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Binuclear Palladium(I) and Palladium(II) Complexes of *ortho*-Functionalized 1,3-Bis(aryl)triazenido Ligands

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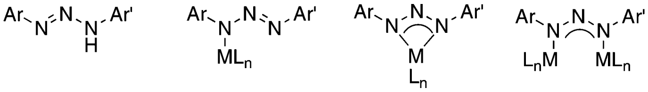
Three new bis(aryl)triazene ligands, Ar-NNNH-Ar′ [Ar = *o*-C_6H_4-CO_2Me, Ar′ = *p*-C_6H_4-CH_3 (**2**); Ar = Ar′ = *o*-C_6H_4-CO_2Me (**3**); Ar = *o*-C_6H_4-SMe, Ar′ = *p*-C_6H_4-CH_3) (**4**)], have been synthesized. The reaction of **1**–**4** with $PdCl_2(NCCH_3)_2$ in the presence of a base afforded a series of binuclear diamagnetic palladium complexes. In these reactions, ligands **1**–**3** afforded the palladium(I) complexes $[Pd^I$(*o*-MeO_2C-C_6H_4-NNN-*o*-C_6H_4-$CO_2Me)]_2$ (**5**, monoclinic, space group $P2_1/c$, $a = 8.6070(10)$ Å, $b = 14.3220(10)$ Å, $c = 12.7310(10)$ Å, $\beta = 100.2950(10)°$, $Z = 2$), $[Pd^I$(*o*-MeO-C_6H_4-NNN-*o*-C_6H_4-OMe)$]_2$ (**6**, triclinic, space group $P\bar{1}$, $a = 6.6288(5)$ Å, $b = 10.2631(10)$ Å, $c = 11.0246(11)$ Å, $\alpha = 85.579(6)°$, $\beta = 80.885(6)°$, $\gamma = 74.607(6)°$, $Z = 1$), and $[Pd^I$(*o*-MeO_2C-C_6H_4-NNN-*p*-C_6H_4-$CH_3)]_2$ (**7**, tetragonal, space group $I41/a$, $a = 20.866(3)$ Å, $b = 20.866(3)$ Å, $c = 13.156(2)$ Å, $Z = 8$). In contrast, the reaction of ligand **4** with $PdCl_2(NCCH_3)_2$ resulted in the formation of a palladium(II) dimer, $[Pd^{II}$(*o*-MeS-C_6H_4-NNN-*p*-C_6H_4-$CH_3)Cl]_2$ (**8**, orthorhombic, space group $P2_12_12$, $a = 10.4058(5)$ Å, $b = 16.2488(8)$ Å, $c = 9.9500(5)$ Å, $Z = 2$).

Introduction

A fundamental aim of inorganic chemistry is the synthesis of complexes that exhibit new reactivity. An approach toward this important goal is the preparation of unique ligands that impart novel chemistry when incorporated into the metal coordination sphere. As such, a class of ligands that has attracted our attention is the triazenido ligands (Chart 1), because these ligands exhibit a variety of bonding modes with distinct properties.[1,2] Triazenido ligands in monomeric complexes can bind through a single nitrogen or can form metallocycles through chelation. They are also well-known to bridge two metal centers (Chart 1).[3,4]

Chart 1. Generic Triazene and Triazenido Binding Modes



Triazenido ligands are isoelectronic with amidinates,[5,6] which have been successfully used in transition metal chemistry. The central nitrogen of the triazene imparts greater acidity on the N−H[7,8] relative to the amidine N−H, making the triazenido less electron donating and more amenable to binding to late transition metals. Our initial studies involved the use of simple 1,3-bis(aryl) triazines to prepare main group complexes.[9,10] More recently, we have turned our attention

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to the application of 1,3-bis(aryl) triazenido ligands bearing Lewis basic *ortho*-substituents,[11,12] such as esters,[13,14] which can form additional chelating rings and induce novel coordination environments. The weakly coordinating ester carbonyl groups can behave as hemilabile ligands[15] to open a coordination site for substrate activation. The ability of the Lewis basic *ortho*-substituents to coordinate to soft metals could be modulated by choice of hard weakly coordinating groups, such as esters and ethers, or softer more-electron donating substituents, such as the methylmercapto group. We have found that the nature of the Lewis basic *ortho*-substituent can have a dramatic impact on the chemistry of these complexes.

In this paper, we examine the synthesis and structure of palladium complexes bearing 1,3-bis(aryl) triazenido ligands with Lewis basic substituents in the *ortho*-positions. Unlike unfunctionalized 1,3-bis(aryl) triazenido ligands, which give palladium(II) complexes when palladium(II) is employed as starting material, we were surprised to find that use of our *ortho*-functionalized triazenes gave rise to palladium(I) or palladium(II) dimers, depending on the characteristics of the *ortho*-substituent. We are unaware of previously characterized examples of palladium(I) employing triazenido ligands. These novel palladium(I) complexes have been fully characterized, including by X-ray crystallography.

Experimental Section

All reactions were performed under air. Unless otherwise specified all chemicals were purchased from Aldrich Chemical Co. and were used without further purification. Methyl anthranilate was purchased from Spectrum, while [1,3-bis(2-carboxymethyl)benzene]triazene (**1**)[11] and bis(acetonitrile)palladium(II) dichloride[16] were synthesized according to literature procedures. NMR spectra were recorded on a Varian Gemini 2000-BB FT. ^{1}H NMR (200 MHz) and ^{13}C{^{1}H} NMR (50 MHz) are reported in parts per million relative to Me_4Si as an internal standard. Coupling constants, *J*, are given in Hertz (Hz). IR spectra were recorded on a Perkin-Elmer Model 1605 FT-IR spectrometer. UV−vis absorption spectra were measured on a HP 8452A diode array spectrophotometer. EI mass spectra were obtained with a HP 5989 MS Engine, and ES mass spectra were measured with an Agilent 110 MSD ion trap. Melting points were measured in a Gallenkamp apparatus and are uncorrected. Elemental analyses were performed at Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Zaragoza, Spain. Samples for elemental analysis were dried at room temperature under vacuum for at least 24 h.

