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REACTION OF THIOLATO-LIGANDS WITH RHENIUM HYDRIDES—III. COMPLEXES OF MERCAPTOPYRIDINES. THE SYNTHESES AND X-RAY CRYSTAL STRUCTURES OF [ReHF(2-SC$_5$H$_4$N)$_2$(PMe$_2$Ph)$_2$]BF$_4$ AND [ReH(2-SC$_5$H$_4$N)(PMe$_2$Ph)$_4$]BF$_4$

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Abstract—The hydride complex [ReH$_5$(PMe$_2$Ph)$_3$] reacted with 2-mercaptopyridine (pySH) in the presence of HBF$_4$ giving [ReH(pyS)(PMe$_2$Ph)$_4$]BF$_4$ (**1**) and [ReHF(pyS)$_2$(PMe$_2$Ph)$_2$]BF$_4$ (**2**). The X-ray structures of both complexes have been determined and are discussed. The known complex [ReH(pyS)$_2$(PPh$_3$)$_2$] and new [ReH(SipyS)$_2$(PPh$_3$)$_2$] (**3**) have been prepared directly from [ReOCl$_3$(PPh$_3$)$_2$], NaBH$_4$ and the appropriate thiol. Analogous reaction of [ReOCl$_3$(dppe)] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) with pySH gave [ReH$_4$(pyS)(dppe)] (**4**).

There has been considerable recent interest in molybdenum hybride complexes with thiolate ligands due to their possible relevance to the nitrogenase enzyme and to molybdenum hydridesulphurization.[1,2] There are, however, comparatively few examples of hydride complexes with other transition metals with a comparatively high proportion of sulphur in the coordination sphere. We have carried out a systematic investigation of the reaction of thiolate ligands with rhenium polyhdride complexes (parts I[3] and II[4]) with a view to creating metal sites capable of binding small molecules. We have by this route *inter alia* prepared dinitrogen complexes,[4] isocyanide complexes,[4] complexes with agostic metal–hydrogen interactions,[4] and carbonyl complexes.[4] We here report the reactions of [ReH$_5$(PPh$_3$)$_5$] and [ReH$_5$(PMe$_2$Ph)$_3$] with 2-mercaptopyridine (pySH) and 2-mercapto-6-trimethylsilylpyridine (SipySH). The reactions of pySH with [ReH$_7$(PPh$_3$)$_2$] to give [ReH(pyS)$_2$(PPh$_3$)$_2$] have been reported[5] and we now describe the syntheses and structures of some new pyS hydrides obtained by reaction of Re hydride precursors with dimethylphenylphosphine or 1,2-diphenylphosphinoethane (dppe).

RESULTS AND DISCUSSION

Reactions of [ReH$_5$(PMe$_2$Ph)$_3$]

The pentahydride [ReH$_5$(PMe$_2$Ph)$_3$] is surprisingly unreactive towards a range of thiolate ligands, including the 2-mercaptopyridines. In order to activate the complex towards the loss of hydride ligands it was reacted with anhydrous HBF$_4$ in tetrahydrofuran prior to addition of the

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mercaptopyridines. This led to the isolation of two complexes as mildly air-sensitive yellow solids, $[ReH(pyS)(PMe_2Ph)_4]BF_4$ (**1**) and $[ReHF(pyS)_2(PMe_2Ph)_2]BF_4$ (**2**), in yields of 21 and 51%, respectively. There has evidently been transfer of a phosphine ligand during the reaction.

