

From a Mercury(II) Bis(yldiide) Complex to Actinide Yldiides

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1. Experimental

1.1. General considerations

All syntheses were carried out under inert atmosphere of nitrogen using standard Schlenk and glovebox techniques. All glassware used (including NMR tubes) were siliated with Me_3SiCl , at reduced pressure, inside of a glass vacuum desiccator. $[(\text{C}_5\text{Me}_5)_2\text{UCl}_2]^{[1]}$ $[(\text{C}_5\text{Me}_5)_2\text{ThCl}_2]^{[1]}$ $[\text{K}[\text{C}(\text{PPh}_3)\{\text{P}(\text{S})\text{Ph}_2\}]]^{[2]}$ and $\text{K}(\text{CH}_2\text{C}_6\text{H}_5)^{[3]}$ were synthesized according to literature procedure. $[\text{K}[\text{C}(\text{PPh}_3)\{\text{P}(\text{S})\text{Ph}_2\}]]$ was prepared from $\text{HC}(\text{PPh}_3)\{\text{P}(\text{S})\text{Ph}_2\}^{[2]}$ and $\text{K}(\text{CH}_2\text{C}_6\text{H}_5)$ in toluene. Single crystals suitable for X-ray diffraction analyses were grown by slow evaporation of a saturated solution of $\text{HC}(\text{PPh}_3)\{\text{P}(\text{S})\text{Ph}_2\}$ in cyclohexane. Single crystals of $[\text{K}[\text{C}(\text{PPh}_3)\{\text{P}(\text{S})\text{Ph}_2\}]] \cdot (18\text{-crown-6})$ suitable for X-ray diffraction analyses were grown for a saturated solution of $[\text{K}[\text{C}(\text{PPh}_3)\{\text{P}(\text{S})\text{Ph}_2\}]]$ and 1 eq of 18-crown-6 in THF. Benzene- d_6 was dried over molecular sieves and degassed with three freeze-pump-thaw cycles. All ^1H and ^{13}C NMR spectrum were collected either on Bruker Avance III 500 or 600 MHz spectrometer. ^{31}P NMR spectrum were collected on Bruker AVII+ 300MHz spectrometer. ^1H and ^{13}C NMR chemical shifts were reported referenced internally to the residual solvent peak at 7.16 ppm (C_6D_6) and 128.06 (C_6D_6). ^{31}P NMR chemical shifts were reported referenced externally to H_3PO_4 at 0 ppm. All heteronuclear NMR spectra were recorded proton decoupled. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analysis was performed on a Carlo Erba 1108 elemental analyzer, outfitted with an A/D converter for analysis using Eager Xperience software. SCXRD data were measured on a Bruker SMART diffractometer with an Apex II area detector (Bruker AXS LLC, USA) using Mo $\text{K}\alpha$ radiation from a sealed source with focusing optics. Collection temperatures were controlled using Cryostream 700 and 800 cryostats (Oxford Cryosystems, UK). Hemispheres of data were collected using strategies of scans about the omega and phi axes. The Bruker Apex3 software suite was used for unit cell determination, data collection, and data reduction.

Caution! ^{232}Th (1.41×10^{10} a, 4.081 MeV) and ^{238}U (4.47×10^{10} a, 4.267 MeV) are alpha emitters, and should be handled with proper radiological controls and safety protocols. Organomercury complexes are highly toxic and must be handled with multiple layers of butyl or nitrile gloves.

1.1 Synthesis of $[\text{Hg}(\text{C}(\text{PPh}_3)\{\text{P}(\text{S})\text{Ph}_2\})_2]$

HgI_2 (500 mg, 1.10 mmol) was dissolved in a scintillation vial using 5 mL of THF, producing a colorless solution. This was placed in a freezer at $-45\text{ }^\circ\text{C}$. In a separate vial, a suspension of benzyl potassium, (157 mg, 1.21 mmol) in 5 mL of toluene was added to a toluene solution of $\text{HC}(\text{PPh}_3)\{\text{P}(\text{S})\text{Ph}_2\}$ (542 mg, 1.10 mmol) at room temperature. The deprotonation reaction was allowed to stir for 30 min, and the resultant orange suspension was filtered to yield a light-yellow solution of $\text{K}[\text{C}(\text{PPh}_3)\{\text{P}(\text{S})\text{Ph}_2\}]$. This solution was allowed to cool for 15 minutes at $-45\text{ }^\circ\text{C}$. After this, the mercuric iodide solution was added dropwise over the course of 10 minutes with vigorous stirring. After 30 min, the solution produced a suspended precipitate. The reaction was allowed to stir for 1 hour and subsequently filtered through Celite, yielding a pale-yellow solution. Solvent was removed *in vacuo* and was replaced with a minimal amount of toluene. X-ray quality crystals were obtained overnight after storing at $-25\text{ }^\circ\text{C}$. 937 mg, 72%.

^1H NMR (600 MHz, THF-*d*₈, 300 K): δ 7.07 – 7.15 (m, 6H, $\text{PPh}_3H_{\text{Ph},\text{meta}}$), 7.18 – 7.25 (m, 12H, $\text{PPh}_3H_{\text{Ph},\text{para},\text{meta}}$), 7.32 – 7.38 (m, 10H $\text{SPPH}_2H_{\text{Ph},\text{para}}$, $\text{PPh}_3H_{\text{Ph},\text{ortho}}$), 7.37 – 7.42 (m, 4H, $\text{SPPH}_2H_{\text{Ph},\text{meta}}$), 7.43 – 7.49 (m, 4H, $\text{SPPH}_2H_{\text{Ph},\text{meta}}$), 7.62 – 7.75 (m, 10H, $\text{SPPH}_2H_{\text{Ph},\text{ortho}}$, $\text{PPh}_3H_{\text{Ph},\text{ortho}}$), 7.81 – 7.95 (m, 4H, $\text{SPPH}_2H_{\text{Ph},\text{ortho}}$) ppm. **$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, THF-*d*₈, 300 K):** δ 43.94 (m, PCP), 128.14 (d, $^3J_{\text{CP}} = 11.5\text{ Hz}$, $\text{SPPH}_2\text{CH}_{\text{Ph},\text{meta}}$), 128.24 (d, $^3J_{\text{CP}} = 12.1\text{ Hz}$, $\text{SPPH}_2\text{CH}_{\text{Ph},\text{meta}}$), 128.88 (d, $^3J_{\text{CP}} = 11.8\text{ Hz}$, $\text{PPh}_3\text{CH}_{\text{Ph},\text{meta}}$), 129.12 (d, $^3J_{\text{CP}} = 12.3\text{ Hz}$, $\text{PPh}_3\text{CH}_{\text{Ph},\text{meta}}$), 129.76 (d, $^4J_{\text{CP}} = 2.9\text{ Hz}$, $\text{SPPH}_2\text{CH}_{\text{Ph},\text{para}}$), 129.83 (d, $^4J_{\text{CP}} = 2.8\text{ Hz}$, $\text{SPPH}_2\text{CH}_{\text{Ph},\text{para}}$), 131.75 (d, $^2J_{\text{CP}} = 10.7\text{ Hz}$, $\text{SPPH}_2\text{CH}_{\text{Ph},\text{ortho}}$), 131.82 (d, $^4J_{\text{CP}} = 2.8\text{ Hz}$, $\text{PPh}_3\text{CH}_{\text{Ph},\text{para}}$), 132.27 (d, $^4J_{\text{CP}} = 3.1\text{ Hz}$, $\text{PPh}_3\text{CH}_{\text{Ph},\text{para}}$), 132.47 (d, $^2J_{\text{CP}} = 10.4\text{ Hz}$, $\text{SPPH}_2\text{CH}_{\text{Ph},\text{ortho}}$), 134.54 (d, $^2J_{\text{CP}} = 10.3\text{ Hz}$, $\text{PPh}_3\text{CH}_{\text{Ph},\text{ortho}}$), 134.82 (d, $^2J_{\text{CP}} = 9.5\text{ Hz}$, $\text{PPh}_3\text{CH}_{\text{Ph},\text{ortho}}$) ppm. **$^{31}\text{P}\{^1\text{H}\}$ NMR (120 MHz, THF-*d*₈, 298 K):** δ 21.82 (d, $^2J_{\text{PP}} = 19.8\text{ Hz}$, PPh_3), 43.61 (d, $^2J_{\text{PP}} = 19.8\text{ Hz}$, SPPH_2). **IR (KBr, cm^{-1}):** 3450 (w), 3052 (m), 1486 (m), 1436 (s), 1390 (w), 1309 (w), 1097 (s), 1044 (s), 1313 (w), 966 (m), 854 (s), 746 (s), 691 (s), 638 (m), 505 (s).

The ipso carbon atoms as well as the central bridging carbon could not be resolved in the regular $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The bridging carbon was subsequently detected through $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy on **1** with a ^{13}C labelled ylidic carbon atom. For the labelled species, the $^{13}\text{C}\{^1\text{H}\}$ NMR signal of the central carbon atom appears as a multiplet at 43.9 ppm. The signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum show the expected splitting to a doublet of doublets, because of the additional coupling with the ^{13}C enriched C1 atom. While the $^2J_{\text{PP}}$ coupling amounts to 19.9 Hz, the $^1J_{\text{PC}}$ couplings are measured to be 67.1 (P(S) signal) and 79.4 Hz (PPh_3 group), respectively.

Supporting Information

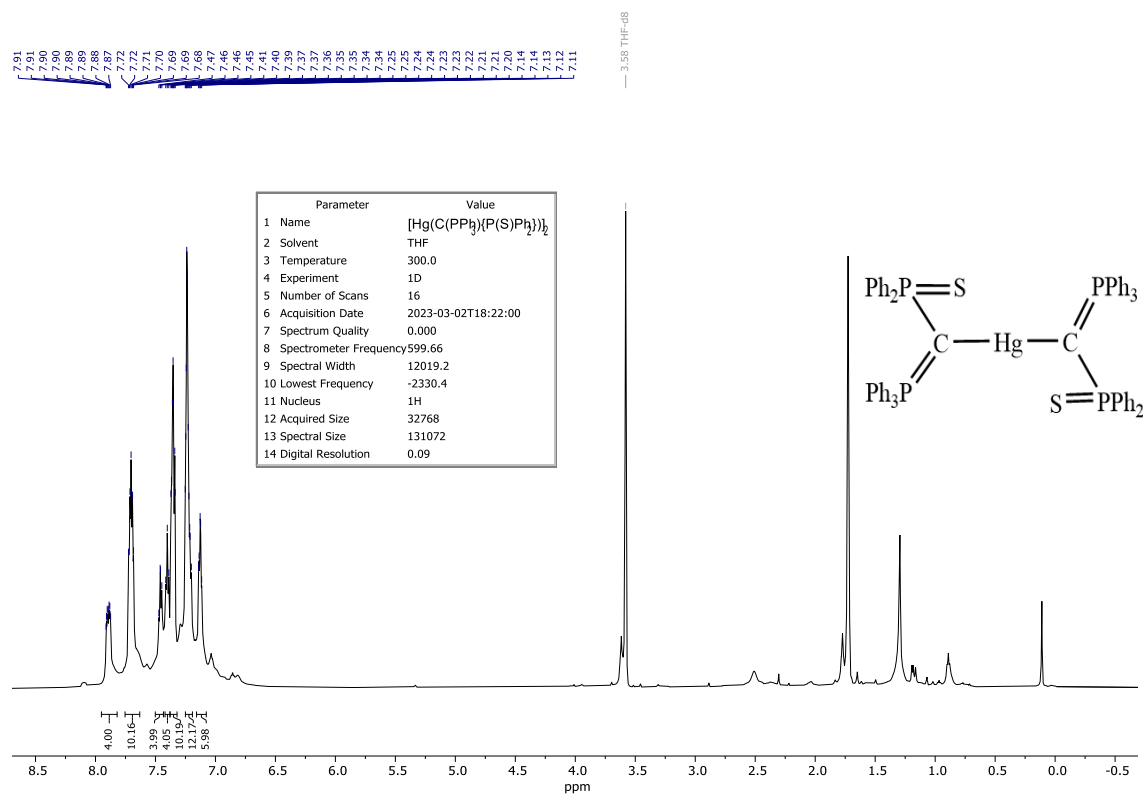


Figure S1: ¹H NMR (600 MHz, THF-d₈, 300 K): spectrum of [Hg(C(PPh₃){P(S)Ph₂)}₂].

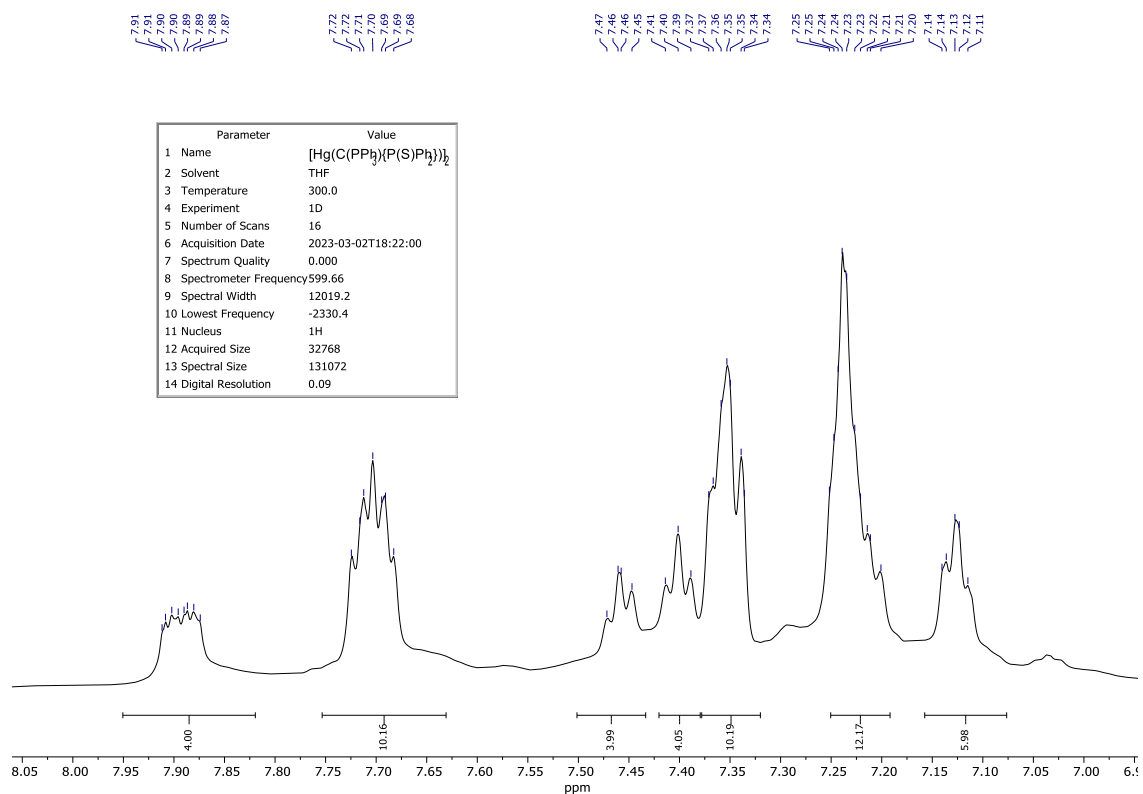


Figure S2: Aryl region of ¹H NMR (600 MHz, THF-d₈, 300 K) spectrum of [Hg(C(PPh₃){P(S)Ph₂)}₂].

