Preparation of a bis(hydrosulfido) complex of Mo having a tetraphosphine co-ligand and its transformation into MoRh₂ and MoIr₂ mixed-metal sulfido clusters[†]

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The treatment of a Mo(0) complex with a tetraphosphine co-ligand $[Mo(\kappa^4-P4)(Ph_2PCH_2CH_2PPh_2)]$ (P4 = meso-o-C₆H₄(PPhCH₂CH₂PPh₂)₂) with H₂S gas in toluene at room temperature afforded [Mo(SH)₂(κ^4 -P4)] (1), which demonstrates the first Mo(II) bis(hydrosulfido) complex. Its trigonal-prismatic structure rarely observed for Mo(II) complexes has been determined by X-ray analysis. The reactions of 1 with [RhCl(CO)₂]₂ and [IrCl(CO)₂(*p*-toluidine)] in the presence of NEt₃ resulted in the formation of the sulfido-bridged trinuclear clusters [Mo(κ^4 -P4)(μ_3 -S)₂{Rh(CO)₂}₂] (4) and [Mo(κ^4 -P4)(μ_3 -S)₂{Ir(CO)₂}₂] (5), respectively. The X-ray diffraction study has disclosed that the MoRh₂ cluster 4 in the solid state exists in two isomeric forms arising from the different orientation of P4 to the trigonal-prismatic Mo center, whereas the crystals of the Ir analogue 5 contains the molecules corresponding to only one of the two isomers observed for 4. The fluxional features of 1, 4, and 5 in solution have been confirmed by VT NMR studies.

Introduction

Hydrosulfido complexes are attracting much attention because of their relevance to the active sites of commercial hydrodesulfurization catalysts as well as certain metalloenzymes.¹ Recent studies in this laboratory have demonstrated the importance of hydrosulfido complexes as precursors in the synthesis of sulfido-bridged homo- and heterometallic clusters.² Thus, the dinuclear µ-bis(hydrosulfido) complexes such as [(Cp*MCl)₂(µ-SH)₂] (M = Ru, Rh, Ir; Cp^{*} = η^5 -C₅Me₅) and [(RuLCl)₂(μ -SH)₂] (L = π -arene) have turned out to be readily converted into a variety of homo- and heterometallic µ-sulfido clusters with the nuclearities ranging from 3 to 10 by treatment with numerous transition metal and main-group metal species.^{2,3} On the other hand, examples of well-defined mononuclear bis(hydrosulfido) complexes are still limited and their transformations into sulfur-bridged multinuclear complexes have barely been explored.1,4

In this paper, we wish to report the synthesis of a new bis(hydrosulfido) complex of Mo containing a linear tetraphosphine co-ligand, $[Mo(SH)_2(\kappa^4-P4)]$ (1; P4 = *meso-o*-C₆H₄(PPhCH₂CH₂PPh₂)₂), and its reaction with Rh and Ir complexes, affording sulfido-bridged MoRh₂ and MoIr₂ clusters. The facile formation of new, early to late, Group 6 to Group 9, mixed-metal sulfido clusters observed here are noteworthy, as it may lead to the syntheses of a number of homo- and heterobimetallic clusters of a new class.

Table 1 Selected bond distances (Å) and angles (°) in 1 $\,$

| | 0.455(1) | | 2 200/1) |
|--------------|-----------|--------------|-----------|
| Mo-S(1) | 2.455(1) | Mo-S(2) | 2.389(1) |
| Mo-P(1) | 2.4713(8) | Mo-P(2) | 2.4333(8) |
| Mo-P(3) | 2.4292(8) | Mo-P(4) | 2.4659(8) |
| S(1)-Mo-S(2) | 77.50(3) | S(1)-Mo-P(1) | 85.90(3) |
| S(1)-Mo-P(2) | 138.42(3) | S(1)–Mo–P(3) | 144.82(3) |
| S(1)–Mo–P(4) | 87.00(4) | S(2)-Mo-P(1) | 137.73(3) |
| S(2)-Mo-P(2) | 91.45(3) | S(2)-Mo-P(3) | 91.28(3) |
| S(2)–Mo–P(4) | 130.21(3) | P(1)-Mo-P(2) | 75.71(2) |
| P(1)-Mo-P(3) | 121.98(2) | P(1)-Mo-P(4) | 86.56(3) |
| P(2)-Mo-P(3) | 74.09(2) | P(2)-Mo-P(4) | 127.73(3) |
| P(3)-Mo-P(4) | 74.96(3) | | |
| | | | |

