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Preparation of Sulfide-Bridged Di- or Trinuclear Pyrrolylimido and Diazoalkane Complexes Derived from a Tungsten Dinitrogen Complex[1]

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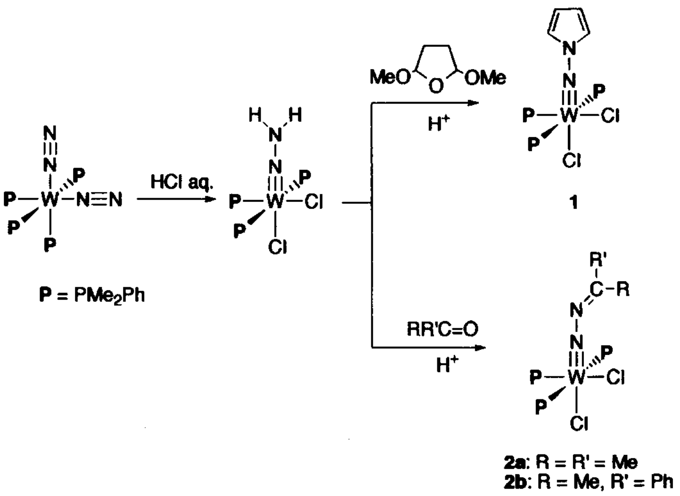
Tungsten pyrrolylimido and diazoalkane complexes, *cis,mer*-$[WCl_2(NNC_4H_4)(PMe_2Ph)_3]$ and *cis,mer*-$[WCl_2(NN{=}CRR')(PMe_2Ph)_3]$, which are readily derived from the dinitrogen complex *cis*-$[W(N_2)_2(PMe_2Ph)_4]$, reacted with $[PPh_4]_2[WS_4]$ to give the sulfide-bridged di- or trinuclear pyrrolylimido and diazoalkane complexes, $[PPh_4][WCl(NNC_4H_4)(PMe_2Ph)_2(\mu\text{-}S)_2WS_2]$ (**4**) and $[PPh_4][WCl(NN{=}CRR')(PMe_2Ph)_2(\mu\text{-}S)_2WS_2]$ (R = R′ = Me (**5a**); R = Me, R′ = Ph; R = H, R′ = *p*-MeC_6H_4), or $[\{WCl(NNC_4H_4)(PMe_2Ph)_2(\mu\text{-}S)_2\}_2W]$ (**7**) and $[\{WCl(NN{=}CMePh)(PMe_2Ph)_2(\mu\text{-}S)_2\}_2W]$. Treatment of **4** or **5a** with tetraalkylthiuram disulfide resulted in the formation of sulfide-dithiocarbamate complexes: $[W(NNC_4H_4)(PMe_2Ph)(S_2CNR_2)(\mu\text{-}S)_2WS(S_2CNR_2)]$ (R = Et, Pr^i (**9b**)) and $[W(NN{=}CMe_2)(PMe_2Ph)(S_2CNEt_2)(\mu\text{-}S)_2WS(S_2CNEt_2)]$. On the other hand, replacement of two PMe_2Ph ligands in **4** and **5** by $Ph_2PCH_2CH_2PPh_2$ (dppe) afforded $[PPh_4][WCl(NNC_4H_4)(dppe)(\mu\text{-}S)_2WS_2]$ and $[PPh_4][WCl(NN{=}CRR')(dppe)(\mu\text{-}S)_2WS_2]$ (R = R′ = Me; R = Me, R′ = Ph (**12b**)), where **12b** has been shown to react further with $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) to give a bimetallic trinuclear complex $[WCl(NN{=}CMePh)(dppe)(\mu\text{-}S)_2W(\mu\text{-}S)_2Rh(cod)]$ (**13**). Detailed structures have been determined by X-ray analyses for **4**, **5a**, **7**, **9b**, and **13**.

The complexes containing organodinitrogen ligands[2] have been attracting much attention owing to their relevance to biological and chemical N_2-fixing systems. Thus, organodiazenido (MNNR), organohydrazido (MNNRR′), and diazoalkane (MNN=CRR′) complexes serve not only as the potential models for the active sites of nitrogenase to produce NH_3 from N_2 but also as the intermediates on the new synthetic routes to organonitrogen compounds from N_2. On the other hand, in relation to the structure of FeMo-cofactor of nitrogenase,[3] complexes of Mo and its congener W with both sulfide and organodinitrogen ligands are of particular interest. Although some Mo and W organodinitrogen complexes of this type are known,[4] they are not derived from N_2 complexes.

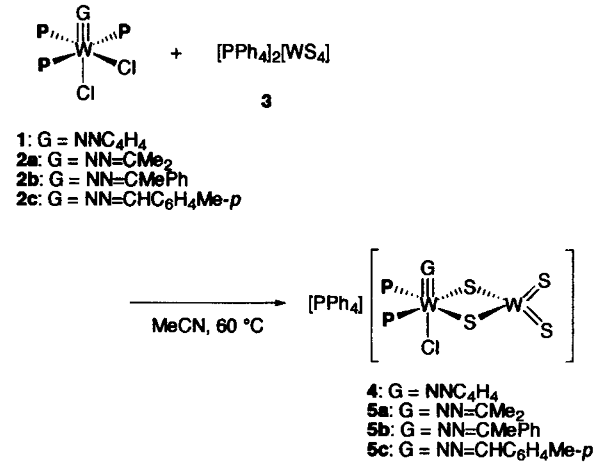
In the course of our extensive studies on the reactivities of Mo and W dinitrogen complexes with tertiary phosphine coligands,[5] we have shown that a variety of organodinitrogen complexes can be derived from *trans*-$[M(N_2)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) and *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, W). Among these, pyrrolylimido and diazoalkane complexes *cis,mer*-$[WCl_2(NNC_4H_4)(PMe_2Ph)_3]$ (**1**)[6] and *cis,mer*-$[WCl_2(NN{=}CRR')(PMe_2Ph)_3]$ (**2**)[7] (Scheme 1) are of great importance, since organonitrogen compounds are readily liberated from these complexes under certain mild conditions; viz., pyrrole and aminopyrrole from the former[6a,8] and azines or amines from the latter.[7] Now we have found that **1** and **2** react with $[WS_4]^{2-}$ to give the sulfide-bridged di- or trinuclear pyrrolylimido and diazoalkane complexes. In this paper, syntheses and characterization of these new complexes are described, together with the details of several other organodinitrogen complexes derived therefrom.

Results and Discussion

Reactions of Pyrrolylimido and Diazoalkane Complexes 1 and 2 with $[WS_4]^{2-}$ Anion. Reactions of **1** and **2** with one equiv of $[PPh_4]_2[WS_4]$ (**3**) in acetonitrile at 60 °C afforded the sulfide-bridged dinuclear complexes $[PPh_4][WCl(NNC_4H_4)(PMe_2Ph)_2(\mu\text{-}S)_2WS_2]$ (**4**) and $[PPh_4][WCl(NN{=}CRR')(PMe_2Ph)_2(\mu\text{-}S)_2WS_2]$ (**5a**: R = R′ = Me; **5b**: R = Me, R′ = Ph; **5c**: R = H, R′ = *p*-MeC_6H_4) (Eq. 1). The yields were moderate for **4**, **5a**, and **5b**, whereas **5c** was obtained in only 11% yield due to the formation of a significant amount of uncharacterizable solid. The reactions forming **5** proceeded considerably faster than the reaction giving **4**. One of the mutually *trans* PMe_2Ph ligands and the Cl *cis* to the organodinitrogen ligand in **1** and **2** underwent substitution by the η^2-WS_4 ligand, which has been verified by the spectroscopic and microanalytical data as well as the X-ray analyses of **4** and **5a** (Figs. 1 and 2). A related reaction was reported previously for the formation of the dimethylhydrazido(2−) complex $[W(NNMe_2)_2(PPh_3)(\mu\text{-}S)_2WS_2]$ (**6**) from $[WCl(NNMe_2)_2(PPh_3)_2]Cl$ and $[NBu^n_4]_2[WS_4]$.[4a]



Scheme 1.