Supporting Information

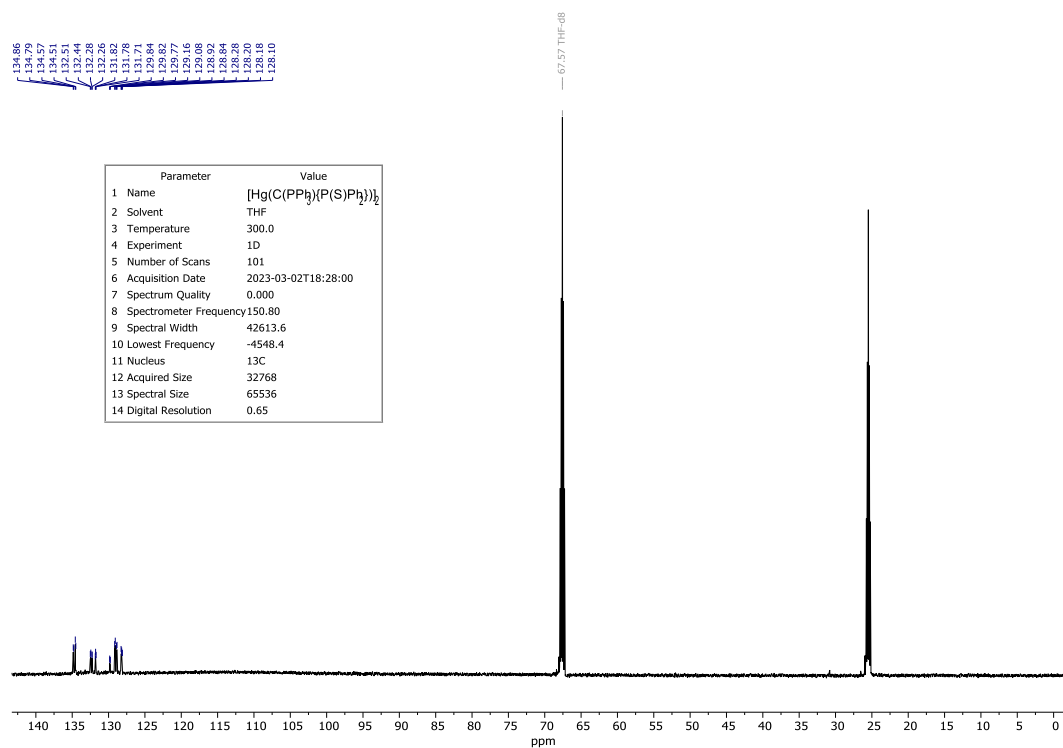


Figure S3: $^{13}\text{C}\{^1\text{H}\}$ (150 MHz, THF- d_8 , 300 K) spectrum of [Hg(C(PPh₃){P(S)Ph₂})₂].

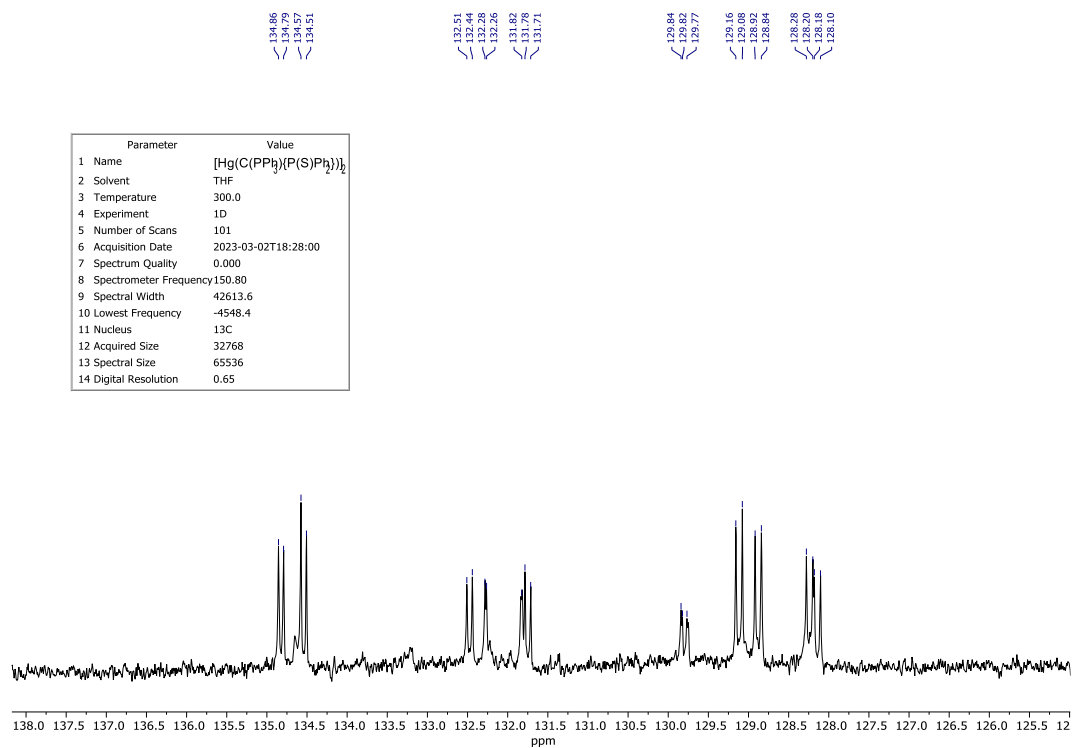


Figure S4: Aryl region of $^{13}\text{C}\{^1\text{H}\}$ (150 MHz, THF- d_8 , 300 K) spectrum of [Hg(C(PPh₃){P(S)Ph₂})₂].

Supporting Information

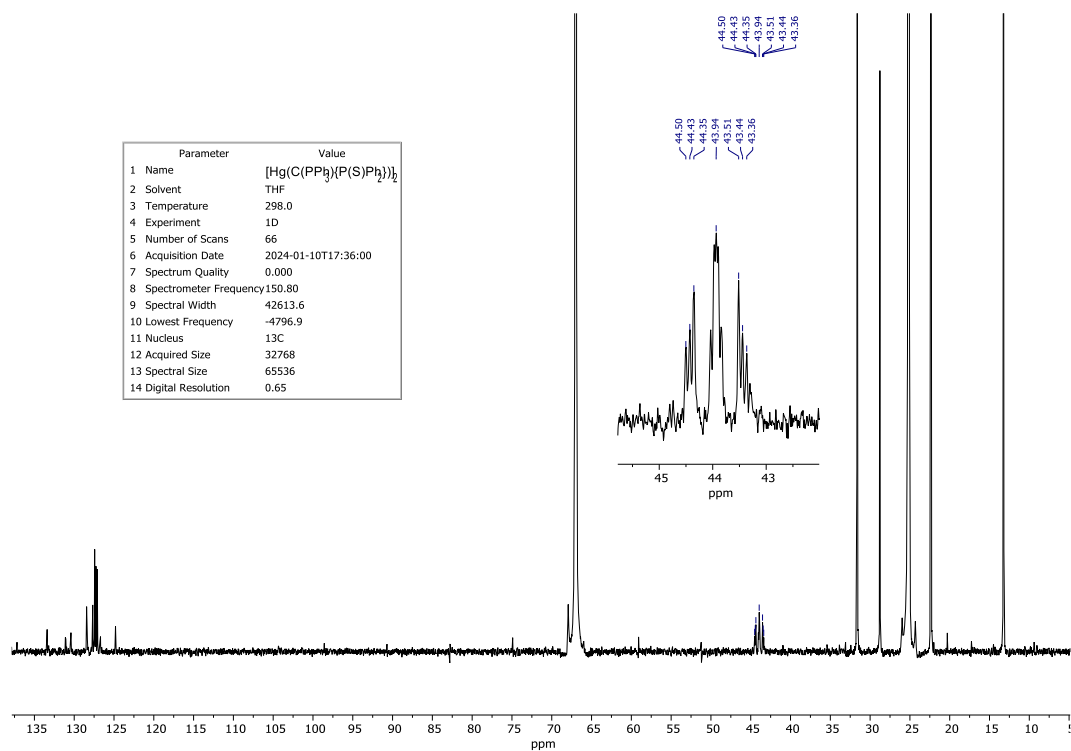


Figure S5: $^{13}\text{C}\{^1\text{H}\}$ (150 MHz, THF, 298 K) spectrum of ^{13}C -labeled $[\text{Hg}(\text{C}(\text{PPh}_3)\{\text{P}(\text{S})\text{Ph}_2\})_2]$. The sample was only prepared on a milligram scale and not fully purified, but only used for detection of the ylidic carbon atom.

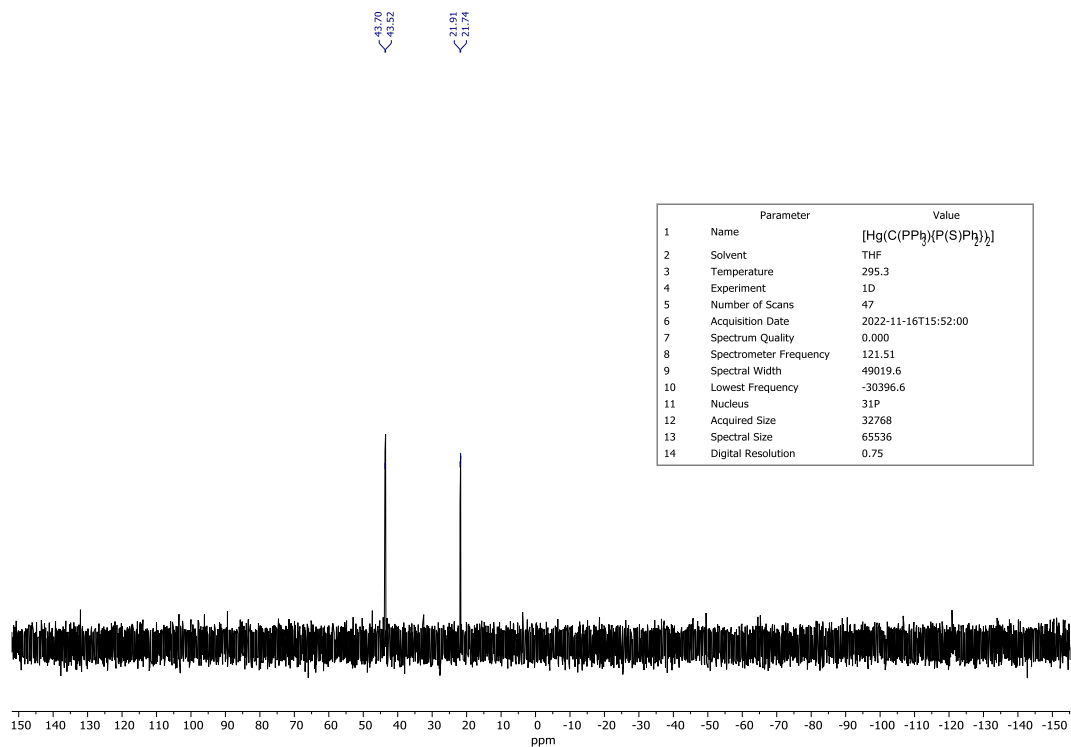


Figure S6: $^{31}\text{P}\{^1\text{H}\}$ NMR (120 MHz, THF-*d*₈, 298 K) spectrum of $[\text{Hg}(\text{C}(\text{PPh}_3)\{\text{P}(\text{S})\text{Ph}_2\})_2]$.

Supporting Information

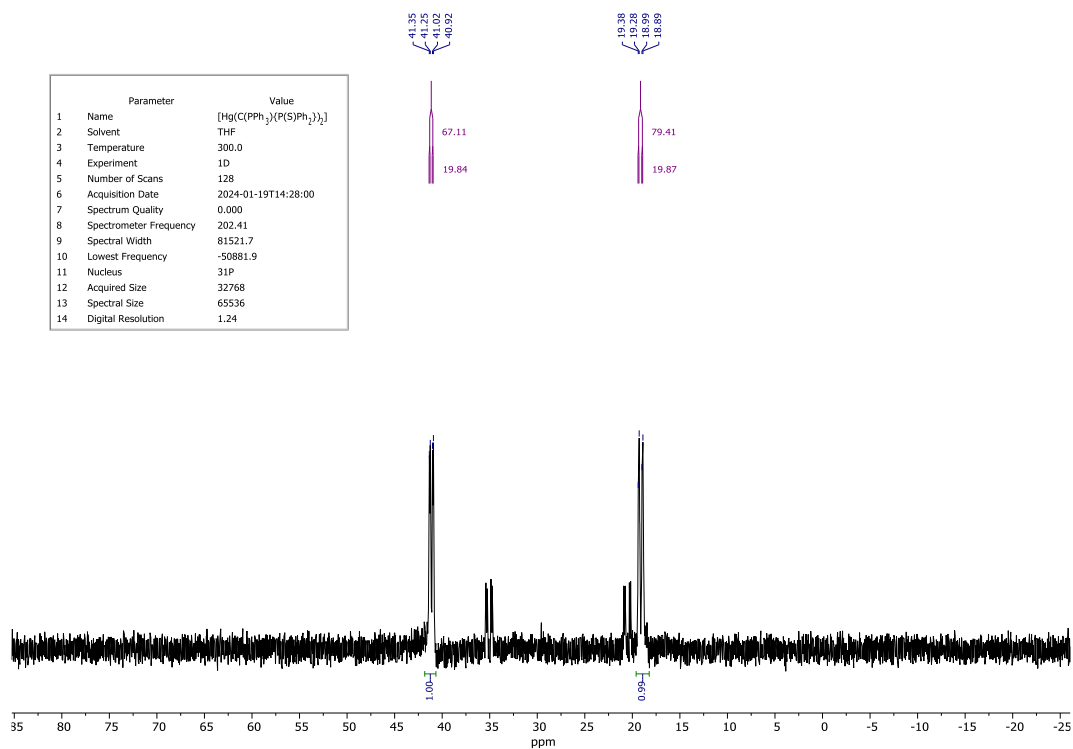


Figure S7: $^{31}\text{P}\{^1\text{H}\}$ NMR (120 MHz, THF- d_8 , 298 K) spectrum of ^{13}C -labeled $[\text{Hg}(\text{C}(\text{PPh}_3)\{\text{P}(\text{S})\text{Ph}_2\})_2]$. The sample was only prepared on a milligram scale and not fully purified, but only used for detection of the ylidic carbon atom. The NMR spectrum thus shows $^{31}\text{P}\{^1\text{H}\}$ NMR signals of the still present ^{13}C -labeled ylide ($\delta = 20.5, 35.1$ ppm).

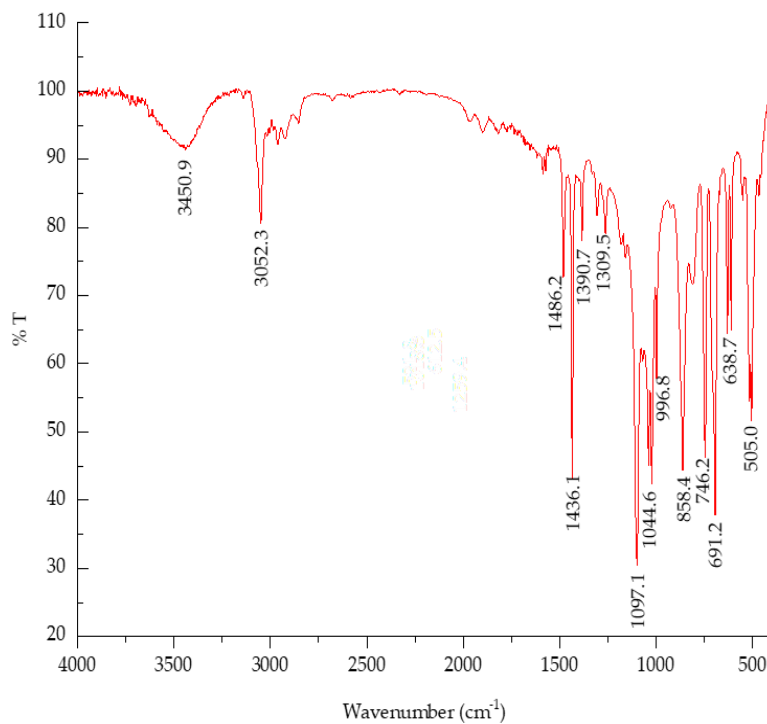


Figure S8: FTIR vibrational spectrum of $[\text{Hg}(\text{C}(\text{PPh}_3)\{\text{P}(\text{S})\text{Ph}_2\})_2]$.

1.2 Synthesis of $[(C_5Me_5)_2Th(\kappa^2-(C,S)-C(PPh_3)\{P(S)Ph_2\})](Cl)$

Method A: To a vial containing $[(C_5Me_5)_2ThCl_2]$ (200 mg, 0.348 mmol), 10 mL of toluene was added, producing an off-white suspension, this was allowed to stir at room temperature for 3h. In a separate vial, a suspension of benzyl potassium, (54 mg, 0.0418 mmol) in 5 mL of toluene was added to a toluene solution of $HC(PPh_3)\{P(S)Ph_2\}$ (171 mg, 0.348 mmol). The deprotonation reaction was allowed to stir for 30 min, and the resultant orange suspension was filtered through Celite to yield a pale-yellow solution of $K(CH_2C_6H_5)$. This solution was then added dropwise to the suspension of $[(C_5Me_5)_2ThCl_2]$ and allowed to stir for 4 hr. The resultant off-white solution was filtered through Celite, and solvent was removed under reduced pressure. Colorless crystals were obtained from a slow vapor diffusion of *n*-pentane into THF at RT over the course of two days, 97 mg, 28%ⁱ.

