Synthesis of the Tetra-phosphine Complexes trans-$MCl_2(PH_3)_4$ (M = Ru, Os)

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Supplementary material

EXPERIMENTAL

General Considerations

All reagents were used as obtained without further purification. ACS grade methanol was obtained from Fisher, electronic grade phosphine was obtained from Linde, $RuCl_3 \cdot 3H_2O$ and $OsCl_3 \cdot 3H_2O$ were obtained from Strem. Methanol was degassed by sparging thoroughly with nitrogen before use. All reactions were preformed under an atmosphere of nitrogen. *CAUTION:* Phosphine is an extremely toxic and reactive gas, which can form spontaneously combustible mixtures in air. The entire experimental apparatus must be thoroughly evacuated and flushed with inert gas prior to use. ^{1}H and ^{31}P NMR spectra at 600 and 243 MHz respectively, were obtained on a Varian INOVA 600 spectrometer in DMSO-d_6 at room temperature. FTIR spectra were obtained on a Thermo Nicolet Avatar 330 spectrometer using a Smart Performer ATR attachment. ESI Mass spectra were obtained from methanolic solutions on an Ionspec QFT FT-ICR mass spectrometer. Elemental analysis was performed by Galbraith Laboratories. Melting points were obtained on an Electrothermal IA6304 melting point apparatus in sealed capillaries (N_2, 1 atm.) and are uncorrected. TGA and DSC analyses were performed on a Mettler Toledo TGA/DSC 1 with a constant heating rate of 10 °C min^{-1}, using a standard 40 μL aluminum sample pan under a constant flow of N_2 (120 mL min^{-1}).

X-ray Diffraction

Crystals of **1** and **2** for X-ray diffraction were grown from methanolic solutions at -50 °C. Diffraction data were collected on a Nonius KappaCCD diffractometer with a graphite monochromator using Mo-Kα radiation (λ = 0.71073 Å) at 153 K. Reflections were collected from phi scans with omega scans to fill the asymmetric unit and a multiscan absorption correction was performed using Scalepack. Structures were solved by direct methods using SHELXS-97 and refined against F^2 by full-matrix least squares methods using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Disorder of the hydrogens due to rotation of the phosphine ligands about the Ru-P axis was modeled by two opposing groups located from the difference Fourier maps with the sum of the group occupancies restrained to unity. The P-H, H-H, and Ru-H distances were restrained to a single set of values and a

single isotropic displacement parameter refined for all hydrogens. Structures **1** and **2** were deposited with FIZ Karlsruhe and assigned CSD reference numbers 421660 and 421661 respectively. Further details of the crystal structure investigation(s) may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the appropriate CSD number. See http://www.rsc.org/suppdata/cc/ for crystallographic data in CIF format.

CHARACTERIZATION DATA

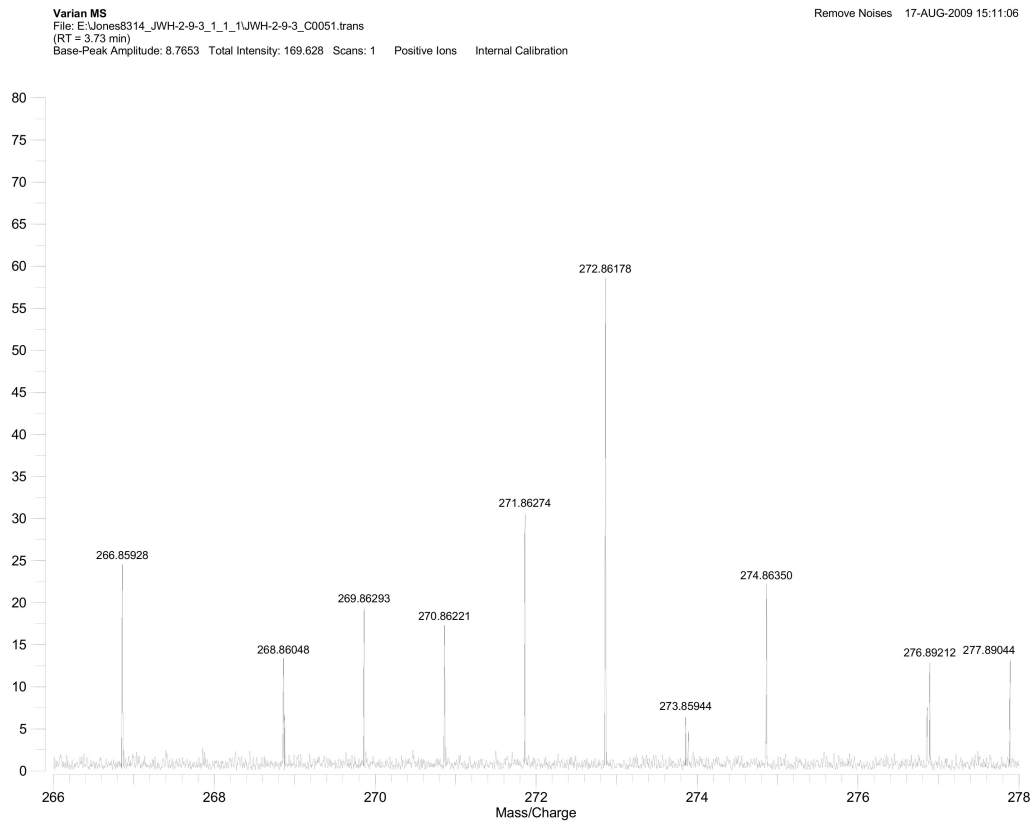

Figure S1. FT-ICR ESI mass spectrum of **1**.

Exact Mass Calculator (Ver 9.0.15)
Varian, Inc.