Results and discussion

Preparation and characterization of 1

The Mo(0) complex [Mo(κ^4 -P4)(dppe)] (2; dppe = Ph₂PCH₂CH₂-PPh₂) which is obtained from the reaction of trans- $[Mo(N_2)_2(dppe)_2]$ with dppe under forcing conditions through the condensation of two dppe ligands in the coordination sphere of Mo,⁵ has been proven to react with a number of substrate molecules to give a variety of Mo(0) and Mo(II) complexes with the P4 co-ligand, which is bonded to the Mo center in either κ^4 , κ^3 , or κ^2 fashion.^{5,6} These include the formation of dihalido complexes $[MoX_2(\kappa^4-P4)]$ (X = Cl (3), Br) by treatment of 2 with PhCH₂X, having a trigonal-prismatic geometry rarely observed for Mo(II) complexes.^{6a} Now we have found that the reaction of 2 with H_2S gas in toluene at room temperature affords cleanly the Mo(II) complex 1 as a green solid in 93% yield (Scheme 1). The structure of 1 in the solid state has been determined by X-ray analysis using a single crystal grown from CH₂Cl₂-hexane, which is shown in Fig. 1 and Table 1.

Complex 1 has a trigonal-prismatic structure analogous to 3, however, the orientation of P4 differs. Thus, as depicted in

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Fig. 1 An ORTEP drawing for 1 at 30% probability level. Hydrogen atoms except for the SH protons are omitted for clarity.



Scheme 1 Reactions of 2 with H_2S gas (this work) and PhCH₂X.^{6a}

Scheme 1, two inner P atoms of P4 are present in the same basal triangular plane in 1, whereas they occupy the site of different basal planes in 3. Despite the difference in the orientation of binding, the interatomic angles associated with P4 are almost comparable: e.g., the P(1)-Mo-P(2), P(2)-Mo-P(3), P(3)-Mo-P(4), and P(1)-Mo-P(4) angles in 1 are 75.71(2), 74.09(2), 74.96(3), and 86.56(3)°, while those in **3** are 73.16(2), 73.30(2), 74.32(2), and 90.20(2)°, respectively. The Mo-P bond lengths in 1 are in the range of 2.4292(8)-2.4713(8) Å and are somewhat longer than those of the chloro complex **3** (2.3792(7)–2.4499(5) $Å^{6a}$), but are not exceptional for the Mo-P bond lengths in the phosphine complexes. The S-Mo-S angle in 1 at 77.50(3)° is slightly smaller than the Cl-Mo-Cl angle in 3 at $81.14(2)^\circ$, where the Mo-S(1) distance at 2.455(1) Å associated with the S atom comprising the basal plane with two terminal P atoms, P(1) and P(4), is significantly longer than the other Mo–S(2) distance at 2.389(1) Å. Consistent with this X-ray structure, the IR spectrum of 1 (KBr method)

displays two characteristic bands assignable to v(SH) at 2537 and 2487 cm⁻¹. For comparison, the v(SH) values of the Mo hydrosulfido complexes were reported for some Mo(IV) complexes, *e.g.* 2498 cm⁻¹ for [Cp₂Mo(SH)₂],⁷ 2480 cm⁻¹ for [Mo(SH)(S₂CNEt₂)₃],⁸ and 2568 cm⁻¹ for [Mo(SH)(=S)(dmpe)₂][OSO₂Me] (dmpe = Me₂PCH₂CH₂PMe₂).⁹

On the other hand, despite the presence of two inequivalent SH protons in the solid state, the ¹H NMR spectrum of **1** in CD₂Cl₂ at 20 °C showed only one quintet at δ 1.53 ppm, while the ³¹P{¹H} NMR spectrum at the same temperature exhibited two multiplets of the AA'XX' pattern at δ 131.2 and 91.8 ppm, assignable to the inner and outer P atoms, respectively. These spectral features may be interpreted in terms of the pseudo rotation of the P4 ligand around the Mo center in addition to the accidental coincidence of the coupling constants of the SH protons with the inner P atoms and the terminal P atoms. Although the ¹H NMR spectra were recorded at lower temperatures, only the broadening of the SH signal was observed, indicating that **1** is still fluxional even at -70 °C (*vide infra*).

