**Electronic supplementary materials** *Mendeleev Commun.*, 2019, **29**, 463–465

# N,S-containing soft ligands for extractive separation of *f*-metals: synthesis and unexpected inverse selectivity

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## Experimental

### General remarks

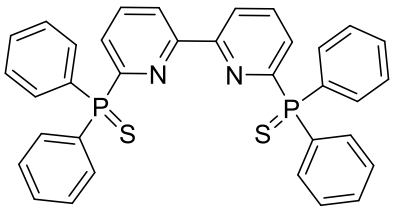
All reagents and solvents were purchased from commercial sources and used as received unless otherwise stated. $P_4S_{10}$ (98%) was purchased from Sigma Aldrich and used as received. Chlorobenzene was dried over MS 4 Å for 24 h prior to use. Commercial deuterated solvents for NMR spectroscopy were stored over MS 4 Å. NMR spectra were recorded using Bruker AVANCE 400 and Bruker AVANCE II 600 spectrometers. High-resolution mass spectra were obtained on an Orbitrap Elite ESI mass spectrometer in positive mode.

### General procedure for the synthesis of phosphine sulfides

To a solution of phosphine oxide (0.8 mmol) in PhCl (35 ml), $P_4S_{10}$ (2 eq, 1.6 mmol) was added. The mixture was heated at 120°C overnight in an argon atmosphere, then cooled to room temperature and diluted with $CH_2Cl_2$ (70 ml). The organic layer was washed with a solution of $Na_2CO_3$ (2×30 ml) and brine (2×20 ml), then dried over $Na_2SO_4$ and concentrated *in vacuo*. Product was isolated by column chromatography with $CH_2Cl_2$–MeOH as eluent.

### Spectral Data

#### 2,2'-Bipyridine-6,6'-diylbis(diphenylphosphine sulfide) 2a

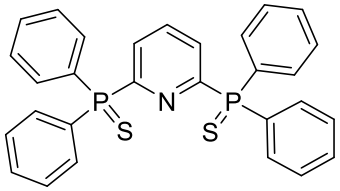



Yellow solid (86%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.43–7.53 (m, 12H), 7.90–7.95 (m, 10H), 8.18 (dd, 2H, *J* 7.8 Hz, 1.9 Hz), 8.57 (t, 2H, *J* 7.2 Hz).

$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$: 124.83, 124.86, 130.87, 130.99, 131.49, 131.74, 134.21, 134.69, 135.01, 135.12, 135.54, 140.27, 140.37, 157.23, 157.41, 157.65, 158.76.$^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$) $\delta$: 38.31.

HRMS: calc. for $[C_{34}H_{26}N_2S_2P_2+H]^+$: 589.1085; found: 589.1100.

**Pyridine-2,6-diylbis(diphenylphosphine sulfide) 2b**



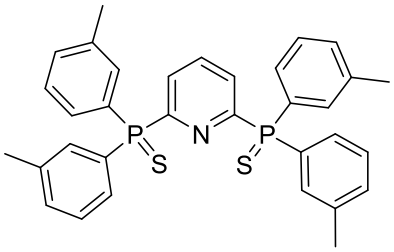
Yellow solid (81%). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.29 (m, 8H), 7.48 (m, 4H), 7.58 (m, 8H), 8.05 (tt, 1H, *J* 7.8 Hz, 3.9 Hz), 8.69 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) $\delta$: 127.77, 127.83, 127.90, 128.65, 128.68, 128.90, 128.93, 130.78, 131.11, 131.64, 131.83, 131.84, 131.88, 136.94, 155.62, 155.78, 156.69, 156.85.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta$: 37.83.

HRMS: calc. for $[C_{29}H_{23}NS_2P_2+H]^+$: 512.0819; found: 512.0833.

**Pyridine-2,6-diylbis(di-*m*-tolylphosphine sulfide) 2c**



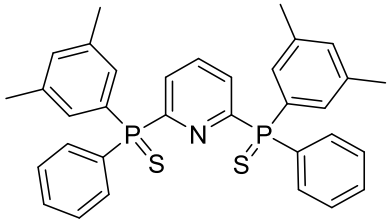
Yellow solid (87%). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$: 2.24 (s, 12H), 7.09 (td, 4H, *J* 7.7 Hz, 3.6 Hz), 7.26 (q, 8H, *J* 6.8 Hz), 7.55 (d, 4H, *J* 14.3 Hz), 8.05 (tt, 1H, *J* 7.8 Hz, 3.9 Hz), 8.70 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) $\delta$: 21.00, 127.47, 127.54, 127.60, 128.73, 128.76, 128.91, 128.97, 128.99, 129.01, 130.79, 131.64, 131.93, 132.23, 132.29, 132.35, 136.72, 136.82, 136.92, 137.68, 137.75, 137.82, 155.53, 155.69, 156.60, 156.76.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta$: 38.14.