(1)

When **3** was treated with 2 equiv of **1** or **2b** (R = Me, R′ = Ph),trinuclear complexes [{WCl(NNC$_4$H$_4$)(PMe$_2$Ph)$_2$(μ- S)$_2$}$_2$W] (**7**) and [{WCl(NN=CMePh)(PMe$_2$Ph)$_2$(μ-S)$_2$}$_2$W] (**8**) were obtained, although the yields were not satisfactory even after the prolonged reaction time (Eq. 2). By monitoring these reactions using ^{1}H NMR spectroscopy, the presence of **4** and **5b** as the intermediates leading to **7** and **8** has been demonstrated unambiguously. The structure containing two W-pyrrolylimido moieties connected by the bridging WS$_4$ unit is unequivocally demonstrated by using X-ray diffraction method for **7** (Fig. 3).

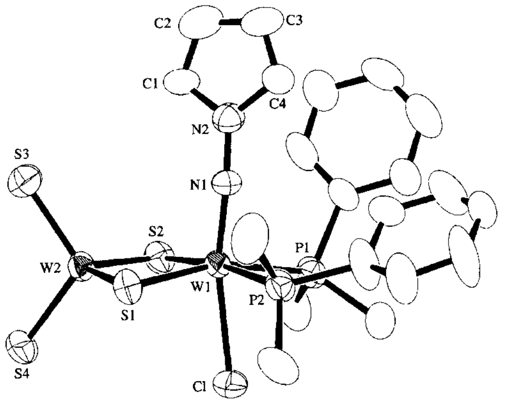


Fig. 1. ORTEP drawing of the anion in **4**. One Ph group with the higher occupancy is shown for the two disordered Ph groups attached to the P(2) atom. Hydrogen atoms are omitted for clarity.

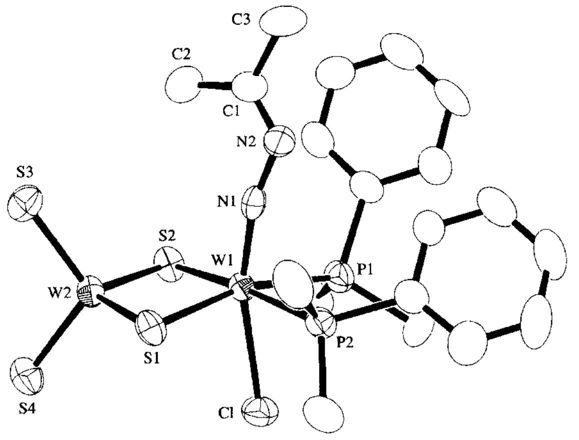


Fig. 2. ORTEP drawing of the anion in **5a**. Hydrogen atoms are omitted for clarity.

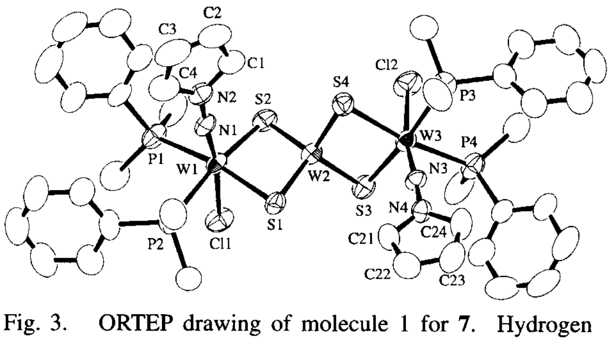


Fig. 3. ORTEP drawing of molecule 1 for **7**. Hydrogen atoms are omitted for clarity.

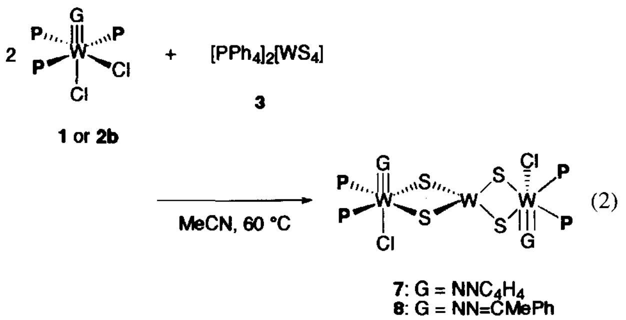


Table 1. Selected Bond Distances and Angles in **4** and **5a**

	4	**5a**
(a) Bond distance (Å)		
W(1)–W(2)	2.905(1)	2.9062(8)
W(1)–S(1)	2.436(2)	2.421(2)
W(1)–S(2)	2.417(3)	2.430(2)
W(2)–S(1)	2.272(2)	2.274(2)
W(2)–S(2)	2.253(2)	2.254(2)
W(2)–S(3)	2.154(3)	2.157(3)
W(2)–S(4)	2.162(3)	2.159(2)
(b) Bond angle (°)		
Cl–W(1)–S(1)	88.70(8)	89.25(8)
Cl–W(1)–S(2)	89.49(8)	89.84(8)
Cl–W(1)–N(1)	167.6(2)	164.4(2)
S(1)–W(1)–S(2)	98.04(7)	98.14(7)
S(1)–W(1)–P(1)	165.19(9)	165.42(8)
S(1)–W(1)–P(2)	81.82(7)	82.92(7)
S(1)–W(1)–N(1)	101.6(2)	102.2(2)
S(2)–W(1)–P(1)	81.69(8)	81.92(7)
S(2)–W(1)–P(2)	173.05(9)	173.85(8)
S(2)–W(1)–N(1)	95.9(2)	98.8(2)
P(1)–W(1)–N(1)	93.2(2)	92.1(2)
P(2)–W(1)–N(1)	90.9(2)	86.8(2)
S(1)–W(2)–S(2)	108.14(8)	108.06(8)
S(1)–W(2)–S(3)	111.02(9)	111.14(10)
S(1)–W(2)–S(4)	109.61(9)	109.09(9)
S(2)–W(2)–S(3)	110.57(10)	110.56(9)
S(2)–W(2)–S(4)	107.24(9)	107.37(9)
S(3)–W(2)–S(4)	110.16(10)	110.5(1)
W(1)–S(1)–W(2)	76.12(6)	76.42(7)
W(1)–S(2)–W(2)	76.86(7)	76.59(6)

Reactions of *cis,mer*-[$WCl_2(NNH_2)(PMe_2Ph)_3$] with **3** were also carried out under various conditions but isolation of the characterizable products was unsuccessful. Similarly, **1** reacted with $[MoS_4]^{2-}$ or $[ReS_4]^-$ to give only some untractable products.

X-Ray Structures of 4, 5a, and 7. As shown in Figs. 1 and 2, the structures of **4** and **5a** are quite analogous except for the organodinitrogen ligands,and pertinent bonding parameters for these two are also in good agreement (Table 1). The W(1) atoms with a formal oxidation state of +IV have a distorted octahedral structure, while the W(2) atoms with a formal +VI state are essentially tetrahedral, if the W–W bond due to the donation of the electron pair from W(1) to W(2) is ignored. The presence of some bonding interaction between the two W atoms is manifested by the W–W distances at 2.905(1) and 2.9062(8) Å in **4** and **5a**, respectively, which are considerably shorter than that of the formal d^0–d^0 complex **6** (3.024(1) Å).[4a] The W_2S_2 planes are folded with the disposition of the bridging S atoms toward the direction of the Cl ligand, where the dihedral angles between the two W_2S planes are 171° and 172° for **4** and **5a**, respectively. The W–S bond distances for the terminal sulfide ligands (2.15—2.16 Å) are apparently shorter than those for the bridging sulfide ligands; among the latter, the W(2)–S bonds (2.25—2.28 Å) are shorter than the W(1)–S bonds (2.41—2.44 Å). This may be explained by the preferential π-donation of the lone pair electron density from the bridging S atom to the W atoms with a higher oxidation state.