It is to be noted that **1** demonstrates the first Mo(II) hydrosulfido complex to be fully characterized. As the related reaction, treatment of $[Mo(PMe_3)_6]$ with H₂S was claimed to result in the initial formation of $[MoH_2(SH)_2(PMe_3)_4]$, although it was not confirmed because of its immediate conversion into *trans*- $[Mo(=S)_2(PMe_3)_4]$.¹⁰ On the other hand, the W analogue $[WH_2(SH)_2(PMe_3)_4]$ was able to be spectroscopically characterized, but it was not isolable due to the similar rapid conversion into *trans*- $[W(=S)_2(PMe_3)_4]$.¹¹

Preparation and characterization of MoRh₂ and MoIr₂ sulfido clusters

When the bis(hydrosulfido) complex 1 was allowed to react with one equivalent of [RhCl(CO)₂]₂ in CH₂Cl₂ in the presence of excess NEt₃ initially at -78 °C and then with gradual warming to room temperature, a sulfido-bridged Mo(11)Rh(1)₂ cluster [Mo(κ^4 -P4)(μ_3 -S)₂{Rh(CO)₂}₂] (4) was isolated in 44% yield after crystallization from CH₂Cl₂-hexane (Scheme 2). The product is a mixture of black crystals of two different shapes and the subsequent X-ray diffraction study of these two different shaped crystals has revealed that the one with rhomboidal faces contains the molecule 4a shown in Fig. 2, while the other has rectangular faces consisting of its isomer 4b depicted in Fig. 3. Interatomic distances and angles therein are listed in Tables 2 and 3, respectively.

Table 2Selected interatomic distances (Å) in 4a, 4b, and 5

| | 4a (M = Rh) | $\mathbf{4b}\left(M=Rh\right)$ | 5 (M = Ir) | |
|---------------------|-------------|--------------------------------|------------|--|
| M(1)-M(2) | 2.9626(4) | 2.970(2) | 2,9856(6) | |
| $Mo \cdots M(1)$ | 3.2325(3) | 3.208 (2) | 3.1436(7) | |
| $Mo \cdots M(2)$ | 3.1430(3) | 3.281(1) | 3.2325(8) | |
| Mo-S(1) | 2.4693(9) | 2.487(3) | 2.468(2) | |
| Mo-S(2) | 2.4417(8) | 2.478(3) | 2.452(2) | |
| Mo-P(1) | 2.4929(8) | 2.494(3) | 2.502(2) | |
| Mo-P(2) | 2.4558(9) | 2.415(3) | 2.471(2) | |
| Mo-P(3) | 2.4490(9) | 2.452(3) | 2.451(2) | |
| Mo-P(4) | 2.4656(8) | 2.433(3) | 2.479(2) | |
| $M(1) - \hat{S}(1)$ | 2.338(1) | 2.347(4) | 2.352(3) | |
| M(1) - S(2) | 2.3311(9) | 2.320(3) | 2.349(2) | |
| M(2) - S(1) | 2.3359(8) | 2.346(3) | 2.357(2) | |
| M(2)-S(2) | 2.3271(9) | 2.330(3) | 2.339(2) | |



Scheme 2 Structures of MoRh₂ and Molr₂ sulfido dusters 4 and 5 in the crystalline form.

Table 3 Selected bond angles (°) in 4a, 4b, and 5

| | $4a \ (M = Rh)$ | $\textbf{4b}\left(M=Rh\right)$ | 5 (M = Ir) |
|-------------------|-----------------|--------------------------------|------------|
| $M_{0}-S(1)-M(1)$ | 84.46(3) | 83.1(1) | 84.21(9) |
| Mo-S(1)-M(2) | 81.65(2) | 85.5(1) | 81.29(9) |
| Mo-S(2)-M(1) | 85.23(2) | 83.9(1) | 84.61(8) |
| Mo-S(2)-M(2) | 82.42(2) | 86.0(1) | 81.99(8) |
| M(1)-S(1)-M(2) | 78.67(2) | 78.5(1) | 78.70(8) |
| M(1)-S(2)-M(2) | 78.99(3) | 79.4(1) | 79.12(8) |
| S(1) - Mo - S(2) | 78.29(2) | 76.7(1) | 78.95(8) |
| P(1)-Mo-P(2) | 74.17(2) | 73.4(11) | 73.92(8) |
| P(1)-Mo-P(3) | 130.91(2) | 141.33(1) | 131.01(8) |
| P(1)-Mo-P(4) | 86.97(2) | 89.2(1) | 87.15(8) |
| P(2)-Mo-P(3) | 74.29(2) | 76.0(1) | 74.32(9) |
| P(2)-Mo-P(4) | 118.31(2) | 105.3(1) | 118.14(8) |
| P(3)-Mo-P(4) | 76.17(2) | 76.6(1) | 76.22(8) |
| S(1)-M(1)-S(2) | 83.22(3) | 82.6(1) | 83.39(9) |
| S(1)-M(2)-S(2) | 83.35(3) | 82.4(1) | 83.52(9) |



