Synthesis of New Transition Metal Carbene Complexes from π-Sulfurane Compounds: Reaction of 10-S-3 Tetraazapentalene Derivatives with Pd(PPh$_3$)$_4$ and RhCl(PPh$_3$)$_3$

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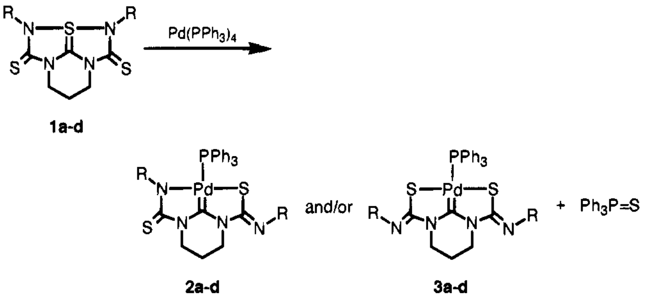
Since the discovery of an unusual structure of trithiapentalene[1] which is sometimes refered to as "no bond resonance", the chemistry of π-hypervalent heterocyclic systems has been a subject of considerable interest. A number of π-electron systems containing a 10-S-3 framework have been prepared,[2] and their structures and reactivities have been investigated.[2,3] However, little is known about the reactivity of the equatorial bonds (S^{IV}=C) of 1,6,6a-trithia(6a-S^{IV})pentalenes and their analogs. Recently, we reported the synthesis and reactivity of 10-S-3 tetraazapentalene derivatives, 2,3-disubstituted 6,7-dihydro-5*H*-2a-thia(2a-S^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithiones (**1a**−**d**).[4,5] These compounds underwent unique reactions due to the nature of hypervalent sulfur. For example, the reaction of **1a** with NaBH$_4$ gave the ring-opening compound 1,3-bis((methylthio)carbamoyl)perhydropyrimidine in good yield with release of the hypervalent sulfur.[6] This reaction was the first example of the cleavage of an equatorial bond (S^{IV}=C) in π-sulfurane compounds and indicated that the carbon atom of the S^{IV}=C(7b) bond of **1a** has an electrophilic nature. The electrophilic nature of the 7b carbon atom was also supported by the MNDO calculation.[7]

Scheme 1[a]



[a] **a**, R = CH$_3$; **b**, R = C$_2$H$_5$; **c**, R = *p*-ClC$_6$H$_4$; **d**, R = *p*-CH$_3$OC$_6$H$_4$.

Table 1. Reactions of **1** with Pd(PPh$_3$)$_4$ and RhCl(PPh$_3$)$_3$[a]

entry	tetraazapentalene (R)	complex	time/h	solvent	product (yield/%[b])
1	**1a** (Me)	Pd(PPh$_3$)$_4$	48	C$_6$H$_6$	**2a** (23), **3a** (39)
2	**1b** (Et)	Pd(PPh$_3$)$_4$	48	C$_6$H$_6$	**2b** (−),[d] **3b** (55)
3	**1c** (*p*-ClC$_6$H$_4$)	Pd(PPh$_3$)$_4$	48	C$_6$H$_6$/CH$_2$Cl$_2$[c]	**2c** (0), **3d** (91)
4	**1d** (*p*-CH$_3$OC$_6$H$_4$)	Pd(PPh$_3$)$_4$	48	C$_6$H$_6$	**2d** (0), **3d** (98)
5	**1a** (Me)	RhCl(PPh$_3$)$_3$	72	C$_6$H$_6$/CH$_2$Cl$_2$	**4a** (94), **5a** (0)
6	**1b** (Et)	RhCl(PPh$_3$)$_3$	72	C$_6$H$_6$/CH$_2$Cl$_2$	**4b** (38), **5b** (−)
7	**1c** (*p*-ClC$_6$H$_4$)	RhCl(PPh$_3$)$_3$	72	C$_6$H$_6$/CH$_2$Cl$_2$	**4c** (0), **5c** (99)
8	**1d** (*p*-CH$_3$OC$_6$H$_4$)	RhCl(PPh$_3$)$_3$	72	C$_6$H$_6$/CH$_2$Cl$_2$	**4d** (0), **5d** (86)

[a] All reactions were carried out at room temperature in a sealed tube. Molar ratio 1:complex = 1:1. [b] Isolated yields based on **1a**−**d**. [c] In C$_6$H$_6$/CH$_2$Cl$_2$ (1:1). [d] The dash signifies that the product could not be isolated.

