A 16 Electron Cyclobutadiene—benzene-1,2-dithiolate Complex of Palladium(II) Bearing A Two-legged Piano-stool Geometry: $(\eta^4\text{-}C_4Me_2(^tBu)_2)Pd(1,2\text{-}S_2C_6H_4)$

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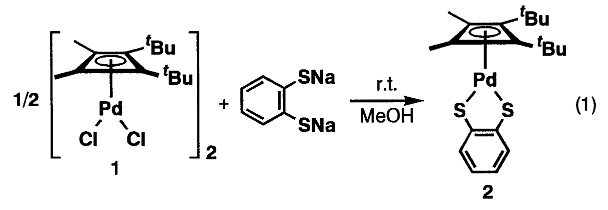
A 16-electron cyclobutadiene—palladium(II)—thiolate complex $(\eta^4\text{-}C_4Me_2(^tBu)_2)Pd(S_2C_6H_4)$ (**2**: $S_2C_6H_4$ = 1,2-benzenedithiolate) is prepared by treatment of $[(\eta^4\text{-}C_4Me_2(^tBu)_2)PdCl_2]_2$ (**1**) with disodium 1,2-benzenedithiolate, and its monomeric two-legged piano-stool structure was characterized by X-ray analysis as well as its LMCT band caused by donation of the filled S(pπ) electrons to the empty Pd(dπ*) orbital.

Recently electron deficiency and coordinative unsaturation around transition metal centers have been alleviated with π donation by a lone pair on a coordinating atom. Thiolate ligand possesses a σ-donor orbital along with lone-pair orbitals suitable for π-interaction with a metal d orbital. Half-sandwich complexes of a general formula $(\eta^n\text{-}C_nR_n)ML_2$ are predicted theoretically to stabilize 16-electron and coordinatively unsaturated species.[1] Thiolate complexes of an n = 6 system, $(\eta^6\text{-}C_6R_6)M(SR)_2$ (M = Ru[2,3] and Os[4,5]), and an n = 5 system, $(\eta^5\text{-}C_5Me_5)Ir(SAr)_2$,[6,7] have recently been prepared. As an extension, an n = 4 system, $(\eta^4\text{-}C_4R_4)M(SR)_2$ (M = group 10 metals), is also expected to be present. However, this type of complex has not been prepared, although 18 electron complexes $(\eta^4\text{-}C_4Me_4)Ni(PMe_2Ph)(\mu\text{-}S_2WS_2)$[8] and $[(\eta^4\text{-}C_4Me_2(^tBu)_2)\text{-}PdCl_2]_2$ (**1**)[9] have been noted and d^8 metal complexes have generally a 16 electron square planar geometry. Herein we report on the preparation and the crystal structure of a mononuclear 16-electron palladium(II) complex, $(\eta^4\text{-}C_4Me_2(^tBu)_2)Pd(S_2C_6H_4)$ (**2**: $S_2C_6H_4$ = 1,2-benzenedithiolate).

Addition of **1**[9] to an excess of disodium 1,2-benzenedithiolate in methanol resulted in the rapid precipitation of deep purple crystalline solid of **2** in 77% yield.[10] The ^1H NMR spectrum of **2** in $CDCl_3$ displayed an AA'BB' pattern due to the 1,2-benzenedithiolate moiety as well as two singlet signals at δ 1.44 and 2.09 due to *tert*-butyl and methyl protons of the cyclobutadiene ring system in a 3:1 integral ratio. The FAB mass spectrum of **2** showed a parent ion, suggesting that **2** is monomeric. The intense purple color (λ_{max} = 560 nm) of **2** is due to a LMCT band where the filled S(pπ) orbital donates to the empty Pd(dπ*) orbital. This unique donation stabilizes the coordinatively unsaturated electron deficient **2**. Such an intense LMCT band corresponds to those found for coordinatively unsaturated transition metal complexes such as $Cp^*Ir(SC_6F_4H\text{-}p)_2$ (Cp^* = $\eta^5\text{-}C_5Me_5$),[6,7] $Cp^*Ru(PR_3)X$,[11,12] $(\eta^6\text{-}p\text{-cymene})Ru(SXy)_2$ (Xy = 2,6-dimethylphenyl),[2] $(\eta^6\text{-}C_6Me_6)\text{-}Ru(1,2\text{-}S_2C_6H_4)$ (**3**),[3] $(\eta^6\text{-}p\text{-cymene})Os(S^tBu)_2$,[4,5] $[Cr(CO)_3(1,2\text{-}S_2C_6H_4)]^{2-}$,[13] and $CpMo(NO)(SPh)_2$.[14]



(1)

The structure of **2** is provided in Figure 1 with selected bond distances and angles.[15] It is noteworthy that complex **2** adopts monomeric two-legged piano-stool geometry similar to that of **3**, although a sterically less demanding thiolate ligand tends to dimerize or oligomerize metal centers. The distances (2.286(1) and 2.288(1) Å) of the Pd—S bonds are longer than those of the Ru—S bonds (2.263(1) and 2.256(1) Å) found for **3**.[3] The distances of the S—C bond (1.744(5) and 1.736(5) Å) are similar to those of some 1,2-benzenedithiolate complexes of Mo,[16] W,[17] Fe,[18] and Ru (**3**)[3]; being consistent with the presence of some contribution of S=C double-bond character as witnessed by the comparison with the double-bonded S=C distance of 1.67(2)—1.75(1) Å in thiourea derivatives.[19]

The summation of angles around the palladium atom of **2** defined by the centroid of the η^4-cyclobutadiene ring carbons and the two sulfur atoms is 360.0° and the angle between the best plane defined by η^4-cyclobutadiene ring carbons and that of the 1,2-benzenedithiolate aromatic carbons is 92.8°, indicating also the two-legged piano-stool geometry of **2**.