Fig. 2 An ORTEP drawing for **4a** at 30% probability level. All hydrogens as well as the phenyl carbons (except for *ipso*-carbons) are omitted for clarity.

Both **4a** and **4b** are 48-electron clusters containing one trigonalprismatic Mo(II) and two square-planar Rh(I) centers. The P4



Fig. 3 An ORTEP drawing for **4b** at 30% probability level. All hydrogens as well as the phenyl carbons (except for *ipso*-carbons) are omitted for clarity.

ligand in 4a is bound to Mo in a manner that the two inner P atoms are included in the same basal triangle around Mo, whereas in 4b the two inner P atoms are located in the different triangular planes. These orientations of P4 in the former and the latter correspond to those in 1 and 3, respectively. The corresponding P-Mo-P chelating angles in 4a and 4b are well comparable, but despite the pseudo $C_{\rm s}$ symmetrical structure for both compounds the difference between the P(1)-Mo-P(3) and P(2)-Mo-P(4) angles in **4b** of 36° is much larger than that in **4a** of 13°, indicating the presence of considerable distortion with respect to the coordination of four P atoms in 4b as compared to 4a. This feature is also confirmed by much larger deviations of the P atoms from the least-squares plane defined by four P atoms in 4b at +0.30, -0.36, +0.39, and -0.30 Å for P(1), P(2), P(3), and P(4) in contrast to those at +0.11, -0.13, +0.13 and -0.11 Å in 4a. For comparison, these values in the less distorted 1 are +0.05, -0.06, +0.06, and -0.07 Å, respectively.

The Mo–Rh separations in the range 3.14–3.28 Å are presumed to be indicative of the absence of significant bonding interactions between Mo and Rh atoms, while the Rh–Rh distances at 2.9625(5) and 2.970(2) Å in **4a** and **4b**, respectively, might suggest that weak interactions are present between the two Rh atoms. The IR and NMR spectra in solution recorded independently for **4a** and **4b** are identical, which is interpreted in terms of the rapid interconversion between these two structures due to the fluxional feature involving the pseudo rotation of P4 around Mo for **4** (*vide infra*).

The Ir analogue $[Mo(\kappa^4-P4)(\mu_3-S)_2\{Ir(CO)_2\}_2](5)$ was prepared from the reaction of 1 with two equivalents of $[IrCl(CO)_2(p-$ toluidine)] according to the analogous procedure to that for preparing 4, except that THF was used as solvent to dissolve the latter in addition to CH₂Cl₂ for 1. In the case of 5, however, isolated crystals contained only the molecule that is isostructural with 4a (Scheme 2). The ORTEP drawing is shown in Fig. 4, while the selected interatomic distances and angles are listed in Tables 2 and 3. The Ir–Ir and Ir–S distances in 5 are longer than the Rh–Rh and Rh–S distances in 4a, but only slightly, and the deviations of P atoms of P4 from the least-squares plane defined by these four P atoms at +0.10, -0.16, +0.16, and -0.10 Å observed for P(1), P(2), P(3), and P(4) are almost identical with those for 4a.



Fig. 4 An ORTEP drawing for **5** at 30% probability level. All hydrogens as well as the phenyl carbons (except for *ipso*-carbons) are omitted for clarity.