The Re—H stretching frequency for complex **1** is not detectable in the IR spectrum, and strong bands at 1050 and 1090 cm^{-1} are assigned to the BF_4 anion. The hydride ligand gives rise to a 12-line multiplet comprising four triplets centred at −7.79 ppm in the ^1H NMR spectrum. The *trans*-phosphine ligands are equivalent (see Fig. 2) and produces the triplet splitting [$J\{P(1)—H\} = J\{P(2)—H\} = 20$ Hz]. Further coupling with the two other inequivalent phosphine ligands result in the observed four triplets [$J\{P(3)—H\} = 61$ Hz and $J\{P(2)—H\} = 65$ Hz]. In the ^{31}P NMR spectrum three triplets are observed centred at −35.41, 25.33 and 20.22 ppm. The most intense triplet at −35.41 ppm is assigned to the *trans*-phosphine ligands and is assumed to comprise two overlapping doublets. The two remaining triplets are assigned to P(3) and P(4) with $J\{P(3)—P(4)\}$ either zero or unobservable at the frequency used. The analytical data for this and the other complexes are summarized in Table 1.

For complex **2** ν(Re—H) appears as a medium intensity band at 2040 cm^{-1} and again broad bands at 1050 and 1090 cm^{-1} were attributed to the BF_4 anion. In the ^1H NMR spectrum the hydride resonance appears as an overlapping pair of triplets due to coupling with the two equivalent phosphine ligands and the single fluorine ligands. The ^{31}P NMR spectrum shows a singlet at −32.4 pm and J(P—F) is presumably zero.

X-ray crystal structure of $[ReH(pyS)(PMe_2Ph)_4]BF_4$ (1)

An ORTEP representation of the structure of complex (**1**) is shown in Fig. 1. Selected bond lengths and angles in appear in Table 2. The overall geometry about the Re is best described as distorted pentagonal bipyramidal with the (unobserved) hydride, pyridine thiol and two phosphine ligands in the pentagonal plane. Least-squares planes for the pentagonal plane (excluding the hydride) show that the largest displacement from the plane is 0.027 Å. Due to steric repulsions with the equatorial phosphines the P(1)—Re—P(2) angle is distorted from the ideal value of 180° to 163.89(7)°.

X-ray crystal structure of $[ReHF(pyS)_2(PMe_2Ph)_2]BF_4$ (2)

An ORTEP representation of the structure of complex **2** appears in Fig. 2. Selected bond lengths and angles are shown in Table 3. The overall geometry is best described as distorted pentagonal bipyramidal, excluding the unobserved hydride ligand. The fluoride ligand is located close to the pentadgonal plane in a position bisecting the P(1)—Re—P(2) angle. The observed structure makes an interesting contrast with that of $[ReH_2(mhp)_2(PPh_3)_2]PF_6$,[6] which exists in two iso-

Table 1. Analytical and spectroscopic data for hydrido mercaptopyridine complexes

	Elemental analyses (C,H,N%)[a]	IR (ν cm^{-1})	^1H NMR[b] δ(Re—H) ppm	$^{31}P\{^1H\}$ NMR[b] (δ, ppm)
$[ReH(2\text{-}SC_5H_4N)(PMe_2Ph)_4]BF_4\cdot CH_2Cl_2$	C 45.2(45.2) H 5.7(5.2), N 1.5(1.4)	ν(Re—H)NO[c]	−7.79 [ddt, J(P—H), 20, 20, 61, 65Hz]	−35.41(t) −25.33(t) −20.22(t)
$[ReH(2\text{-}SC_5H_4N]_2F(PMe_2Ph)_2BF_4$	C 39.6(39.5) H 3.8(4.2) N 3.5(3.5)	ν(Re—H) 2040	−8.58 d, −8.82d [J(P—H) = 52 Hz, J(P—F) = 64 Hz]	−32.4(s)
$[ReH(C_5H_3N\text{-}2\text{-}S\text{-}3\text{-}SiMe_3)_2(PPh_3)_2]$		ν(Re—H) 2019	−2.37 [t, J(P—H) 63.50 Hz]	29.13 (s)
$[ReH_4(C_5H_4NS)(dppe)]\cdot 0.25C_7H_8$	C 54.7(54.5) H 5.3(4.8) N 1.9(1.9)	ν(Re-H) NO[c]	−4.26(t)	−9.84(s)

[a] Calculated values in parentheses.