Base Formula: H12 Cl2 P4 Ru +
Plus Adducts:
Minus Fragment Losses: Cl
Isotopic Enrichment: H12ClP4Ru+
Monoisotopic Mass: 272.86160

Calculated Isotope Distribution
Mass Resolving Power: 60,000

Peak	Mass	Rel. Abun.
A	266.86485	17.22
A+2	268.86223	11.11
A+3	269.86319	39.64
A+4	270.86142	40.13
A+5	271.86260	56.88
A+6	272.86152	100.00
A+6	272.86763	0.19
A+7	273.85988	16.94
A+8	274.86254	58.73
A+10	276.85973	18.49

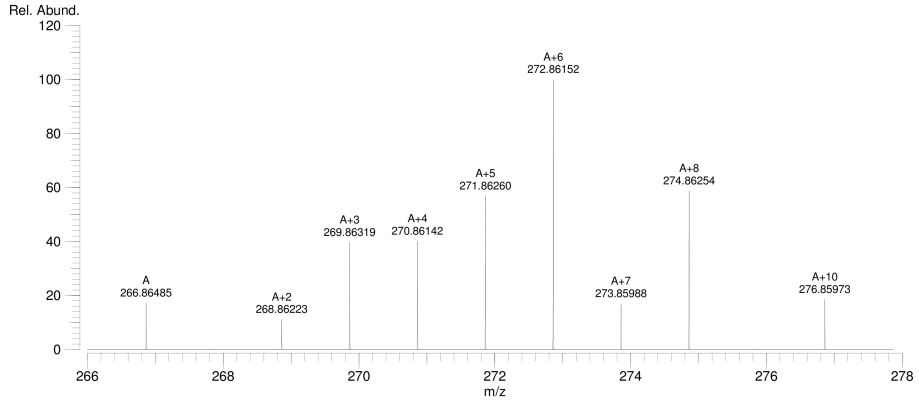

Figure S2. Theoretical isotope pattern of **1**.

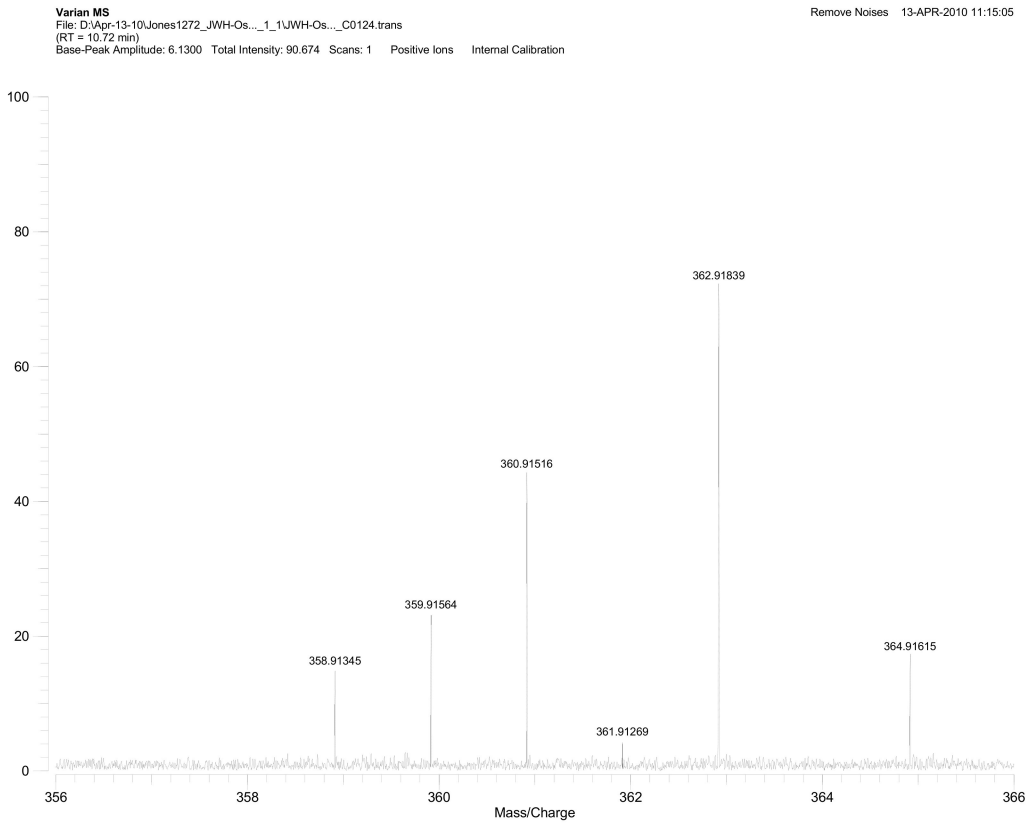

Figure S3. FT-ICR ESI mass spectrum of **2**.

Exact Mass Calculator (Ver 9.0.15)
Varian, Inc.

Base Formula: H12 Cl2 Os P4 +
Plus Adducts:
Minus Fragment Losses: Cl
Isotopic Enrichment: H12ClOsP4+
Monoisotopic Mass: 362.91873

Calculated Isotope Distribution
Mass Resolving Power: 60,000

Peak	Mass	Rel. Abun.
A+2	356.91109	3.90
A+3	357.91300	4.80
A+4	358.91307	32.50
A+5	359.91539	39.60
A+6	360.91566	64.50
A+7	361.91245	12.65
A+8	362.91870	100.00
A+10	364.91578	31.93

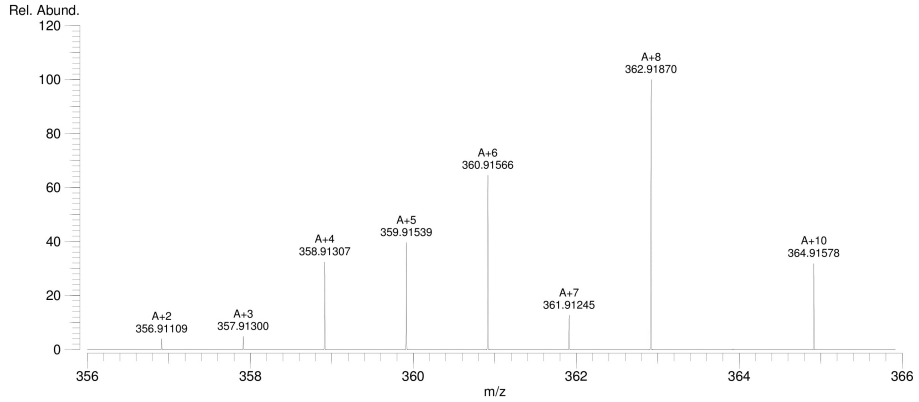

Figure S4. Theoretical isotope pattern of **2**.