For the organodinitrogen ligands, the W(1), N(1), N(2), and C(1)–C(4) atoms in **4** as well as the W(1), N(1), N(2), and C(1)–C(3) atoms in **5a** are essentially coplanar. Important bond distances and angles in pyrrolylimido and diazoalkane ligands are summarized in Table 2. If compared with the data for the Br analogue of **1**[6a]

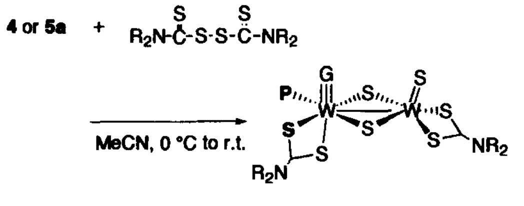
Table 2. Selected Bond Distances (Å) and Angles (°) in Organodinitrogen Ligands

Complex	W–N	N–N	N–C	W–N–N	N–N–C
(a) Pyrrolylimido complex					
4	1.739(7)	1.367(9)	1.35(1), 1.37(1)	171.2(6)	122.8(8), 128.1(8)
7 (molecule 1)	1.748(7)	1.344(9)	1.37(1), 1.37(1)	174.3(6)	125.4(8), 125.7(8)
	1.748(6)	1.337(9)	1.35(1), 1.38(1)	177.3(6)	125.1(7), 126.1(8)
7 (molecule 2)	1.741(7)	1.352(9)	1.35(1), 1.38(1)	174.3(6)	123.5(7), 128.5(8)
	1.761(7)	1.330(9)	1.38(1), 1.37(1)	175.4(6)	124.3(8), 127.0(9)
9b (molecule 1)	1.74(1)	1.34(2)	1.39(2), 1.36(2)	169(1)	125(1), 126(1)
9b (molecule 2)	1.72(1)	1.32(2)	1.37(2), 1.35(3)	171(1)	124(1), 127(1)
[$WBr_2(NNC_4H_4)(PMe_2Ph)_3$]	1.743(4)	1.365(4)	1.38(1), 1.38(1)	177.9(3)	125.4(4), 125.3(4)
(b) Diazoalkane complex					
5a	1.729(7)	1.367(9)	1.28(1)	166.4(5)	119.0(7)
13 (molecule 1)	1.742(7)	1.341(9)	1.29(1)	161.7(6)	118.8(8)
13 (molecule 2)	1.746(8)	1.321(10)	1.29(1)	162.0(7)	119.4(9)
[$WCl_2(NN{=}CMe_2)(PMe_2Ph)_2(CH_2{=}CH_2)$]	1.750(6)	1.34(1)	1.29(1)	167.3(6)	116.7(7)
[$WCl_2(NN{=}CMePh)(PMe_2Ph)_2(p\text{-}MeC_6H_4CHO)$]	1.79(1)	1.29(2)	1.27(2)	166(1)	121(1)

and the diazoalkane complex *cis,mer*-[$WCl_2(NN{=}CMe_2)(PMe_2Ph)_2(CH_2{=}CH_2)$][9] added in Table 2, it might be concluded that the structural features of the organodinitrogen ligands in **4** and **5a** are quite analogous to those of these complexes; viz. the substitution of the η^2-$[WS_4]^{2-}$ ligand for the Cl anion and one PMe_2Ph ligand in **1** and **2a** hardly affects the structures of these nitrogenous ligands.

The X-ray analysis of **7** disclosed that two crystallographically independent molecules are present in the crystal, whose structures are essentially identical. Selected bond distances and angles in **7** are listed in Table 3, while an ORTEP drawing of one of the two molecules is depicted in Fig. 3. Complex **7** has a pseudo C_2 symmetry around the axis through the tetrahedral W(2) or W(5) atom. The W–W–W aray is almost linear with the angle of 173.35(2) and 165.45(2) Å, where the W–W distances in the range 2.8784(5)–2.8894(5) Å are comparable to those in **4** (2.905(1) Å). Important bond distances and angles in the pyrrolylimido ligands are shown in Table 2. These data as well as the order of the bond lengths, W(IV)–S(bridging) > W(VI)–S(bridging), also correspond well to those for **4** described above.

Conversion of 4 and 5 into Dinuclear Sulfide-Dithiocarbamate Complexes. Conversion of **4** and **5** into the pyrrolylimido or diazoalkane complexes of more sulfur-rich environment has been attempted by treatment with tetraethylthiuram disulfide. We have found that the reactions of **4** and **5a** in MeCN at 0 °C to room temperature result in the formation of the sulfide-dithiocarbamate complexes $[W(NNC_4H_4)(PMe_2Ph)(S_2CNEt_2)(\mu\text{-}S)_2WS(S_2CNEt_2)]$ (**9a**) and $[W(NN{=}CMe_2)(PMe_2Ph)(S_2CNEt_2)(\mu\text{-}S)_2WS(S_2CNEt_2)]$ (**10**) (Eq. 3). Reactions of thiuram disulfide with $[MS_4]^{2-}$ (M = Mo, W) were reported previously, which resulted in the formation of the disulfide-dithiocarbamate complex $[Mo(S_2)(S_2CNR_2)_3]$ (R = Et) or the sulfide-disulfide-dithiocarbamate complex $[WS(S_2)(S_2CNR_2)_2]$ (R = Bu^i).[10] High quality single crystals were obtained for the Pr^i complex $[W(NNC_4H_4)(PMe_2Ph)(S_2CNPr^i_2)(\mu\text{-}S)_2WS(S_2CNPr^i_2)]$ (**9b**) prepared similarly from **4** and tetraisopropylthiuram disulfide, whose structure has been determined in detail by the X-ray crystallography.



(3)