[b] s, singlet; t, triplet; ddt, doublet of doublet of triplets; dt, doublet of triplets. Spectra run in $CDCl_3$ solution.

[c] NO = not observable.

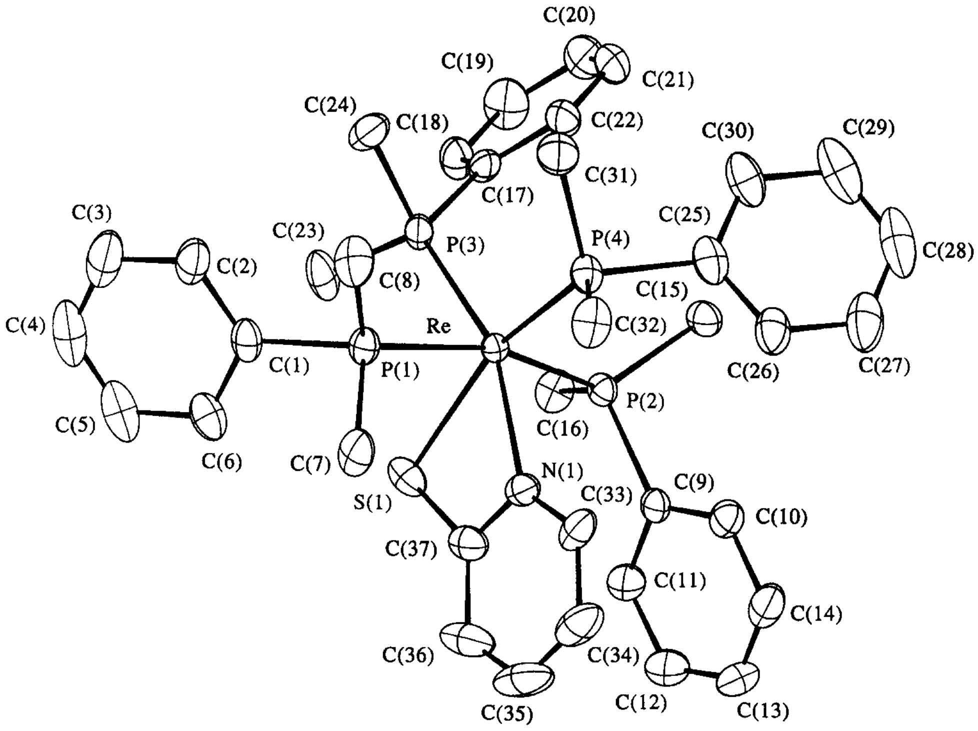

Fig. 1. ORTEP representation of the structure of the cation of [ReH(pyS)(PMe$_2$Ph)$_4$][BF$_4$] (**1**), together with a partial atom labelling scheme.

mers, *cis* and *trans*, both of which have been structurally characterized. In the so-called *trans* isomer the two hydride ligands are located symmetrically approximately in the P—Re—P plane. In complex **2** the location of the hydride is more problematic as there are no immediately obvious distortions in the coordination sphere. A possible location is such that it bisects the S—Re—S angle. Assuming that the Re—H distance is *ca* 1.6 Å the S—H distances would be of the order 1.58 Å, which is longer than a normal S—H bond (*ca* 1.31 Å), but substantially less than the sum of the van der Waals radii (3.05 Å).