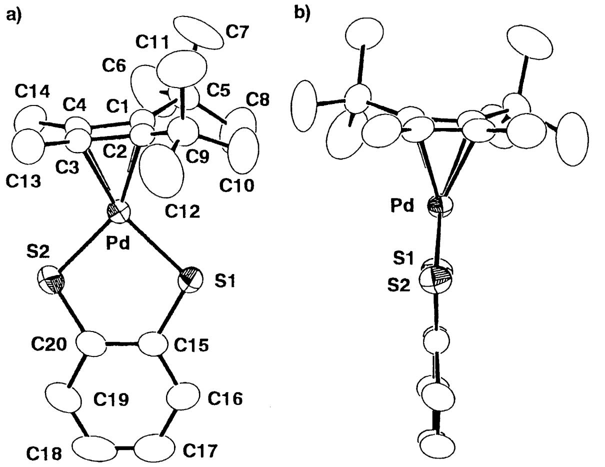
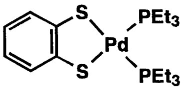


Figure 1. The molecular structures of **2** with a numbering scheme; (a) front-view and (b) side-view. Selected bond distances (Å) and angles (deg): Pd—S1 = 2.286(1), Pd—S2 = 2.288(1), Pd—C1 = 2.155(4), Pd—C2 = 2.149(5), Pd—C3 = 2.153(5), Pd—C4 = 2.127(5), C1—C2 = 1.433(6), C1—C4 = 1.488(6), C2—C3 = 1.483(6), C3—C4 = 1.437(7); S1—Pd—S2 = 89.86(5), Pd—S1—C15 = 103.9(2), Pd—S2—C20 = 103.7(2).

The cyclobutadiene ligand of **2** was found to be labile and thus square planar complexes of the type $Pd(S_2C_6H_4)L_2$ were obtained; being in consistent with the favorable square planar geometry for the Pd(II) complex. Treatment of **2** with an excess of triethylphosphine in THF resulted in the release of the cyclobutadiene ligand and the formation of **4** in 72% yield.[20] Similarly, reaction of **2** with 2,6-xylylisocyanide in THF afforded **5** in 31% yield.[21] These were characterized spectroscopically.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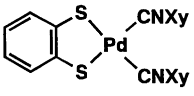
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Thus, we prepared and characterized crystallographically the first 16 electron thiolate complexes of palladium(II) bearing a cyclobutadiene ligand.

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10 **2**: deep purple mirocrystals, mp 200—203 °C. ^{1}H NMR ($CDCl_3$, 35 °C): δ 1.44 (s, 18H, $C_4Me_2(^tBu)_2$), 2.09 (s, 6H, $C_4\mathit{Me}_2(^tBu)_2$), 7.05 (m, 2H, 1,2-$S_2C_6H_4$), 7.76 (m, 2H, 1,2-$S_2C_6H_4$); FAB mass spectrum: *m/z* 438 (M^+); UV/vis (THF): λ_{max} 560 nm (ε = 5600 $M^{-1}cm^{-1}$). Anal. Found: C, 54.79; H, 6.19; S, 14.46%. Calcd for $C_{20}H_{28}PdS_2$: C, 54.72; H, 6.43; S, 14.61%.

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15 Crystal data for **2**: crystals were grown from a mixture of ethanol and THF; orthorhombic space group $P2_12_12_1$, a = 12.884(2), b = 14.540(2), c = 10.973(2) Å, V = 2055.6(5) Å^3, Z = 4, d_{calcd} = 1.418 gcm^{-3}, μ(MoKα) = 11.04 cm^{-1}, unique relfections = 2687, used reflections = 2476 ($I > 1.5\sigma(I)$), R = 0.030, R_w = 0.024, GOF = 2.73 for 208 variables.

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20 **4**: reddish orange crystals, 72% yield, mp 187—191 °C. ^{1}H NMR ($CDCl_3$, 35 °C): δ 1.18 (m, 18H, $PCH_2C\mathit{H}_3$), 2.09 (m, 12H, $PC\mathit{H}_2CH_3$), 6.84 (m, 2H, 1,2-$S_2C_6H_4$), 7.33 (m, 2H, 1,2-$S_2C_6H_4$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 35 °C): δ 15.4 (s); FAB mass spectrum: *m/z* 482 (M^+); Anal. Found: C, 44.11; H, 7.10%. Calcd for $C_{18}H_{34}P_2PdS_2$: C, 44.79; H, 7.10%.

21 **5**: red crystals, 31% yield, mp 189—193 °C. ^{1}H NMR ($CDCl_3$, 35 °C): δ 2.52 (s, 12H, Me), 6.95 (m, 2H, $S_2C_6\mathit{H}_4$), 7.36 (m, 2H, $S_2C_6\mathit{H}_4$), 7.17 (d, 4H, J = 7.9 Hz, $C_6H_3Me_2$), 7.30 (t, 2H, $C_6H_3Me_2$); FAB mass spectrum: *m/z* 507 (M^+ - 1); IR (nujol): ν(CN) 2177 and 2200 cm^{-1}; Anal. Found: C, 55.90; H, 4.34; N, 5.44%. Calcd for $C_{24}H_{22}N_2PdS_2$: C, 56.63; H, 4.36; N, 5.50%.