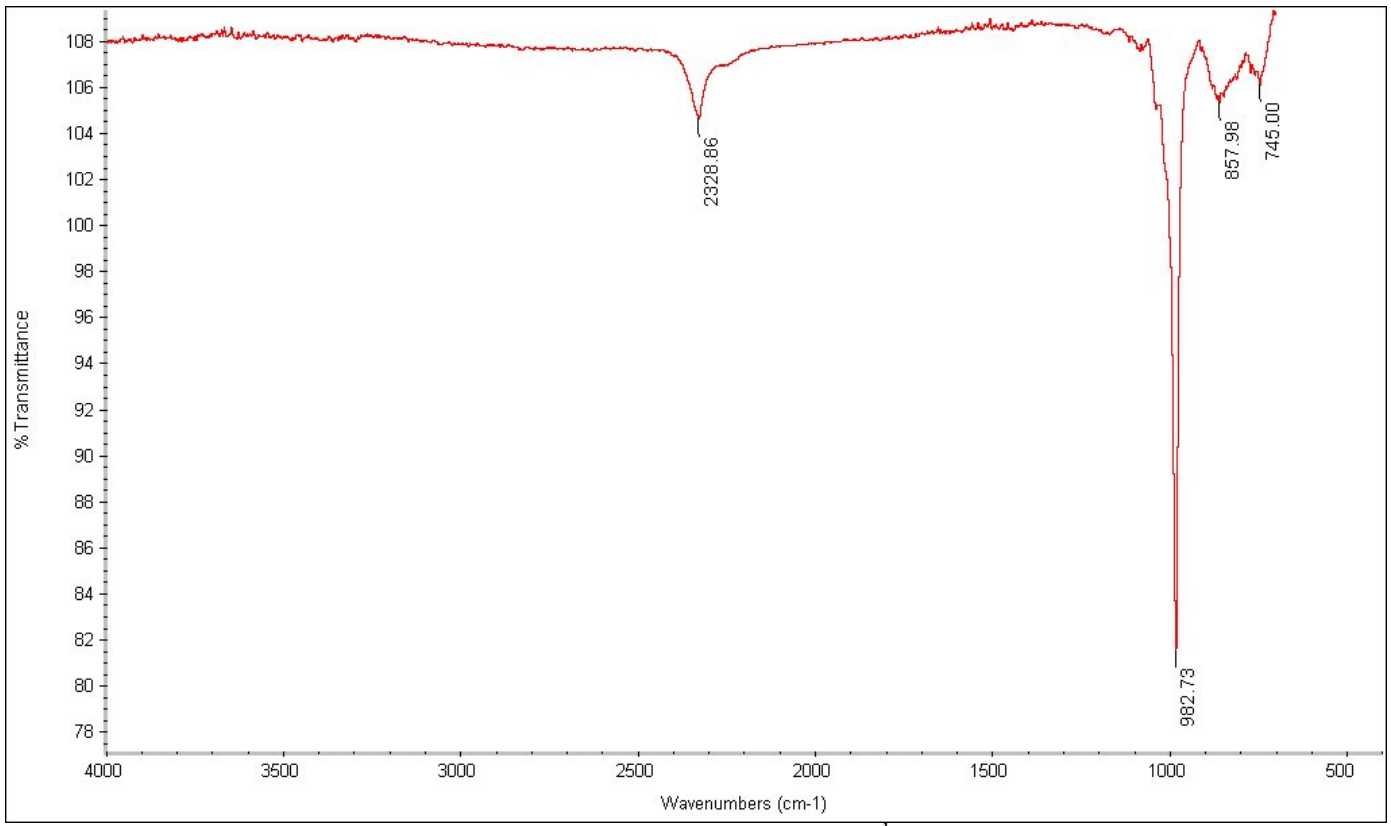

Figure S5. FTIR spectrum of solid **1** in air (ATR, resolution: 1 cm^{-1}).