9a: G = NNC_4H_4, R = Et
9b: G = NNC_4H_4, R = Pr^i
10: G = $NN{-}CMe_2$, R = Et

Table 3. Selected Bond Distances and Angles in **7**

(a) Bond distance (Å)			
Molecule 1			
W(1)–W(2)	2.8846(5)	W(1)–S(1)	2.449(2)
W(1)–S(2)	2.426(2)	W(2)–W(3)	2.8850(5)
W(2)–S(1)	2.227(2)	W(2)–S(2)	2.232(2)
W(2)–S(3)	2.237(2)	W(2)–S(4)	2.236(2)
W(3)–S(3)	2.433(2)	W(3)–S(4)	2.440(2)
Molecule 2			
W(4)–W(5)	2.8894(5)	W(4)–S(5)	2.419(2)
W(4)–S(6)	2.450(2)	W(5)–W(6)	2.8784(5)
W(5)–S(5)	2.228(2)	W(5)–S(6)	2.235(2)
W(5)–S(7)	2.228(3)	W(5)–S(8)	2.230(2)
W(6)–S(7)	2.443(2)	W(6)–S(8)	2.424(3)
(b) Bond angle (°)			
Molecule 1			
Cl(1)–W(1)–S(1)	89.30(8)	Cl(1)–W(1)–S(2)	85.98(8)
Cl(1)–W(1)–N(1)	170.8(2)	S(1)–W(1)–S(2)	96.85(8)
S(1)–W(1)–P(1)	168.64(8)	S(1)–W(1)–P(2)	80.53(8)
S(1)–W(1)–N(1)	97.8(2)	S(2)–W(1)–P(1)	85.06(8)
S(2)–W(1)–P(2)	168.63(8)	S(2)–W(1)–N(1)	98.8(2)
P(1)–W(1)–N(1)	92.9(2)	P(2)–W(1)–N(1)	92.5(2)
W(1)–W(2)–W(3)	173.35(2)	S(1)–W(2)–S(2)	109.75(8)
S(1)–W(2)–S(3)	109.61(9)	S(1)–W(2)–S(4)	110.64(9)
S(2)–W(2)–S(3)	108.31(9)	S(2)–W(2)–S(4)	108.68(9)
S(3)–W(2)–S(4)	109.83(9)	Cl(2)–W(3)–S(3)	88.60(9)
Cl(2)–W(3)–S(4)	89.55(8)	Cl(2)–W(3)–N(3)	169.0(2)
S(3)–W(3)–S(4)	97.36(8)	S(3)–W(3)–P(3)	171.29(8)
S(3)–W(3)–P(4)	84.56(8)	S(3)–W(3)–N(3)	97.6(2)
S(4)–W(3)–P(3)	78.94(8)	S(4)–W(3)–P(4)	168.75(8)
S(4)–W(3)–N(3)	98.6(2)	P(3)–W(3)–N(3)	90.8(2)
P(4)–W(3)–N(3)	92.1(2)	W(1)–S(1)–W(2)	76.03(6)
W(1)–S(2)–W(2)	76.41(7)	W(2)–S(3)–W(3)	76.18(7)
W(2)–S(4)–W(3)	76.05(7)		
Molecule 2			
Cl(3)–W(4)–S(5)	88.68(8)	Cl(3)–W(4)–S(6)	86.55(9)
Cl(3)–W(4)–N(5)	170.7(2)	S(5)–W(4)–S(6)	96.80(8)
S(5)–W(4)–P(5)	165.97(8)	S(5)–W(4)–P(6)	82.11(8)
S(5)–W(4)–N(5)	99.3(2)	S(6)–W(4)–P(5)	85.99(8)
S(6)–W(4)–P(6)	171.82(9)	S(6)–W(4)–N(5)	97.2(2)
P(5)–W(4)–N(5)	99.3(2)	P(6)–W(4)–N(5)	91.0(2)
W(4)–W(5)–W(6)	165.45(2)	S(5)–W(5)–S(6)	109.32(9)
S(5)–W(5)–S(7)	109.00(9)	S(5)–W(5)–S(8)	109.54(10)
S(6)–W(5)–S(7)	111.32(9)	S(6)–W(5)–S(8)	109.14(9)
S(7)–W(5)–S(8)	108.49(9)	Cl(4)–W(6)–S(7)	89.93(9)
Cl(4)–W(6)–S(8)	90.1(1)	Cl(4)–W(6)–N(7)	164.7(2)
S(7)–W(6)–S(8)	96.05(8)	S(7)–W(6)–P(7)	168.37(9)
S(7)–W(6)–P(8)	80.36(8)	S(7)–W(6)–N(7)	101.3(2)
S(8)–W(6)–P(7)	83.64(9)	S(8)–W(6)–P(8)	170.39(9)
S(8)–W(6)–N(7)	98.8(2)	P(7)–W(6)–N(7)	90.2(2)
P(8)–W(6)–N(7)	90.7(2)	W(4)–S(5)–W(5)	76.77(7)
W(4)–S(6)–W(5)	76.00(7)	W(5)–S(7)–W(6)	75.93(7)
W(5)–S(8)–W(6)	76.28(8)		

X-Ray Structure of 9b. Selected bond distances and angles for two crystallographically independent molecules in **9b** determined by the X-ray analysis are summarized in Table 4, while an ORTEP drawing of molecule 1, which is essentially similar to that of molecule 2, is depicted in Fig. 4. The W(1) (or W(3)) atom has a highly distorted octahedral structure, while the W(2) or W(4) atom is square pyramidal with a terminal sulfide ligand at the apical position. The W–W distances at 2.7957(9) and 2.816(1) Å are significantly shorter than that in **4** and the bridging sulfides are bonded to two W atoms more symmetrically in **9b** than those in **4**,

Table 4. Selected Bond Distances and Angles in **9b**

(a) Bond distance (Å)			
Molecule 1			
W(1)-W(2)	2.7957(9)	W(1)-S(1)	2.372(4)
W(1)-S(2)	2.353(4)	W(1)-S(4)	2.574(4)
W(1)-S(5)	2.503(4)	W(2)-S(1)	2.274(4)
W(2)-S(2)	2.304(4)	W(2)-S(3)	2.103(4)
W(2)-S(6)	2.436(4)	W(2)-S(7)	2.448(5)
Molecule 2			
W(3)-W(4)	2.816(1)	W(3)-S(8)	2.367(4)
W(3)-S(9)	2.338(4)	W(3)-S(11)	2.586(4)
W(3)-S(12)	2.521(4)	W(4)-S(8)	2.280(4)
W(4)-S(9)	2.294(4)	W(4)-S(10)	2.114(4)
W(4)-S(13)	2.448(4)	W(4)-S(14)	2.443(5)
(b) Bond angle (°)			
Molecule 1			
S(1)-W(1)-S(2)	98.5(1)	S(1)-W(1)-S(4)	84.7(1)
S(1)-W(1)-S(5)	85.0(1)	S(1)-W(1)-P(1)	163.7(1)
S(1)-W(1)-N(1)	106.3(4)	S(2)-W(1)-S(4)	90.9(1)
S(2)-W(1)-S(5)	158.5(1)	S(2)-W(1)-P(1)	83.2(1)
S(2)-W(1)-N(1)	108.6(4)	S(4)-W(1)-S(5)	68.2(1)
S(4)-W(1)-P(1)	79.1(1)	S(4)-W(1)-N(1)	155.5(4)
S(5)-W(1)-P(1)	87.7(1)	S(5)-W(1)-N(1)	90.6(4)
P(1)-W(1)-N(1)	88.3(4)	S(1)-W(2)-S(2)	102.9(1)
S(1)-W(2)-S(3)	109.0(2)	S(1)-W(2)-S(6)	138.5(1)
S(1)-W(2)-S(7)	83.7(1)	S(2)-W(2)-S(3)	108.4(2)
S(2)-W(2)-S(6)	82.0(1)	S(2)-W(2)-S(7)	142.4(2)
S(3)-W(2)-S(6)	108.3(2)	S(3)-W(2)-S(7)	104.0(2)
S(6)-W(2)-S(7)	70.0(1)	W(1)-S(1)-W(2)	74.0(1)
W(1)-S(2)-W(2)	73.8(1)		
Molecule 2			
S(8)-W(3)-S(9)	100.2(1)	S(8)-W(3)-S(11)	87.0(1)
S(8)-W(3)-S(12)	85.6(1)	S(8)-W(3)-P(2)	167.0(1)
S(8)-W(3)-N(5)	102.9(4)	S(9)-W(3)-S(11)	89.0(1)
S(9)-W(3)-S(12)	155.2(1)	S(9)-W(3)-P(2)	81.4(1)
S(9)-W(3)-N(5)	107.0(4)	S(11)-W(3)-S(12)	67.1(1)
S(11)-W(3)-P(2)	80.1(1)	S(11)-W(3)-N(5)	159.1(4)
S(12)-W(3)-P(2)	87.8(1)	S(12)-W(3)-N(5)	95.0(4)
P(2)-W(3)-N(5)	88.9(4)	S(8)-W(4)-S(9)	104.2(1)
S(8)-W(4)-S(10)	109.4(2)	S(8)-W(4)-S(13)	141.0(2)
S(8)-W(4)-S(14)	82.2(1)	S(9)-W(4)-S(10)	107.6(2)
S(9)-W(4)-S(13)	82.1(1)	S(9)-W(4)-S(14)	139.5(1)
S(10)-W(4)-S(13)	104.8(2)	S(10)-W(4)-S(14)	107.6(2)
S(13)-W(4)-S(14)	70.1(1)	W(3)-S(8)-W(4)	74.6(1)
W(3)-S(9)-W(4)	74.9(1)		

although the W–S bonds associated with the pyrrolylimido unit are still slightly longer. These findings might suggest that **9b** is formally assignable to be a W(V)–W(V) complex with a W–W single bond rather than a W(IV)–W(VI) species, although the choice is somewhat arbitrary. The central W_2S_2 plane is considerably folded with the dihedral angle along the W–W bond of 149 or 157°. The bonding parameters in the pyrrolylimido ligand are not exceptional, as summarized in Table 2.