Method B: A scintillation vial was charged with 10 mL of toluene and $[(C_5Me_5)_2ThCl_2]$ (83 mg, 0.144 mmol) To this stirring suspension, a colorless THF solution of $[Hg(C(PPh_3)\{P(S)Ph_2\})_2]$ (85 mg, 0.072 mmol) was added dropwise over the course of 5 min, immediately producing a yellow solution and causing the suspended $(C_5Me_5)_2ThCl_2$ to visibly become solubilized. This reaction was allowed to stir for 4 hr, after which, a fine white precipitate had formed. The contents of the scintillation vial were filtered through Celite, and solvent was subsequently removed to yield an off-white powder. Colorless crystals were obtained from a slow vapor diffusion of *n*-pentane into THF at RT over the course of two days, 51 mg, 36%ⁱ.

¹H NMR (300 MHz, THF-*d*₈, 297 K): δ 1.94 (s, 30H, $C_5(CH_3)_5$), 7.03 – 7.29 (m, 10 H), 7.30 – 7.51 (m, 15H) ppm. **¹³C{¹H} NMR (150 MHz, C₆D₆, 300 K):** δ 13.3 (CH_3 , C_5Me_5), 41.96 (PCP, dd, $J_{CP} = 38.24$, 16.52), 125.7 (s, C_5Me_5), 127.9 (d, $^3J_{CP} = 11.9$ Hz, $SPPH_2CH_{Ph,meta}$), 128.4 (d, $^3J_{CP} = 11.7$ Hz, $PPh_3CH_{Ph,meta}$), 130.4 (s, $SPPH_3CH_{Ph,para}$), 131.3 (s, $PPh_3CH_{Ph,para}$), 133.4 (d, $^2J_{CP} = 11.6$, $SPPH_2CH_{Ph,ortho}$), 134.8 (dd, $^1,^3J_{CP} = 84.6 + 8.1$ Hz, $SPPH_2CH_{Ph,ipso}$), 135.6 (d, $^2J_{CP} = 9.8$ Hz, $PPh_3CH_{Ph,ortho}$), 142.9 (d, $^1J_{CP} = 73.5$ Hz $PPh_3CH_{Ph,ipso}$) ppm. **³¹P{¹H} NMR (120 MHz, THF-*d*₈, 297 K):** δ 9.45 (d, $^2J_{PP} = 8.1$ Hz, PPh_3) 20.47 (d, $^2J_{PP} = 8.2$ Hz, $SPPH_3$). **FT-IR (KBr, cm^{-1}):** 3053 (w), 2901 (m), 2859 (m), 2244 (w), 2082 (w), 1488 (m), 1435 (s), 1376 (m), 1313 (w), 1106 (s), 1074 (s), 1023 (w), 767 (s), 692 (m), 591 (m), 522 (m). **Anal. Calcd. (found) for $C_{51}H_{55}P_2SClTh$:** C, 61.65 (62.12%); H, 5.58 (5.10%); S, 3.23 (3.58%).

The central bridging carbon could not be resolved in the regular $^{13}C\{^1H\}$ NMR spectrum, but could be detected through $^{13}C\{^1H\}$ NMR spectroscopy on **2** with a ^{13}C -labelled ylidic carbon atom (Figure S12). The ^{13}C signal of this atom appears as doublet of doublets at 42.0 ppm with $^1J_{PC}$ coupling constants of 16.5 and 38.2 Hz, respectively. These coupling patterns could be confirmed in the $^{31}P\{^1H\}$ NMR spectrum of the labelled compound, which shows the expected splitting and with the coupling constants already observed in the $^{13}C\{^1H\}$ NMR spectrum (Figure S14).

ⁱ Note that the NMR spectrum of the complex repeatedly showed large amounts (e.g. four equivalents in Figure S9) of residual toluene, which we were not able to remove under vacuum. Therefore the isolated yield of the complex might be even lower than indicated herein.

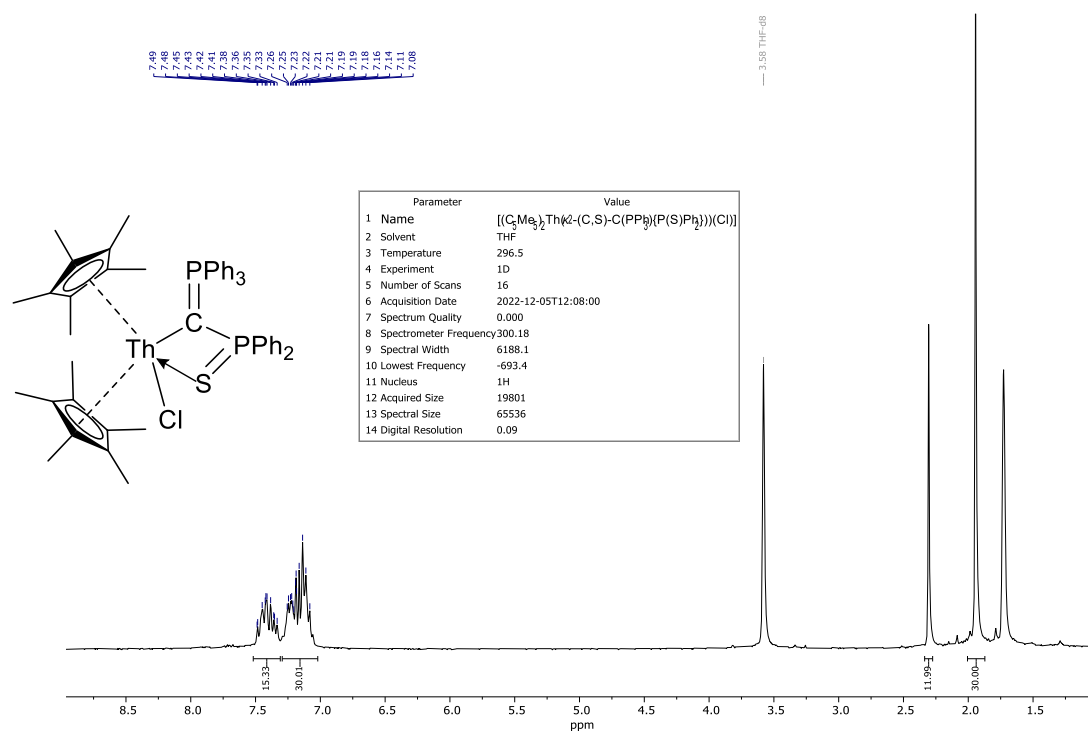


Figure S9: 1H NMR (300 MHz, THF- d_8 , 297 K) spectrum of $[(C_5Me_5)_2Th(\kappa^2-(C,S)-C(PPh_3)\{P(S)Ph_2\})](Cl)]$. The 1H NMR spectrum shows residues of toluene ($\delta = 2.3 + 7.0 - 7.2$ ppm). The integration of the aromatic region in the 1H NMR spectrum reveals the anticipated 25 H signals, along with 20 H signals from toluene, corresponding to the signal intensity of the associated methyl group at 2.3 ppm.

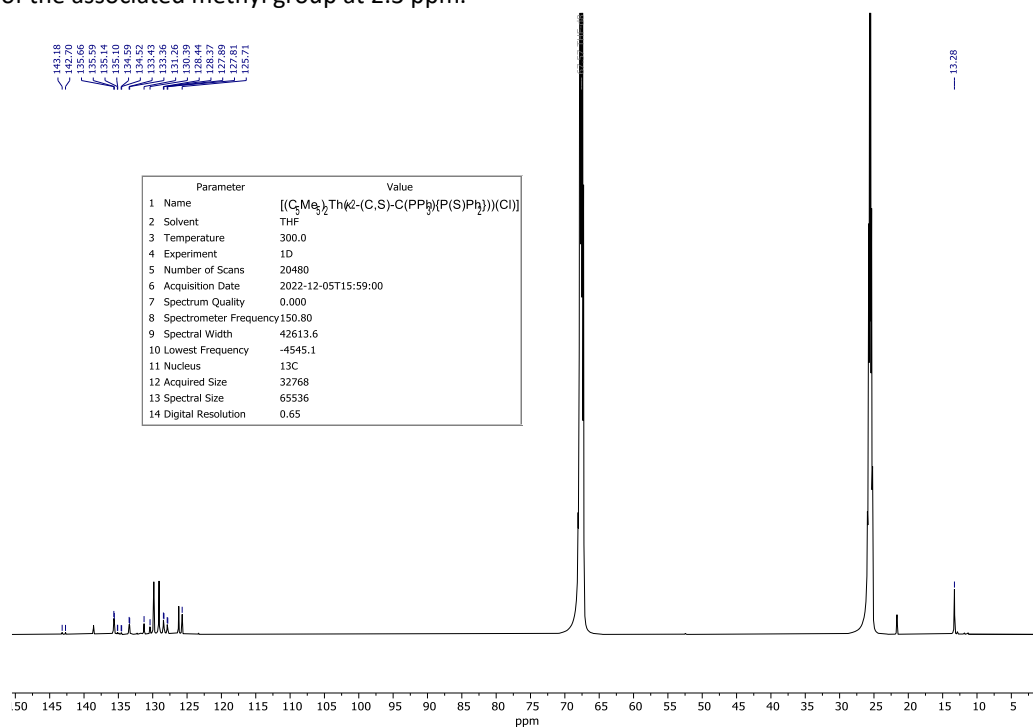


Figure S10: $^{13}C\{^1H\}$ (150 MHz, THF- d_8 , 300 K): spectrum of $[(C_5Me_5)_2Th(\kappa^2-(C,S)-C(PPh_3)\{P(S)Ph_2\})](Cl)]$. The $^{13}C\{^1H\}$ NMR spectrum shows residues of toluene ($\delta = 21.3, 125.9, 128.7, 129.5, 138.2$ ppm).

Supporting Information

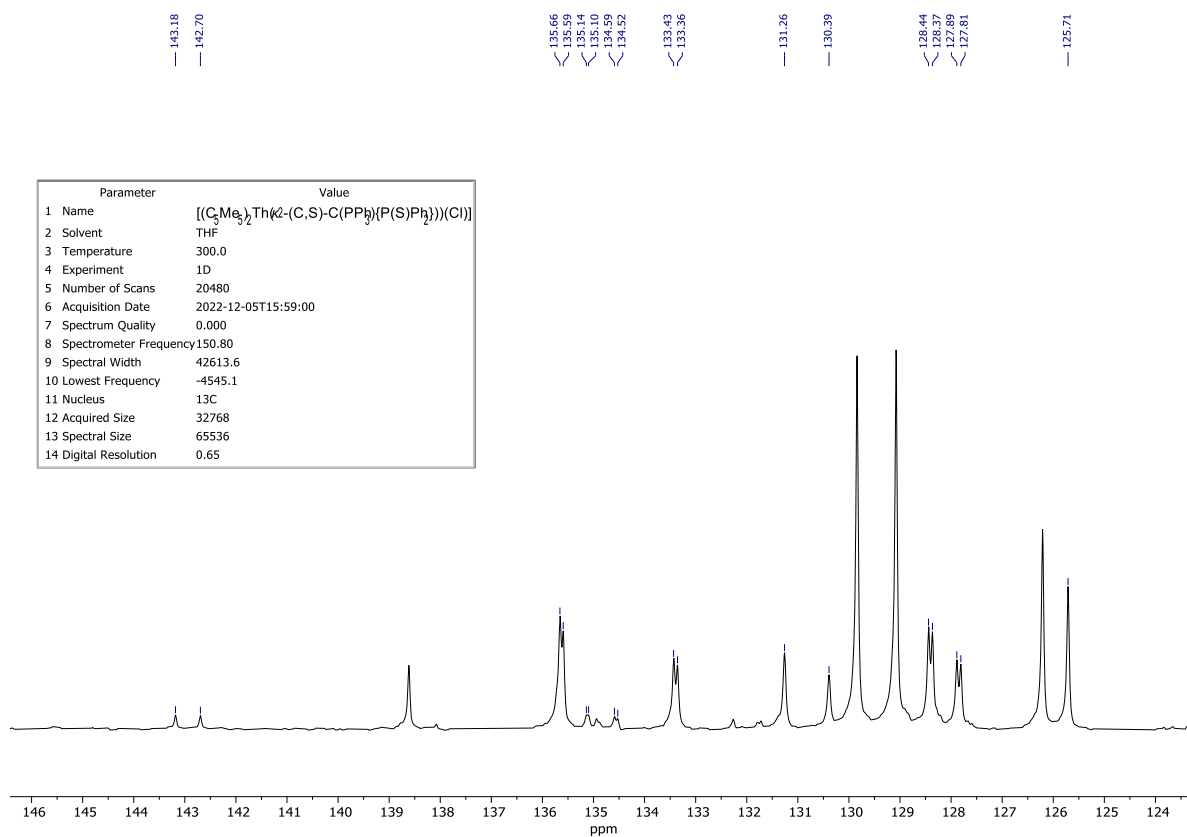


Figure S11: Aryl region of $^{13}C\{^1H\}$ (150 MHz, THF- d_8 , 300 K): spectrum of $[(C_5Me_5)_2Th(\kappa^2-(C,S)-C(PPh_3)\{P(S)Ph_2\})](Cl)]$.

Supporting Information

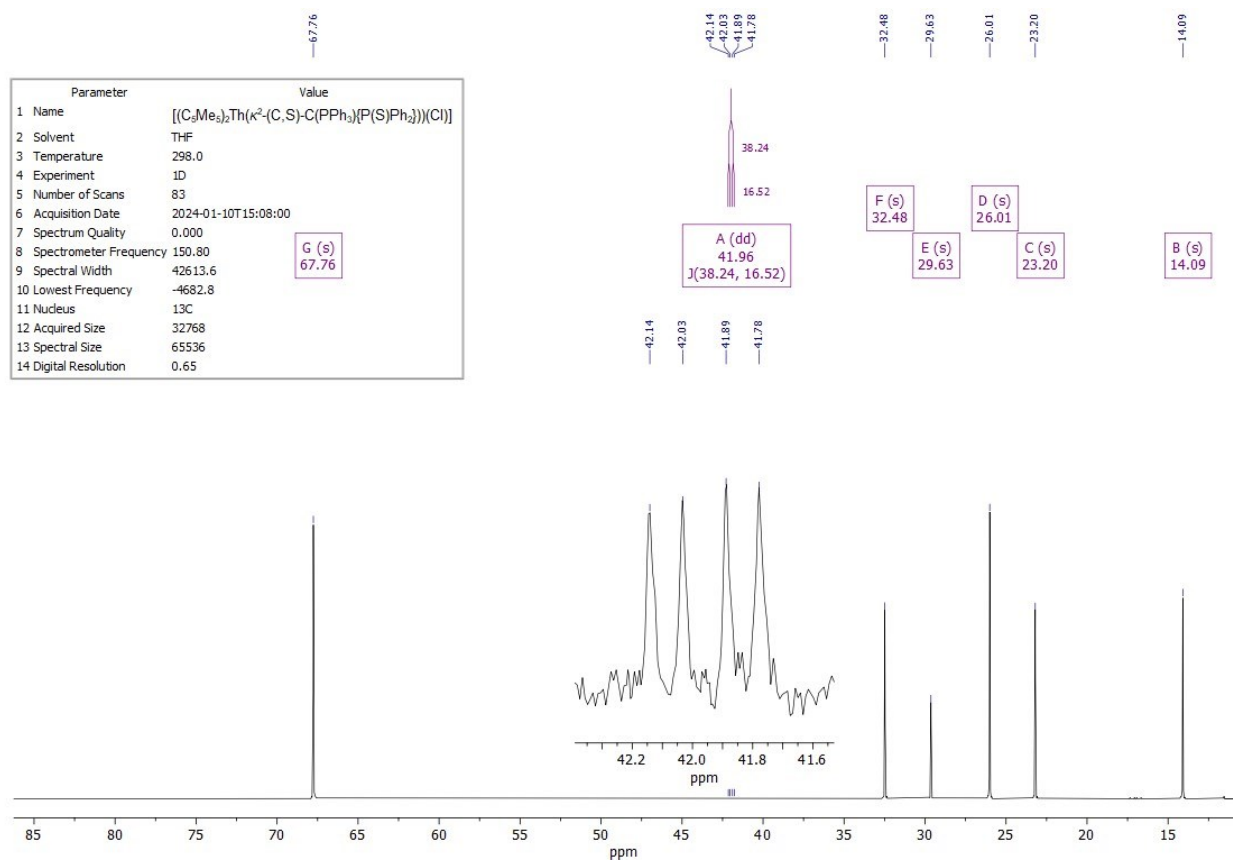


Figure S12: $^{13}C\{^1H\}$ (150 MHz, THF, 298 K): Aliphatic region of ^{13}C -labeled $[(C_5Me_5)_2Th(\kappa^2-(C,S)-C(PPh_3)\{P(S)Ph_2\})\{Cl\})]$. Peaks at 26.0 and 67.8 ppm correspond to non-deuterated THF, peaks at 14.1, 23.2, 29.6 and 32.5 to *n*-heptane. The sample was only prepared on a milligram scale and not fully purified, but only used for detection of the ylidic carbon atom.

