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A Bimetallic Bis-pentalene Sandwich Complex: Synthesis and Structure of $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$

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Summary: The reaction between $K_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]$ and $Mo_2(OAc)_4$ yields $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$, the first example of a bimetallic bis-pentalene sandwich complex to be structurally characterized by X-ray diffraction. Structural data show that the carbon frameworks of the two pentalene ligands are eclipsed and effectively planar with fold angles of ca. 2° and 3° while the $SiPr^i{}_3$ groups are staggered; the Mo−Mo distance is 2.340(1) Å.

The pentalenyl dianion $[C_8H_6]^{2-}$, first synthesized by Katz in 1962,[1] its substituted derivatives $[C_8H_{6-n}R_n]^{2-}$, and neutral counterparts C_8H_6 and $[C_8H_{6-n}R_n]$ have been infrequently used as ligands in organometallic chemistry.[2] The scarcity of pentalene metal complexes[3] is perhaps a result of the synthetic difficulty in accessing stable pentalene and pentalenyl dianion precursors (i.e., pentalenes and dihydropentalenes).[4] Historically, structurally characterized metal compounds containing pentalene ligands were those in which the pentalene serves as a bridge between two or more metal centers bound to different five-membered rings of the pentalene ligand in a cis or trans arrangement.[5] Examples of such complexes are *trans*-$\{[(C_3H_5)Ni]_2(\eta^5{:}\eta^5\text{-}C_8H_6)\}$,[6] *cis*-$\{[Ru(CO)_2GeMe_3]_2(\eta^5{:}\eta^5\text{-}C_8H_6)\}$,[7] *cis*-$\{Ru_3(CO)_8[\eta^5{:}\eta^5\text{-}C_8H_4(1,5\text{-}SiMe_3)_2]\}$,[8] *cis*-$\{Ru_3(CO)_8[\eta^5{:}\eta^5\text{-}C_8H_3(1,3,5\text{-}SiMe_3)_3]\}$,[9] *cis*-$\{Ru_3(CO)_8[\eta^5{:}\eta^5\text{-}C_8H_6]\}$,[10] *trans*-$[(Li{\cdot}DME)_2C_8H_6]$,[11] *trans*-$\{[(\eta^5\text{-}C_5Me_5)M]_2(\eta^5{:}\eta^5\text{-}C_8H_6)\}$ (M = Fe,[12] Co[13]), and *trans*-$\{[(\eta^5\text{-}C_5Me_5)Fe]_2(\eta^5{:}\eta^5\text{-}C_8H_6)\}\{BF_4\}$.[13] Very recently, the first complexes in which a pentalene ligand binds to a single metal center in an η^8-fashion, i.e., $[\eta^8\text{-}C_8H_4(1,5\text{-}SiMe_3)_2]TaCl_3$,[14] $(\eta^8\text{-}C_8H_6)V(\eta^5\text{-}Cp')$ ($Cp' = C_5Me_5$, C_5H_4Me), $[\eta^8\text{-}C_8H_5(2\text{-}Me)]V(\eta^5\text{-}C_5H_5)$, $(\eta^8\text{-}C_8H_6)V(\eta^5\text{-}C_9H_7)$,[15] $(\eta^8\text{-}C_8H_6)Ti(\eta^5\text{-}C_5H_5)$, $(\eta^8\text{-}C_8H_6)M(\eta^5\text{-}C_5H_5)X$ (M = Ti, Zr; X = Cl, Br), $(\eta^8\text{-}C_8H_6)ZrCl_2(THF)_2$,[16] and $[\eta^8\text{-}C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2Th$,[17] have been synthesized and structurally characterized.[18] Somewhat surprisingly, one class of pentalene compounds which has not been structurally characterized by X-ray diffraction is that of simple bimetallic bis-pentalene sandwich complexes, $M_2[C_8H_{6-n}R_n]_2$, even though such complexes were proposed by Katz 26 years ago.[19,20] Herein, we extend our studies with the $SiPr^i{}_3$-substituted pentalene ligand[17] $[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]^{2-}$ and report the synthesis and structural characterization of the dimolybdenum sandwich complex $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$.

The reaction of 2 equiv of $K_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]$ with $Mo_2(OAc)_4$ in THF at room temperature results in the formation of a mixture of two compounds. The nearly identical spectroscopic data (^1H and ^{13}C NMR and mass spectroscopies) observed for these two compounds

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(3) For simplicity, in this paper any complexes containing a $[C_8H_{6-n}R_n]$ ligand will be referred to as a "pentalene complex" regardless of the nature of the ligand (i.e., neutral or anionic).