We now report the conversion of 10-S-3 tetraazapentalene derivatives into their Pd and Rh carbene complexes by reaction with Pd(PPh$_3$)$_4$ and RhCl(PPh$_3$)$_3$. When **1a** was treated with 1 equiv of Pd(PPh$_3$)$_4$ in degassed benzene at room temperature for 48 h (Scheme 1), new Pd(II) carbene complexes **2a**, Pd[CN(S=CNCH$_3$)CH$_2$CH$_2$CH$_2$NC(S)=NCH$_3$](PPh$_3$), and **3a**, Pd[CN(C(S)=NCH$_3$)CH$_2$CH$_2$CH$_2$NC(S)=NCH$_3$](PPh$_3$), were obtained as yellowish solids in 23 and 39% yields, respectively, accompanying the formation of triphenylphosphine sulfide (Ph$_3$P=S) in the same amount as that of the carbene complexes. The other tetraazapentalene derivatives (**1b**−**d**) reacted similarly with Pd(PPh$_3$)$_4$ to give **3b**−**d**. The results are shown in Table 1. The structure of **3a**[8] was determined by X-ray crystallographic analysis. Figure 1 shows an ORTEP drawing of **3a**. The Pd atom has a square planar-coordinated structure surrounded by two sulfur ligands, one phosphorus ligand, and one carbene ligand. The bond length of the C(1)−Pd bond is 2.005 Å, similar to the bond length of the C−Pd bond of other Pd(II) carbene complexes.[10] The configuration of the two methyl groups attached to the imino nitrogens of **3a** is syn to the S−C bond. Complex **3a** was very stable in organic solvents under air atmosphere. The structure of **2a**[11] was determined by comparison of its spectral data with those of **3a**. Complex **2a** is stable to air in solid state but unstable in organic solvents at room temperature. In dichloromethane and benzene, **2a** changed to **3a** by an intramolecular ligand exchange. This ligand exchange reaction was followed by measuring the ^{1}H NMR spectrum of **2a** at several different times. Complex **2a** was completely converted into **3a** after 15 days in benzene and 25

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(7) Tomura, M. A Ph.D. dissertation. Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Japan, 1992, p 43. The sulfur atoms of the thiocarbonyl groups at the 1- and 4-positions of **1a** have a large coefficient in the HOMO, and the carbon atom at the 7b-position, which bonded to the S^{IV} atom, has a large coefficient in the LUMO.

(8) X-ray data of **3a**.[17] Selected bond distances (Å): Pd(1)−S(2), 2.293(1); Pd(1)−S(3), 2.281(1); Pd(1)−C(1), 2.005(5); Pd(1)−P(1), 2.332(1); S(3)−C(3), 1.759(5); S(2)−C(2), 1.755(6); N(2)−C(1), 1.342(6); N(2)−C(2), 1.430(5); N(3)−C(1), 1.336(4); N(3)−C(3), 1.417(6); N(1)−C(2), 1.265(7); N(1)−C(7), 1.467(7). Selected bond angles (deg): S(3)−Pd(1)−S(2), 169.24(5); S(3)−Pd(1)−C(1), 84.7(1); S(3)−Pd(1)−P(1), 96.80(4); S(2)−Pd(1)−C(1), 84.5(1); S(2)−Pd(1)−P(1), 93.95(5).

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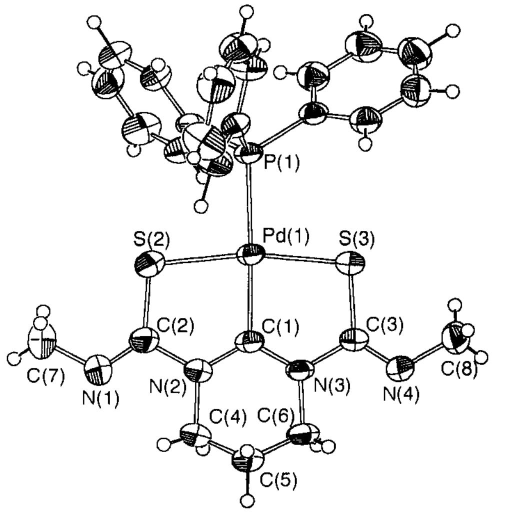
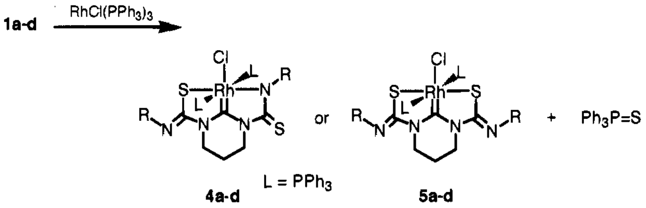


Figure 1. ORTEP drawing of **3a** viewed on the pentalene framework.[9] Non-hydrogen atoms are represented as a themal ellipsoid of 50% probability.