Synthesis of Ligands. 1-[(2-Carboxymethyl)benzene]-3-[(4-methyl)benzene]triazene (2). Methyl anthranilate (2.5 mL, 19.3 mmol) in water (5 mL) was mixed with 1 M HCl (57.9 mL, 57.9 mmol, 3 equiv) at 0 °C. An aqueous solution (15%) of sodium nitrite (1.997 g, 28.9 mmol, 1.5 equiv) was added dropwise with stirring. Once the amine was dissolved, a 15% solution of *p*-toluidine in ethanol (2.07 g, 19.3 mmol, 1 equiv) was added at 0 °C and stirred for 30 min. The reaction mixture was neutralized with a 15% aqueous solution of NaOAc (31.6 mL) to give a yellow precipitate. The reaction mixture was filtered, and the solid was dried under vacuum. The product was purified by crystallization at −4 °C from 9:1 ethyl acetate/hexanes to obtain a yellow crystalline solid (2.25 g, 8.35 mmol, 87%). mp: 108−110 °C. IR (KBr): ν 3256, 2951, 1684, 1579, 1496, 1460, 1264, 1152, 1129, 750 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ 7.92 (d, $J = 5.4$ Hz, 1H, Ar), 7.88 (d, $J = 5.2$ Hz, 1H, Ar), 7.70 (d, $J = 8.0$ Hz, 2H, Ar), 7.14 (t, $J = 5.6$ Hz, 1H, Ar), 7.02 (d, $J = 8.6$ Hz, 2H, Ar), 6.67 (t, $J = 7.5$ Hz, 1H, Ar), 3.32 (s, 3H, $-O-CH_3$), 2.09 (s, 3H, $Ar-CH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz, 25 °C): δ 167.7 (C=O), 147.4 ($C_{Ar}-N$), 144.1 ($C_{Ar}-N$), 137.9 ($C_{Ar}-C=O$), 134.4 ($C_{Ar}-H$), 131.1 ($C_{Ar}-H$), 129.7 (2 $C_{Ar}-H$), 121.6 ($C_{Ar}-H$), 120.8 ($C_{Ar}-H$), 114.5 (2 $C_{Ar}-H$), 111.7 ($C_{Ar}-CH_3$), 52.1 ($-O-CH_3$), 21.2 ($Ar-CH_3$). MS-EI: *m/z* [M]$^+$ 269 (23), [$M^+ - N_3(C_6H_4)$-$COOCH_3$] 91 (100). Anal. Found: C, 66.61; H, 5.43; N, 15.71. Calcd for $C_{15}H_{15}N_3O_2$: C, 66.90; H, 5.61; N, 15.60.

[1,3-Bis(2-methoxy)benzene]triazene (3). At −5 °C, *o*-anisidine (2.0 mL, 17.7 mmol) was mixed with an excess isoamyl nitrite (2.4 mL, 17.7 mmol, 1 equiv) in toluene (5 mL), and the mixture was vigorously stirred for 6 h. The reaction mixture was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed in vacuo to obtain a red solid. The product was purified by flash chromatography (alumina, ethyl acetate/hexane 9:1), and a red fraction was collected. The product was crystallized from a 9:1 ethyl acetate/hexane solution at −4 °C to obtain **2** as a red crystalline solid (784 mg, 3.05 mmol, 34%). mp: 87−90 °C. IR (KBr): ν 3158, 2833, 1597, 1257, 790 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ 10.25 (bs, 1H, N*H*), 7.66 (dd, $J = 7.9$, 1.6 Hz, 2H, Ar), 7.13 (dt, $J = 7.7$, 1.2 Hz, 2H, Ar), 7.01−6.94 (m, 4H, Ar), 3.91 (s, 6H, $-OCH_3$). ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ 120.9 ($C_{Ar}-H$), 111.1 ($C_{Ar}-H$), 55.7 ($O-CH_3$) (only observed signals). MS-ESI (negative mode): *m/e* [M − H]$^-$ 256. Anal. Found: C, 65.45; H, 5.60; N, 16.12. Calcd for $C_{14}H_{15}N_3O_2$: C, 65.35; H, 5.88; N, 16.33.

1-[2-(Thiomethyl)benzene]-3-[4-(methyl)benzene]triazene (4). 2-(Methylthio)aniline (1.10 g, 7.91 mmol) in water (5 mL) was mixed with 1 M HCl (24.3 mL, 24.3 mmol, 3 equiv) at 0 °C. A 15% $NaNO_2$ aqueous solution (0.838 g, 12.1 mmol, 1.5 equiv) was then added dropwise with stirring. Once the amine was dissolved, a 15% solution of *p*-toluidine in ethanol (0.868 mg, 8.1 mmol, 1 equiv) was added at 0 °C. The reaction mixture was stirred for 30 min, and then it was neutralized with 15% NaOAc (40 mL) to obtain a yellow solution. The mixture was extracted with ethyl acetate, and the organic layer was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to obtain an orange solid, which was purified by flash chromatography (alumina, 9:1 ethyl acetate/hexanes). The product was crystallized from ethyl acetate/hexanes (9:1) at −4 °C to obtain yellow crystals (0.951 g, 3.69 mmol, 93%). mp: 66−68 °C. IR(KBr): ν 3254, 2852, 1522, 1419, 1256, 1167, 724 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ 10.22 (bs, 1H, N*H*), 7.68 (dd, $J = 8.1$, 1.4 Hz, 1H, Ar), 7.47−7.18 (m, 6H, Ar), 7.04 (dt, $J = 7.5$, 1.6 Hz, 1H, Ar), 2.40 (s, 3H, $-SCH_3$), 2.37 (s, 3H, $Ar-CH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz, 25 °C): δ 142.1 ($C_{Ar}-N$), 136.4 ($C_{Ar}-H$), 132.3 ($C_{Ar}-H$), 129.4 (2 $C_{Ar}-H$), 128.3 ($C_{Ar}-Me$), 123.3 ($C_{Ar}-H$), 119.7 ($C_{Ar}-H$), 114.6 (2 $C_{Ar}-H$), 21.1 ($Ar-CH_3$), 18.4 ($S-CH_3$) (only observed signals). Anal. Found: C, 65.14; H, 5.71; N, 16.39; S, 12.41. Calcd for $C_{14}H_{15}N_3S$: C, 65.34; H, 5.87; N, 16.33; S, 12.46.

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Table 1. Crystallographic Data and Refinement Parameters for Compounds **5**−**8**

	5	**6**	**7**	**8**
empirical formula	$C_{32}H_{28}N_6O_8Pd_2$	$C_{30}H_{28}N_6O_4Pd_2$	$C_{28}H_{28}N_6O_4Pd_2$	$C_{29}H_{30}N_6S_2Cl_4Pd_2$
fw	837.44	749.38	725.36	881.31
cryst syst	monoclinic	triclinic	tetragonal	orthorhombic
space group	$P2_1/c$	$P\bar{1}$	$I41/a$	$P2_12_12$
a (Å)	8.6070(10)	6.6288(5)	20.866(3)	10.4058(5)
b (Å)	14.3220(10)	10.2631(10)	20,866(3)	16.2488(8)
c (Å)	12.7310(10)	11.0246(11)	13.156(2)	9.9500(5)
α (deg)	90	85.579(6)	90	90
β (deg)	100.2950(10)	80.885(6)	90	90
γ (deg)	90	74.607(6)	90	90
V (Å^3)	1544.1(2)	713.51(11)	5728(2)	1682.36(14)
Z	2	1	8	2
ρ_{calcd} (g cm^{-3})	1.801	1.744	1.62	1.740
T (K)	293	143	293	143
λ(Mo Kα) (Å)	0.71073	0.71069	0.71073	0.71069
μ (mm^{-1})	1.228	1.308	1.300	1.541
R1^a (%)	0.0352	0.0190	0.0318	0.0424
wR2^b (%)	0.0765	0.0464	0.0540	0.1083