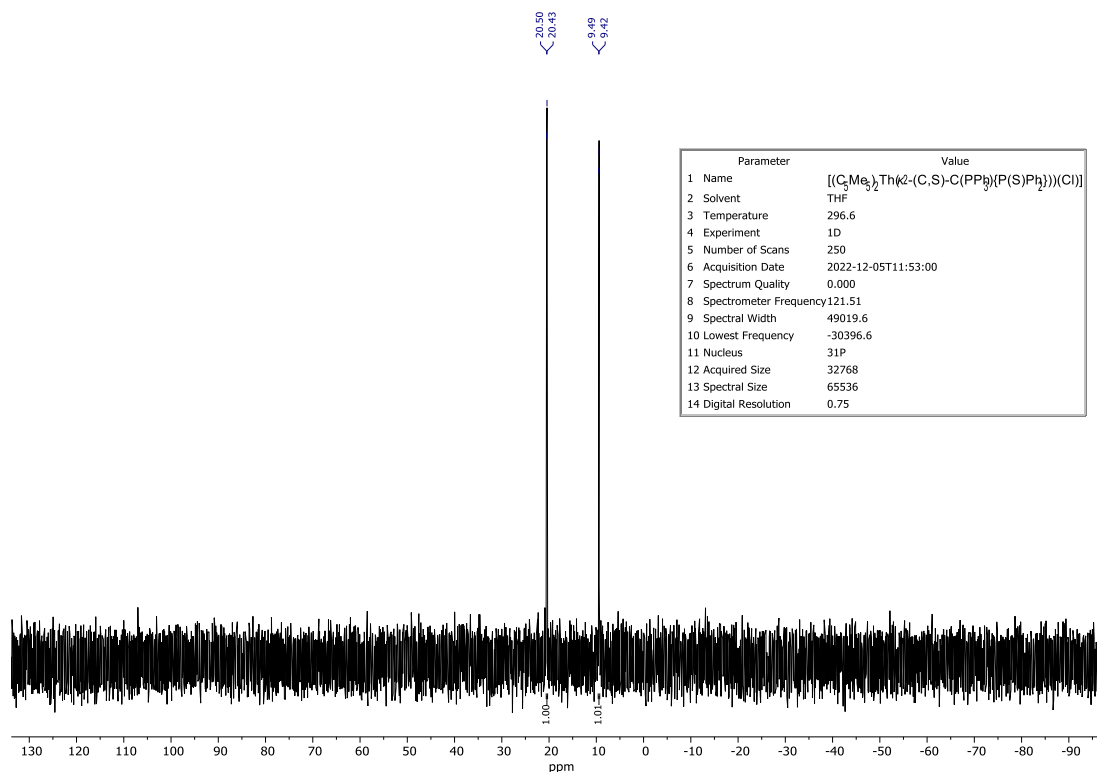


Figure S13: $^{31}\text{P}\{^1\text{H}\}$ (120 MHz, THF- d_8 , 297 K) NMR spectrum of [(C5Me5)2Th(k2-(C,S)-C(PPh3){P(S)Ph2})(Cl)].

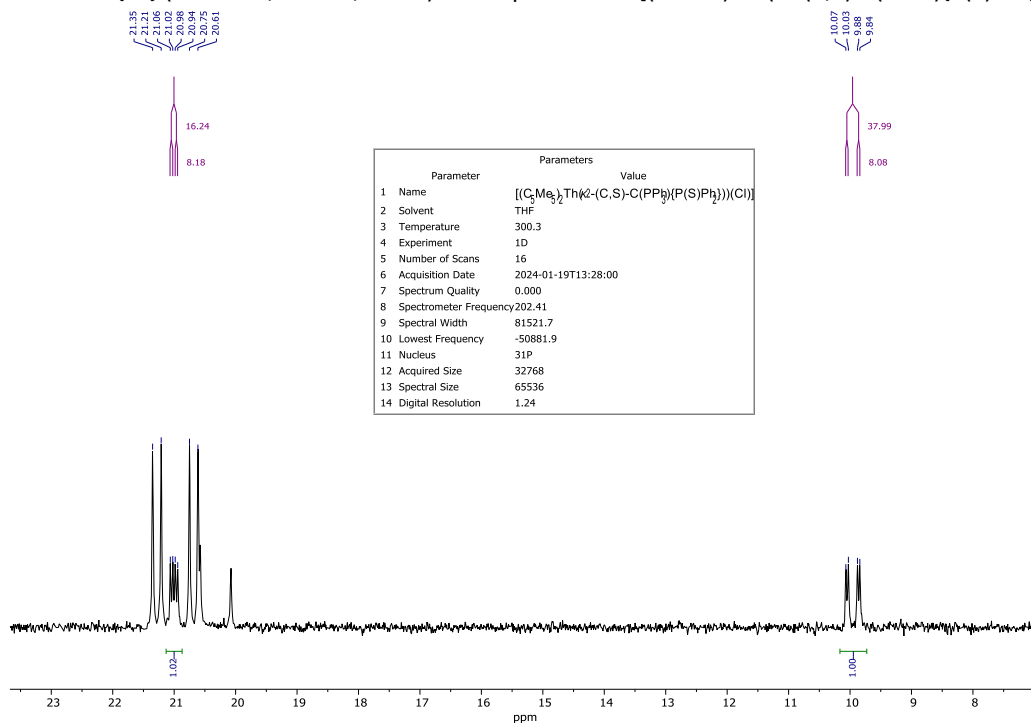


Figure S14: $^{31}\text{P}\{^1\text{H}\}$ (200 MHz, THF- d_8 , 297 K) NMR spectrum of the ^{13}C -labeled [(C5Me5)2Th(k2-(C,S)-C(PPh3){P(S)Ph2})(Cl)]. The sample was only prepared on a milligram scale and not fully purified, but only used for detection of the ylidic carbon atom. Therefore, the spectrum shows $^{31}\text{P}\{^1\text{H}\}$ NMR signals of the still present ^{13}C -labeled ylide [$\delta = 20.98$ (dd, $^1J_{\text{CP}} = 121.3$ Hz + $^2J_{\text{PP}} = 28.0$ Hz) ppm] along with the signals at 9.95 and 21.0 ppm for thorium complex **3**.

Supporting Information

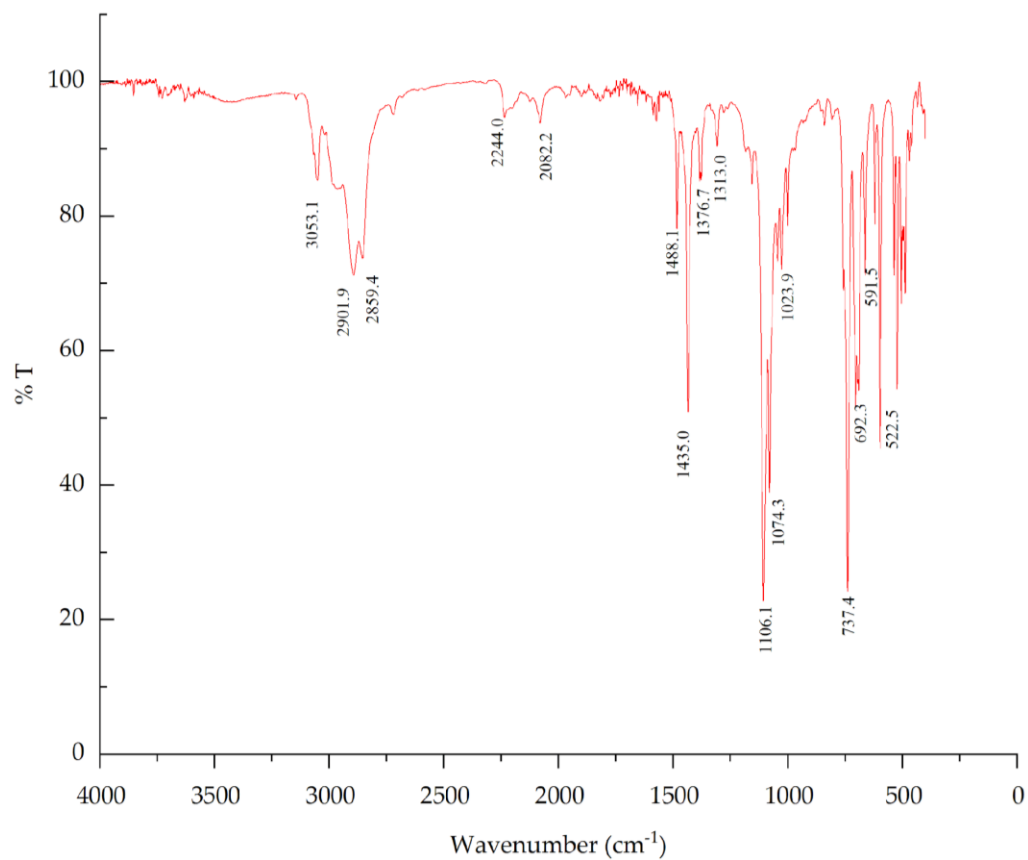


Figure S15: FTIR vibrational spectrum of $[(C_5Me_5)_2Th(\kappa^2-(C,S)-C(PPh_3)\{P(S)Ph_2\})](Cl)]$.

1.3 Synthesis of $[(C_5Me_5)_2U(\kappa^2-(C,S)-C(PPh_3)\{P(S)Ph_2\})](Cl)$

Method A: To a vial containing $[(C_5Me_5)_2UCl_2]$ (152 mg, 0.262 mmol), ca. 10 mL of toluene was added, producing a dark red solution, this was allowed to stir at RT. In a separate vial, a suspension of benzyl potassium, (37 mg, 0.0288 mmol) in 5 mL of toluene, was added to a toluene solution of $HC(PPh_3)\{P(S)Ph_2\}$ (129 mg, 0.262 mmol). The deprotonation reaction was allowed to stir for 30 min, and the resultant orange suspension was filtered to yield a light-yellow solution of $K[C(PPh_3)\{P(S)Ph_2\}]$. This solution was then added dropwise to the solution of $[(C_5Me_5)_2UCl_2]$ and allowed to stir for 4 hr, resulting in a slow color change from red to light orange. The solution was filtered through Celite and solvent was removed under reduced pressure. The resulting powder was dissolved in a minimal amount of *n*-pentane. Orange crystals were obtained from a concentrated *n*-pentane solution at $-45\text{ }^\circ\text{C}$, 86 mg, 33%.

Method B: A scintillation vial was charged with 10 mL of toluene and $[(C_5Me_5)_2UCl_2]$ (72 mg, 0.124 mmol), producing a dark red solution. To this stirring solution, a colorless THF solution of $[Hg(C(PPh_3)\{P(S)Ph_2\})_2]$ (146 mg, 0.124 mmol) was added dropwise over the course of 5 min. The solution remained dark red in color with the formation of a flocculent precipitate. This reaction was allowed to stir for 4 hr, after which, a fine white precipitate was obtained, rinsed with toluene and THF and discarded. Solvent was subsequently removed *in vacuo* to yield a reddish orange powder of **4**, 54 mg, 38%.

1H NMR (600 MHz, C_6D_6 , 298 K)/ $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6 , 298 K): *The unequivocal assignment of signals in both the 1H and $^{13}C\{^1H\}$ NMR spectra was not feasible due to the paramagnetic properties of the compound.*

$^{31}P\{^1H\}$ NMR (120 MHz, C_6D_6 , 298 K): δ -47.68, -506.90 FT-IR (KBr, cm^{-1}): 3067.6 (m), 2909.5 (m), 2852.8 (w), 1477.1 (w), 1432.4 (s), 1375.7 (s), 1175.7 (m), 1101.1 (s), 1023.5 (s), 996.8 (s), 811.7 (w), 737.1 (s), 686.3 (m), 593.8 (m), 522.2 (m). **Anal. Calcd. (found) for $C_{51}H_{55}P_2SCIU$:** C, 59.16 (59.07%); H, 5.35 (5.58%).

Comparison method A and B

Salt metathesis with **2** showed similar success to salt metathesis using the potassium compound **1-K**. However, the mercury transmetalation may prove ideal when moving to oxidation states that are less stable such as U(VI) where reduction to U(V) is often observed with alkali metal salts.¹⁸

Supporting Information

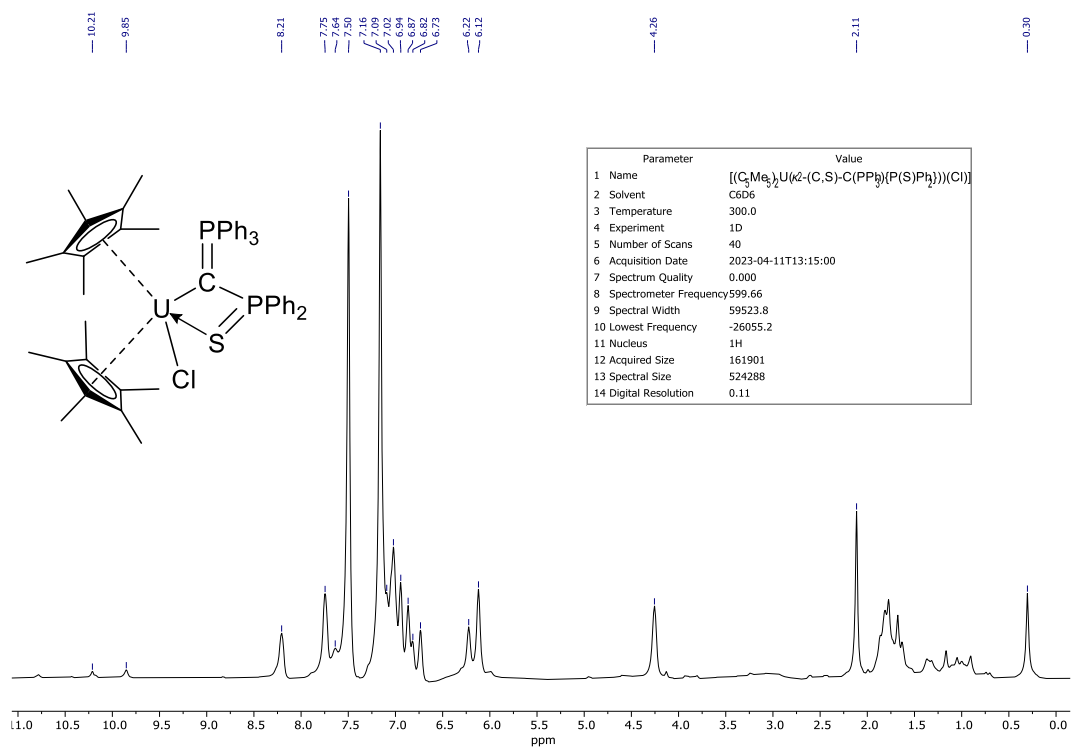


Figure S16: ¹H NMR spectrum (600 MHz, C₆D₆, 298 K) of $[(C_5Me_5)_2U(\kappa^2-(C,S)-C(PPh_3)\{P(S)Ph_2\})](Cl)$.