(4) For references on the synthesis of pentalenes and dihydropentalenes, including a review article, see the following and references therein: (a) Lindner, H.-J. In *Methoden der organischen Chemie*, 4th ed.; Georg Thieme Verlag: Stuttgart, 1985; Vol. 5/2c, p 103−122. (b) Meier, H.; Pauli, A.; Kolshorn, H.; Kochhan, P. *Chem. Ber.* **1987**, *120*, 1607−1610. (c) Griesbeck, A. G. *Synthesis* **1990**, 144−147. (d) Meier, H.; Pauli, A.; Kochhan, P. *Synthesis* **1987**, 573−574.

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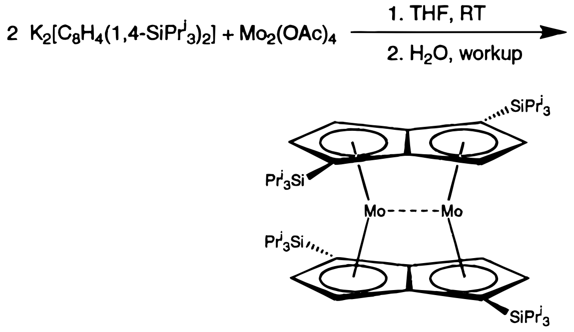
suggest that they are isomers. Attempts to separate these compounds by standard methods (i.e., fractional crystallization, sublimation, and chromatography) have proved unsuccessful. In addition, variable-temperature ^{1}H NMR experiments in the range from ca. −60 to +120 °C showed no signs that these two compounds interconvert. However, we have been able to isolate one of these compounds by selective degradation of the other.[21] Thus, addition of oxygen-free[22] water to a benzene solution of the two compounds gives, after workup, $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$ as a green solid in 22% yield (eq 1).[23]



(1)

The ^{1}H NMR spectrum (toluene-d_8) of $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$ is unusual in the sense that one ring hydrogen appears in the typical aromatic region at δ 7.13 while the other is observed upfield at δ 2.64. Heteronuclear NOE experiments have assigned the resonances at δ 2.64 and 7.13 to the hydrogens occupying the 2- and 3-positions, respectively.

The molecular structure of $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$, as determined by X-ray diffraction,[24] is shown in Figure 1, from which several features are noteworthy. The pentalene ligands of $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$ are effectively planar with fold angles, about the bridgehead carbons, of ca. 2° and 3°, which are within the range (0°−9°) observed for *cis*-bi- and trimetallic pentalene complexes.[7−10] In contrast, mononuclear compounds containing an η^8-pentalene are characterized by bent pentalene ligands with large fold angles in the range of 24−43°.[14−17] The pentalene ligands of $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$ are parallel, as indicated by an angle of only ca. 2° between the mean planes of the two ligands (Figure 1a). As seen in Figure 1b, the carbon frameworks of the $[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]$ ligands are only slightly twisted (ca. 10°) from an eclipsed conformation whereas the $SiPr^i{}_3$ substituents are staggered. The distances of the molybdenum atoms to the bridgehead carbons (2.360(3)−Å-2.419(3) Å) are slightly longer than those to the other carbons (2.258(3)−Å-2.297(3) Å), which is a feature observed in the majority of bimetallic pentalene complexes. In contrast, the shortest metal−carbon distances in the mononuclear η^8-bound pentalene complexes, where the pentalene ligands are highly folded, are those to the bridgehead carbons.