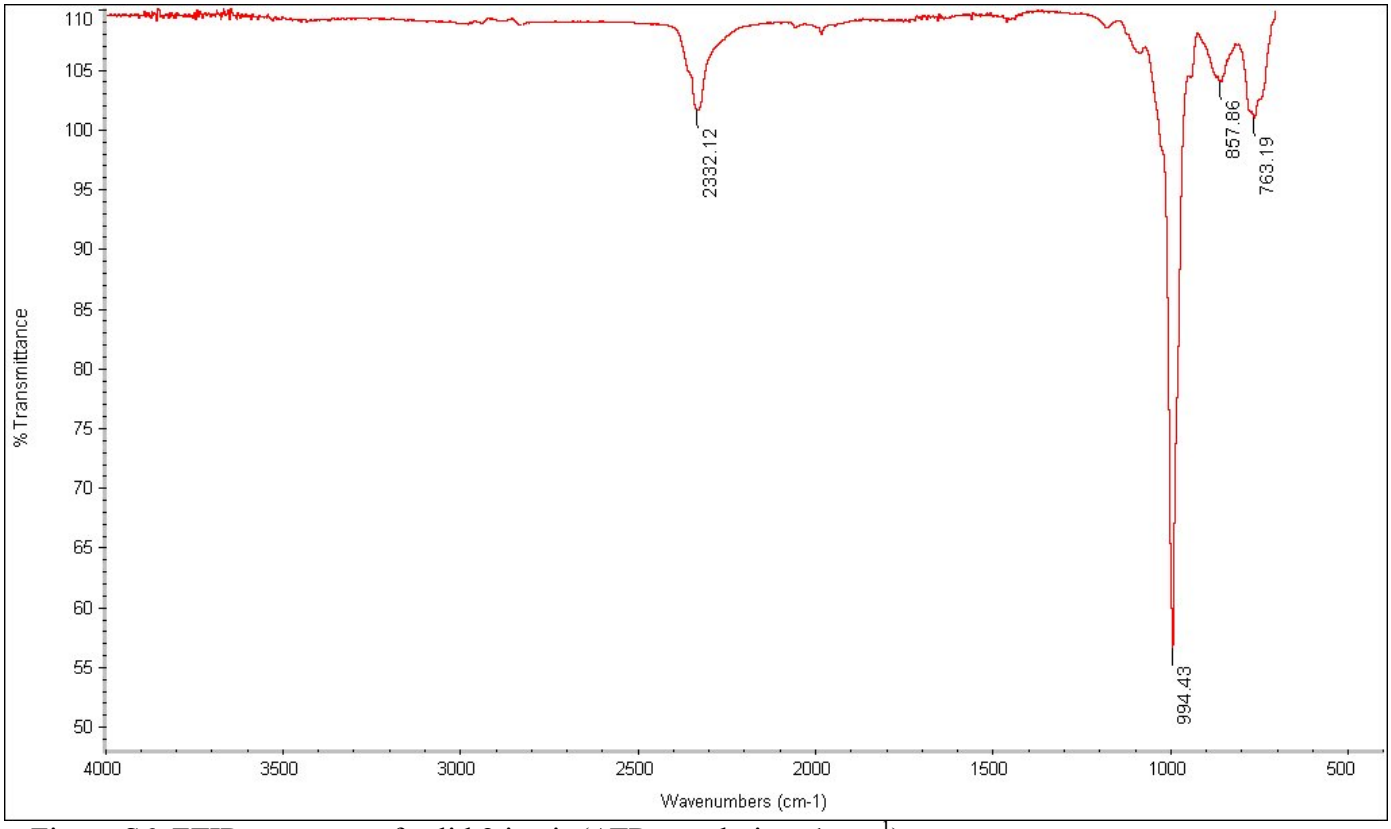

Figure S6. FTIR spectrum of solid **2** in air (ATR, resolution: 1 cm^{-1}).

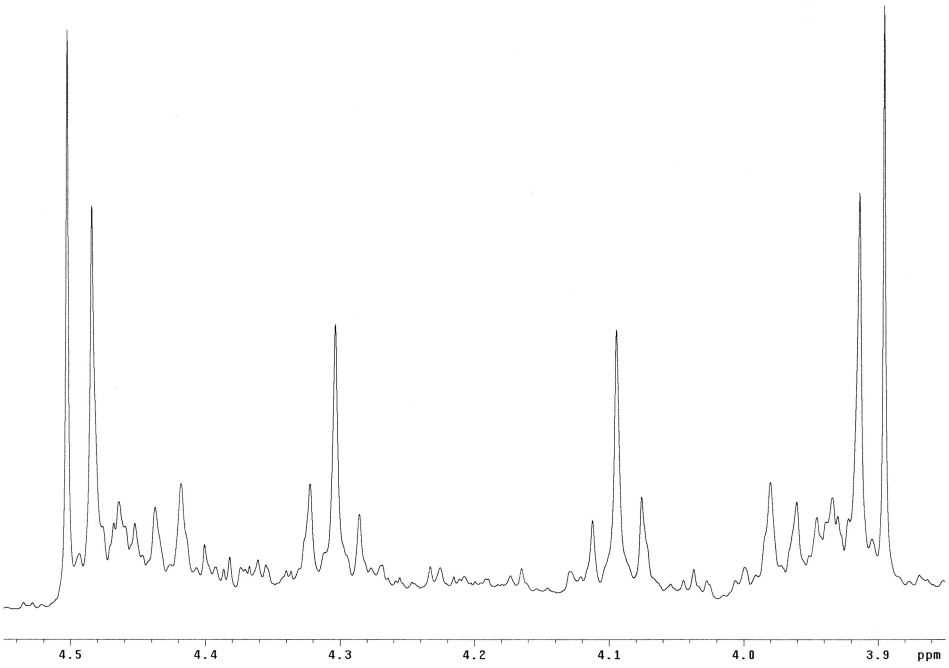

Figure S7. ^{1}H NMR spectrum of **1** in DMSO-d_6 at room temperature.