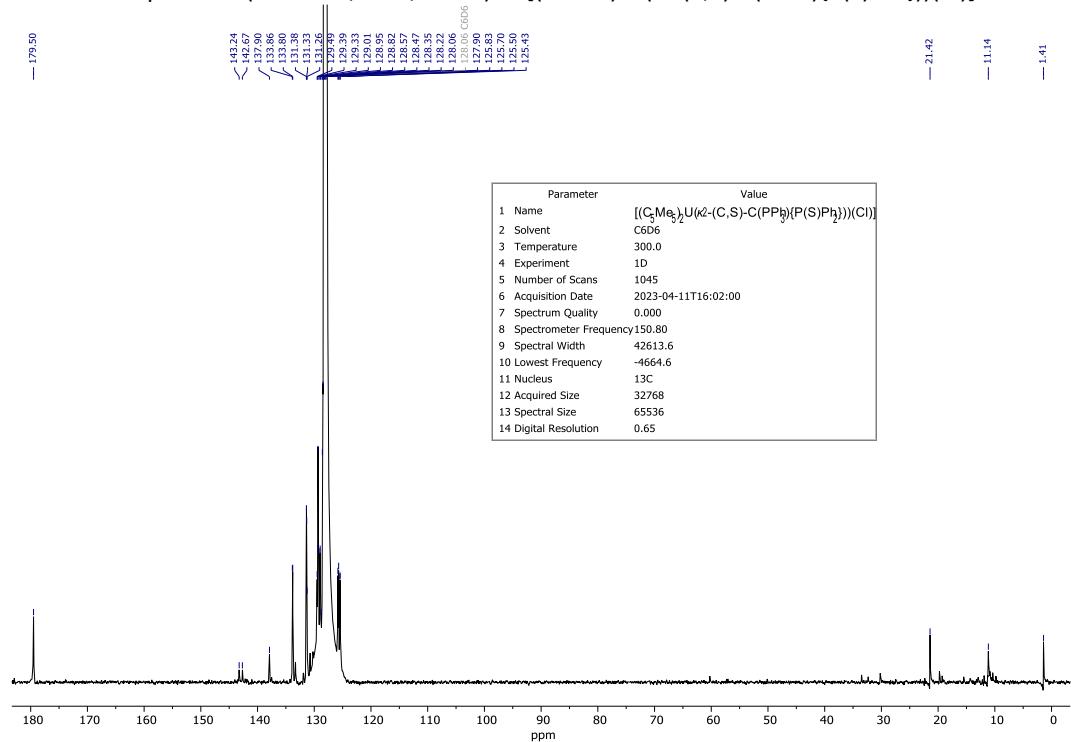


Figure S17: ¹³C{¹H} (150 MHz, C₆D₆, 298 K) NMR spectrum of $[(C_5Me_5)_2U(\kappa^2-(C,S)-C(PPh_3)\{P(S)Ph_2\})](Cl)$.

Supporting Information

Parameter	Value
1 Name	$[(C_5Me_5)_2U(\kappa^2-(C,S)-C(PPh_3)\{P(S)Ph_2\})](Cl)]$
2 Solvent	C6D6
3 Temperature	297.3
4 Experiment	1D
5 Number of Scans	2048
6 Acquisition Date	2022-12-14T09:25:00
7 Spectrum Quality	0.000
8 Spectrometer Frequency	121.51
9 Spectral Width	178571.4
10 Lowest Frequency	-95172.5
11 Nucleus	^{31}P
12 Acquired Size	119276
13 Spectral Size	262144
14 Digital Resolution	0.68

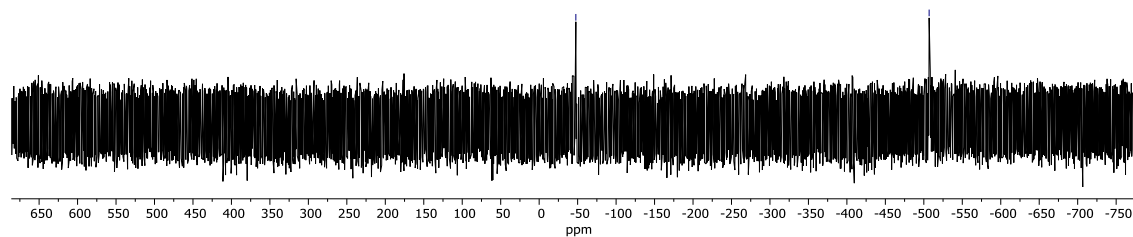


Figure S18: $^{31}P\{^1H\}$ NMR (120 MHz, C_6D_6 , 298 K) spectrum of $[(C_5Me_5)_2U(\kappa^2-(C,S)-C(PPh_3)\{P(S)Ph_2\})](Cl)$.

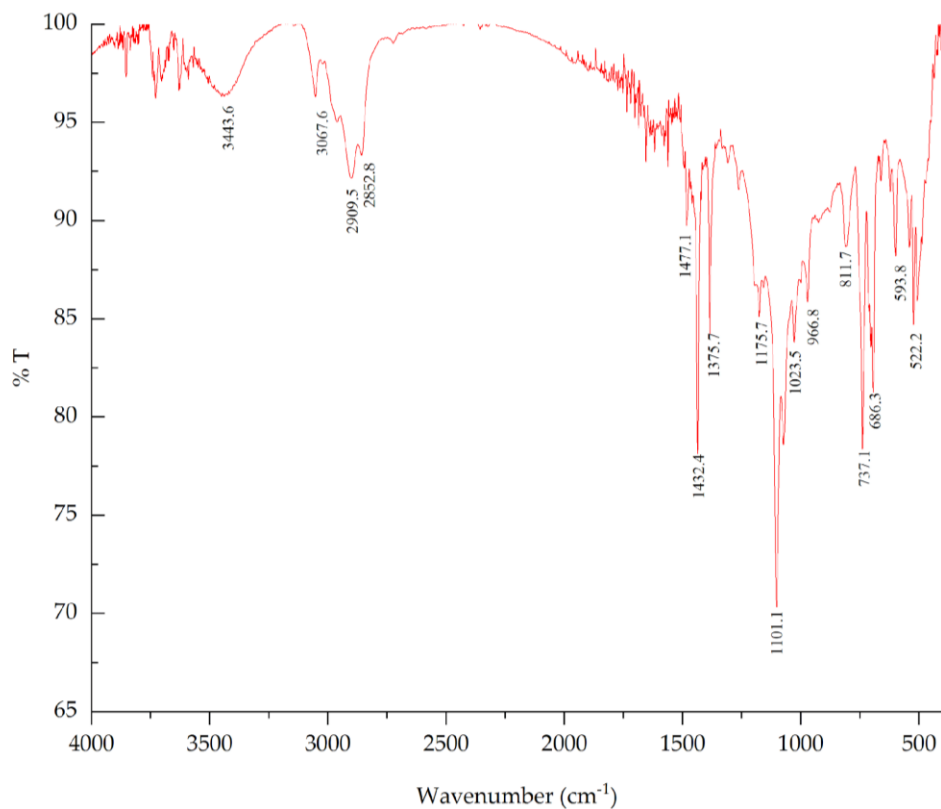


Figure S19: FTIR spectrum of $[(C_5Me_5)_2U(\kappa^2-(C,S)-C(PPh_3)\{P(S)Ph_2\})](Cl)$.

2 Crystal structure determination

2.1 General information

Good quality single crystals were hand-picked under polarized optical microscopy in an inert oil such as perfluoropolyalkylether and then mounted on the diffractometer in random orientations. The data collection was done at 100 K. X-ray intensity data measurements of ylide **1-H** and ylide **1-K** were carried out on a Rigaku Synergy instrument (κ -goniometer) with a PILATUS3 R 200K hybrid pixel array detector using $\text{CuK}\alpha$ (1.54184 Å) radiation monochromated by means of multilayer optics. The X-ray generator was operated at 50 kV and 30 mA. SC-XRD data for complexes **2**, **3** and **4** were measured on a Bruker SMART diffractometer with an Apex II area detector (Bruker AXS LLC, USA) using $\text{Mo K}\alpha$ radiation from a sealed source with focusing optics. Collection temperatures were controlled using Cryostream 700 and 800 cryostats (Oxford Cryosystems, UK). Hemispheres of data were collected using strategies of scans about the omega and phi axes. The Bruker Apex3 software suite was used for unit cell determination, data collection, and data reduction.

All the structures were solved using direct methods, refined with the Shelx software package and expanded using Fourier techniques.^[4] Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were inserted at the calculated positions and refined as riding atoms.

Crystallographic data including structure factors have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2307044-2307048. Copies of the data can be gained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk]. An *ORTEP III*⁵ view of all compounds were drawn with 50% probability displacement ellipsoids and H atoms omitted for clarity.

Table S1 Data collection and structure refinement details for compounds **1-H**, **1**, and **2**.

Compound	1-H	1	2
Formula	C ₃₁ H ₂₆ P ₂ S	C ₄₃ H ₄₉ KO ₆ P ₂ S	C ₆₆ H ₅₈ OP ₄ S ₂ Hg
CCDC	2307045	2307046	2307044
Formula weight	492.52	794.92	1255.71
Temperature [K]	100(2)	100(2)	173.0
Wave length [Å]	1.54184	1.54184	1.54184
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 21/ <i>n</i>	<i>P</i> -1	C2/ <i>c</i>
a [Å]	9.72967(4)	9.46920(10)	24.571(5)
b [Å]	15.22975(6)	10.89450(10)	14.090(3)
c [Å]	16.93649(8)	21.4146(3)	20.038(4)
α [°]	90	77.0360(10)	90
β [°]	91.2641(4)	83.3740(10)	122.893(5)
γ [°]	90	73.6670(10)	90
Volumen [Å ³]	2509.046(19)	2062.75(4)	5824.8(19)
Z	4	2	4
Calc. density [Mg·m ⁻³]	1.304	1.280	1.432
μ (MoKα) [mm ⁻¹]	5.812	2.700	2.866
F(000)	1032	840	2536.0
Crystal dimensions [mm]	0.630 x 0.408 x 0.257	0.175 x 0.115 x 0.092	0.08 x 0.04 x 0.02
Theta range θ [°]	3.904 to 76.807	4.244 to 67.997	3.948 to 52.848
Index ranges	-11 ≤ h ≤ 12 -19 ≤ k ≤ 19 -21 ≤ l ≤ 21	-11 ≤ h ≤ 11 -13 ≤ k ≤ 13 -25 ≤ l ≤ 25	-30 ≤ h ≤ 30 -17 ≤ k ≤ 17 -24 ≤ l ≤ 24
Reflections collected	74641	56837	57926
Independent reflections	5211 [Rint = 0.0406, Rsigma = 0.0143]	7494 [Rint = 0.1110, Rsigma = 0.0504]	5923 [Rint = 0.1259, Rsigma = 0.0621]
Data/Restraints/Parameter	5211/0/307	7494/0/530	5923/0/335
Goodness-of-fit on F ²	1.061	1.050	1.183
Final R indices [I > 2σ(I)]	R1 = 0.0306 wR2 = 0.0785	R1 = 0.0753 wR2 = 0.1355	R1 = 0.0923, wR2 = 0.2182
Largest diff. peak and hole [e·Å ⁻³]	0.431 and -0.396	0.606 and -0.411	5.08/-3.24

Table S2 Data collection and structure refinement details for the actinide complexes **3** and **4**.

Compound	3	4
Formula	C ₅₈ H ₆₃ P ₂ SClTh	C ₅₁ H ₅₅ P ₂ SCIU
CCDC	2307048	2307047
Formula weight	1121.57	908.36
Temperature [K]	173.0	173.0
Wave length [Å]	1.54184	0.71073
Crystal system	orthorhombic	Triclinic
Space group	<i>Pca2₁</i>	<i>P-1</i>
a [Å]	12.1389(3)	12.0774(7)
b [Å]	14.1799(4)	14.1627(7)
c [Å]	14.3984(4)	14.3748(8)
α [°]	94.1930(10)	94.016(2)
β [°]	90.4360(10)	90.702(2)
γ [°]	93.0160(10)	93.297(2)
Volumen [Å ³]	2468.15(12)	2448.4(2)
Z	4	2
Calc. density [Mg·m ⁻³]	3.018	1.529
μ (MoKα) [mm ⁻¹]	6.440	3.516
F(000)	2256.0	1132.0
Crystal dimensions [mm]	0.11x 0.07x 0.03	0.04x 0.04 x 0.01
Theta range θ [°]	5.064 to 59.998	3.904 to 55.762
Index ranges	-17 ≤ h ≤ 17 -19 ≤ k ≤ 19 -20 ≤ l ≤ 20	-15 ≤ h ≤ 15 -18 ≤ k ≤ 18 -18 ≤ l ≤ 18
Reflections collected	129878	65581
Independent reflections	14377 [Rint = 0.0368, Rsigma = 0.0220]	11657 [Rint = 0.0560, Rsigma = 0.0489]
Data/Restraints/Parameter	14377/0/579	1167/0/579
Goodness-of-fit on F ²	1.091	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0193, wR2 = 0.0393	R1 = 0.0341, wR2 = 0.0635
Largest diff. peak and hole [e·Å ⁻³]	1.77/-0.76	1.20 and -0.97

2.2 Crystal Structure Determination of Ylide 1-H and Yldiide 1-K

Ylide 1-H

The ylide was prepared as described in reference 2. Single crystals were obtained by slow concentration of a cyclohexane solution.

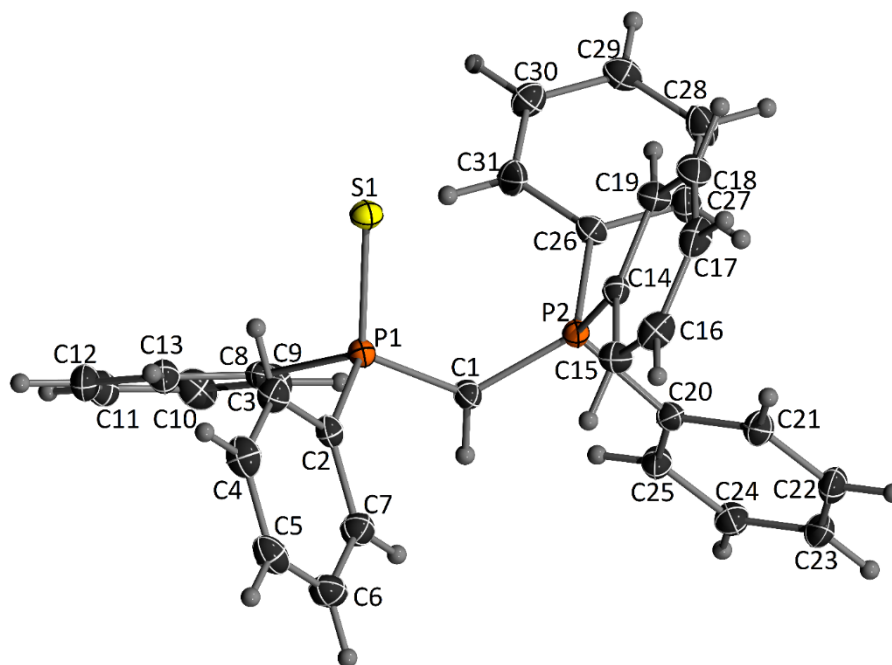


Figure S20: Molecular structure of compound **1-H**. Thermal ellipsoids at 50% probability level. Selected bond lengths [Å] and angles [°]: P1-C1 1.7294(13), C1-P2 1.6959(13), P1-S1 1.9729(4), P1-C1-P2 110.60(6). Symmetry operations: $-x+1/2, y+1/2, -z+1/2$; $-x, -y, -z$; $x-1/2, -y-1/2, z-1/2$

Yldiide 1-K

The yldiide was synthesized as described in ref 2. The yldiide was dissolved in as little THF as possible and 1 eq 18-crown-6 was added. Single crystals were obtained at room temperature by diffusion of hexane into the thf solution.

The crown ether and phenyl rings of the phosphonium moiety were disordered. The disorder was refined by using the PART keyword and free variables. Refinement led to approx. ratios of 68:32 in case of the phenyl groups and 55:45 for the disordered crown ether. The ellipsoids of the crown ether were additionally treated with EADP constraints.