Scheme 2[a]



[a] **a**, R = CH_3; **b**, R = C_2H_5; **c**, R = *p*-ClC_6H_4; **d**, R = *p*-$CH_3OC_6H_4$.

days in $CDCl_3$.[12] In general, the carbene complexes having two sulfur ligands are more stable than the carbene complexes having nitrogen and sulfur ligands. Thus, when **1b** was treated with $Pd(PPh_3)_4$, **3b** was obtained as a sole isolable product in moderate yield with recovery of **1b**. The reaction of **1c** and **1d**[13] with $Pd(PPh_3)_4$ in C_6H_6/CH_2Cl_2 (1:1) at room temperature for 48 h gave **3c** and **3d** in high yields, respectively (Table 1). The formation of **3a−d** in preference to **2a−d** suggests that a severe steric repulsion exists between the substituents in the 2 and 3 positions of the latter compounds. The same method was applied to the synthesis of Rh(III) carbene complexes[14] (Scheme 2). The reaction of **1a** with $RhCl(PPh_3)_3$ in C_6H_6/CH_2Cl_2 (1:1) at room temperature for 72 h gave the unsymmetrical Rh(III) carbene complex **4a**, $RhCl[CN(S{=}CNCH_3)CH_2CH_2CH_2NC(S){=}NCH_3](PPh_3)_2$, in 94% yield. In this reaction, $Ph_3P{=}S$ was produced in an amount equivalent to that of **4a**. The reaction of **1b** with $RhCl(PPh_3)_3$ under similar conditions gave **4b** in low yield. The results are given in Table 1. The low reactivity of **1b** may be due to a steric repulsion between two ethyl groups, attached to the pentalene ring, and the Ph_3P groups of $RhCl(PPh_3)_3$ at the transition state (see ref 5a). The structure of the complex **4a** was determined from the spectral data[15] and X-ray crystallographic analysis.[16] Figure 2 shows an ORTEP drawing of the molecular structure of **4a**. The X-ray crystallographic analysis showed the following structural features for **4a**. (1) The Rh atom is octahedrally coordinated. (2) The six coordinated sites are occupied by one chloro ligand, two trans phosphine ligands, and one tridentate ligand formed by release of a hypervalent sulfur. The C(1)−Rh bond length is 1.937 Å, very similar to that of known Rh(III) carbene complexes.[14] This carbene complex is stable in refluxed benzene under air atmosphere. The reaction of **1c** and **1d** with $RhCl(PPh_3)_3$ gave the carbene complexes **5c**, $RhCl[CN(C(S){=}N\text{-}C_6H_4\text{-}p\text{-}Cl)CH_2CH_2CH_2N(C(S){=}N\text{-}C_6H_4\text{-}p\text{-}Cl)](PPh_3)_2$, and **5d**, $RhCl[CN(C(S){=}N\text{-}C_6H_4\text{-}p\text{-}OCH_3)CH_2CH_2CH_2N(C(S){=}N\text{-}C_6H_4\text{-}p\text{-}OCH_3)](PPh_3)_2$, in 99 and 86% yields, respectively, without the formation of **4c** and **4d** (Table 1).

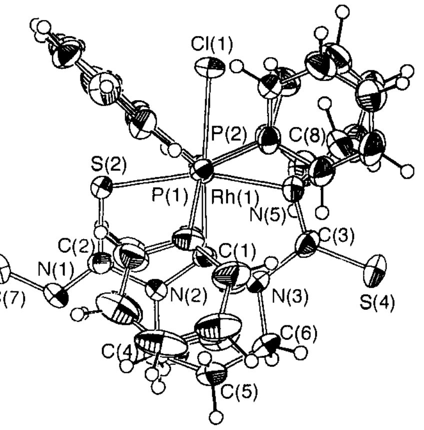


Figure 2. ORTEP drawing of **4a** viewed on the pentalene framework.[9] Non-hydrogen atoms are represented as a thermal ellipsoid of 50% probability.