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Synthesis of Complexes. [1,3-Bis(2-carboxymethyl)benzene(triazenido)palladium(I)]$_2$ (5). 1,3-Bis(2-carboxymethyl)benzene triazene (**1**) (50.0 mg, 0.160 mmol) was dissolved in CH_3CN (5 mL), and triethylamine (32.3 mg, 0.319 mmol, 2 equiv) was added with stirring. To the resulting solution, $(CH_3CN)_2PdCl_2$ (41.4 mg, 0.160 mmol, 1 equiv) in CH_3CN (5 mL) was slowly added, and the mixture was stirred for 30 min at room temperature, during which time a red precipitate formed. The reaction mixture was filtered to obtain a reddish microcrystalline solid, which was recrystallized by slow evaporation of a solution of **5** in CH_2Cl_2 to give dark red crystals (56.5 mg, 0.068 mmol, 85%). mp: 215 °C. IR (KBr): ν 2947, 1713, 1643, 1595, 1562, 1381, 1157, 750 cm^{-1}. UV−vis (CH_2Cl_2, 2.2688×10^{-4} M): λ (ϵ) 242 (5382.98), 340 (15 534.52), 406 (16 012.73), 512 (2637.63), 600 nm (526.75 L cm^{-1} mol^{-1}). ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ 7.79 (dd, J = 7.8, 1.6 Hz, 2H, Ar), 7.46 (dd, J = 8.4, 1.4 Hz, 2H, Ar), 7.36 (dt, J = 7.0, 1.6 Hz, 2H, Ar), 7.06 (dt, J = 8.4, 1.4 Hz, 2H, Ar), 3.77 (s, 6H, O−CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz, 25 °C): δ 168.5 (C=O), 150.4 (C_{Ar}−N), 132.3 (C_{Ar}−H), 130.6 (C_{Ar}−H), 123.4 (C_{Ar}−H), 122.5 (C_{Ar}−C=O), 121.3 (C_{Ar}−H), 52.8 (−O−CH$_3$). Anal. Found: C, 45.60; H, 3.12; N, 10.07. Calcd for $C_{32}H_{28}N_6O_8Pd_2$: C, 45.89; H, 3.37; N, 10.04.

{1-[(2-Carboxymethyl)benzene]-3-[(4-methyl)benzene](triazenido)palladium(I)}$_2$ (6). Complex **6** was prepared in the same manner as **5** using ligand **2** to obtain a reddish microcrystalline solid that was first purified by column chromatography (florisil, CH_2Cl_2). Next, the product crystallized by vapor diffusion of pentane into a concentrated solution of the product in CH_2Cl_2 at room temperature to give dark red crystals (43.8 mg, 0.058 mmol, 45%). mp: 233−235 °C. IR (KBr): ν 3014, 2852, 1642, 1557, 1375, 1151 cm^{-1}. UV−vis (CH_2Cl_2, 2.9355×10^{-4} M): λ (ϵ) 220 (4174), 282 (5008.7), 342 (13 256), 396 (13 186), 422 (13 042), 506 (3312), 598 nm (666 L cm^{-1} mol^{-1}). ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ 7.82 (dd, J = 8.2, 1.6 Hz, 2H, Ar), 7.57 (dd, J = 8.6, 1.2 Hz, 2H, Ar), 7.35−7.25 (m, 6H, Ar), 7.07 (d, J = 8.2 Hz, 4H, Ar), 6.89 (dt, J = 8.2, 1.2 Hz, 2H, Ar), 3.62 (s, 6H, O−CH_3), 2.32 (s, 6H, Ar−CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz, 25 °C): δ 169.1 (C=O), 151.6 (C_{Ar}−N), 147.9 (C_{Ar}−N), 135.0 (C_{Ar}−C=O), 133.6 (C_{Ar}−H), 131.3 (2C_{Ar}−H), 128.1 (C_{Ar}−CH_3), 122.7 (C_{Ar}−H), 121.9 (C_{Ar}−H), 119.6 (C_{Ar}−H), 116.2 (2C_{Ar}−H), 53.5 (−O−CH$_3$), 20.9 (Ar−CH$_3$). Anal. Found: C, 48.18; H, 3.62; N, 11.37. Calcd for $C_{30}H_{28}N_6O_4Pd_2$: C, 48.08; H, 3.77; N, 11.21.

[1,3-Bis(2-Methoxy)benzene(triazenido)palladium(I)]$_2$ (7). Complex **7** was prepared in the same manner as **5**, using ligand **3**, to obtain a red microcrystalline solid that was purified by column chromatography (florisil, CH_2Cl_2). The resultant product was crystallized by vapor diffusion of pentane into a concentrated solution of the product in $CHCl_3$ at room temperature to give red crystals (28.8 mg, 0.040 mmol, 51%). mp: 160−162 °C. IR (KBr): ν 2826, 1584, 1489, 1358, 1244, 747, cm^{-1}. UV−vis (CH_2Cl_2, 1.7581×10^{-4} M): λ (ϵ) 302 (8959.69), 390 (12 084.64), 504 (1398.1), 562 (1030.66), 656 nm (384.51 L cm^{-1} mol^{-1}). ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ 7.28 (dd, J = 7.4, 2.4 Hz, 2H, Ar), 7.97 (td, J = 8.2, 1.8 Hz, 2H, Ar), 6.88−6.79 (m, 4H, Ar), 3.64 (s, 6H, O−CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz, 25 °C): δ 151.4 (C_{Ar}−O), 138.8 (C_{Ar}−N), 124.2 (C_{Ar}−H), 121.4 (C_{Ar}−H), 120.0 (C_{Ar}−H), 111.4 (C_{Ar}−H), 57.1 (O−CH$_3$). Anal. Found: C, 46.50; H, 3.28; N, 11.48. Calcd for $C_{28}H_{28}N_6O_4Pd_2$: C, 46.36; H, 3.89; N, 11.59.

{1-[2-(Thiomethyl)benzene]-3-[4(methyl)benzene](triazenido)]-(chloro)palladium(II)}$_2$ (8). Complex **8** was prepared in the same manner as **5**, using ligand **4**. The reaction provided a brown precipitate that was crystallized by vapor diffusion of pentane into a concentrated solution of the product in CH_2Cl_2 at room temperature to provide amber crystals (50.6 mg, 0.057 mmol, 59%). mp: 199 °C. IR (KBr): ν 2930, 1575, 1426, 1286, 1164, 819, 768 cm^{-1}. UV−vis (CH_2Cl_2, 7.375×10^{-4} M): λ (ϵ) 258 (2154.19), 286 (2370.85), 334 (5580.71), 382 (5577.46), 446 (5510.21), 632 nm (1263.84 L cm^{-1} mol^{-1}). ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ 7.75−7.65 (m, 6H, Ar), 7.56 (dd, J = 7.8, 1.2 Hz, 2H, Ar), 7.40−7.03 (m, 8H, Ar), 2.88 (s, 6H, -SCH_3), 2.28 (s, 6H, Ar−CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz, 25 °C): δ 155.7 (C_{Ar}−N), 146.7 (C_{Ar}−N), 136.1 (C_{Ar}−H), 132.0 (C_{Ar}−H), 130.9 (2 C_{Ar}−H), 129.3 (C_{Ar}−S), 124.7 (C_{Ar}−CH_3), 122.4 (C_{Ar}−H), 121.9 (C_{Ar}−H), 118.5 (2 C_{Ar}−H), 29.5 (−S−CH$_3$), 20.9 (Ar−CH$_3$). Anal. Found: C, 39.64; H, 3.18; N, 9.91; S, 6.97. Calcd for $C_{29}H_{30}N_6S_2Cl_4Pd_2$: C, 39.52; H, 3.43; N, 9.54; S, 7.28.