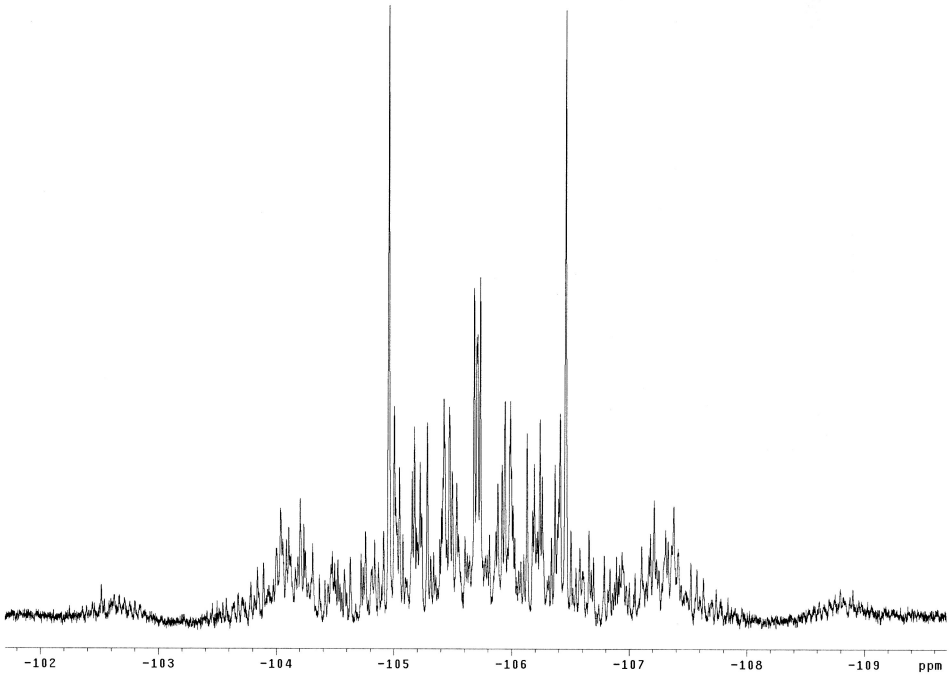

Figure S8. ^{31}P NMR spectrum of **1** in DMSO-d_6 at room temperature.

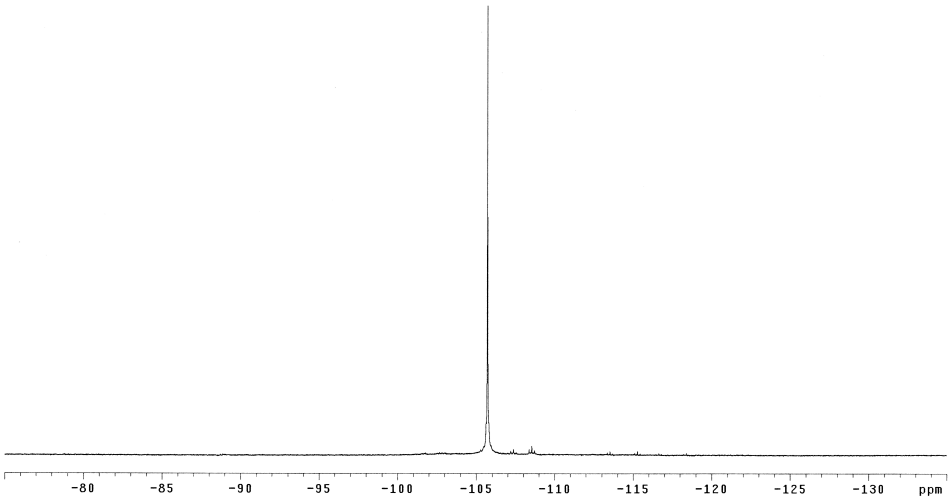

Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of **1** in DMSO-d_6 at room temperature.

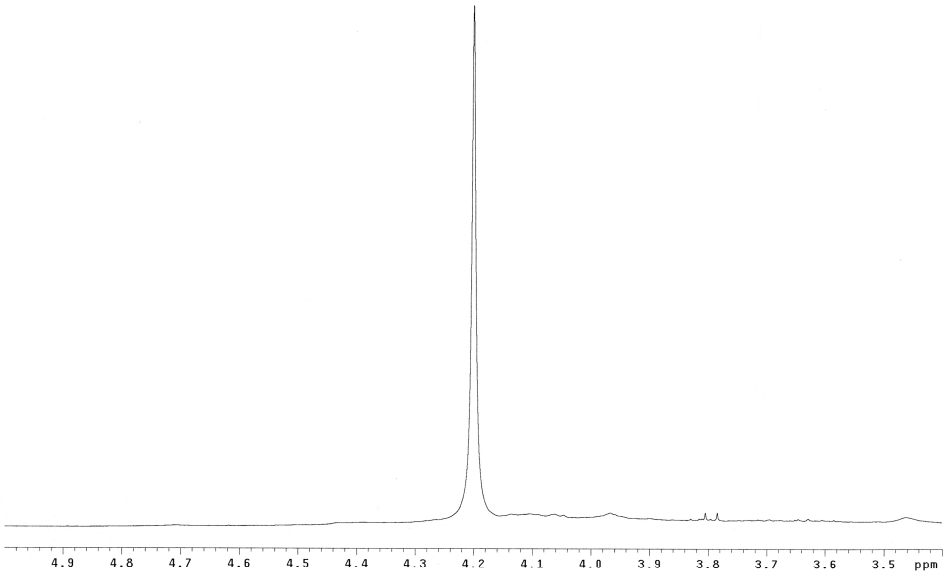

Figure S10. $^{1}H\{^{31}P\}$ NMR spectrum of **1** in DMSO-d_6 at room temperature.