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Supplementary Material Available: Spectroscopic and analytical data for complexes **2a**, **3a**, **3b**, **3c**, **3d**, **4a**, **4b**, **5c**, and **5d**; ORTEP drawing of **3a** and **4a**; and tables of crystal data and experimental details and selected bond lengths and angles (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(11) **2a**: mp 260−261 °C; FT-IR (KBr, cm^{-1}) 1611, 1535, 1487, 1435, 1398, 1309, 1098, 745, 694; ^1H NMR (270 MHz, $CDCl_3$) δ 2.05 (quint, 2H, J = 6.1 Hz, $NCH_2CH_2CH_2N$), 2.93 (d, 3H, J(PH) = 1.8 Hz, $PPdNCH_3$), 3.10 (s, 3H, NCH_3), 3.73 (t, 2H, J = 6.1 Hz, $NCH_2CH_2CH_2N$), 4.19 (t, 2H, J = 6.1 Hz, $NCH_2CH_2CH_2N$), 7.40−7.60 (m, 15H, ArH); UV (CH_3CN) λ_{max} (ϵ) 262.0 (26 300), 356 nm (2700). Anal. Calcd for $C_{26}H_{27}N_4S_2PPd$: C, 52.30; H, 4.56; N, 9.38. Found: C, 52.38; H, 4.49; N, 9.23. **3a**: mp 265−266 °C; FT-IR (KBr, cm^{-1}) 1605, 1518, 1435, 1396, 1348, 743, 692; ^1H NMR (270 MHz, $CDCl_3$) δ 1.97 (quint, 2H, J = 6.1 Hz, $NCH_2CH_2CH_2N$), 3.17 (s, 6H, 2 × NCH_3), 3.85 (t, 4H, J = 6.1 Hz, $NCH_2CH_2CH_2N$), 7.40−7.60 (m, 15H, ArH); UV (CH_3CN) λ_{max} (ϵ) 244 (sh, 26 700), 355.5 nm (2200). Anal. Calcd for $C_{26}H_{27}N_4S_2PPd$: C, 52.27; H, 4.56; N, 9.38. Found: C, 52.30; H, 4.47; N, 9.42.

(12) The signals at 2.93 (CH_3NCS-) and 3.10 ppm ($CH_3N{=}C$) of **2a** decreased as time elapsed, and the singlet at 3.17 ppm ($=NCH_3$) of **3a** appeared as time elapsed. Finally, the spectrum of **2a** changed to the spectrum of **3a**.

(13) Compound **1d** was prepared according to a method similar to that for the synthesis of **1c** (see ref 5h): ^1H NMR (270 MHz, $CDCl_3$) δ 2.39 (quint, 2H, J = 6.0 Hz, $NCH_2CH_2CH_2N$), 3.79 (s, 6H, 2 × OCH_3), 4.47 (t, 4H, J = 5.8 Hz, $NCH_2CH_2CH_2N$), 6.91−7.29 (m, 8H, ArH).

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(15) **4a**: FT-IR (KBr, cm^{-1}) 1605, 1520, 1504, 1435, 1398, 1344, 1309, 1164, 1100, 1062, 748, 696, 654, 522, 493; ^1H NMR (270 MHz, $CDCl_3$) δ 0.59 (quint, 2H, J = 4.9 Hz, $NCH_2CH_2CH_2N$), 2.07 (s, 3H, NCH_3), 2.49 (t, 2H, J = 5.8 Hz, $NCH_2CH_2CH_2N$), 3.02 (s, 3H, $=NCH_3$), 3.71 (t, 2H, J = 6.1 Hz, $NCH_2CH_2CH_2N$), 7.30−7.75 (m, 30H, 2 × $P(C_6H_5)_3$); UV (CH_3CN) λ_{max} (ϵ) 355 (9600), 272 nm (23 300).

(16) X-ray data of **4a**.[17] Selected bond distances (Å): Rh(1)−S(2), 2.344(1); Rh(1)−C(1), 1.937(5); Rh(1)−P(1), 2.388(2); Rh(1)−P(2), 2.364(2); Rh(1)−N(5), 2.073(4); Rh(1)−Cl(1), 2.446(1); S(2)−C(2), 1.753(6); N(2)−C(1), 1.331(7); N(2)−C(2), 1.427(7); N(5)−C(3), 1.312(8); N(3)−C(3), 1.426(7). Selected bond angles (deg): S(2)−Rh(1)−C(1), 83.1(2); S(2)−Rh(1)−P(1), 87.90(6); S(2)−Rh(1)−P(2), 90.25(6); N(5)−Rh(1)−C(1), 78.8(2); N(5)−Rh(1)−P(1), 90.7(2); N(5)−Rh(1)−P(2), 92.8(2); Cl(1)−Rh(1)−S(2), 101.16(6); Cl(1)−Rh(1)−N(5), 97.0(2); Cl(1)−Rh(1)−C(1), 174.7(2).

(17) There are several interesting points in these structures, and details of X-ray structure will be published elsewhere together with related compounds by M. Yasui, F. Iwasaki, and N. Matsumura.