Reactions of 4 and 5 with Rh Complex to Give Bimetallic Complexes. Preparation of bimetallic polynuclear complexes containing both the early and late transition metals is of particular interest because novel catalytic activities are expected to arise from the cooperation of two kinds of metals different in nature. Since **4** and **5** still consist of the terminal WS_2 unit that can bind another metal fragment, as manifested by the formation of **7** and **8**, synthesis of trinuclear mixed-metal complexes was attempted by reacting, e.g., **5a** with $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) or $[RuCl_2(p\text{-cymene})]_2$. However, the reactions did not proceed cleanly, because, at least in part, transfer of the ligating phosphines took place from **5a** to the noble metal center. Hence, substitution of the relatively labile PMe_2Ph ligands in **4** and **5** with more firmly coordinating ligands was undertaken.

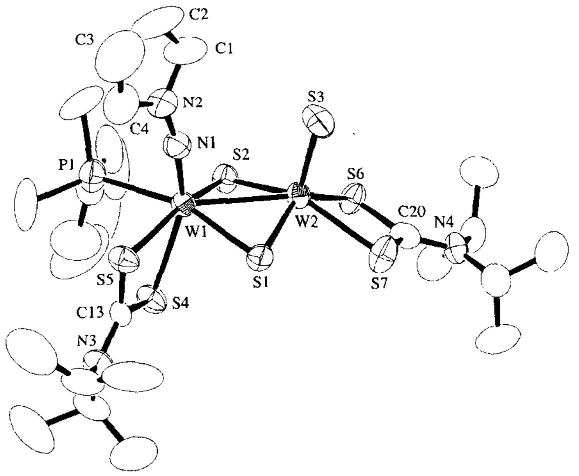
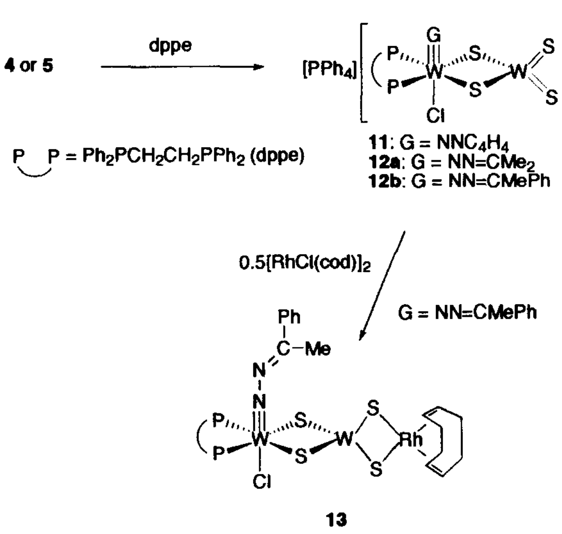


Fig. 4. ORTEP drawing of molecule 1 for **9b**. Hydrogen atoms are omitted for clarity.

It has been found that two PMe_2Ph ligands cis to the organodinitrogen ligand in **1** and **2** are readily replaced by a bidentate phosphine $Ph_2PCH_2CH_2PPh_2$ (dppe) to give $[PPh_4][WCl(NNC_4H_4)(dppe)(\mu\text{-}S)_2WS_2]$ (**11**) or $[PPh_4][WCl(NN{=}CRR')(dppe)(\mu\text{-}S)_2WS_2]$ (**12a**: R = R′ = Me; **12b**: R = Me, R′ = Ph) (Scheme 2). Structures of these complexes are essentially similar to those of the corresponding PMe_2Ph complexes, as confirmed by the preliminary X-ray diffraction study of **12a** (see Experimental part).



Scheme 2.

As expected, treatment of **12b** with 0.5 equiv of [RhCl(cod)]$_2$ afforded the trinuclear bimetallic complex [WCl(NN=CMePh)(dppe)(μ-S)$_2$W(μ-S)$_2$Rh(cod)] (**13**) (Scheme 2), which has been fully characterized by the X-ray analysis. Besides numerous di- or trinuclear complexes containing one or two terminal (μ-S)$_2$MS$_2$ moieties (M = Mo, W), trinuclear complexes with a (μ-S)$_2$M(μ-S)$_2$ bridge are well precedented.[11] For example, [{Rh(cod)(μ-S)$_2$}$_2$W] (**14**) is known as the related W–Rh complex.[12] However, trinuclear complexes containing two different metal units bridged by (μ-S)$_2$M(μ-S)$_2$ are relatively rare.[13]

X-Ray Structure of 13. Single crystals of **13** contain two crystallographically independent molecules whose structures are almost identical. An ORTEP drawing of molecule 1 is shown in Fig. 5, while selected bond distances and angles are listed in Table 5. Complex **13** contains one distorted octahedral W atom, one tetrahedral W atom, and a square planar Rh atom, where the W–W–Rh linkage is almost linear (173.59(3) and 177.50(3)°) with the W–W distances at 2.8486(6) and 2.845(1) Å and the W–Rh distances of 2.8613(9) and 2.845(2) Å. Complex **13** may be formulated as a W(IV)–W(VI)–Rh(I) species. The observed W–Rh distances are comparable to those in a Rh(I)–W(VI)–Rh(I) complex **14** (2.87 and 2.84 Å;[14] 2.854 Å[12b]) and are only slightly shorter than those in the Rh(III)/W(VI) complexes [{(C$_5$Me$_5$)RhCl(μ-S)$_2$}$_2$W] (2.908(2) and 2.892(2) Å),[14] [(C$_5$Me$_5$)Rh{P(OEt)$_3$}(μ-S)$_2$WS$_2$] (2.9044(7) Å), and [(C$_5$Me$_5$)Rh{P(OEt)$_3$}(μ-S)$_2$W(μ-S)$_2$CuCl] (2.8996(9) Å).[13a] The W$_2$S$_2$ plane is slightly folded with the dihedral angle along the W–W vector of 171—172°, while two WRhS triangles are almost coplanar. Pertinent bonding distances and angles in the diazoalkane ligand are comparable to those in **5a** and the other diazoalkane complexes are shown in Table 2.