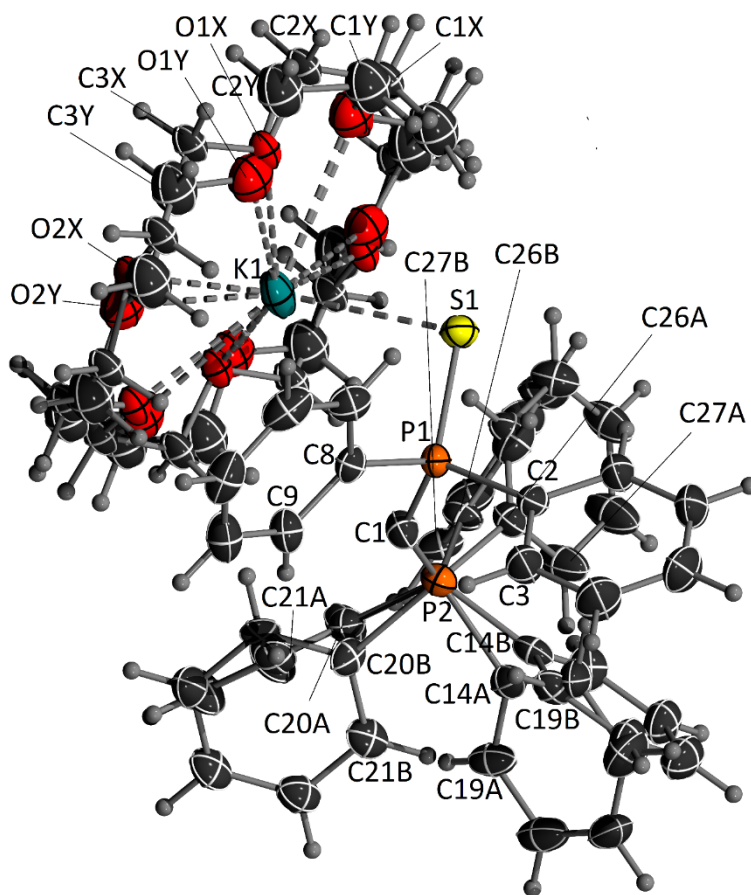


Figure S21: Molecular structure of compound **1-K**. Thermal ellipsoids at 50% probability level. Selected bond lengths [Å] and angles [°]: P1-C1 1.664(3), C1-P2 1.607(3), P1-S1 2.0179(9), P1-C1-P2 141.25(19). Symmetry operations: $-x, -y, -z$

2.3 Crystal Structure Determination of the mercury and actinide complexes

Mercury yldiide 2

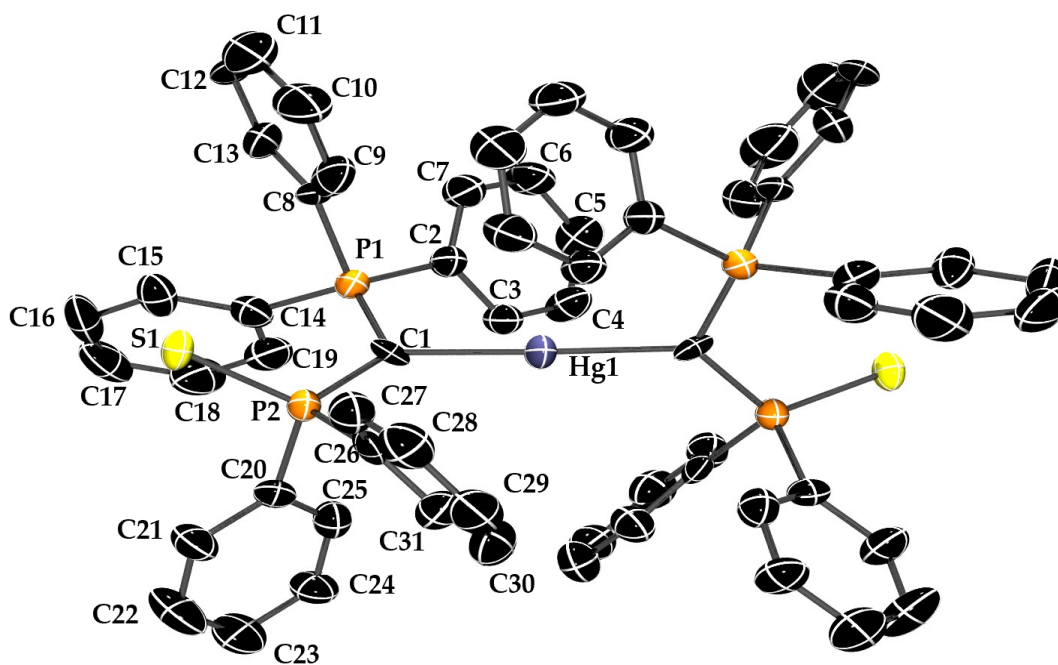


Figure S22: Molecular structure of compound **2**. Thermal ellipsoids at 50% probability level. Selected bond lengths [Å] and angles [°]: Hg1-C1 2.096(11), C1-P1 1.750(11), P1-S1 1.994(4), P2-C1-P1 120.5(7). Symmetry operations: 1-X,+Y,3/2-Z

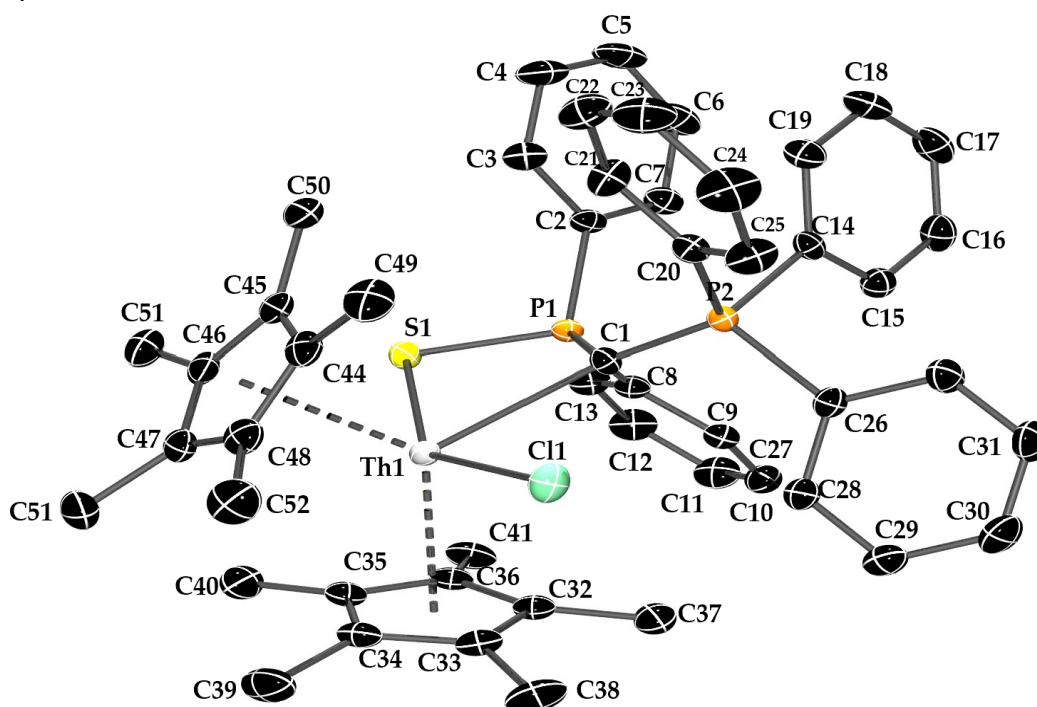
Thorium yldiide **3**

Figure S23: Molecular structure of compound **3**. Thermal ellipsoids at 50% probability level. Selected bond lengths [Å] and angles [°]: Th1-C1 2.6620(16), Th1-S1 2.8885(4), P1-S1 2.0317(6), P1-C1-P2 123.73(10).

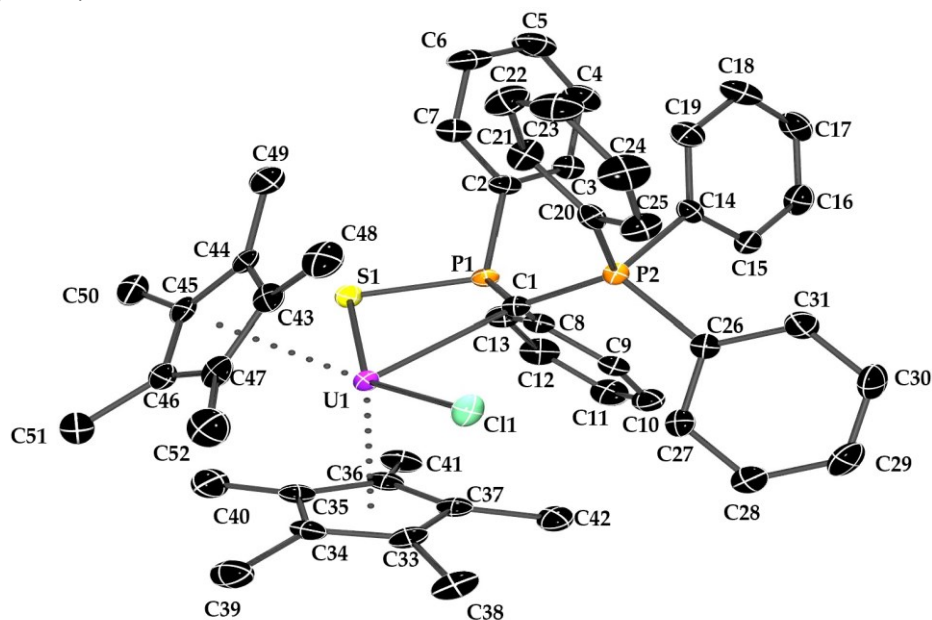
Uranium yldiide, **4**

Figure S24: Molecular structure of compound **4**. Thermal ellipsoids at 50% probability level. Selected bond lengths [Å] and angles [°]: U1-C1 2.554(3), Th1-S1 2.8357(8), P1-S1 2.0308(12), P1-C1-P2 123.30(19).

3 Computational details

3.1 General

All calculations were performed without symmetry restrictions. Starting coordinates were obtained with GaussView 6.0^[5] or directly from the crystal structure analyses. The geometry optimizations were carried out with the Gaussian16 (Revision C.01) program package.^[6]

Energy optimizations were performed using Density Functional Theory (DFT) with the B3PW91 functional^[7] using the double- ζ basis set def2svp^[8] basis set in conjunction with Grimme's D3 dispersion correction. Dolg's MWB60-ECP was employed for the heavy atoms (Hg, U, Th).^[9] Frequency analyses were performed on the same level of theory and showed no imaginary frequency, thus confirming the structures to be local minima on the potential energy surface. The geometries obtained after energy optimization were used for subsequent single point energy calculations on a higher level of theory (def2tzvp)^[7] and bonding analyses. The NBO analyses were performed with NBO Version 7.0,^[10] Quantum Theory of Atoms in Molecules (QTAIM) analyses^[11] using Multiwfn^[12] to depict the topological properties of the respective molecules. The results were visualized using the ChemCraft software^[13] and are depicted below.

3.2 Results of the bonding analysis of yldiide 1 and its complexes 2-4

Table S3: Results of the computational studies of the yldiide **1-K** and yldiide complexes **2-4**; WBIs and NPA charges and features of the bond critical points; (b3pw91/def2TZVP/MWB60)

	1-K	1 ₂ Hg (2)	Th complex 3	U complex 4
WBI (C-M)	0.0180	0.4607	0.605	0.7229
WBI (C-P(S))	1.1775	0.9855	1.077	1.0857
WBI (C-P _{PPh₃})	1.3865	1.1642	1.1467	1.15
WBI (P=S)	1.1605	1.3118	1.0077	1.0464
q(C1) [e]	-1.556	-1.634	-1.488	-1.421
q(P _{PPh₃}) [e]	1.560	1.624	1.652	1.651
q(P(S)) [e]	1.395	1.383	1.515	1.492
q(M) [e]	0.876	1.249	0.755	0.575
q(S) [e]	-0.789	-0.661	-0.388	-0.389
Σ q(ligand)	-0.954	-0.625	-0.007	-0.011
ρ (BCP-MC)	0.014	0.126	0.062	0.069
ϵ (BCP-MC)	0.039	0.041	0.018	0.041

Quantum Theory of Atoms in Molecules

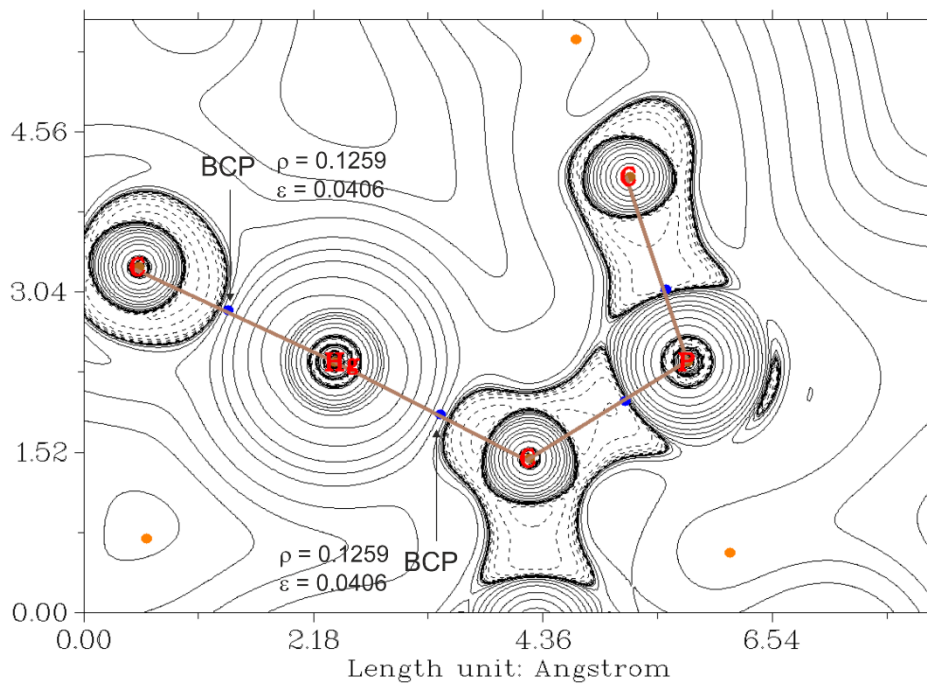


Figure S25: Contour plots of the Laplacian of the electron density in the plane of the Hg-C-P plane of compound **2**. Blue points indicate bond-critical points (BCPs), values for electron density and ellipticity are indicated in the figure.

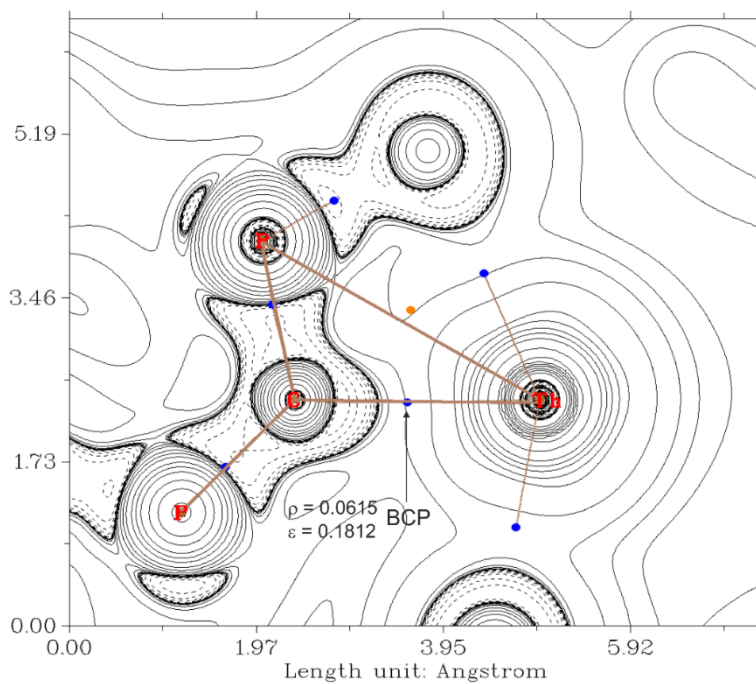


Figure S26: Contour plots of the Laplacian of the electron density in the plane of the Th-C-P plane of compound **3**. Blue points indicate bond-critical points (BCPs), values for electron density and ellipticity are indicated in the figure.