Structural Determination. A summary of crystal data and refinement parameters for the structural analyses is given in Table 1.

Compounds 5 and 7. A deep-red prismlike crystal of complex **5** with approximate dimensions of 0.460 × 0.296 × 0.268 mm and a red prismlike crystal of **7** with approximate dimensions of 0.278 × 0.232 × 0.086 mm were used for X-ray crystallographic analysis. The X-ray intensity data were measured at 295 K on a Bruker SMART CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å). The detector was placed at a distance of 4.837 cm from the crystal.

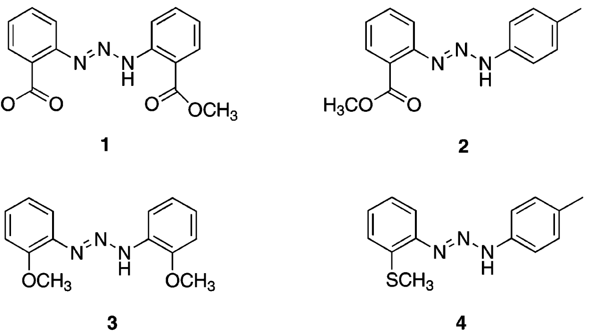
A total of 1200 frames were collected with a scan width of 0.3° in ω and an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT Software package[17] using a narrow-frame integration algorithm. The integration of the data using a monoclinic unit cell for **5** yielded a total of 20 653 reflections to a maximum 2θ angle of 65.04° (0.66 Å resolution), of which 5571 were independent ($R_{\mathrm{int}} = 5.65\%$). The integration of the data using a tetragonal unit cell for **7** yielded a total of 33 610 reflections to a maximum 2θ angle of 60.06° (0.70 Å resolution), of which 4183 were independent ($R_{\mathrm{int}} = 5.14\%$).

The final cell constants for **5** and **7** are based on the refinement of the XYZ-centroids of 6240 and 5098 reflections, respectively, above $20\sigma(I)$. Analysis of the data showed negligible decay during data collection; the intensities were corrected for Lorentz and polarization factors, and an analytical absorption correction was applied based on the face index.

The structures were solved and refined on F^2 values by full-matrix least-squares with anisotropic thermal parameters for non-hydrogen atoms, using the Bruker SHELXTL (version 5.1) Software Package.[18] Positions of hydrogen atoms H atoms in these structures were introduced at calculated positions as riding atoms, with C−H = 0.96 (CH_2) or 0.93 Å (aromatic) and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\ U_{\mathrm{eq}}(\mathrm{C})$ or $U_{\mathrm{iso}}(\mathrm{H}) = 10.08$ Å.^{2}

Compounds 6 and 8. A deep-red prismlike crystal of complex **6** with approximate dimensions of 0.44 × 0.11 × 0.05 mm and a reddish-black prismlike crystal of **8** with approximate dimensions of 0.32 × 0.27 × 0.10 mm were used for X-ray crystallographic analysis. X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at a temperature of 143 K. Preliminary indexing was performed from a series of four 0.5° rotation images with exposures of 30 s. A total of 830 (for **6**) and 440 (for **8**) rotation images were collected with a crystal-to-detector distance of 36 mm, 2θ swing angles of −12° for **6** and −10° (for **8**), a rotation width of 0.5°, and exposures of 30 (**6**) and 10 s (**8**): scan 1 was a ϕ-scan from 225 to 405° at $\omega = 0°$ and $\chi = 0°$ (for **6**) and a ϕ-scan from −90 to 90° at $\omega = 0°$ and $\chi = 0°$; scan 2 was a ϕ-scan from 270 to 450° at $\omega = 0°$ and $\chi = -30°$ (for **6**) and a ω-scan from −20 to 20° at $\chi = -90°$ and $\phi = 0-30°$ (for **8**); scan 3 was an ω-scan from −20 to 4° at $\chi = -90°$ and $\phi = 315°$ (for **6**); scan 4 was an ω-scan from −20 to 11° at $\chi = -90°$ and $\phi = 135°$ (for **6**). Rotation images were processed using CrystalClear,[19] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the CrystalStructure[20] program package for further processing and structure solution on a Dell Pentium 111 computer. For **6**, a total of 8129 reflections were measured over the ranges of $5.46 \le 2\theta \le 54.96°$, $-8 \le h \le 6$, $-13 \le k \le 10$, $-14 \le 1 \le 14$, yielding 3063 unique reflections ($R_{\mathrm{int}} = 0.0160$). The intensity data were corrected for Lorentz and polarization effects and for absorption using REQAB[21] (min and max transmission, 0.733 and 1.000). For **8**, subsequent inspection of the rotation images indicated that there were a large number of diffraction spots that did not fit the orientation matrix from CrystalClear. The crystal was found to be twinned by a rotation of 2.4° about the normal to 5.9, 5.5−1 (it can be surmised that the crystal was cracked or split into two components or that there was a misalignment of the stacking of crystal plates). Twin indexing and processing of twinned data was performed by the TwinSolve[22] module of CrystalClear. A total of 18 491 reflections were measured over the ranges of $5.02 \le 2\theta \le 55.08°$, $-12 \le h \le 12$, $-12 \le k \le 20$, $-9 \le l \le 12$, yielding 18 491 unique reflections ($R_{\mathrm{int}} = 0.0000$). The intensity data were corrected for Lorentz and polarization effects and for absorption using REQAB[21] (min and max transmission, 0.688 and 1.000). The structures were solved by direct methods (SIR97).[23] Refinement was by full-matrix least-squares based on F^2 using SHELXL-97.[24] All reflections were used during refinement (F^2 values that were experimentally negative were replaced by F^2 = O). For **6**, the weighting scheme used was $W = 1/[\sigma^2(F_o^2) + 0.0172P^2 + 0.5506P]$, where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a "riding" model. Refinement converged to R1 = 0.0190 and wRr_2=0.0464 for 2994 reflections for which $F > 4\sigma(F)$ and R_1 = 0.0196, wRr_2 = 0.0470, and GOF = 1.097 for all 3063 unique, nonzero reflections and 192 variables.[25] The maximum Δ/σ in the final cycle of least-squares was 0.005, and the two most prominent peaks in the final difference Fourier were +0.396 and 0.656 e Å^{-3}. For **8**, the weighting scheme used was $w = 1/[\sigma^2(F_o^2) + 0.0512P^2 + 5.8696P]$, where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a "riding" model. Refinement converged to R_1 = 0.0424 and wR_2 = 0.1083 for 17 763 reflections for which $F > 4\sigma(F)$ and R_1 = 0.0462, wRr_2 = 1129, and GOF = 1.129 for all 18 491 unique, nonzero reflections and 198 variables.[25] The maximum Δ/σ in the final cycle of least-squares was 0.001, and the two most prominent peaks in the final difference Fourier were +0.788 and 0.849 e Å^{-3}.