HRMS: calc. for $[C_{33}H_{31}NS_2P_2+H]^+$: 568.1446; found: 568.1459.

**Pyridine-2,6-diylbis[(3,5-dimethylphenyl)(phenyl)phosphine sulfide] 2d**



Yellow solid (90%). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$: 2.16 (d, 12H, *J* 14.5 Hz), 7.08 (d, 2H, *J* 13.7 Hz), 7.23 (m, 6H), 7.43 (m, 2H), 7.60 (m, 4H), 8.05 (m, 1H), 8.69 (m, 2H).

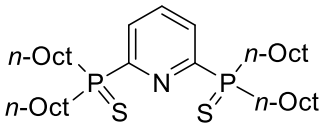
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) $\delta$: 23.83, 23.95, 130.63, 130.71, 130.76, 130.84, 131.86, 132.11, 132.30, 132.36, 132.41, 132.46, 132.52, 132.57, 133.34, 133.67, 133.95, 134.03, 134.19,

134.46, 134.52, 134.81, 134.87, 134.94, 134.99, 135.05, 135.32, 136.04, 136.15, 139.88, 139.98, 140.48, 140.56, 140.62, 140.70, 158.54, 158.70, 159.60, 159.78.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta$: 38.19, 38.22.

HRMS: calc. for $[C_{33}H_{31}NS_2P_2+H]^+$: 568.1446; found: 557.1453.

**Pyridine-2,6-diylbis(dioctylphosphine sulfide) 2e**



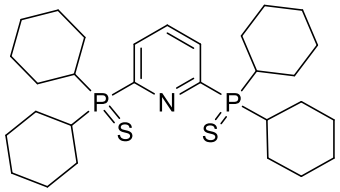

Yellow solid (86%). $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$: 0.86 (t, 12H, *J* 6.8 Hz), 1.23 (m, 44H), 1.68 (m, 4H), 2.08 (m, 4H), 2.25 (m, 4H), 8.02 (m, 1H), 8.48 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) $\delta$: 13.64, 21.82, 22.18, 28.72, 28.79, 30.32, 30.48, 31.09, 31.35, 31.62, 129.00, 129.03, 129.22, 129.25, 136.51, 154.90, 155.05, 155.85, 156.00.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta$: 48.28.

HRMS: calc. for $[C_{37}H_{71}NS_2P_2+H]^+$: 656.4576; found: 656.4594.

**Pyridine-2,6-diylbis(dicyclohexylphosphine sulfide) 2f**



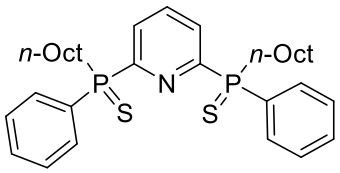

Yellow solid (73%). $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$: 1.25 (m, 24H), 1.78 (m, 12H), 2.11 (m, 4H), 2.44 (m, 4H), 7.97 (tt, 1H, *J* 7.8 Hz, 3.1 Hz), 8.48 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) $\delta$: 28.04, 28.34, 28.83, 28.92, 29.04, 29.06, 29.17, 39.33, 39.83, 133.78, 133.80, 133.98, 134.01, 138.92, 156.52, 156.66, 157.40, 157.55.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta$: 59.45.

HRMS: calc. for $[C_{29}H_{47}NS_2P_2+H]^+$: 536.2698; found: 536.2711.