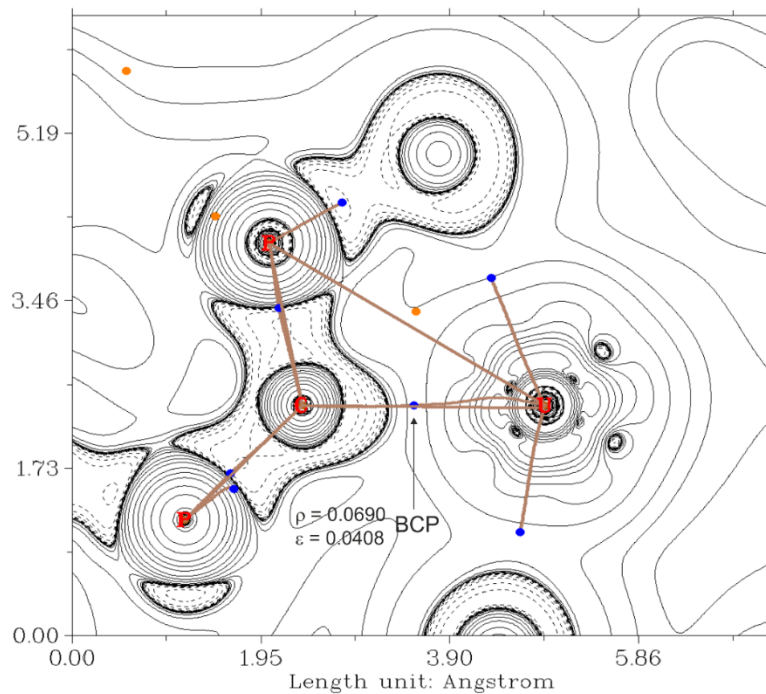


Figure S27: Contour plots of the Laplacian of the electron density in the plane of the U-C-P plane of compound 4. Blue points indicate bond-critical points (BCPs), values for electron density and ellipticity are indicated in the figure.

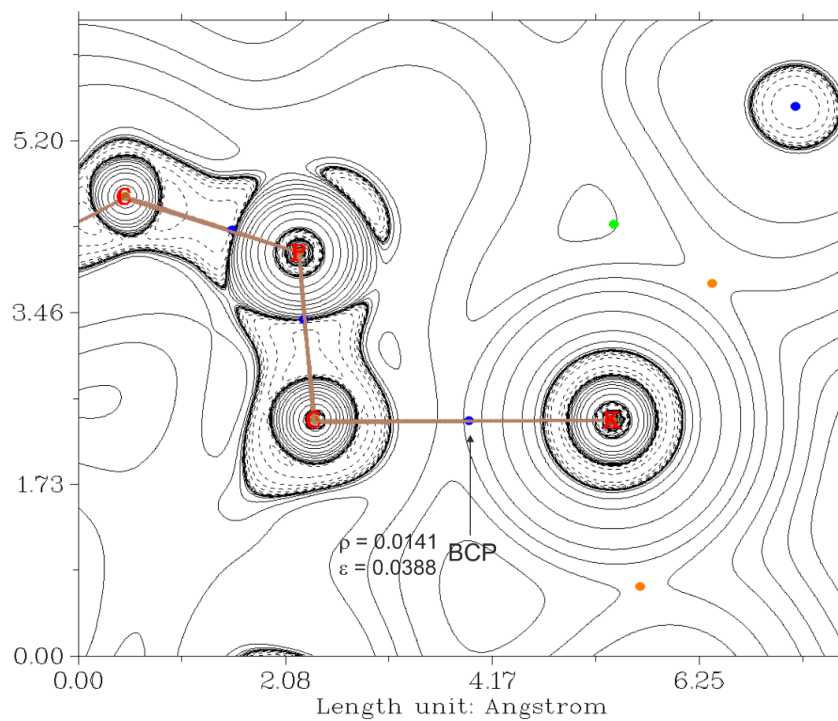


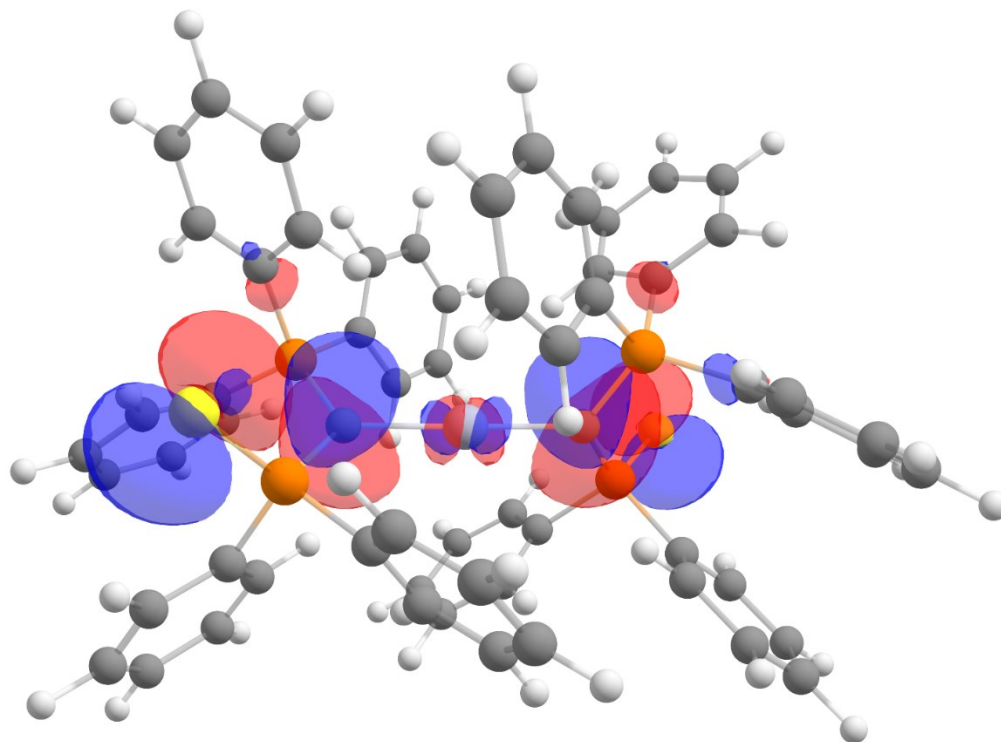
Figure S28: Contour plots of the Laplacian of the electron density in the plane of the K-C-P plane of compound 1-K. Blue points indicate bond-critical points (BCPs), values for electron density and ellipticity are indicated in the figure.

Supporting Information

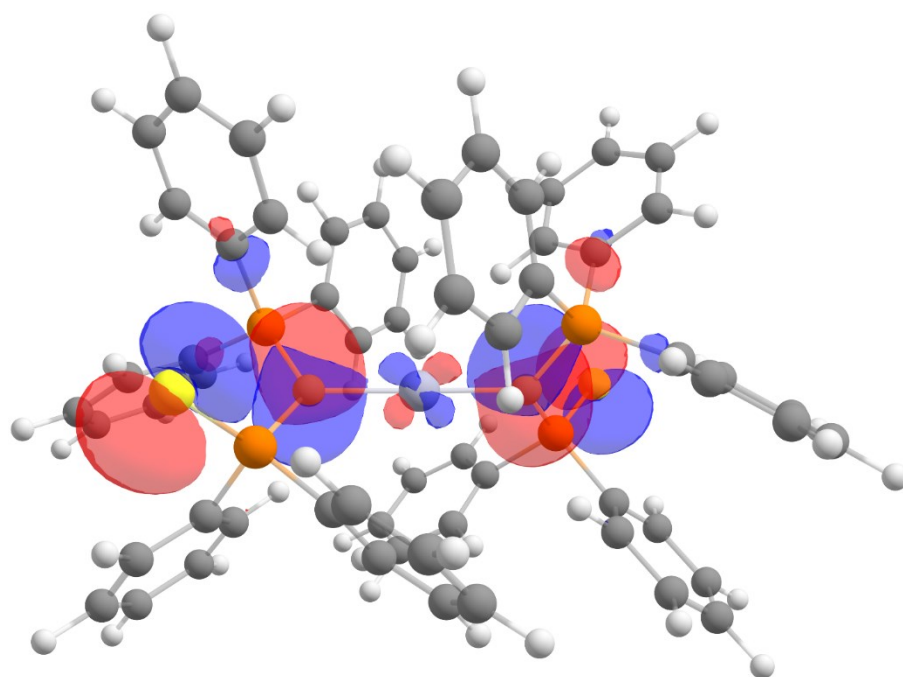
Molecular orbitals

HgY₂ (Compound 2)

HOMO



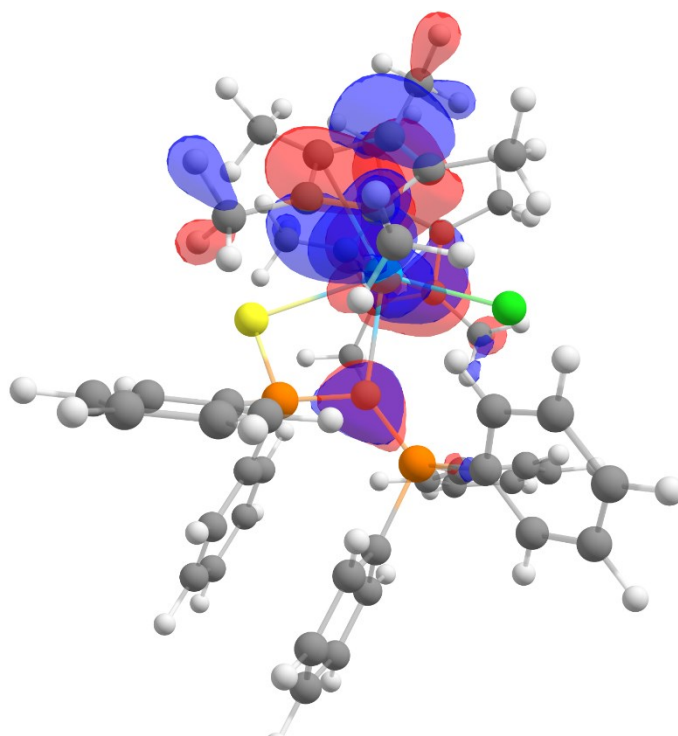
HOMO -1



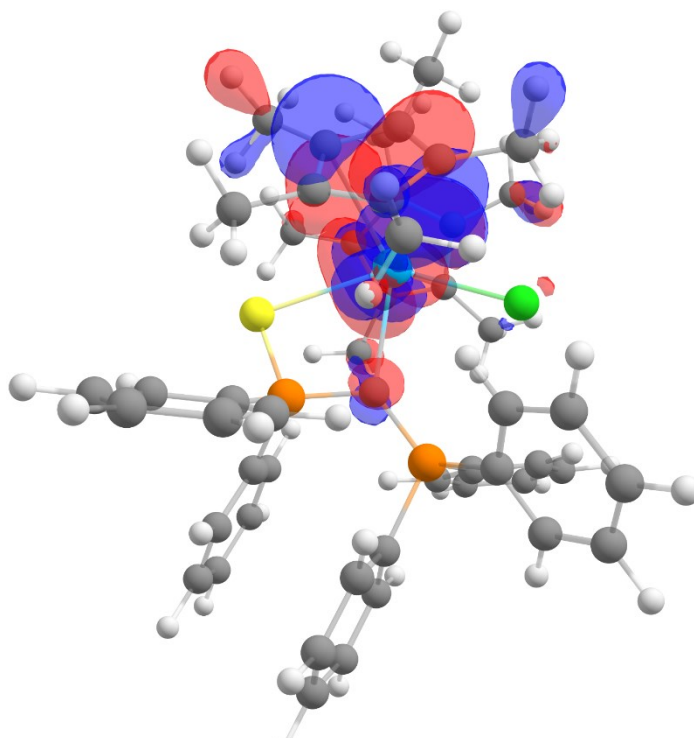
Supporting Information

YThClCp₂ (Compound 3)

HOMO

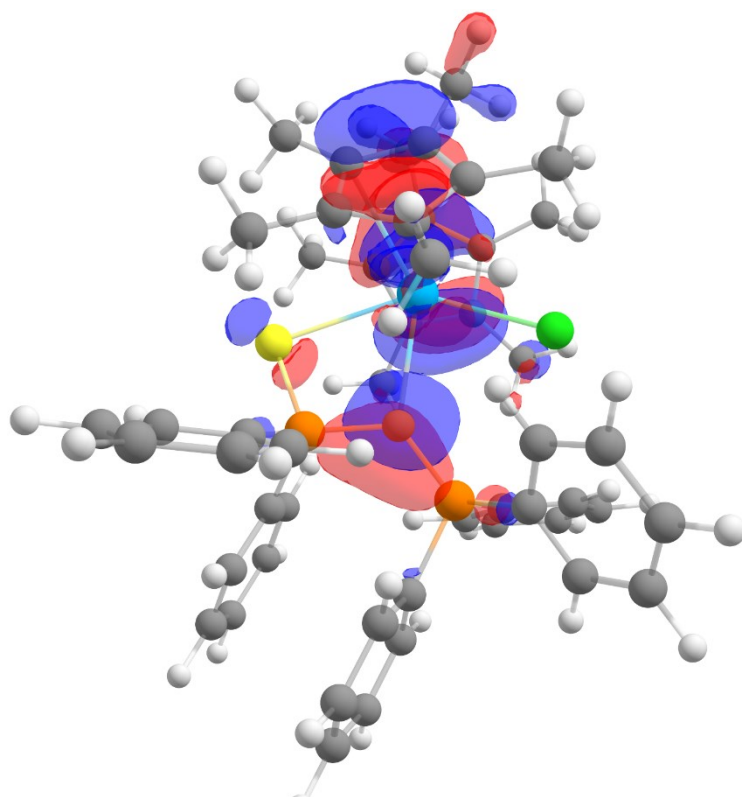


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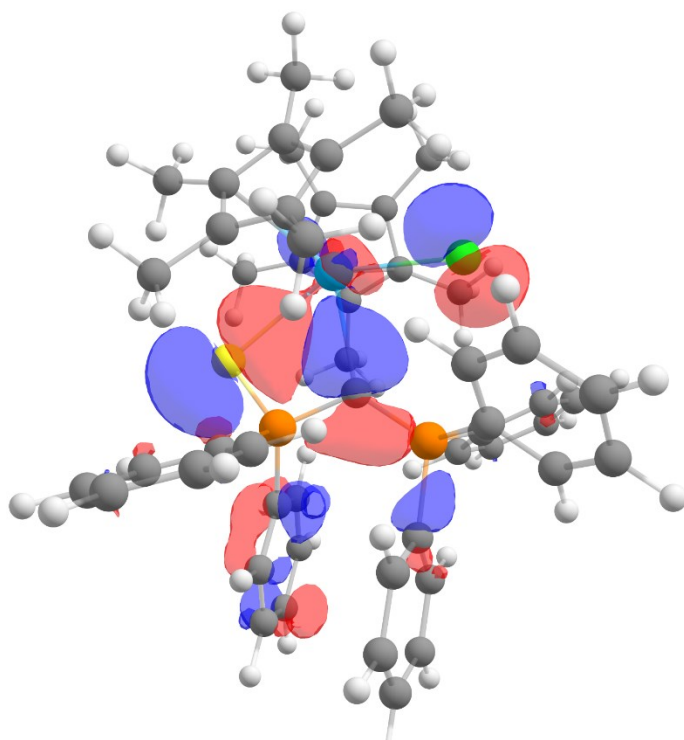


Supporting Information

HOMO -2



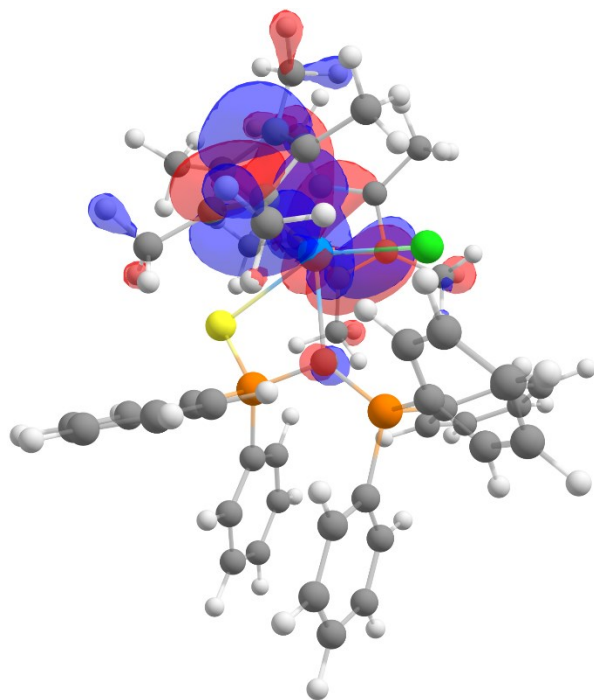
HOMO -6



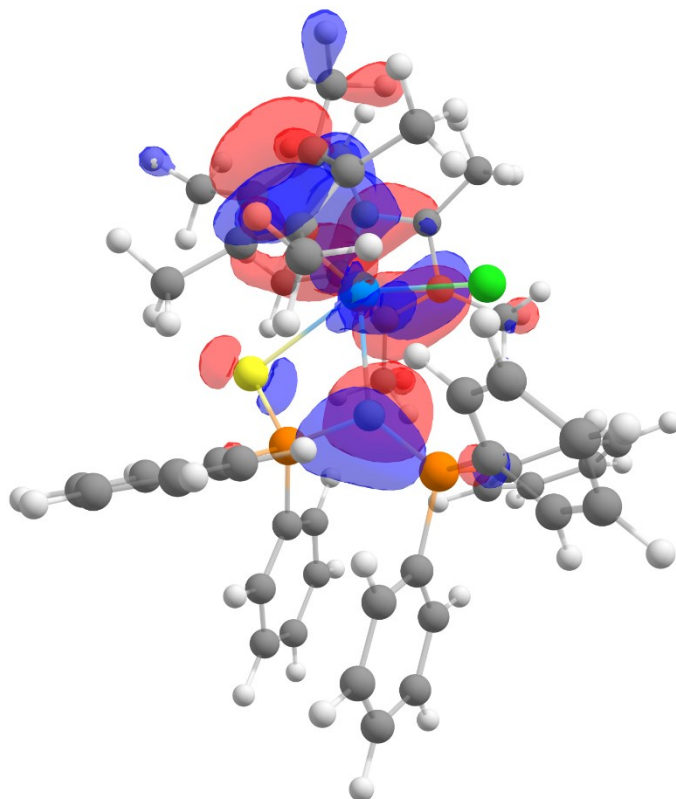
Supporting Information

YUClCp₂ (Compound 4)