Chart 2. Structures of Ligands **1**−**4**



Results and Discussion

Ligand Syntheses. Triazenes **1**−**4** (Chart 2) were synthesized following modified literature procedures. Ligands **1** and **3** were obtained in one step by coupling of methyl anthranilate and *o*-anisidine, respectively, in toluene using isoamyl nitrite.[11] Synthesis of triazenes **2** and **4** was performed by diazotization of the corresponding functionalized aniline with sodium nitrite, followed by coupling with *p*-toluidine.[12] The triazenes were isolated by crystallization from 9:1 ethyl acetate/hexanes at −4 °C with yields in the range of 34−93%.

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(17) *Saint-plus*, version 6.04; Bruker AXS Inc.: Madison, WI, 2000.

(18) Sheldrick, G. M. *SHELXTL*, version 6.10; Bruker AXS Inc.: Madison, WI, 2000.

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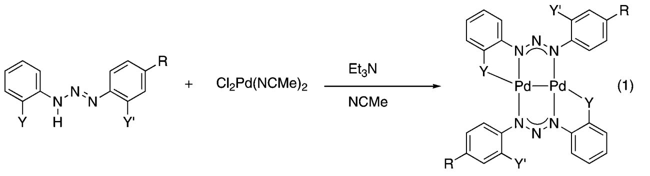
(25) $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $GOF = \{\sum[w(F_o^2 - F_c^2)^2/(n - p)\}^{1/2}$, where n = the number of reflections and p = the number of parameters refined.

Synthesis of Palladium(I) Complexes. Palladium complexes of **1**−**3** were prepared by combination of bis(acetonitrile)palladium(II) dichloride in acetonitrile with a mixture of the corresponding triazenes and triethylamine to obtain reddish microcrystalline compounds **5**−**7** (eq 1). The products were isolated by filtration and purified by recrystallization (**5**) or column chromatography on florisil in dichloromethane, followed by crystallization (**6**, **7**). The palladium triazenido complexes were isolated as analytically pure solids **5**, **6**, and **7** in 85, 45, and 51% yield, respectively.

We were surprised to find that elemental analyses of the crystalline solids **5**−**7** were not consistent with simple substitution of a chloride or a chloride and acetonitrile by the triazenido ligand. Instead, the analyses were consistent with palladium(I) bearing a single triazenido, as outlined in eq 1.



1, Y = Y' = CO$_2$Me, R = H
2, Y = CO$_2$Me, Y' = H, R = Me
3, Y = Y' = OMe, R = H

5, Y = Y' = CO$_2$Me, R = H 85% yield
6, Y = CO$_2$Me, Y' = H, R = Me 45% yield
7, Y = Y' = OMe, R = H 51% yield

Palladium(I), which has the d^9 configuration, is expected to exhibit paramagnetic behavior. Compounds **5**, **6**, and **7**, however, are diamagnetic and amenable to NMR analysis. The ^{1}H and ^{13}C{^{1}H} NMR spectra of all three complexes are indicative of a single-ligand environment. ^{1}H resonances are found in the range of 7.8−6.8 ppm for the aromatic protons, 3.8−3.6 ppm for the methoxy groups in **5**−**7**, and 2.3 ppm for the tolyl methyl protons in **6**. A single ^{13}C resonance at 168.5 ppm was observed for the esters of **5**, which is virtually unchanged from that of the unbound ligand (168.2 ppm). Similarly, the ester carbonyl resonance of **6** was located at 169.1 ppm, only slightly downfield from the unbound ligand **2** (167.7 ppm). The equivalence of the two ester substituents in **5** and methoxy groups in **7** on the NMR time scale can be explained by rapid exchange of bound and free carbonyl groups. Analogous behavior has been observed for the [Cu(Ar-NNN-Ar)]$_2$ and [Ag(Ar-NNN-Ar)]$_2$ complexes of ligand **1**.[14] On the basis of the NMR behavior, it is assumed that the d^9 Pd(I) centers are spin-coupled through a Pd−Pd bond, as observed in other dinuclear Pd(I) complexes.[26]

The positions of IR absorptions of pendent carbonyl groups in **5** and **6** can provide insight into their interaction with palladium. Interpretation of changes in ester ν_{CO} absorptions of unbound **1** and **2** versus their adducts **5** and **6** is not straightforward. First, the triazenes must be deprotonated to bind to the metals in these complexes, which will cause a change in the C═O stretching frequency. Second, each ligand binds to two metal centers compared to a single proton in the triazenes. The IR spectrum of unbound diester **1** (KBr) shows absorptions for the carbonyl groups at 1714 and 1698 cm^{-1}.[13] Compound **5** (KBr) exhibits two absorptions at 1713 and 1643 cm^{-1}. From the IR spectrum of **5**, we believe that one of the carbonyl oxygens is coordinated to palladium and the other is unbound. The IR spectrum of unbound monoester **2** (KBr) shows a single absorption for the carbonyl group at 1684 cm^{-1}, which is shifted to 1642 cm^{-1} in compound **6** (KBr). This shift is indicative of coordination of the ester carbonyl to palladium.

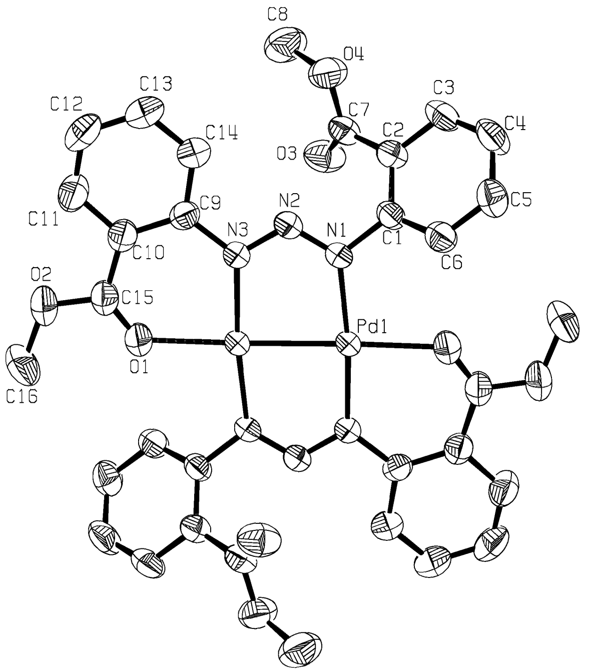


Figure 1. ORTEP of **5**. Bond distances and angles are given in Table 2.