The IR spectrum of **5** in CH₂Cl₂ displayed three characteristic v(CO) bands at 2032, 2010, and 1959 cm⁻¹, which are considerably lower than those of the Rh analogue **4** at 2043, 2024, and 1976 cm⁻¹, as expected from the greater electron-donating ability of the Ir(1) center than Rh(1). This difference corresponds well to that observed previously between $[Cp^{u_2}Zr(\mu_3-S)_2\{Rh(CO)_2\}_2]$ ($Cp^{u} = \eta^5$ -1,3-¹Bu₂C₃H₃) and its Ir analogue: 2066, 2041, and 1994 cm⁻¹ for the former and 2056, 2027, and 1979 cm⁻¹ for the latter.^{4h} The ³¹P{¹H} NMR spectrum recorded at room temperature is essentially similar to that of **4** and the VT NMR study has revealed the fluxional behavior for **5** as described below.

Fluxional feature of 1, 4, and 5 in solution

As demonstrated by X-ray analysis, two SH protons in 1 are inequivalent in the solid form. However, these protons are recorded in its ¹H NMR spectrum at room temperature as one quintet at δ 1.53 ppm, indicating the fluxional nature of 1 in solution. As the recording temperature was lowered to -10, -40, and -70 °C, this signal gradually shifted towards the higher field with concurrent severe broadening, but even at -70 °C separation of the peak was not observed. The VT³¹P{¹H} NMR spectra of 1 are in accordance with this finding. Thus, as shown in Fig. 5, the spectrum at 20 °C exhibited two multiplets of AA'XX' pattern at δ 131.2 and 91.8 ppm assignable to inner and terminal P atoms, respectively, which broadened significantly as the temperature decreased, and at -70 °C the signal for the inner P atoms almost coalesced.



VT ${}^{31}P{}^{1}H$ NMR studies were also conducted for 4 and 5. Although 4 exists as two isomeric forms in the solid state as described above, their spectral features in solution are the same. Fig. 6 depicts the ${}^{31}P{}^{1}H$ NMR spectra of 4, which indicates that by lowering the recording temperature to -70 °C both of the two signals due to the inner and terminal P atoms separated into two signals, indicating the presence of two slowly interconverting species at this temperature. This is consistent with the finding about the solid state structures of 4 by X-ray analysis. Similar spectral features were also observed for the Ir analogue 5 as shown in Fig. 7, although two signals assignable to the inner and terminal P atoms are still quite broad even at -70 °C. Based on the structures of two isomers demonstrated for 4 in a well-defined manner by the X-ray analysis, the fluxional feature of 1, 4, and 5 may be interpreted by the rotation of the P4 ligand occurring around the Mo center, which is shown in Scheme 3.





Scheme 3 Fluxional feature observed for 1, 4, and 5 due to the rotation of the P4 ligand around Mo.

Experimental

General comments

All manipulations were carried out under N_2 using standard Schlenk techniques. Solvents were dried by common methods and distilled under N_2 before use. Complexes **2**,⁵ [RhCl(CO)₂]₂,¹² and [IrCl(CO)₂(*p*-toluidine)]¹³ were prepared according to literature procedures, while the chemicals were obtained commercially and used as received except for NEt₃, which was treated with KOH and distilled under N_2 before use.

IR spectra were recorded on a JASCO FT/IR-420 spectrometer, while ¹H and ³¹P{¹H} NMR spectra were obtained from a JEOL alpha-400 spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 series II CHN analyzer.

Preparation of complexes

Synthesis of 1. Through a stirred suspension of 2 (1.80 g, 1.39 mmol) in toluene (50 mL), H_2S gas was bubbled for 15 min,

and the mixture was stirred continuously for 2 h under H₂S atmosphere. A green solid precipitated, which was filtered off, washed with toluene (20 mL × 2) and ether (20 mL × 5), and then dried *in vacuo*. Complex 1 was obtained as a green powder (1.14 g, 93% yield). Single crystals suitable for X-ray diffraction were obtained by crystallization of the solid from CH₂Cl₂–hexane. Anal. Found: C, 62.92; H, 5.02. C₄₆H₄₄MoP₄S₂ requires C, 62.73; H, 5.04. IR (KBr): *v*(SH) 2537, 2487 cm⁻¹. $\delta_{\rm H}$ (400 MHz; CD₂Cl₂, 20 °C): 7.85–7.75, 7.65–7.55 (m, 2H each, aromatic), 7.3–7.0 (m, 22H, aromatic), 6.91 (t, 4H, aromatic), 6.7–6.6 (m, 4H, aromatic), 2.45–2.25 (br, 2H, PCH₂), 2.1–1.7 (br, 6H, PCH₂), 1.53 (quint, *J* = 2.2 Hz, 2H, SH). $\delta_{\rm P}$ (162 MHz, CD₂Cl₂, 20 °C): 131.2 (m, 2P, inner P), 91.8 (m, 2P, outer P), AA'XX' pattern: $J_{\rm AX} + J_{\rm AX} = 30$ Hz.