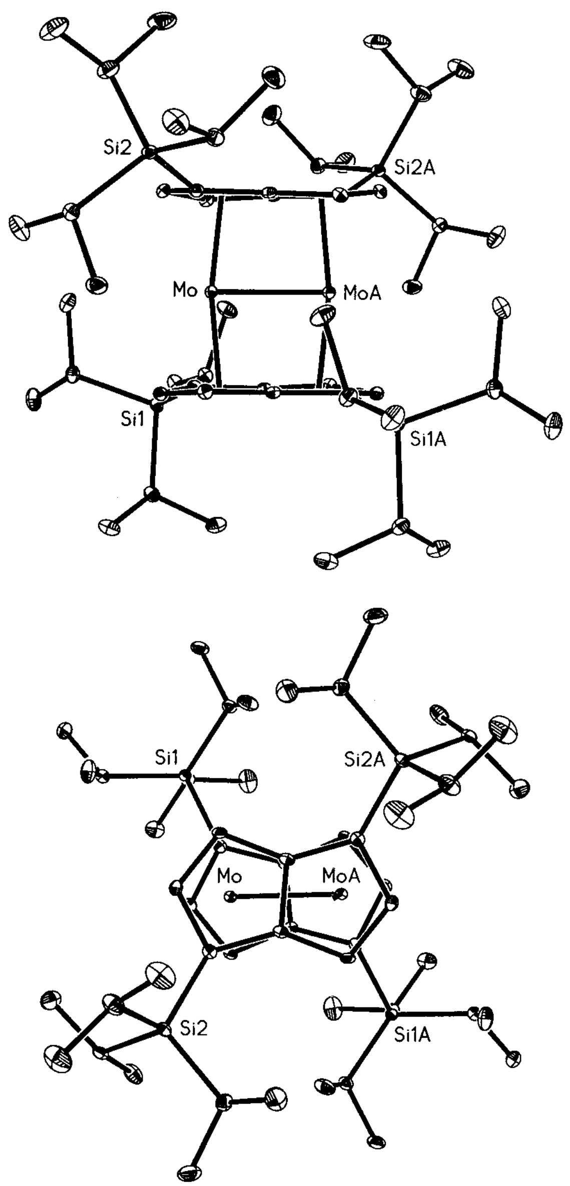


Figure 1. Two orthogonal views of the molecular structure of $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$.

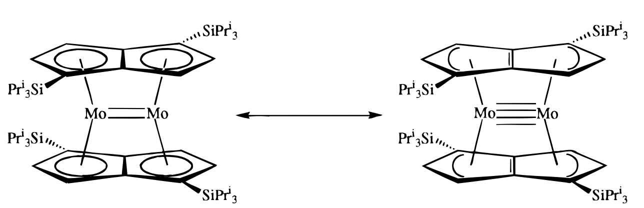


Figure 2. Two possible resonance structures for $Mo_2[C_8H_4\text{-}(1,4\text{-}SiPr^i{}_3)_2]_2$.

$Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$ is diamagnetic, which implies that the Mo−Mo bonding interaction has a formal bond order of two or four. In this regard, a simplified description of the nature of $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$ is provided by the two resonance structures shown in Figure 2, i.e., a doubly bonded 18-electron complex and a quadruply bonded 16-electron complex.[25] The Mo−Mo distance of 2.340(1) Å in $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$ is

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(21) Although the identity of the other compound is unknown, it is possible that it is an isomer of $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$. Two possibilities include: (i) an isomer in which the $SiPr^i{}_3$ subsituents are eclipsed and (ii) an isomer in which each $C_8H_4(1,4\text{−}SiPr^i{}_3)_2$ ligand binds in an η^8-fashion to a single Mo atom, resulting in an unsupported (i.e., unbridged) Mo−Mo bond.

(22) Both compounds react rapidly with oxygen in solution.

(23) For comparison, the reaction of NaCp with $Mo_2(OAc)_4$ does not yield the analogous [Cp2Mo]2 complex. See the following and references therein: (a) Smart, J. C.; Curtis, C. J. *Inorg. Chem.* **1978**, *17*, 3290−3292. (b) Bashkin, J.; Green, M. L. H.; Poveda, M. L.; Prout, K. *J. Chem. Soc., Dalton. Trans.* **1982**, 2485−2494.

(24) $Mo_2[C_8H_4(1,4\text{−}SiPr^i{}_3)_2]$ is orthorhombic *Pccn* (No. 56) with a = 13.7859(11) Å, b = 15.3758(12) Å, c = 25.442(3) Å, and Z = 4 at 173 K. For refinement on F^2 using SHELXL93, R = 0.036 for 3689 reflections with $I > 2\sigma(I)$ and R_w = 0.086 for all 4741 reflections.

shorter than the range observed for Mo−Mo double bonds, ca. 2.49−Å-2.89 Å,[26] and longer than most complexes containing Mo−Mo quadruple bonds, ca.. 2.01−Å-2.24 Å.[27] We are aware of one quadruply bonded dimolybdenum complex, namely $Mo_2(C_8H_8)_3$,[28] with a Mo−Mo distance (2.302(2) Å) which is similar to that of $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$. Photoelectron spectroscopy and molecular orbital calculations are in progress to provide more insight into the nature of the bonding in $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$. Finally, it is noteworthy that $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$ is the first bimetallic bis-pentalene sandwich complex to be structurally characterized by X-ray diffraction.

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Supporting Information Available: Tables of spectroscopic, analytical, and X-ray data and experimental details for the synthesis of $Mo_2[C_8H_4(1,4\text{-}SiPr^i{}_3)_2]_2$ (13 pages). Ordering information is given on any current masthead page.

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