Structures of Pd(I) Complexes. X-ray quality crystals of **5** were grown from dichloromethane by slow evaporation of the solvent, while crystals of **6** and **7** formed upon vapor-phase diffusion of pentane into concentrated solutions of the complexes in dichloromethane. ORTEP diagrams for complexes **5**, **6**, and **7** are illustrated in Figures 1, 2, and 3, respectively. Crystallographic data and refinement parameters are located in Table 1, and the bond distances and angles for **5**−**7** are displayed in Table 2. The gross structural features of **5**−**7** consist of two palladium centers bridged by two triazenido ligands with one pendent Lewis basic ester carbonyl oxygen (**5**, **6**) or methoxy oxygen (**7**) coordinated to each palladium center. The absence of counterions indicates that the palladium(II) starting material has been reduced to palladium(I) during the syntheses.

The Pd(I) structures are similar to those of the Cu(I) and Ag(I) dimeric complexes [Cu(Ph-NNN-Ph)]$_2$,[27] [Cu(Ar-NNN-Ar)]$_2$, and [Ag(Ar-NNN-Ar)]$_2$ (Ar = *o*-C$_6$H$_4$-COOCH$_3$)[14] and the related amidinato complexes [Ag(R-NCPhN-R)]$_2$ (R = *o*-C$_6$H$_4$-COOCH$_3$, *o*-C$_6$H$_4$-SCH$_3$).[28] In these complexes, each ligand bridges two metal centers, as observed in the structures of **5**−**7**. Complexes **5**−**7** have nearly planar bicyclic cores formed by the two N$_3$ units and the palladium centers (Figures 1−3). The *trans* nitrogens

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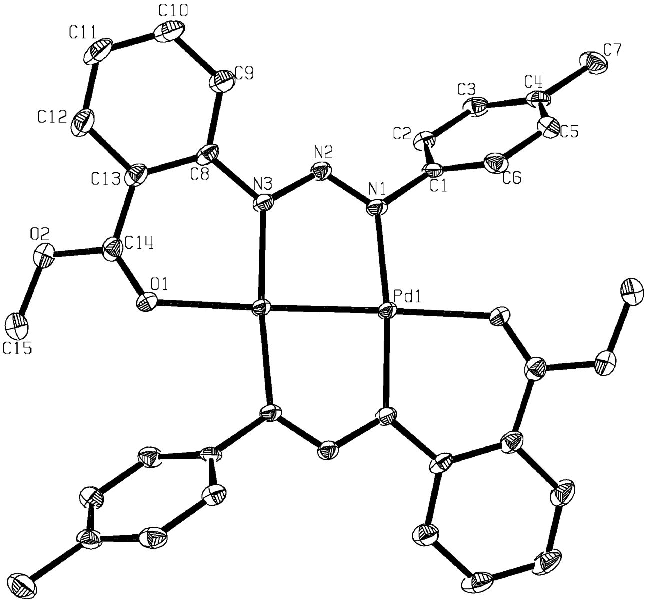

Figure 2. ORTEP of **6**. Bond distances and angles are given in Table 2.

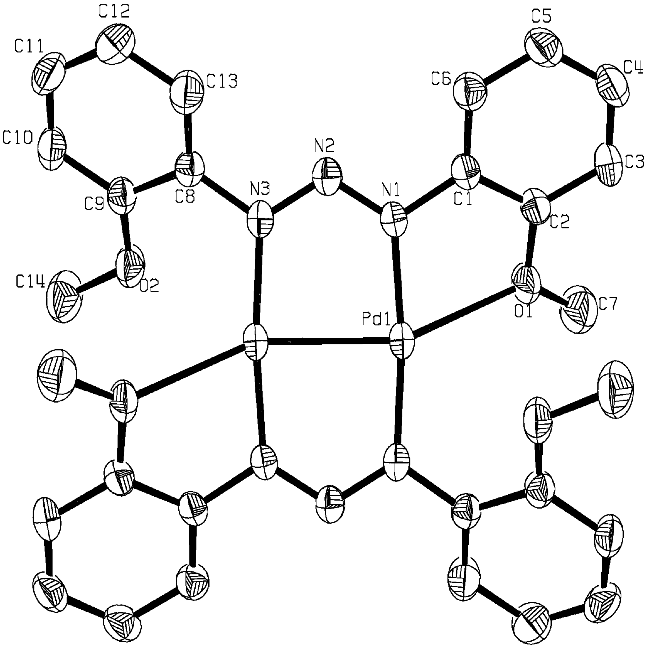

Figure 3. ORTEP of **7**. Bond distances and angles are given in Table 2.

Table 2. Bond Distances (Å) and Angles (deg) for Compounds **5**−**7**

	5	**6**	**7**
Pd(1)−Pd(1a)	2.4309(3)	2.4202(3)	2.4158(4)
Pd(1)−N(1)	2.0341(17)	2.0302(14)	2.0069(19)
Pd(1)−N(3a)	2.0177(17)	2.0264(15)	2.024(2)
Pd(1)−O(1a)	2.1631(16)	2.1641(13)	
Pd(1)−O(1)			2.4464(17)
C(15/14)−O(1)	1.219(2)	1.217(2)	
C(2)−O(1)			1.380(3)
C(7)−O(1)			1.398(3)
C(9)−O(2)			1.356(3)
C(14)−O(2)			1.420(3)
C(7)−O(3)	1.195(3)		
N(1)−N(2)	1.286(2)	1.289(2)	1.303(2)
N(2)−N(3)	1.318(2)	1.321(2)	1.305(2)
N(1)−N(2)−N(3)	116.76(16)	116.05(14)	114.47(19)
N(3a)−Pd(1)−N(1)	173.95(7)	173.25(6)	173.61(7)
N(3a)−Pd(1)−Pd(1a)	89.63(5)	89.39(4)	87.21(5)
N(2)−N(3)−Pd(1a)	121.72(13)	121.68(11)	125.01(15)
C(15/14)−O(1)−Pd(1a)	127.41(14)	125.66(12)	
C(2)−O(1)−Pd(1)			108.06(14)
N(3a)−Pd(1)−O(1a)	88.33(6)	88.55(5)	
N(3a)−Pd(1)−O(1)			114.37(7)
N(1)−Pd(1)−Pd(1a)	84.34(5)	84.68(4)	86.45(5)
N(2)−N(1)−Pd(1)	127.54(13)	127.70(12)	126.82(15)
N(1)−Pd(1)−O(1a)	97.70(6)	97.56(5)	
N(1)−Pd(1)−O(1)			71.89(7)
O(1a)−Pd(1)−Pd(1a)	177.88(4)	175.95(4)	
O(1)−Pd(1)−Pd(1a)			151.12(5)