Synthesis of 4. Complex 1 (441 mg, 0.500 mmol) and [RhCl(CO)₂]₂ (195 mg, 0.501 mmol) were dissolved in CH₂Cl₂ (30 mL) and then NEt₃ (280 µL, 2.01 mmol) was added at -78 °C. The mixture was gradually warmed to room temperature with stirring. After 18 h, the solution was concentrated to ca. 5 mL in vacuo and the resultant mixture was filtered to give a dark green solid and a green filtrate. The solid was washed with CH₂Cl₂ $(5 \text{ mL} \times 2)$ and dried, while the filtrate was concentrated again to ca. 3 mL and the mixture was filtered off. The solid remained, which was washed with CH_2Cl_2 (2 mL \times 2) and dried. Two crops of crude product were combined and crystallized from CH₂Cl₂-hexane, yielding 4 as black crystals (263 mg, 44%). These consisted of thin rhomboidal crystals containing 4a and thin rectangular crystals containing 4b, where large crystals were able to be separated manually. Anal. for the mixture of 4a and 4b. Found: C, 50.01; H, 3.39. C₅₀H₄₂O₄MoP₄Rh₂S₂ requires C, 50.19; H, 3.54. The data below recorded independently for 4a and 4b are the same. IR (CH₂Cl₂): v(CO) 2043, 2024, 1976 cm⁻¹. $\delta_{\rm H}$ (400 MHz; CD₂Cl₂, 20 °C): 7.85 (br, 4H, aromatic), 7.76 (br, 2H, aromatic), 7.5-7.3 (m, 10H, aromatic), 7.2–7.1 (m, 10H, aromatic), 6.99 (t, 4H, aromatic), 6.62 (br, 4H, aromatic), 2.87, 2.29, 2.20, 1.43 (br, 2H each, PCH₂). $\delta_{\rm P}$ (162 MHz, CD₂Cl₂, 20 °C): 118.8 (br, 2P, inner P), 81.9 (br, 2P, outer P).

Synthesis of 5. A solution of [IrCl(CO)₂(*p*-toluidine)] (392 mg, 1.00 mmol) and NEt₃ (280 μ L, 2.01 mmol) in THF (10 mL) cooled to -78 °C was poured into a stirred solution of 1 (441 mg, 0.500 mmol) in CH₂Cl₂ (20 mL) at -78 °C. The solution was stirred continuously with gradual warming to room temperature, affording a green suspension. The product mixture was filtered off and the green solid obtained was washed with CH_2Cl_2 (5 mL \times 3). Drying in vacuo of the residue gave analytically pure 5 (519 mg, 76% yield). Single crystals for X-ray analysis were available by recrystallization from CH₂Cl₂-hexane. Found: C, 43.81; H, 3.04. $C_{50}H_{42}O_4MoP_4Ir_2S_2$ requires C, 43.67; H, 3.08. IR (CH₂Cl₂): v(CO) 2032, 2010, 1959 cm⁻¹. $\delta_{\rm H}$ (400 MHz; CD₂Cl₂, 20 °C): 7.83 (br, 4H, aromatic), 7.76, 7.50 (br, 2H each, aromatic), 7.38 (m, 8H, aromatic), 7.23 (m, 6H, aromatic), 7.13, 7.03 (t, 4H each, aromatic), 6.59 (br, 4H, aromatic), 2.62, 2.11, 2.03, 1.54 (br, 2H each, PCH₂). δ_P (162 MHz, CD₂Cl₂, 20 °C): 116.0 (m, 2P, inner P), 76.3 (m, 2P, outer P).