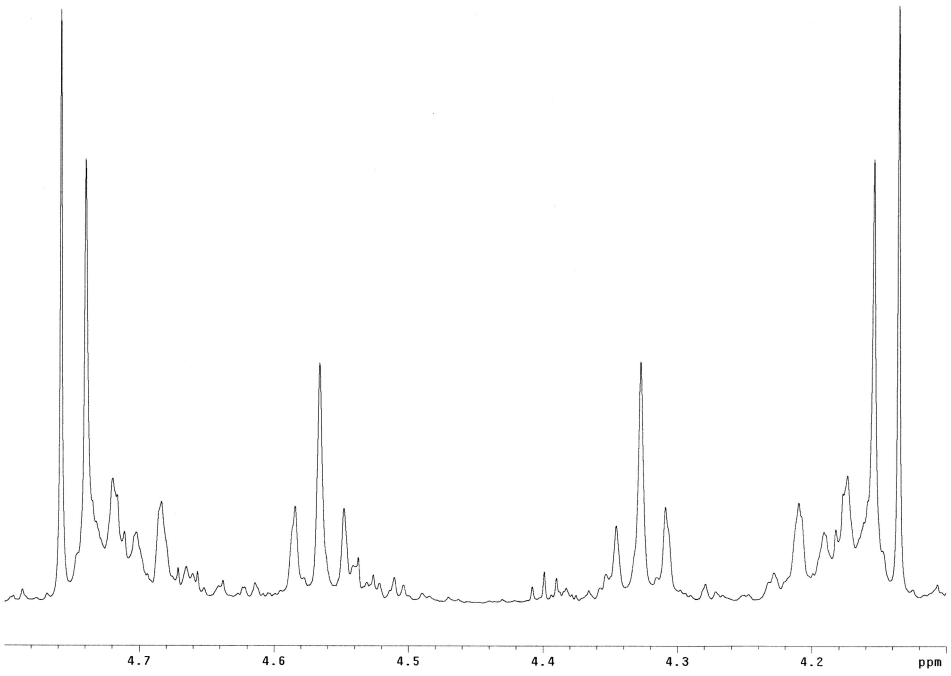

Figure S11. ^{1}H NMR spectrum of **2** in DMSO-d_6 at room temperature.

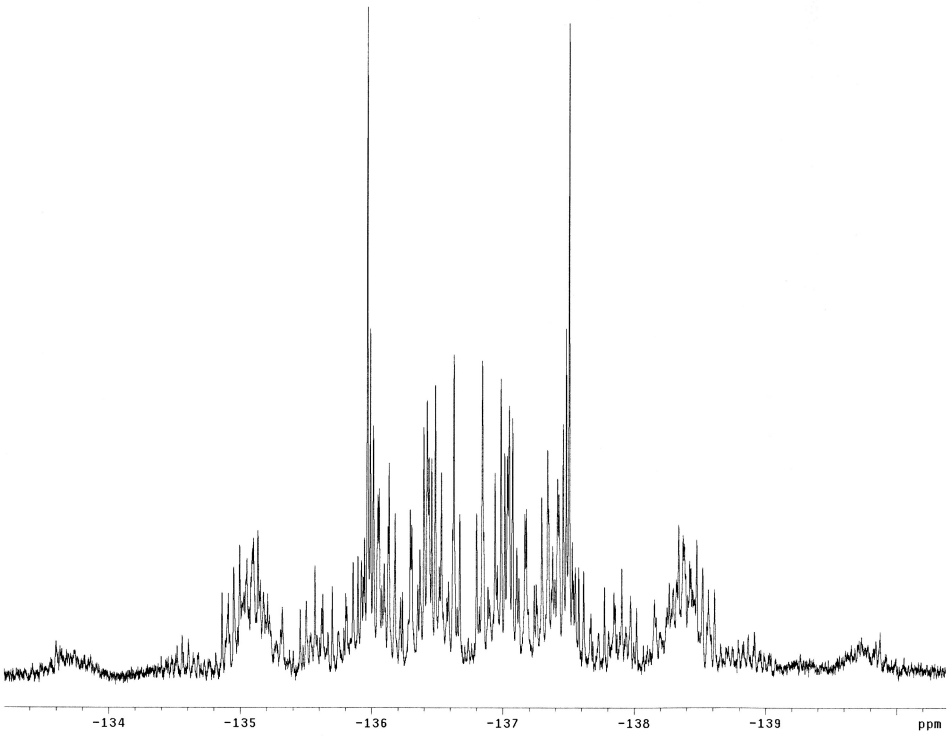

Figure S12. ^{31}P NMR spectrum of **2** in DMSO-d_6 at room temperature.

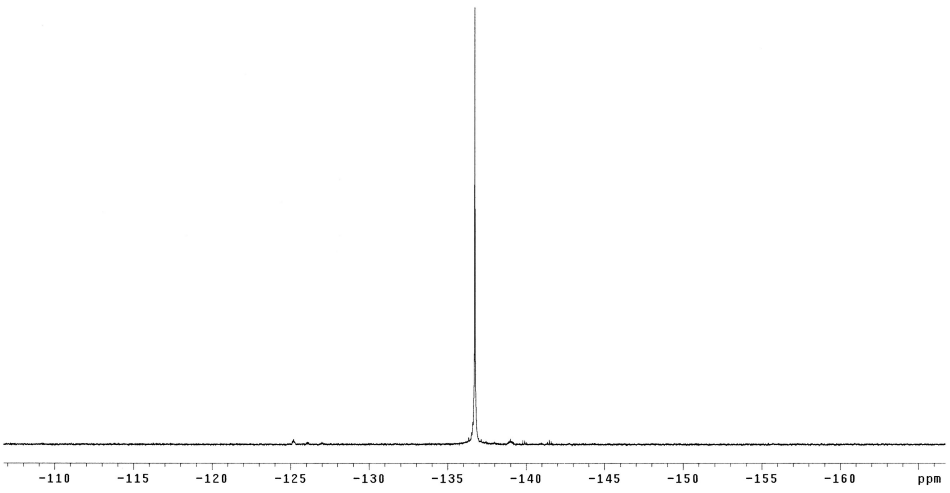

Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in DMSO-d_6 at room temperature.