Table 3. Pd−Pd Bond Distances in Some Bridged Dinuclear Pd(I) Complexes

complex	$d_{\text{Pd−Pd}}$ (Å)	ref
$Pd_2(\mu\text{-}Me_2PCH_2PMe_2)_2Br_2$	2.603(1)	34
$[(i\text{-}Pr)_3Pd]_2(\mu\text{-allyl})(\mu\text{-CCH})$	2.6597(4)	35
$[Pd_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2)_2(2,4,6\text{-}Me_3C_6H_2NC)_2]^{2+}$	2.617(2)	36
$Pd_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(SnCl_3)Cl$	2.644(2)	37
$Pd_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(C_6Cl_5)_2$	2.670(2)	38
$Pd_2(\mu\text{-}Ph_2PCH_2PPh_2)_2Br_2$	2.699(5)	39
$[Pd_2\{Ph_2P(CH_2)_3PPh_2\}_2]^{2+}$	2.701(3)	40

exhibit N−Pd−N bond angles of 173.95, 173.25, and 173.61° in **5**−**7**, respectively, indicating a small distortion from planarity of the Pd-triazenido framework resulting from the coordination of the ester carbonyl (**5** and **6**) or methoxy groups (**7**). Like the Cu(I) and Ag(I) analogs, the coordinated carbonyl oxygens in **5** and **6** lie slightly above and below the planar core with Pd−Pd−O bond angles of 177.88 and 175.95°, respectively. In **7**, a greater deviation from planarity with the Pd-triazenido core is observed with a Pd−Pd−O angle of 151.12°. The difference is attributed to the reduced size of the metallocycle. The C−O distances of the coordinated carbonyl oxygens in **5** and **6** are slightly elongated [1.2119(16) and 1.217(13) Å, respectively] with respect to the carbonyl group in the unbound ligand **1** [1.183(6) Å].[13] The Pd−N(1) and Pd−N(3) bond lengths in **5**−**7** are very similar at 2.0341(17) and 2.0177(17) Å in **5**, 2.0302(14) and 2.026(2) Å in **6**, and 2.0069(19) and 2.024(2) in **7**.

The Pd−Pd distances of 2.4309(3) Å in **5**, 2.4202(3) Å in **6,** and 2.4158(4) in **7** are consistent with Pd−Pd bonds. These distances are considerably shorter than most of the Pd−Pd bonds reported for dinuclear Pd(I)−Pd(I) complexes (see Table 3 for examples).[29−36] A comparison of the M−M distances in dimeric complexes prepared from ligand **1** is informative. The metal−metal distances in the Pd(I) [2.4309(3) Å] and Cu(I) [2.439(12) Å] dimers are in close contact; however, in the Ag(I) dimer, the Ag−Ag distances is quite long [2.704(2) Å].[14] This observation leads us to conclude

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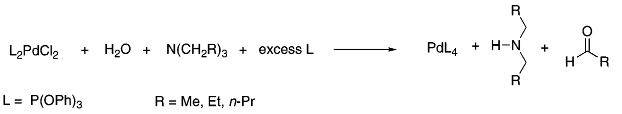
that the triazenide ligands are not solely responsible for the short M−M contacts observed in the Pd(I) complexes reported herein. It is noteworthy that the Pd(I) oxidation state is rare, whereas Cu(I) and Ag(I) complexes are common. We hypothesize that the triazenido ligands derived from **1**−**3** facilitate the reduction of the Pd(II) to Pd(I) and stabilize the Pd(I) oxidation state.

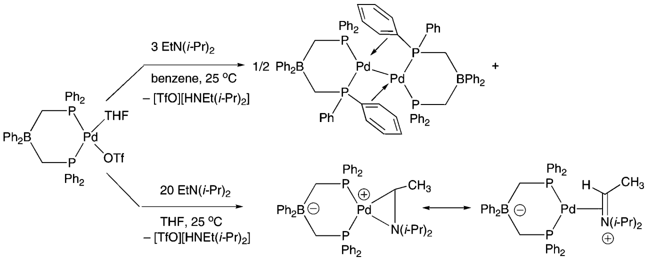
During the course of the synthesis of the dimeric Pd(I) complexes outlined above, the Pd(II) is reduced by one electron. At this time, we do not have experimental data concerning this process. It is well-known, however, that the reduction of Pd(II) starting materials to Pd(0) is common in cross-coupling reactions initiated with Pd(II).[37] Trzeciak, Ciunik, and Ziolkowski[38] have reported that tertiary amines can reduce Pd(II) to Pd(0) in the presence of trace amounts of water with formation of the corresponding secondary amine and aldehyde oxidation products (eq 2). The mechanism is proposed to begin with amine coordination to Pd(II), followed by C−H activation. The observation of aldehyde formation and labeling experiments support their proposed mechanism.



(2)

In a detailed study of a related process, Lu and Peters found that a Pd(II) complex bearing an anionic bis(phosphine) ligand undergoes reduction to Pd(I) in approximately 70% yield when exposed to 3 equiv of tertiary amine (Scheme 1). In THF, however, the cyclometallation product is observed quantitatively when the same Pd(II) complex is exposed to a large excess of tertiary amine. In this case, a mechanism involving binding of the amine, β-hydride elimination, and deprotonation of the resulting palladium hydride by free amine is favored.[39] The cyclometalated amine, of course, has a second resonance form in which the palladium is formally Pd(0). Dissociation of the iminium would lead to Pd(0). Iminium hydrolysis would generate a secondary amine and an aldehyde, as observed in eq 2.

Scheme 1. Reactions of a Pd(II) Complex with Amine in Different Solvents



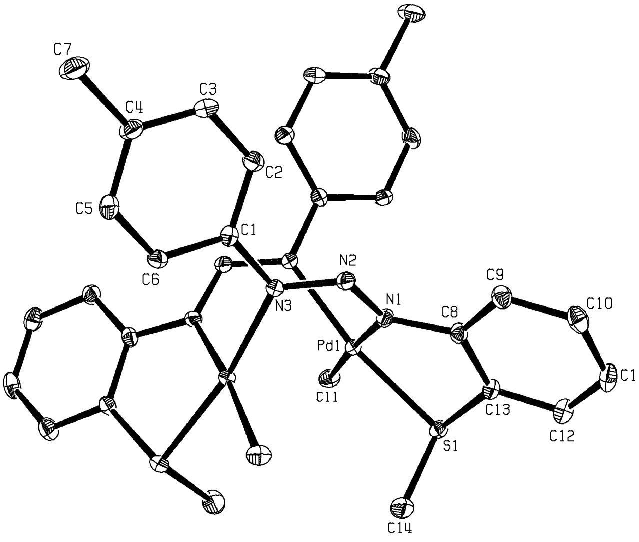
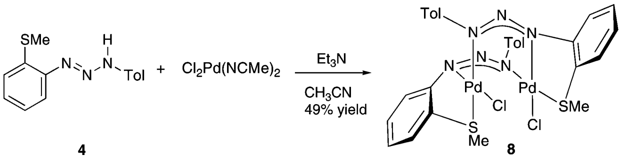


Figure 4. ORTEP of **8**·CH_2Cl_2. Bond distances and angles are given in Table 4. CH_2Cl_2 is omitted for clarity.