Table 2. Selected bond lengths (Å) and angles (°) for [ReH(pyS)(PMe$_2$Ph)$_4$][BF$_4$]

Re—N(1)	2.196(5)	Re—P(3)	2.371(2)
Re—P(4)	2.378(2)	Re—P(2)	2.427(3)
Re—P(1)	2.491(4)	Re—S(1)	2.513(2)
S(1)—C(37)	1.726(9)	P(1)—C(7)	1.822(8)
P(1)—C(8)	1.844(8)	P(1)—C(1)	1.851(7)
P(2)—C(9)	1.824(7)	P(2)—C(16)	1.826(7)
P(2)—C(15)	1.833(7)	P(3)—C(23)	1.816(8)
P(3)—C(24)	1.830(8)	P(3)—C(17)	1.847(7)
P(4)—C(31)	1.825(8)	P(4)—C(32)	1.828(8)
P(4)—C(25)	1.844(8)		
N(1)—Re—P(3)	156.5(2)	N(1)—Re—P(4)	94.1(2)
P(3)—Re—P(4)	108.56(7)	N(1)—Re—P(2)	84.6(2)
P(3)—Re—P(2)	95.08(6)	P(4)—Re—P(2)	104.58(7)
N(1)—Re—P(1)	85.90(14)	P(3)—Re—P(1)	88.49(6)
P(4)—Re—P(1)	89.05(6)	P(2)—Re—P(1)	163.89(7)
N(1)—Re—S(1)	64.5(2)	P(3)—Re—S(1)	92.27(7)
P(4)—Re—S(1)	157.89(7)	P(2)—Re—S(1)	80.12(8)
P(1)—Re—S(1)	84.05(7)		

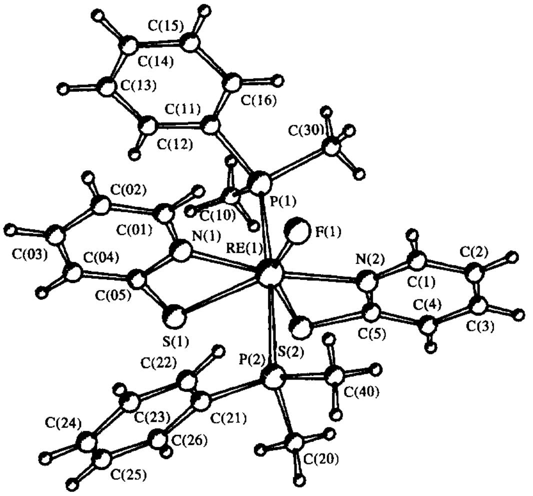

Fig. 2. PLUTO representation of the structure of the cation of $[ReHF(pyS)_2(PMe_2Ph)_2][BF_4]$ (**2**), together with a partial atom labelling scheme.

This would require a four-centre Re—S—H—S system. A related structure involving a three-centre Fe—S—H bonding has been proposed for the complex $[FeH(SPh)(CO)_3(PPh_3)]^-$.[6]

Syntheses from $[ReH_5(PPh_3)_3]$ *and directly from* $[ReOCl_3L_2]$ ($L = PPh_3$, 1/2 dppe)

The literature synthesis of $[ReH_5(PPh_3)_3]$ from $[ReOCl_3(PPh_3)_2]$ using lithium aluminium hydride is not particularly convenient, as the excess $LiAlH_4$ has to be destroyed during the workup procedure. We have developed an alternative convenient method using sodium borohydride which gives pure product via a simple toluene extraction in a yield of *ca* 60%. Alternatively, the pentahydride can be generated *in situ* from $[ReOCl_3(PPh_3)_2]$ and borohydride and the thiol hydrides prepared directly by the addition of thiol to the reaction solution. The known complex $[ReH(pys)_2(PPh_3)_2]$[6] was prepared from $[ReOCl_3(PPh_3)_2]$ using this procedure and had spectroscopic properties identical to those in the literature. The related but new complex $[ReH(SipyS)_2(PPh_3)_2]$ (**3**) was prepared in a similar manner, but the very high solubility of the complex prevented its isolation in an analytically pure state. The steric bulk of the Me_3Si group does not appear to change the gross structure and the spectroscopic properties of **3** are very similar to those of the pyS derivative.