Table 5. Selected Bond Distances and Angles in **13**

(a) Bond distance (Å)			
Molecule 1			
W(1)–W(2)	2.8486(6)	W(1)–S(1)	2.407(3)
W(1)–S(2)	2.416(3)	W(2)–Rh(1)	2.8613(9)
W(2)–S(1)	2.224(3)	W(2)–S(2)	2.224(3)
W(2)–S(3)	2.190(3)	W(2)–S(4)	2.199(3)
Rh(1)–S(3)	2.324(3)	Rh(1)–S(4)	2.318(3)
Molecule 2			
W(3)–W(4)	2.845(1)	W(3)–S(5)	2.413(3)
W(3)–S(6)	2.408(3)	W(4)–Rh(2)	2.845(2)
W(4)–S(5)	2.229(3)	W(4)–S(6)	2.233(3)
W(4)–S(7)	2.192(3)	W(4)–S(8)	2.190(3)
Rh(2)–S(7)	2.322(3)	Rh(2)–S(8)	2.311(3)
(b) Bond angle (°)			
Molecule 1			
Cl(1)–W(1)–S(1)	89.64(9)	Cl(1)–W(1)–S(2)	90.24(9)
Cl(1)–W(1)–N(1)	163.7(2)	S(1)–W(1)–S(2)	97.85(9)
S(1)–W(1)–P(1)	167.93(9)	S(1)–W(1)–P(2)	91.73(9)
S(1)–W(1)–N(1)	102.2(2)	S(2)–W(1)–P(1)	89.11(9)
S(2)–W(1)–P(2)	168.87(9)	S(2)–W(1)–N(1)	99.0(2)
P(1)–W(1)–N(1)	86.3(2)	P(2)–W(1)–N(1)	84.4(2)
W(1)–W(2)–Rh(1)	173.59(3)	S(1)–W(2)–S(2)	109.65(10)
S(1)–W(2)–S(3)	111.4(1)	S(1)–W(2)–S(4)	111.0(1)
S(2)–W(2)–S(3)	110.24(10)	S(2)–W(2)–S(4)	109.1(1)
S(3)–W(2)–S(4)	105.33(10)	S(3)–Rh(1)–S(4)	97.48(10)
W(1)–S(1)–W(2)	75.81(8)	W(1)–S(2)–W(2)	75.63(8)
W(2)–S(3)–Rh(1)	78.62(9)	W(2)–S(4)–Rh(1)	78.56(9)
Molecule 2			
Cl(2)–W(3)–S(5)	89.95(10)	Cl(2)–W(3)–S(6)	89.11(10)
Cl(2)–W(3)–N(3)	164.4(3)	S(5)–W(3)–S(6)	98.60(10)
S(5)–W(3)–P(3)	169.33(10)	S(5)–W(3)–P(4)	89.14(9)
S(5)–W(3)–N(3)	99.4(3)	S(6)–W(3)–P(3)	90.3(1)
S(6)–W(3)–P(4)	167.06(9)	S(6)–W(3)–N(3)	101.7(3)
P(3)–W(3)–N(3)	84.4(3)	P(4)–W(3)–N(3)	87.1(3)
W(3)–W(4)–Rh(2)	177.50(3)	S(5)–W(4)–S(6)	110.0(1)
S(5)–W(4)–S(7)	111.4(1)	S(5)–W(4)–S(8)	108.4(1)
S(6)–W(4)–S(7)	111.1(1)	S(6)–W(4)–S(8)	110.2(1)
S(7)–W(4)–S(8)	105.7(1)	S(7)–Rh(2)–S(8)	97.9(1)
W(3)–S(5)–W(4)	75.49(8)	W(3)–S(6)–W(4)	75.49(8)
W(4)–S(7)–Rh(2)	78.07(9)	W(4)–S(8)–Rh(2)	78.34(9)

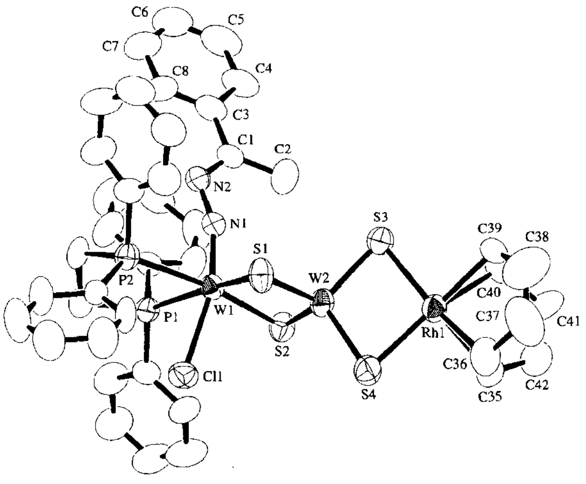


Fig. 5. ORTEP drawing of molecule 1 for **13**. Hydrogen atoms are omitted for clarity.

Experimental

General. All manipulations were carried out under an atmosphere of N$_2$. IR and NMR spectra were recorded on JASCO FT/IR-420 and JEOL EX-270 spectrometers. The signals due to the aromatic protons are omitted in the following ^{1}H NMR data. Elemental analyses were done with a Perkin–Elmer 2400 series II CHN analyzer. Amounts of solvating molecules in the crystals were determined by X-ray crystallography, NMR measurement, and/or GLC analysis. Complexes **4**,[6a] **5**,[7,9] and [RhCl(cod)]$_2$[15] were prepared according to the published methods, while **3** and tetraalkylthiuram disulfides were commercially obtained and used as received.

Preparation of 4. A solution containing **1** (500 mg, 0.667 mmol) and **3** (660 mg, 0.666 mmol) in acetonitrile (50 ml) was heated at 60 °C for 24 h. Then, the solvent was removed under reduced pressure and the residue was washed with ethanol and ether. The orange solid which remained was crystallized from acetonitrile–ether (30 ml/40 ml). Red crystals. Yield: 580 mg (71%). Found: C, 42.93; H, 3.62; N, 2.06%. Calcd for C$_{44}$H$_{46}$N$_2$ClP$_3$S$_4$W$_2$: C, 43.06; H, 3.78; N, 2.28%. ^{1}H NMR (CDCl$_3$) δ = 1.80 and 2.14 (d, $J_{\text{P-H}}$ = 8.9 Hz, 6H each, PMe), 5.37 and 5.53 (t, J = 2.2 Hz, 2H each, C$_4$H$_4$). ^{31}P{^{1}H} NMR (CDCl$_3$) δ = −23.4 (s, $J_{\text{W-P}}$ = 261 Hz, 2P, PMe$_2$Ph), 22.6 (s, 1P, PPh$_4^+$).

Preparation of 5. Complexes **5** were prepared from corresponding **2** and an equimolar amount of **3** by a procedure similar to that for preparing **4**, except for the reaction time (8 h for **5a** and **5b** or 12 h for **5c**).

5a. Red crystals. Yield: 74%. Found: C, 42.28; H, 3.92; N, 2.31%. Calcd for $C_{43}H_{48}N_2ClP_3S_4W_2$: C, 42.43; H, 3.97; N, 2.30%. ^1H NMR ($CDCl_3$) $\delta = 0.76$ and 1.05 (s, 3H each, $NCMe_2$), 1.71 and 2.29 (d, $J_{P-H} = 8.9$ Hz, 6H each, PMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = -23.0$ (s, $J_{W-P} = 257$ Hz, 2P, PMe_2Ph), 22.6 (s, 1P, PPh_4^+). IR (KBr) ν(C=N) 1582 cm^{-1}.

5b. Brown crystals. Yield: 75%. Found: C, 44.81; H, 3.84; N, 2.18%. Calcd for $C_{48}H_{50}N_2ClP_3S_4W_2$: C, 45.07; H, 3.94; N, 2.19%. ^1HNMR ($CDCl_3$) $\delta = 1.07$ (s, 3H, NCMe), 1.75 and 2.30 (d, $J_{P-H} = 8.9$ Hz, 6H each, PMe). $^{31}P\{^1H\}$NMR ($CDCl_3$) $\delta = -23.2$ (s, $J_{W-P} = 252$ Hz, 2P, PMe_2Ph), 22.6 (s, 1P, PPh_4^+). IR (KBr) ν(C=N) 1518 cm^{-1}.