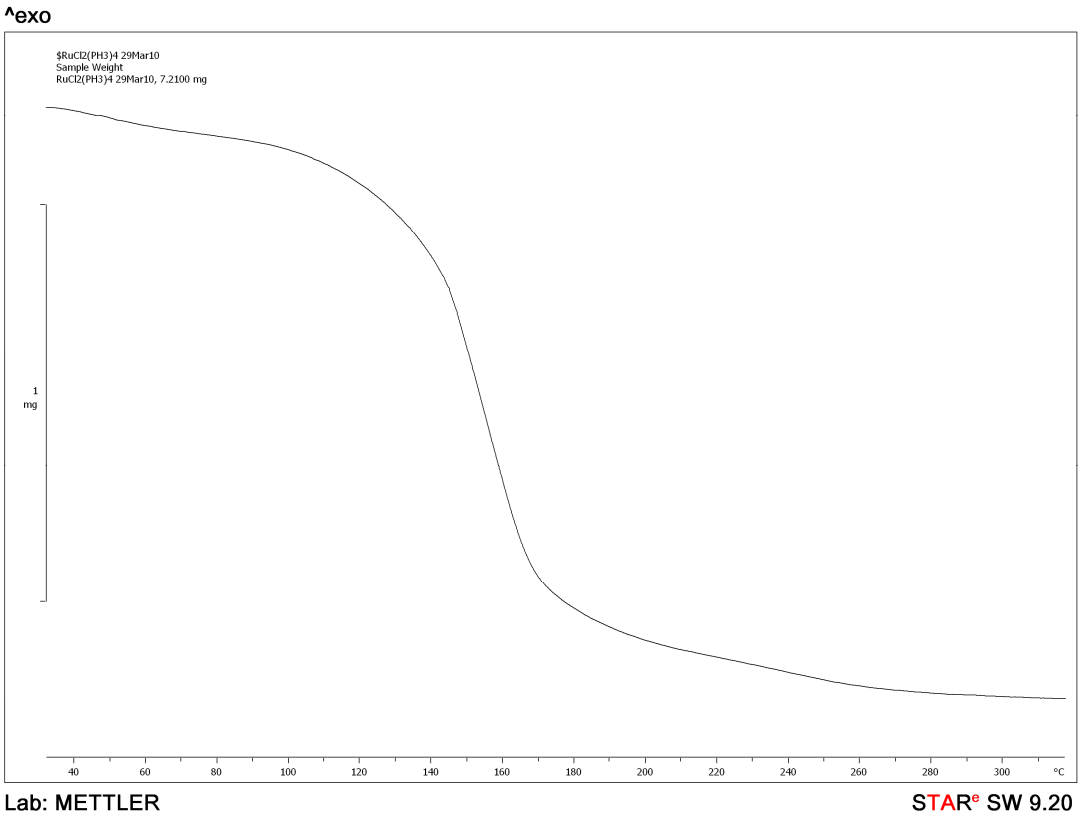

Figure S14. TGA thermogram of **1** (10 °C/min, 120 mL/min N_2).

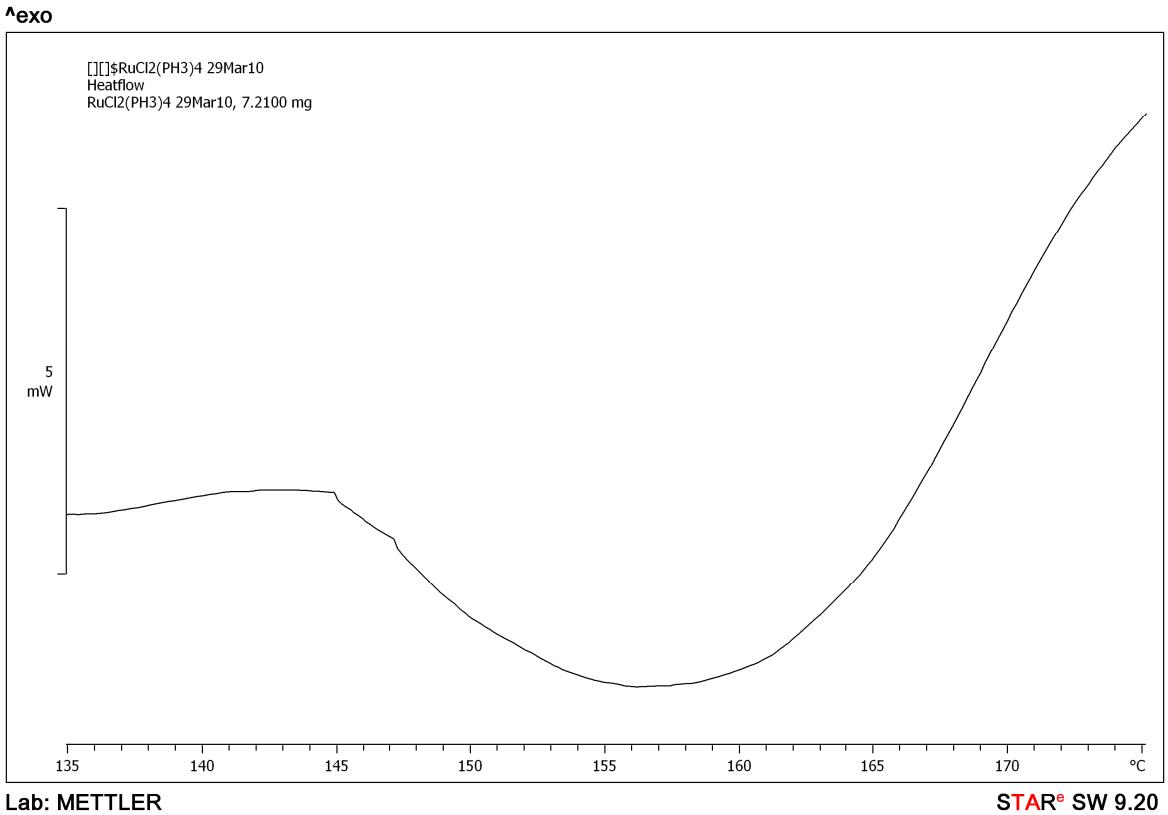

Figure S15. DSC thermogram of **1** (10 °C/min, 120 mL/min N_2).