Reaction of $[ReOCl_3(dppe)]$ ($dppe = Ph_2PCH_2CH_2PPh_2$) with pySH in the presence of sodium borohydride gives a yellow green compound in 73% yield. Elemental analysis suggests the stoichiometry $[ReH_n(pyS)(dppe)]$ (**4**). The complex is diamagnetic and therefore n must be 2 or 4, and integration of the ^1H NMR spectrum suggess the value of 4. This also confers a formal valence electron count of 18 on the complex.

The IR bands due to the Re—H bonds could not be observed, but a triplet centred at −4.26 ppm due to the hydrides is observed in the ^{1}NMR spectrum. The triplet comprises two sharp outer peaks and a broad centre peak which is characteristic of slow exchange mechanisms. Similar spectra have been reported for the hydrides MH_4L_4 ($M = Mo$, W; $L = PMe_2Ph$, PEt_2Ph) and MH_2L_4 [$M = Fe$, Ru; $L = P(OEt)_3$, PEt_2Ph, $PPh(OBu^t)_2$].[7 10] The $^{31}P\{^1H\}$ NMR spectrum of complex **4** comprises a singlet at −9.84 ppm, indicating that the phosphorus donors are in equivalent environments. The probable geometry of the complex is tetrahedral, excluding the hydrides, which can be located in capping sites on the faces of the tetrahedron. This dodecahedral geometry is not the only possibility

Table 3. Selected bond lengths (Å) and angles (°) for $[ReHF(pyS)_2(PMe_2Ph)_2]BF_4$

Re(1)—F(1)	1.701(4)	Re(1)—N(1)	2.152(6)
Re(1)—N(2)	2.168(5)	Re(1)—P(2)	2.460(2)
Re(1)—P(1)	2.463(2)	Re(1)—S(1)	2.544(2)
F(1)—Re(1)—N(1)	81.5(2)	F(1)—Re(1)—N(2)	81.5(2)
F(1)—Re(1)—P(2)	94.6(2)	F(1)—Re(1)—P(1)	95.0(2)
F(1)—Re(1)—S(1)	144.3(2)	F(1)—Re(1)—S(2)	144.0(2)
N(1)—Re(1)—N(2)	163.0(2)	N(1)—Re(1)—P(2)	91.1(1)
N(1)—Re(1)—P(1)	90.2(1)	N(1)—Re(1)—S(1)	62.9(2)
N(1)—Re(1)—S(2)	134.4(2)	N(2)—Re(1)—P(2)	89.6(1)
N(2)—Re(1)—P(1)	92.0(1)	N(2)—Re(1)—S(1)	134.0(2)
N(2)—Re(1)—S(2)	62.7(2)	P(2)—Re(1)—P(1)	170.35(6)
P(2)—Re(1)—S(1)	83.98(7)	P(2)—Re(1)—S(2)	88.31(6)
P(2)—Re(1)—S(1)	88.12(6)	P(1)—Re(1)—S(2)	83.95(6)
S(1)—Re(1)—S(2)	71.65(7)		

giving equivalent phosphorus donors but is preferred on electronic and steric grounds.

EXPERIMENTAL

Materials and methods

All manipulations were performed under dry nitrogen using standard Schlenk- and vacuum-line and syringe techniques unless stated otherwise. The precursors $[ReOCl_3(PPh_3)_2]$ and $[ReOCl_3(dppe)]$[11] were prepared by standard literature methods. $HBF_4 \cdot Et_2O$, 2-mercaptopyridine and 2-SC_5H_3N-$SiMe_3$-3 were used without further purification as purchased from ALDRICH, while PMe_2Ph and DPPE ligands were prepared as described in the literature.[12] Other reagents and solutions were obtained from commercial sources. Elemental analyses were performed by Medac Ltd, University of Brunel. IR spectra were recorded as Nujol mulls (NaCl plates) on a Perkin–Elmer 1330 IR spectrophotometer. ^1H and $^{31}P\{^1H\}$ NMR were recorded on a EX-270 JEOL (270 MHz) NMR spectrometer.