5c. Brown-green crystals. Yield: 11%. Found: C, 45.03; H, 3.85; N, 2.40%. Calcd for $C_{48}H_{50}N_2ClP_3S_4W_2$: C, 45.07; H, 3.94; N, 2.19%. ^1HNMR ($CDCl_3$) $\delta = 1.81$ and 2.22 (d, $J_{P-H} = 8.8$ Hz, 6H each, PMe), 2.20 (s, 3H, C_6H_4Me), 7.42 (s, 1H, NN=CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = -23.2$ (s, $J_{W-P} = 257$ Hz, 2P, PMe_2Ph), 22.6 (s, 1P, PPh_4^+). IR (KBr) ν(C=N) 1530 cm^{-1}.

Preparation of 7. An acetonitrile solution (10 ml) containing **1** (147 mg, 0.196 mmol) and **3** (99 mg, 0.10 mmol) was heated at 60 °C for 110 h and then volatile materials were evaporated under reduced pressure. ^1H NMR spectrum showed that the residue contained **7**, **4**, and **1** in a molar ratio of 5 : 1 : 1. After washing with ether, the resulting brown solid was extracted with ether–benzene (12 ml/3 ml). The extract was dried up and the residue was crystallized from CH_2Cl_2–hexane to give red crystals of **7**·7/4CH_2Cl_2 (55 mg, 35%). Found: C, 31.25; H, 3.52; N, 3.18%. Calcd for $C_{41.75}H_{55.5}N_4Cl_{5.5}P_4S_4W_3$: C,31.11; H, 3.47; N, 3.48%. ^1HNMR ($CDCl_3$) $\delta = 1.94$ and 2.01 (d, $J_{P-H} = 9.4$ Hz, 6H each, PMe), 2.29 (d, 12H, $J_{P-H} = 8.9$ Hz, 12H, PMe), 5.58 and 5.77 (t, $J = 2.3$ Hz, 2H each, C_4H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = -21.6$ (d, $J_{P-P} = 21$ Hz, $J_{W-P} = 269$ Hz, 2P, PMe_2Ph), -20.3 (d, $J_{P-P} = 21$ Hz, $J_{W-P} = 274$ Hz, 2P, PMe_2Ph).

Preparation of 8. A mixture containing **2b** (160 mg, 0.200 mmol) and **3** (99 mg, 0.099 mmol) in acetonitrile (10 ml) was refluxed for 20 h. After the solvent was evaporated in vacuo, the residue was washed with ethanol (10 ml) and ether (3 ml), and then extracted with ether (130 ml). The extract was dried up and the residue was crystallized from CH_2Cl_2–hexane to give brown crystals of **8**·1/2CH_2Cl_2 (15 mg, 9% yield). Found: C, 35.78; H, 3.83; N, 3.14%. Calcd for $C_{48.5}H_{61}N_4Cl_3P_4S_4W_3$: C, 36.18; H, 3.82; N, 3.48%. ^1HNMR ($CDCl_3$) $\delta = 1.35$ (s, 6H, NCMe), 1.73, 2.06, 2.36, and 2.42 (d, $J_{P-H} = 9.0$ Hz, 6H each, PMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = -21.7$ (d, $J_{P-P} = 23$ Hz, $J_{W-P} = 262$ Hz, 2P, PMe_2Ph), -21.0 (d, $J_{P-P} = 23$ Hz, $J_{W-P} = 266$ Hz, 2P, PMe_2Ph). IR (KBr) ν(C=N) 1521 cm^{-1}.

Preparation of 9a. To a solution of **4** (123 mg, 0.100 mmol) in acetonitrile (15 ml) was added tetraethylthiuram disulfide (30 mg, 0.099 mmol) at 0 °C. The mixture was continuously stirred at 0 °C for 7 h and then at room temperature for 19 h. After the solvent was evaporated in vacuo, the residue was washed with ether and then extracted with benzene (20 ml). The extract was dried up and the residue was crystallized from CH_2Cl_2–hexane to give red crystals of **9a** (22 mg, 22% yield). Found: C, 27.38; H, 3.56; N, 5.44%. Calcd for $C_{22}H_{35}N_4PS_7W_2$: C, 27.00; H, 3.60; N, 5.72%. ^1HNMR ($CDCl_3$) $\delta = 1.08$, 1.15, 1.40, and 1.42 (t, $J = 7.1$ Hz, 3H each, CH_2CH_3), 2.03 (d, $J_{P-H} = 8.6$ Hz, 3H, PMe), 2.34 (d, $J_{P-H} = 9.0$ Hz, 3H, PMe), 3.21 and 3.61 (dq, $J = 14.0$ and 7.1 Hz, 1H each, CH_2CH_3), 3.40—3.55 (m, 2H, CH_2CH_3), 3.80—4.05 (m, 4H, CH_2CH_3), 5.76 and 6.42 (t, $J = 2.3$ Hz, 2H each, C_4H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = -23.4$ (s, $J_{W-P} = 204$ Hz, PMe_2Ph). IR (KBr) $\nu(S_2CN)$ 1536 and 1502; ν(W=S) 512 cm^{-1}.

Complexes **9b** and **10** were prepared similarly, except that the final crystallization was carried out from benzene–hexane.

9b·1/4C_6H_6. Orange red crystals. Yield: 40%. Found: C, 31.62; H, 4.31; N, 5.28%. Calcd for $C_{27.5}H_{44.5}N_4PS_7W_2$: C, 31.33; H, 4.25; N, 5.31%. ^1HNMR ($CDCl_3$) $\delta = 0.9$—2.0 (overlapping m, 24H, NCH*Me*), 2.05 (d, $J_{P-H} = 8.6$ Hz, 3H, PMe), 2.32 (d, $J_{P-H} = 9.0$ Hz, 3H, PMe), 3.5—5.5 (m, 4H, NC*H*), 5.74 and 6.41 (t, $J = 2.2$ Hz, 2H each, C_4H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = -23.7$ (s, $J_{W-P} = 204$ Hz, PMe_2Ph). IR (KBr) $\nu(S_2CN)$ 1515 and 1470; ν(W=S) 514 cm^{-1}.

10. Brown crystals. Yield: 21%. Found: C, 26.55; H, 3.88; N, 5.66%. Calcd for $C_{21}H_{37}N_4PS_7W_2$: C, 26.04; H, 3.85; N, 5.78%. ^1HNMR ($CDCl_3$) $\delta = 1.03$, 1.08, 1.387, and 1.394 (t, $J = 7.2$ Hz, 3H each, CH_2CH_3), 1.53 and 1.54 (s, 3H each, NNCMe), 2.29 and 2.39 (d, $J_{P-H} = 9.0$ Hz, 3H each, PMe), 3.10 and 3.39 (dq, $J = 11.1$ and 7.0 Hz, 1H each, CH_2CH_3), 3.45—3.60 (m, 2H, CH_2CH_3), 3.75—4.05 (m, 4H, CH_2CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = -21.9$ (s, $J_{W-P} = 201$ Hz, PMe_2Ph). IR (KBr) ν(C=N) 1580; $\nu(S_2CN)$ 1530 and 1496; ν(W=S) 516 cm^{-1}.

Preparation of 11. A DMF solution (3 ml) containing **4** (122 mg, 0.0997 mmol) and dppe (59 mg, 0.15 mmol) was stirred at room temperature for 27 h. After the volatile materials were evaporated in vacuo, the residue was washed with ether and then extracted with acetonitrile (6 ml). Addition of ether to the concentrated extract afforded orange-red crystals of **11**·MeCN (120 mg, 86%). Found: C, 48.00; H, 3.69; N, 3.03%. Calcd for $C_{56}H_{51}N_3ClP_3S_4W_2$: C, 48.38; H,3.70; N, 3.02%. ^1HNMR (CD_2Cl_2) $\delta = 4.99$ and 5.04 (t, $J = 2.3$ Hz, 2H each, NC_4H_4), 2.95—3.15 and 3.35—3.55 (m, 2H each, PCH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) $\delta = 22.9$ (s, $J_{W-P} = 245$ Hz, dppe); this peak is overlapping with the signal due to PPh_4^+.