**Pyridine-2,6-diylbis[octyl(phenyl)phosphine sulfide] 2g**



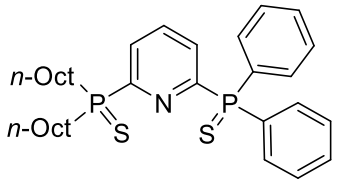

Yellow liquid (87%). $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$: 0.87 (td, 6H, *J* 6.8 Hz, 2.0 Hz), 1.41 (m, 24H), 2.49 (m, 2H), 2.71 (m, 2H), 7.37 (td, 2H, *J* 7.7 Hz, 2.8 Hz), 7.49 (m, 4H), 7.90 (m, 3H), 8.01 (m, 2H), 8.44 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) $\delta$: 13.68, 21.63, 21.73, 22.19, 22.21, 28.70, 28.74, 28.76, 28.86, 30.26, 30.38, 30.43, 30.55, 30.83, 31.01, 31.36, 31.40, 31.58, 127.92, 128.00, 128.05, 128.12, 128.27, 128.30, 128.33, 128.36, 128.51, 128.54, 128.57, 128.60, 130.55, 130.70, 130.73, 130.78, 130.83, 130.87, 130.93, 131.17, 131.34, 131.48, 136.74, 136.80, 136.84, 136.89, 136.93, 136.98, 155.73, 155.85, 155.89, 156.01, 156.74, 156.86, 156.90, 157.02.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta$: 41.47.

HRMS: calc. for $[C_{33}H_{47}NS_2P_2+H]^+$: 584.2698; found: 584.2709.

**[6-(Dioctylphosphorothioyl)pyridin-2-yl]diphenylphosphine sulfide 2h**



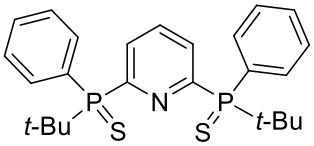

Yellow liquid (81%). $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$: 0.87 (t, 6H, *J* 7.1 Hz), 1.32 (m, 24H), 1.90 (m, 4H), 7.43 (m, 4H), 7.52 (m, 2H), 7.79 (m, 4H), 8.04 (tt, 1H, *J* 7.7 Hz, 3.8 Hz, 3.6 Hz), 8.45 (dddd, 1H, *J* 7.6 Hz, 6.3 Hz, 2.7 Hz, 1.1 Hz), 8.65 (m, 1H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) $\delta$: 13.69, 21.58, 21.61, 22.18, 28.64, 28.67, 30.11, 30.27, 30.92, 31.33, 31.45, 127.82, 127.95, 128.87, 128.90, 128.94, 128.96, 129.09, 129.12, 129.19, 129.21, 131.32, 131.35, 131.80, 131.90, 132.22, 136.88, 154.69, 154.86, 155.43, 155.58, 155.64, 155.80, 156.50, 156.66.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta$: 39.08, 48.75.

HRMS: calc. for $[C_{33}H_{47}NS_2P_2+H]^+$: 584.2698; found: 584.2704.

**Pyridine-2,6-diylbis[*tert*-butyl(phenyl)phosphine sulfide] 2i**




Yellow solid (72%). $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$: 1.28 (d, 9H, *J* 17.1 Hz), 1.35 (d, 9H, *J* 16.9 Hz), 7.36 (td, 2H, *J* 7.8 Hz, 2.9 Hz), 7.43 (m, 2H), 7.51 (m, 2H), 7.98 (m, 1H), 8.15 (m, 4H), 8.77 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) $\delta$: 25.35, 25.41, 35.59, 36.08, 127.45, 127.57, 130.79, 130.93, 131.06, 132.94, 133.04, 133.07, 133.13, 133.17, 136.13, 155.60, 155.65, 155.77, 155.82, 156.54, 156.61, 156.69, 156.76.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) $\delta$: 57.69, 57.89.

HRMS: calc. for $[C_{25}H_{31}NS_2P_2+H]^+$: 472.1446; found: 472.1450.

**Extraction experiments**

Solvent extraction experiments were carried out at temperature 25 ± 1 °C using 0.01 M ligand solutions in *m*-nitrobenzotrifluoride. Volumes of the aqueous and organic phases were 0.5 ml each. Extraction was carried out in 3M $HNO_3$ or 3M $NH_4NO_3$ solutions containing trace amounts of $^{241}Am$ and $^{152}Eu$. The phases were treated with a vortex shaker for 30 minutes, then centrifuged to accelerate the separation of the phases, and 0.35 ml of each phase was taken for analysis. The count rate for the aqueous and organic phases was determined using a GR 3818 high-purity germanium detector (Canberra Ind.) from the γ-irradiation of $^{241}Am$ at 59.1 keV and of $^{152}Eu$ at 122.2 keV. The distribution coefficients were calculated as the ratio of count rates for the corresponding organic and aqueous phases, and separation factors were calculated as the ratio of distribution coefficients for the two elements.

All the solvent extraction experiments were reproduced three times. The relative error of the distribution coefficients did not exceed 15%.