$[ReH_5(PPh_3)_3]$

A slurry of $[ReOCl_3(PPh_3)_2]$ (1.00 g, 1.2 mmol) and PPh_3 (1.00 g, 3.8 mmol) together with $NaBH_4$ (1.00 g, excess) in absolute ethanol (20 cm^3) was heated under reflux for 3 h. After filtration, the solid was extracted with toluene. A yellow powder was obtained by removal of the toluene *in vacuo* and washed with MeOh and then Et_2O. Yield 61%.

$[ReH(2\text{-}SC_5H_4N)_2(PPh_3)_2]$

A slurry of $[ReOCl_3(PPh_3)_2]$ (0.25 g, 0.3 mmol) and $NaBH_4$ (0.25 g, excess) together with 2-mercaptopyridine (0.067 g, 0.6 mmol) in absolute ethanol (20 cm^3) was heated under flux for 30 min. The solution was evaporated to dryness and extracted with toluene. The complex was obtained as a yellow orange powder after removal of solvent *in vacuo*. Yield 81%.

$[ReH(2\text{-}S\text{-}C_5H_3N\text{-}3\text{-}SiMe_3)_2(PPh_3)_2]$

This complex was prepared in similar manner to the preparation of $[ReH(2\text{-}SC_5H_4N)_2(PPh_3)_2]$ with 2-HSC_5H_3N-3-$SiMe_3$ instead of 2-HSC_5H_4N. The crude product was obtained by evaporation of the filtration solution to dryness. Yield 83%.

$[ReH_4(2\text{-}SC_5H_4N)(dppe)]$

A slurry of $[ReOCl_3(dppe)]$ (0.25 g, 0.35 mmol) and 2-mercaptopyridine (0.079 g, 0.7 mmol) together with $NaBH_4$ (0.25 g, excess) in absolute ethanol (20 cm^3) was heated under reflux for 20 min. The solution was evaporated to dryness and then extracted with toluene. A yellow green powder was obtained after removal of the toluene *in vacuo*. Yield 73%.

Reaction between $[ReH_3(PMe_2Ph)_3]$ *and 2-mercaptopyridine*

A solution of $[ReH_5(PMe_2Ph)_3]$ (0.20 g, 0.33 mmol) in THF (10 cm^3) was treated with $HBF_4 \cdot Et_2O$ (0.063 g, 0.33 mmol). The mixture was stirred for 2 h and then evaporated to dryness. A solution of 2-mercaptopyridine (0.073 g, 0.65 mmol) in absolute ethanol (10 cm^3) was added to the reaction, followed by heating under reflux for 1 h. Yellow crystals of $[ReH_4(2\text{-}SC_5H_4N)(PMe_2Ph)_4][BF_4]$ precipitated in 21% yield. Et_2O was added to the filtrate to produced orange–brown crystals of $[ReF(2\text{-}SC_5H_4N)_2(PMe_2Ph)_2][BF_4]$ in a few days in 51% yield.

DETERMINATION OF X-RAY CRYSTAL STRUCTURES

The details of the X-ray crystal structure determinations are also summarized in Table 4.

Structure of $[ReH(pyS)(PMe_2Ph)_4][BF_4]$ (**1**)

Data collection. Intensity data were collected on a Rigaku AFC5R diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å). Cell constants were obtained from least-squares refinement of the setting angles of 20 centred reflections in the range $5 < \theta < 13$. The data were collected in the ω–2θ scan mode and three standard reflections were measured every 1.5 h of exposure. A 0.4% loss of intensity was observed which was linealy corrected during processing. Three standard reflections were measured every 250 reflections to check the crystal orientation. The data were corrected for Lorentz and polarization factors and an absorption correction was applied using ψ-scans of nine reflections.