X-Ray crystallography†

Details of diffraction studies are summarized in Table 4. Single crystals of 1, $4a \cdot 1.3CH_2Cl_2$, $4b \cdot 0.5CH_2Cl_2$, and $5 \cdot 1.375CH_2Cl_2$

Table 4Crystal data for 1, 4a, 4b, and 5

| | 1 | $4\mathbf{a} \cdot 1.3 \mathrm{CH}_2 \mathrm{Cl}_2$ | 4b ·0.5CH ₂ Cl ₂ | 5.1.375CH ₂ Cl ₂ |
|--------------------------------------|--------------------------------|---|---|--|
| Formula | $C_{46}H_{44}P_4S_2Mo$ | $C_{51.6}H_{45.2}O_4P_4S_2Cl_{3.2}MoRh_2$ | $C_{50.5}H_{43}O_4P_4S_2ClMoRh_2$ | C _{51 38} H _{44 75} O ₄ P ₄ S ₂ Cl _{2 75} MoIr |
| $M_{\rm r}$ | 880.81 | 1332.54 | 1239.11 | 1492.12 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ (no. 14) | <i>C</i> 2/ <i>c</i> (no. 15) | $P2_1/c$ (no. 14) | <i>C</i> 2/ <i>c</i> (no. 15) |
| a/Å | 14.054(3) | 41.234(1) | 13.709(4) | 41.213(9) |
| b/Å | 12.073(2) | 11.9799(4) | 17.143(4) | 12.066(2) |
| c/Å | 25.259(5) | 21.7291(9) | 20.980(5) | 21.619(4) |
| $\beta/^{\circ}$ | 103.749(1) | 96.1025(7) | 101.070(1) | 95.852(1) |
| $V/Å^3$ | 4163(2) | 10673.0(7) | 4839(2) | 10 695(4) |
| Ζ | 4 | 8 | 4 | 8 |
| $D_{\rm c}/{\rm Mg}~{\rm m}^{-3}$ | 1.405 | 1.658 | 1.701 | 1.853 |
| Crystal size/mm ³ | $0.40 \times 0.20 \times 0.10$ | $0.10 \times 0.10 \times 0.10$ | $0.50 \times 0.20 \times 0.10$ | $0.50 \times 0.20 \times 0.10$ |
| $2\theta_{\rm max}^{\circ}/^{\circ}$ | 55.74 | 54.96 | 54.96 | 54.96 |
| T/K | 293 | 293 | 293 | 293 |
| Unique reflections | 9892 | 12 020 | 11 062 | 12 245 |
| Data of $I > 2\sigma(I)$ | 5700 | 8735 | 5033 | 5474 |
| Variables | 528 | 638 | 624 | 638 |
| Transmission factor | 0.643-1.000 | 0.586-0.883 | 0.661-0.883 | 0.293-0.572 |
| R_1^a | 0.038 | 0.037 | 0.063 | 0.049 |
| WR_2^b | 0.130 | 0.114 | 0.201 | 0.177 |
| GOF ^c | 1.013 | 1.018 | 1.076 | 1.032 |

were sealed in glass capillaries under argon and mounted on a Rigaku Mercury-CCD diffractometer equipped with a graphitemonochromatized Mo K α source. Data collections were performed by using the CrystalClear program package.¹⁴ All data were corrected for absorption.

Structure solution and refinements were conducted by using the Crystal Structure program package.¹⁵ The positions of non-hydrogen atoms were determined by Patterson methods (PATTY)¹⁶ and subsequent Fourier synthesis (DIRDIF99),¹⁷ which were refined by full-matrix least-squares techniques. Hydrogen atoms were placed at the calculated positions and included at the final stages of the refinements with fixed parameters. For 1, the SH hydrogens were found in the Fourier map and refined isotropically. In 4a·1.3CH2Cl2, two CH2Cl2 molecules are disordered, where the population of the molecule near the 2-fold axis is 0.6. All non-hydrogen atoms in these molecules were refined isotropically, while hydrogens were not added. Some C-Cl bonds were restrained. For 4b.0.5CH₂Cl₂, the solvating CH₂Cl₂ molecules, which are present around the inversion center, are disordered and their structures were refined isotropically with restraints of bond lengths and angles with hydrogens at the calculated positions. In 5.1.375CH₂Cl₂, both solvating CH₂Cl₂ molecules are disordered, for which the Cl atoms were refined anisotropically, while the C atoms were refined isotropically. Hydrogens were not included. The population of the molecule near the 2-fold axis was found to be 0.75. For the other molecule, refinements were carried out with the restrained C-Cl bonds.

CCDC numbers are 719133–719136 for 1, $4a \cdot 1.3CH_2Cl_2$, $4b \cdot 0.5CH_2Cl_2$, and $5 \cdot 1.375CH_2Cl_2$, respectively.

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