Complexes **12** were prepared similarly.

12a·MeCN. Red crystals. Yield: 87%. Found: C, 47.62; H, 3.84; N, 3.03%. Calcd for $C_{55}H_{53}N_3ClP_3S_4W_2$: C, 47.86; H, 3.87; N, 3.04%. ^1HNMR ($CDCl_3$) $\delta = 0.57$ and 0.77 (s, 3H each, NCMe), 2.9—3.4 (m, 4H, PCH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = 24.4$ (s, $J_{W-P} = 240$ Hz, dppe), 22.6 (s, PPh_4^+). IR (KBr) ν(C=N) 1573 cm^{-1}.

12b. Brown crystals. Yield: 77%. Found: C, 48.38; H,3.89; N, 2.08%. Calcd for $C_{58}H_{52}N_2ClP_3S_4W_2$: C, 49.71; H, 3.74; N, 2.00%. ^1HNMR (CD_2Cl_2) $\delta = 0.87$ (s, 3H, NCMe), 3.1—3.5 (m, 4H, PCH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) $\delta = 23.3$ (s, $J_{W-P} = 233$ Hz, dppe), 22.9 (s, PPh_4^+). IR (KBr) ν(C=N) 1521 cm^{-1}. Although this compound was obtained as spectroscopically pure crystals, the C analysis data were somehow not satisfactory even after the repeated purification.

Preparation of 13. To a suspension of **12b** (72 mg, 0.051 mmol) in acetonitrile (5 ml) was added $[RhCl(cod)]_2$ (13 mg, 0.026 mmol) and then the mixture was stirred at room temperature for 6 h. A brown-yellow solid precipitated, which was filtered off and washed with acetonitrile and ether. Crystallization of the remaining solid from CH_2Cl_2–hexane afforded brown crystals of **13**·1/2CH_2Cl_2 (46 mg, 69%). Found: C, 38.98; H, 3.50; N, 2.47%. Calcd for $C_{42.5}H_{45}N_2Cl_2P_2RhS_4W_2$: C, 38.80; H, 3.45; N, 2.13%. ^1HNMR ($CDCl_3$) $\delta = 0.88$ (s, 3H, NCMe), 2.57 (br. s, 8H, CH_2 in cod), 3.3—3.5 (m, 4H, PCH_2), 5.75 and 5.92 (br. s, 2H each, CH=CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = 25.8$ (s, $J_{W-P} = 243$ Hz). IR (KBr) ν(C=N) 1519 cm^{-1}.

X-Ray Crystallographic Studies. Single crystals were sealed

Table 6. Crystallographic Data for **4**, **5a**, **7**·7/4CH$_2$Cl$_2$, **9b**·1/4C$_6$H$_6$, **13**·1/2CH$_2$Cl$_2$

	4	**5a**	**7**·7/4CH$_2$Cl$_2$	**9b**·1/4C$_6$H$_6$	**13**·1/2CH$_2$Cl$_2$
Formula	$C_{44}H_{46}ClN_2P_3S_4W_2$	$C_{43}H_{48}ClN_2P_3S_4W_2$	$C_{41.75}H_{55.5}Cl_{5.5}N_4P_4S_4W_3$	$C_{27.5}H_{44.5}N_4PS_7W_2$	$C_{42.5}H_{45}Cl_2N_2P_2RhS_4W_2$
Formula weight	1227.18	1217.18	1612.10	1054.27	1315.54
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a/Å	10.491(5)	10.456(4)	15.533(2)	11.029(2)	12.189(7)
b/Å	30.014(5)	29.872(2)	19.084(3)	17.11(1)	15.725(3)
c/Å	15.264(5)	15.421(2)	21.004(2)	22.136(6)	24.491(4)
α/deg	90	90	106.499(9)	101.24(4)	92.79(2)
β/deg	103.27(3)	103.22(2)	105.789(8)	101.30(2)	94.43(3)
γ/deg	90	90	91.47(1)	101.64(2)	100.84(3)
V/Å^3	4678(2)	4688(1)	5708(1)	3891(3)	4586(2)
Z	4	4	4	4	4
ρ_{calc}/g cm^{-3}	1.742	1.724	1.875	1.799	1.905
$F(000)$	2392	2376	3094	2050	2540
μ_{calc}/cm^{-1}	52.91	52.78	65.85	63.55	57.65
Transmn factor	0.2664—0.9988	0.6368—0.9997	0.6882—1.0000	0.3039—0.9991	0.9026—0.9999
Cryst size/mm^3	0.7 × 0.7 × 0.1	0.7 × 0.3 × 0.2	0.7 × 0.4 × 0.3	0.6 × 0.25 × 0.1	0.5 × 0.15 × 0.1
Scan type	ω	ω	ω–2θ	ω	ω
2θ range/deg	5—55	5—55	5—45	5—45	5—50
No. measd.	11536	11569	15484	10683	12919
No. unique	10958	10988	14943	10054	12073
No. obsd. ($I > 3.0\sigma(I)$)	6137	7103	12312	6627	8171
No. var.	533	497	1136	749	1010
$R^{a)}$	0.043	0.041	0.033	0.043	0.032
$R_w{}^{b)}$	0.027	0.041	0.040	0.044	0.030
GOF	1.58	1.59	1.92	1.59	1.40
Residual peaks (e$^-$/Å^{-3})	1.42, −1.09	2.08, −1.48	3.31, −1.61	1.94, −1.56	1.07, −0.70

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

in glass capillaries under Ar, which were transferred to a Rigaku AFC7R diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ source. Diffraction studies were done at room temperature. Orientation matrices and unit cell parameters were determined by a least-squares fit of 25 reflections with $35<2\theta<40°$. The intensities of 3 check reflections were monitored every 150 reflections during data collection, which revealed no significant decay for all crystals. Intensity data were corrected for Lorentz and polarization effects and for absorption (ψ scans). Details of crystal and data collection parameters are summarized in Table 6.

Structure solution and refinements were carried out by using a teXsan program package.[16] The positions of non-hydrogen atoms were determined by Patterson methods and subsequent Fourier syntheses (DIRDIF PATTY),[17] which were refined anisotropically by full-matrix least-squares techniques. The Ph group on P(2) in **4** was refined as two disordered moieties with 0.6 and 0.4 occupancies. On the other hand, for **13** one of the two Cl atoms in the solvating CH_2Cl_2 was found in two disordered positions and refined with fixed Cl–C–Cl angles. Hydrogen atoms were placed at the calculated positions and included in the final stages of refinements with fixed parameters.[18]

The X-ray analysis has also been carried out similarly for **12b**. Although the structure of the molecule could be solved and refined to the satisfactory level, one unassignable peak remained at the position far apart from the molecule of **12b**. Crystallographic data for **12b** are as follows, where the unknown peak was tentatively assigned as O and refined anisotropically: $a = 11.304(3)$, $b = 14.685(6)$, $c = 20.33(1)$ Å, $\alpha = 72.03(4)°$, $\beta = 82.63(4)°$, and $\gamma = 73.07°$ with $Z = 2$ in space group $P\bar{1}$ (No. 2). R (R_w) = 0.049 (0.067) for 7391 data with $I>3.0\sigma(I)$.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 137418-137421.

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18 Figures of the whole views with atom-numbering scheme, the tables listing atom coordinates, anisotropic thermal parameters of non-hydrogen atoms,extensive bond distances and angles, and complete F_o-F_c data for **4**, **5a**, **7**$\cdot$7/4CH_2Cl_2, **9b**$\cdot$1/4C_6H_6, and **13**$\cdot$1/2CH_2Cl_2 are deposited as Document No. 73014 at the Office of the Editor of Bull. Chem. Soc. Jpn.