Structure solution and refinement. The structure was solved using direct methods (TEXSAN structure solution package[13]). The remaining non-hydrogen atoms were located in subsequent cycles of Fourier-difference syntheses and least-squares refinement. Full-matrix least-squares refinement on

Table 4. Summary of experimental details for the X-ray crystal structures of [ReH(pyS)$(PMe_2Ph)_4$][BF_4] (**1**) and [ReH(2-SC_5H_4N)$_2$F$(PMe_2Ph)_2$]BF_4 (**2**)

	1	**2**
(a) Crystal parameters		
Formula weight	$C_{37}H_{49}BF_4NP_4SRe$	$C_{26}H_3BF_5N_2P_2S_2Re$
a (Å)	15.692(3)	17.218(8)
b (Å)	14.685(4)	27.913(9)
c (Å)	19.690(3)	12.501(4)
β (°)	109.99	
V (Å^3)	4264(2)	6008(4)
Space group	$P2_1/n$	$Pbca$
D_c (g cm^{-3}) (Calc.)	1.59	1.75
Z	4	8
F(000)	2048	3104
(b) Measurement of intensity data		
Crystal dimensions (mm)	0.3 × 0.3 × 0.3	1.8 × 0.6 × 0.6
Instrument	Enraf–Nonius CAD-4	Rigaku AFC5R
Radiation	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71069 Å)
Scan rate (°min^{-1} in ω)	—	$16/n$ (n = 1,2,3)
Scan mode	ω–θ	ω–2θ
Temperature (°C)	23	23
Scan length	—	$0.92+0.35 \tan\theta$
Scan range (°)	$2\theta < 50$	$2\theta < 50$
Reflections collected	7493	5868
Observed reflections	6157 [$I > 2\sigma(I)$]	3866 [$I > 3\sigma(I)$]
(c) Reduction of intensity data and summary of structure solution and refinement: data corrected for background, attenuators, Lorentz and polarization effects in the usual fashion		
Structure solution	Patterson	Direct method
Absorption corrections	0.84–1.00	0.61–1.0.
Reflection average	Applied	Applied
R	0.040	0.033
R_w	0.113	0.043
Goodness-of-fit	1.212	1.20

F converged with $R = 0.033$, $R_w = 0043$, max shift/error 0.11, and $S = 1.20$. The extinction coefficient was not refined. Hydrogen atoms were added in calculated positions with $B_{eq} = 1.2$ times B_{eq} of the attached atom; they were included in structure-factor calculations but were not refined. Neutral scattering factors were used.[14]

Structure of [ReH(pyS)$_2$F$(PMe_2Ph)_2$][BF_4] (**4**)

Data collection. Intensity data were collected on an Enraf–Nonius CAD-4 diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Cell constants were obtained from least-squares refinement of the setting angles of 25 centred reflections in the range $2 < \theta < 25°$. The data were collected in the ω–2θ scan mode and three standard reflections were measured every 2 h of exposure. A −1.9% loss of intensity was observed which was linearly corrected during processing. Three standard reflections were measured every 200 reflections to check the crystal orientation. The data were corrected for Lorentz and polarization factors and an absorption correction was applied using ψ-scans of nine reflections.

Structure solution and refinement. The structure was solved using the Patterson heavy-atom method (Molen structure solution package[15]). The remaining non-hydrogen atoms were located in subsequent cycles of Fourier-difference syntheses and least-squares refinement. Full-matrix least-squares refinement on F^2 using SHELX-93 software[16] converged with $R1 = 0.040$, $wR2 = 0.113$ for the reflections with $I > 2\sigma(I)$($R1 = 0.055$, $wR2 = 0.120$ for 11 data). Hydrogen atoms were added in calculated positions and refined with in riding mode with U_{iso}H equal to $1.2U_{eq}$(C) of 1.5 U_{eq}(C) for methyl groups. The BF_4 anion was constrained to have tetrahedral symmetry. The CH_2Cl_2 solvate was poorly defined, and was constrained to have roughly equal C—Cl bond lengths. One of the Cl atoms was disordered between two positions, and the H atoms of the solvate molecule were omitted.

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