122. (c) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606.

(4) (a) Kühl, O. *Chem. Soc. Rev.* **2007**, *36*, 592. (b) Normand, A. T.; Cavell, K. J. *Eur. J. Inorg. Chem.* **2008**, *2008*, 2781. (c) John, A.; Ghosh, P. *Dalton Trans.* **2010**, *39*, 7183.

(5) (a) Yuan, D.; Huynh, H. V. *Molecules* **2012**, *17*, 2491. (b) Bierenstiel, M.; Cross, E. D. *Coord. Chem. Rev.* **2011**, *255*, 574.

(6) (a) Fliedel, C.; Braunstein, P. *Organometallics* **2010**, *29*, 5614. (b) Fliedel, C.; Sabbatini, A.; Braunstein, P. *Dalton Trans.* **2010**, *39*, 8820. (c) Huynh, H. V.; Yeo, C. H.; Tan, G. K. *Chem. Commun.* **2006**, 3833. (d) Huynh, H. V.; Yuan, D.; Han, Y. *Dalton Trans.* **2009**, 7262. (e) Huynh, H. V.; Yeo, C. H.; Chew, Y. X. *Organometallics* **2010**, *29*, 1479. (f) Iglesias-Sigüenza, J.; Ros, A.; Díez, E.; Magriz, A.; Vázquez, A.; Álvarez, E.; Fernández, R.; Lassaletta, J. M. *Dalton Trans.* **2009**, 8485. (g) Ros, A.; Monge, D.; Alcarazo, M.; Álvarez, E.; Lassaletta, J. M.; Fernández, R. *Organometallics* **2006**, *25*, 6039. (h) Roseblade, S. J.; Ros, A.; Monge, D.; Alcarazo, M.; Álvarez, E.; Lassaletta, J. M.; Fernández, R. *Organometallics* **2007**, *26*, 2570. (i) Ros, A.; Alcarazo, M.; Iglesias-Sigüenza, J.; Díez, E.; Álvarez, E.; Fernández, R.; Lassaletta, J. M. *Organometallics* **2008**, *27*, 4555.

(7) (a) Sellmann, D.; Allmann, C.; Heinemann, F.; Knoch, F.; Sutter, J. *J. Organomet. Chem.* **1997**, *541*, 291. (b) Sellmann, D.; Prechtel, W.; Knoch, F.; Moll, M. *Inorg. Chem.* **1993**, *32*, 538. (c) Sellmann, D.; Prechtel, W.; Knoch, F.; Moll, M. *Organometallics* **1992**, *11*, 2346. (d) Yuan, D.; Huynh, H. V. *Organometallics* **2010**, *29*, 6020. (e) Yuan, D.; Huynh, H. V. *Dalton Trans.* **2011**, *40*, 11698. (f) Cabeza, J. A.; del Río, I.; Sánchez-Vega, M. G.; Suárez, M. *Organometallics* **2006**, *25*, 1831. (g) Holm, S. C.; Rominger, F.; Straub, B. F. *J. Organomet. Chem.* **2012**, *719*, 54.

(8) Ruiz, J.; Mesa, A. F. *Chem. Eur. J.* **2012**, *18*, 4485.

(9) Gu, S.; Xu, D.; Chen, W. *Dalton Trans.* **2011**, *40*, 1576.

(10) Arduengo, A. J.; Tapu, D.; Marshall, W. J. *J. Am. Chem. Soc.* **2005**, *127*, 16400.

(11) Mechler, M.; Latendorf, K.; Frey, W.; Peters, R. *Organometallics* **2012**, *32*, 112.

(12) (a) Mas-Marzá, E.; Mata, J.; Peris, E. *Angew. Chem., Int. Ed.* **2007**, *46*, 3729. (b) Viciano, M.; Sanaú, M.; Peris, E. *Organometallics* **2007**, *26*, 6050. (c) Zanardi, A.; Corberán, R.; Mata, J. A.; Peris, E. *Organometallics* **2008**, *27*, 3570. (d) Zanardi, A.; Mata, J. A.; Peris, E. *J. Am. Chem. Soc.* **2009**, *131*, 14531. (e) Zanardi, A.; Mata, J. A.; Peris, E. *Chem. Eur. J.* **2010**, *16*, 13109.

(13) Raynal, M.; Cazin, C. S. J.; Vallee, C.; Olivier-Bourbigou, H.; Braunstein, P. *Dalton Trans.* **2009**, 3824.

(14) Zamora, M. T.; Ferguson, M. J.; McDonald, R.; Cowie, M. *Dalton Trans.* **2009**, *0*, 7269.

(15) Herrmann, W. A.; Schwarz, J.; Gardiner, M. G. *Organometallics* **1999**, *18*, 4082.

(16) Wells, K. D.; Ferguson, M. J.; McDonald, R.; Cowie, M. *Organometallics* **2008**, *27*, 691.

(17) Albrecht, M.; Miecznikowski, J. R.; Samuel, A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 3596.

(18) Holm, S. C.; Siegle, A. F.; Loos, C.; Rominger, F.; Straub, B. F. *Synthesis* **2010**, *2010*, 2278.

(19) Berg, R.; Straub, J.; Schreiner, E.; Mader, S.; Rominger, F.; Straub, B. F. *Adv. Synth. Catal.* **2012**, *354*, 3445.

(20) Wildonger, K. J.; Ratcliffe, R. W. *J. Antibiot.* **1993**, *46*, 1866.

(21) Danehy, J. P.; Doherty, B. T.; Egan, C. P. *J. Org. Chem.* **1971**, *36*, 2525.

(22) Epstein, W. W.; Sweat, F. W. *Chem. Rev.* **1967**, *67*, 247.

(23) Huynh, H. V.; Ho, J. H. H.; Neo, T. C.; Koh, L. L. *J. Organomet. Chem.* **2005**, *690*, 3854.

(24) (a) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512. (b) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176.

(25) Sheldrick, G. M. *SADABS*; Bruker Analytical X-ray Division, Madison, WI, 2008.

(26) Sheldrick, G. M. Software Package SHELXTL 2008/4 for Structure Solution and Refinement. *Acta Crystallogr.* **2008**, *A64*, 112.

(27) Farrugia, L. J. ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI). *J. Appl. Crystallogr.* **1997**, *30*, 565; www.ornl.gov/sci/ortep.

(28) *Persistence of Vision Raytracer (POV-Ray) Version 3.6*; www.povray.org.