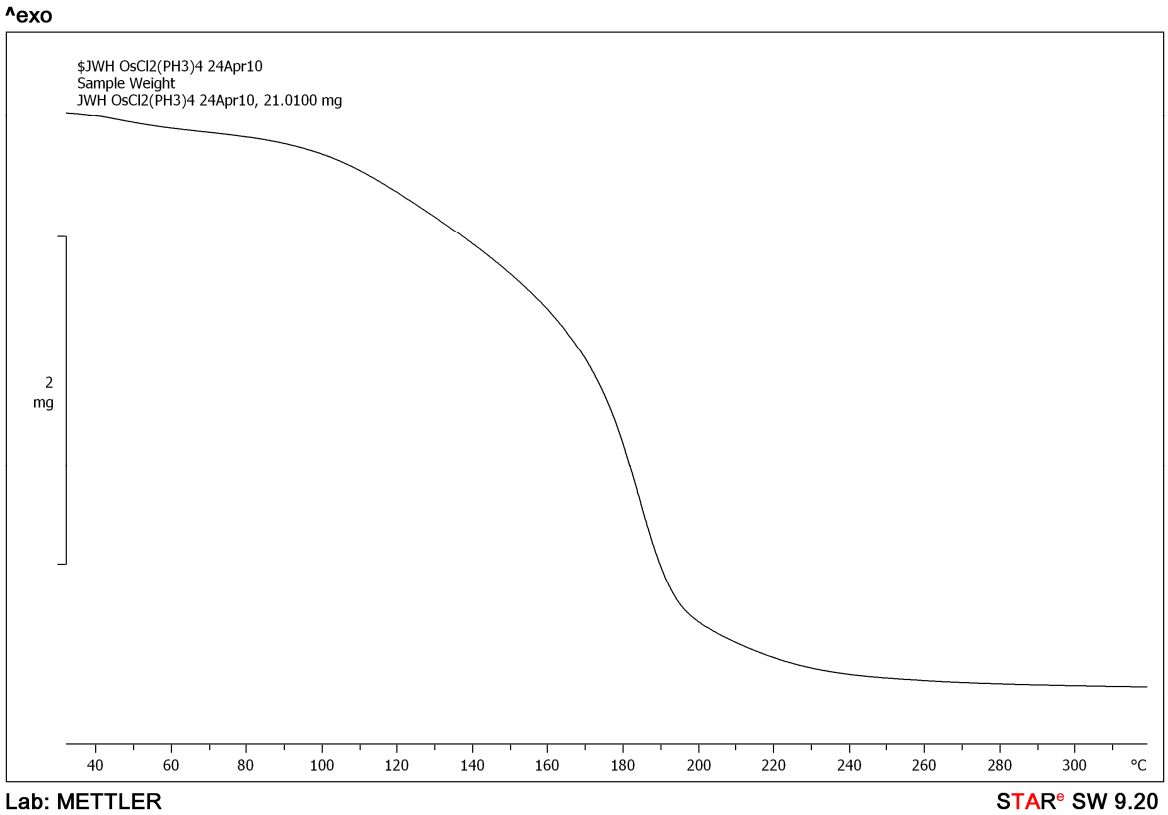

Figure S16. TGA thermogram of **2** (10 °C/min, 120 mL/min N_2).

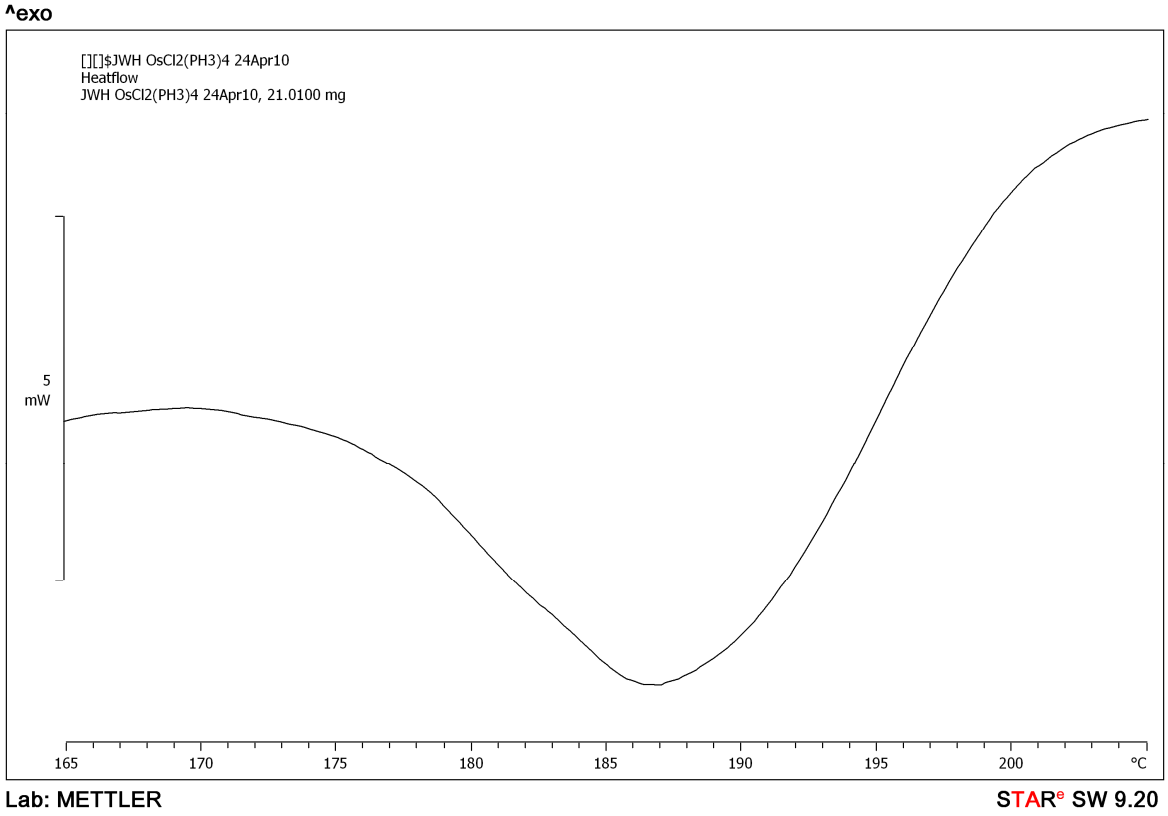

Figure S17. DSC thermogram of **2** (10 °C/min, 120 mL/min N_2).