Synthesis of Palladium(II) Triazenido Complex. Combination of bis(acetonitrile)palladium(II) dichloride in acetonitrile with triazene **4** and triethylamine resulted in the formation of brown microcrystalline **8**. Filtration of **8** was followed by recrystallization to provide analytically pure amber crystals in 59% yield (eq 3). Unlike **5**−**7**, elemental analysis of **8** was not consistent with formation of reduced Pd(I) dimers. The analysis was in line with our initial expectations for the substitution product, [(triazenido)PdCl]$_2$.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **8** indicated a symmetric complex with a single triazenido ligand environment. In the ^{1}H NMR, resonances for the aromatic protons were found between 7.0 and 7.7 ppm. The methyl mercapto protons resonated at 2.88 ppm, and a signal for the tolyl methyl protons was observed at 2.28 ppm. A shift from 2.40 ppm for the S−Me group in the unbound ligand **4** to 2.88 ppm for the S−Me in **8** suggests that the sulfur is coordinated to palladium. The IR spectrum (KBr) of **8** exhibits an absorption at 1575 cm^{-1} assigned to the N−N−N linkage, which is shifted to shorter wavelength compared to that of the free ligand (1522 cm^{-1}).



(3)

Structure of 8. X-ray quality crystals of **8** were grown by vapor-phase diffusion of pentane into a concentrated solution of the complex in dichloromethane. The structure of **8** was determined, and an ORTEP diagram is illustrated in Figure 4. Bond distances and angles are displayed in Table 4. The complex cocrystallizes with one molecule of CH_2Cl_2, which is not included in Figure 4. The structure consists of a dimeric palladium complex with two bridging tridentate triazenide ligands. The S−Me of each ligand is bonded to a palladium, and the remaining coordination sites are occupied by chlorides.

The central eight-membered core formed by the two N_3 units and the palladium centers are found in an “open book”

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Table 4. Bond Distances (Å) and Angles (deg) for **8**·CH_2Cl_2

Pd(1)−Pd(1a)	2.9077(4)
Pd(1)−N(1)	2.010(2)
Pd(1)−N(3a)	2.087(2)
N(1)−N(2)	1.313(3)
N(2)−N(3)	1.293(3)
Pd(1)−S(1)	2.2707(7)
Pd(1)−Cl(1)	2.3108(7)
N(3)−N(2)−N(1)	114.3(2)
N(1)−Pd(1)−N(3a)	93.70(9)
N(1)−Pd(1)−S(1)	84.26(7)
N(3a)−Pd(1)−Cl(1)	89.29(7)
S(1)−Pd(1)−Cl(1)	92.13(3)
S(1)−Pd(1)−Pd(1a)	113.16(2)
N(1)−Pd(1)−Pd(1#1)	76.24(7)
N(3a)−Pd(1)−Pd(1a)	75.44(7)
Cl(1)−Pd(1)−Pd(1a)	108.32(2)
S(1)−Pd(1)−Pd(1a)	113.16(2)

geometry, which has been previously observed in some palladium(II)−triazenido complexes.[15,40,41] The geometry about each palladium is only slightly distorted from idealized square planar, as seen in the bond angles around palladium (Table 4). The angle N(1)−N(2)−N(3) of the triazenide ligand is 114.3°, and the Pd−N(1) and Pd−N(3) bond lengths are 2.010(2) and 2.087(2) Å. The Pd−N distances in this dimer can be compared to the Pd−N lengths in $[Pd(C_6F_5)(CN\text{-}t\text{-}Bu)(\mu\text{-}Ph\text{-}NNN\text{-}Ph)]_2$ [2.073(4) and 2.098(4) Å],[35] as well as those of the amidinate dimer $Pd_2Cl_2\{\mu\text{-}PhNC(Me)NPh\}_2(PMe_2Ph)_2$ [2.097(5) and 2.059(5) Å].[36] The Pd−S distance of 2.2707(7) Å in **8** is within the range found in other mercapto-palladium complexes (2.2716−2.2661 Å).[42]

The Pd−Pd distance in **8** is 2.9077(4) Å. This distance is comparable to that found in other triazenido complexes of Pd(II): $[Pd(C_6F_5)(CN\text{-}t\text{-}Bu)(\mu\text{-}PhNNNPh)]_2$ [2.9007(8) Å],[36] $[Pd(C_6H_4N{=}NC_6H_5)(\mu\text{-}p\text{-}tol\text{-}NNN\text{-}p\text{-}tol)]_2$ [2.895(2) Å],[43] and the related amidinate complex $[Pd_2Cl_2\{\mu\text{-}Ph{-}NC(Me)N{-}Ph\}_2(PMe_2Ph)_2]$ [2.9014(2) Å].[36] Although a shorter Pd−Pd distance, 2.747(1) Å, has been reported for $[Pd_2(\mu\text{-}Ar\text{-}NNN\text{-}Ar)_2]_2(\mu\text{-}Cl)_4$,[44] both are nonbonding, as expected for 16-electron square-planar Pd(II) complexes.

We propose that the electron-donating S−Me group of **8** results in a more electron-rich palladium center. The S−Me group increases the stability of the complex toward reduction more than the weakly donating ester carbonyl groups in **5** and **6** or the methoxy group in **7**.

Concluding Remarks

Reported herein are the structures of three novel Pd(I) dimers (**5**−**7**) supported by 1,3-bis(aryl) triazenido ligands bearing Lewis basic groups in the *ortho*-positions. The Lewis basic ester and methoxy groups coordinate to the palladium(I) centers. These ligands appear to facilitate reduction of Pd(II) to the uncommon Pd(I) and to stabilize metals in the +1 oxidation state. Previous studies from our group have shown that ligand **1** forms similar complexes with Cu(I) and Ag(I).

In contrast to reactions with triazenes **1**−**3**, the reaction of ligand **4**, containing a pendent S−Me group, with $Cl_2Pd(NCCH_3)_2$ does not yield reduced Pd(I), but rather a dimeric Pd(II) with bridging tridentate ligands. We speculate that the greater donating ability of the S−Me group, with respect to that of the CO_2Me and OMe groups, results in a more electron-rich palladium center that is more stable to reduction than complexes prepared from ligands **1**−**3**. These studies illustrate how pendent Lewis basic groups of the 1,3-bis(aryl) triazenido ligands can enable the synthesis of novel palladium complexes in the rare Pd(I) oxidation state. The next step in these studies will be to determine how our ligands impact the reactivity of the resulting Pd(I) complexes.

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Supporting Information Available: Structural data for **5**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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