HOMO -1

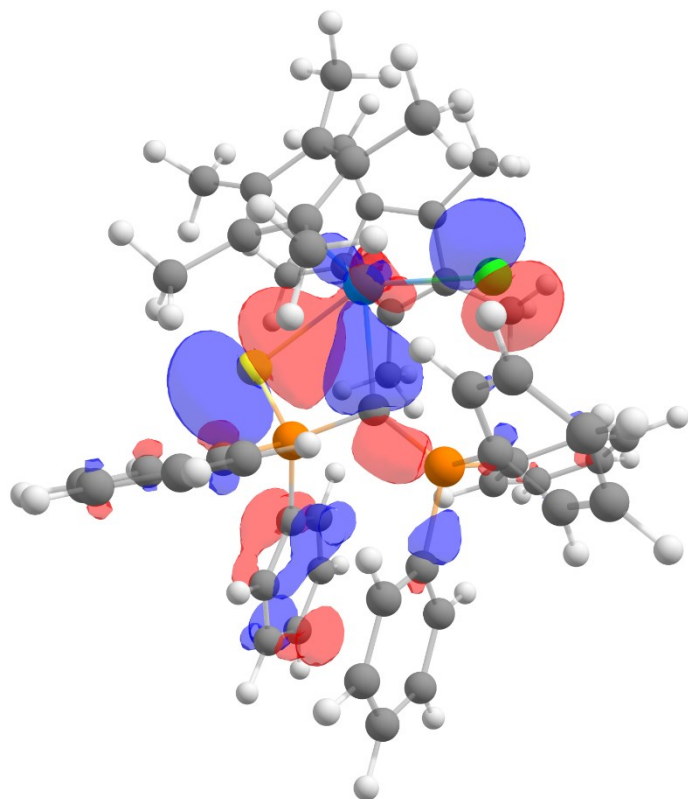


HOMO-4



Supporting Information

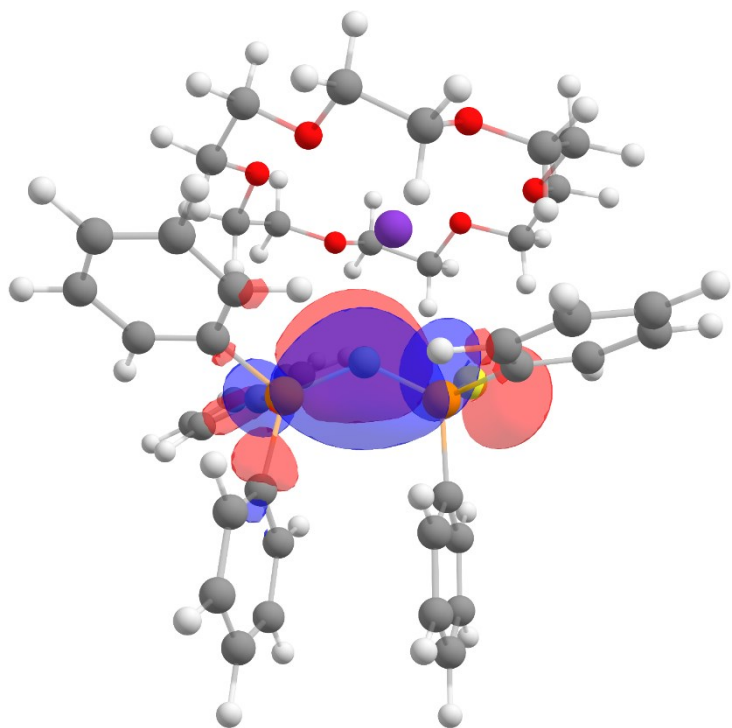
HOMO-7



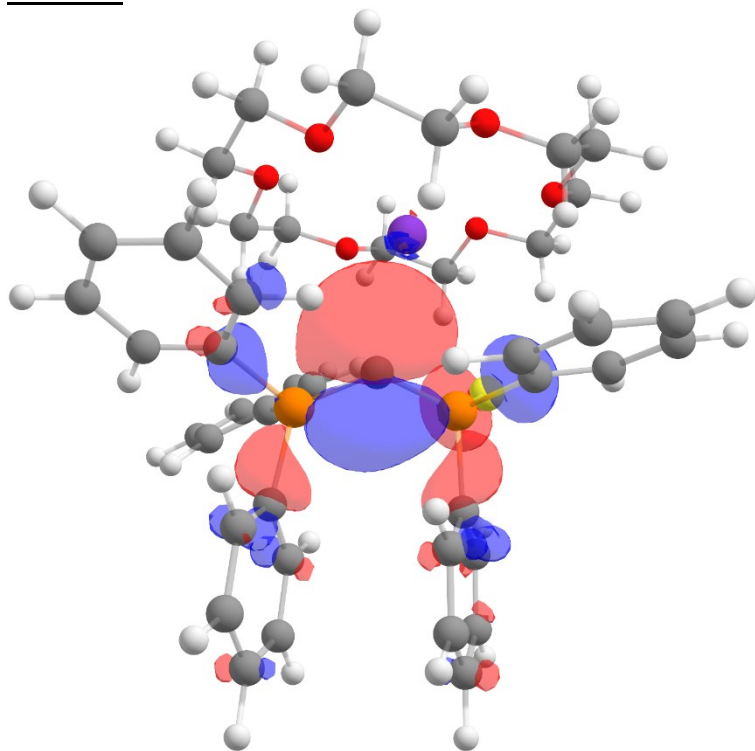
Supporting Information

1-K

HOMO



HOMO-1



3.3 Coordinates of optimized structures

Level of theory: (b3pw91//def2svp)

Y₂Hg

Atom	x	y	z
Hg	4.12370100	3.70102000	12.61920400
C	6.15840900	3.68507700	12.28132800
C	2.08901300	3.68335700	12.95717700
P	7.27956200	4.61082000	13.27031200
P	6.78646000	2.48411200	11.23760700
P	0.96698100	4.60816500	11.96830300
P	1.46209500	2.48154500	14.00061700
S	8.71184100	3.64086200	14.25453600
C	6.19271400	5.55277100	14.42487900
C	8.00321000	5.91807600	12.18764700
C	8.06078900	3.11193700	10.08937000
C	7.52644600	1.03303900	12.06071800
C	5.41074800	1.80565500	10.24137800
S	-0.46425700	3.63700500	10.98375300
C	2.05300000	5.55143700	10.81404300
C	0.24193800	5.91441600	13.05125200
C	0.18724900	3.10797600	15.14905100
C	0.72343200	1.02996600	13.17721600
C	2.83846800	1.80413300	14.99664400
C	6.23009300	5.28565100	15.79492300
C	5.27694300	6.48981500	13.92835000
C	7.37493800	6.25361000	10.98230600
C	9.20573900	6.54083500	12.54024100
C	7.75373700	3.43170200	8.75982800
C	9.31766500	3.45397300	10.61403000
C	8.50174600	0.24143500	11.44302400
C	7.03362500	0.68697000	13.32442200
C	4.52481700	2.68366700	9.59094700
C	5.18671400	0.42459300	10.17047400
C	2.01630100	5.28430100	9.44398200
C	2.96753800	6.48954700	11.31084400
C	0.86975000	6.25021400	14.25676000
C	-0.96119000	6.53606600	12.69873700
C	0.49416000	3.42775900	16.47862400
C	-1.06998000	3.44900800	14.62458700
C	-0.25128200	0.23745100	13.79466700
C	1.21665200	0.68452900	11.91349200
C	3.72361400	2.68281600	15.64723300
C	3.06378000	0.42326200	15.06722200
H	6.98541800	4.58641700	16.16668100
C	5.31633200	5.90115100	16.65373600
C	4.36581600	7.10638100	14.78552800
H	5.27774800	6.72375300	12.86263000
H	6.45212800	5.73736100	10.70471600
C	7.94828800	7.20002500	10.13303400

Supporting Information

C	9.77319400	7.49199400	11.69251900
H	9.70389700	6.24429000	13.46765000
H	6.78479800	3.16115300	8.33512300
C	8.68557800	4.10659400	7.97118200
C	10.23817800	4.13803800	9.82262900
H	9.55687800	3.22363900	11.65703800
H	8.88989900	0.51835200	10.45924900
C	8.98232200	-0.89773700	12.09039100
C	7.50957600	-0.45704400	13.96095400
H	6.28997600	1.32849200	13.80509800
H	4.66870300	3.76594300	9.65930500
C	3.43512600	2.17931600	8.88442700
C	4.09058200	-0.07275300	9.46303500
H	5.85876400	-0.26585200	10.68383500
H	1.26191200	4.58417100	9.07200900
C	2.92958600	5.90087600	8.58543700
C	3.87818400	7.10718800	10.45392400
H	2.96615900	6.72347100	12.37656800
H	1.79306200	5.73481500	14.53426300
C	0.29535300	7.19577500	15.10627600
C	-1.52969700	7.48637900	13.54670400
H	-1.45896000	6.23931100	11.77118700
H	1.46338100	3.15798700	16.90317800
C	-0.43819600	4.10167100	17.26749900
C	-1.99101500	4.13210000	15.41622000
H	-1.30908900	3.21867000	13.58155700
H	-0.63974100	0.51386400	14.77846100
C	-0.73088100	-0.90198300	13.14703700
C	0.74168600	-0.45975000	11.27670300
H	1.95982700	1.32673400	11.43299000
H	3.57869400	3.76497400	15.57916700
C	4.81381200	2.17931600	16.35357900
C	4.16041800	-0.07323000	15.77448000
H	2.39234600	-0.26768800	14.55372900
H	5.34103100	5.67804500	17.72383300
C	4.37355600	6.79924000	16.14883100
H	3.64382800	7.82728500	14.39364800
H	7.46249000	7.44080800	9.18379500
C	9.14813600	7.82030000	10.48632100
H	10.71597900	7.97212300	11.96846700
H	8.43921900	4.35389900	6.93540400
C	9.92302300	4.47100700	8.50435000
H	11.20179400	4.42652000	10.24852400
H	9.74962300	-1.51245400	11.61291600
C	8.48445000	-1.24765100	13.34749100
H	7.12557800	-0.72406100	14.94771600
H	2.74555600	2.86796000	8.39641500
C	3.21602300	0.80199100	8.81904200
H	3.91661300	-1.15092600	9.42729000
H	2.90544400	5.67777400	7.51532500
C	3.87117800	6.80005200	9.09061600
H	4.59921800	7.82893000	10.84601600
H	0.78081300	7.43675100	16.05563900

Supporting Information

C	-0.90509300	7.81493500	14.75307000
H	-2.47294200	7.96563600	13.27081500
H	-0.19194500	4.34899700	18.30329800
C	-1.67601900	4.46509100	16.73453100
H	-2.95493200	4.41981500	14.99048400
H	-1.49773200	-1.51740800	13.62432100
C	-0.23261400	-1.25125600	11.88991900
H	1.12599400	-0.72627000	10.28992900
H	5.50276700	2.86848300	16.84171600
C	5.03420100	0.80218000	16.41862000
H	4.33538500	-1.15124900	15.80998300
H	3.65350200	7.27541800	16.81935800
H	9.60288000	8.55527500	9.81665600
H	10.64387000	5.01702700	7.89052100
H	8.86373500	-2.13881300	13.85461400
H	2.35244500	0.41555500	8.27225400
H	4.59085700	7.27707800	8.42028800
H	-1.36065500	8.54922800	15.42292800
H	-2.39728600	5.01035300	17.34853900
H	-0.61113400	-2.14262600	11.38259100
H	5.89816600	0.41641900	16.96527500

YThClCp₂

Atom	x	y	z
C	4.72812800	9.66559500	3.69970700
Th	2.82910000	10.94201400	2.49261900
P	5.06495800	8.42464300	2.57558000
P	5.69963100	9.97851900	5.06210600
Cl	2.85657200	12.24106100	4.84612300
S	4.17226800	8.96203500	0.81184900
C	0.78979000	9.23169300	3.66648300
C	0.21938200	10.53229900	3.56500900
C	0.02199600	10.82044400	2.18634300
C	0.53250100	9.72315600	1.43166900
C	0.98314300	8.73165600	2.35124800
C	2.27444300	12.95321000	0.42798100
C	2.59740100	13.65956500	1.61993800
C	3.97445800	13.42453700	1.90679300
C	4.48739800	12.54798400	0.91361700
C	3.42917700	12.23355800	0.01295900
C	6.83878300	8.06838900	2.24238700
C	4.41157800	6.77780300	3.04704700
C	7.06592700	8.77647300	5.40262200
C	6.52343100	11.61196000	5.01722100
C	4.84049000	9.91480200	6.67706100
C	0.83501000	8.41467700	4.91983600
C	-0.31714600	11.35768400	4.69270500
C	-0.86497900	11.92931800	1.71067000
C	0.44838600	9.49017300	-0.04530400
C	1.29436200	7.31809300	1.97221300
C	1.10885100	13.20470800	-0.47740800

Supporting Information

C	1.73604800	14.62989800	2.36984900
C	4.77889600	14.15382700	2.93387800
C	5.92638700	12.19405400	0.72513900
C	3.55006200	11.51495800	-1.29553400
C	7.46948000	6.90550500	2.70009400
C	7.58949600	9.02994100	1.55341700
C	3.88556100	6.58360700	4.32414800
C	4.39621400	5.72376800	2.12345800
C	6.69722200	7.52914400	5.93257600
C	8.42402200	9.03541300	5.18127500
C	7.46860800	11.84265900	4.00623400
C	6.22713200	12.63408300	5.92598100
C	3.47308300	9.65286700	6.72608600
C	5.56910100	10.05203500	7.86825900
H	-0.05377800	7.76127400	4.97052800
H	0.81586200	9.04730500	5.81627100
H	1.71292000	7.76063400	4.97424500
H	-0.27522000	12.43142900	4.46142200
H	0.26262500	11.21422200	5.61434300
H	-1.37101900	11.09894400	4.90109400
H	-0.98642300	11.92172400	0.62229200
H	-0.50891800	12.92475900	2.00937700
H	-1.86906500	11.80612500	2.15136800
H	0.20744400	10.40611800	-0.59939600
H	-0.33245900	8.74635600	-0.28266000
H	1.39666700	9.09399300	-0.44254300
H	0.38046400	6.82476100	1.59607500
H	1.65725700	6.73243300	2.82544400
H	2.05510200	7.25799600	1.18124400
H	1.45164400	13.79787900	-1.34351800
H	0.31004300	13.77616400	0.00873900
H	0.67057000	12.28429500	-0.88618400
H	2.13860500	15.65408400	2.29233200
H	1.68874700	14.37789500	3.44114700
H	0.70871100	14.65365700	1.98131500
H	5.21067200	15.07377500	2.50077900
H	5.61073000	13.54544200	3.30257900
H	4.17222600	14.43339000	3.80391900
H	6.03191900	11.28613000	0.11666500
H	6.42775200	12.02653400	1.68623200
H	6.46577000	13.01069700	0.21375700
H	3.66089800	12.23549200	-2.12586800
H	2.66098200	10.90539500	-1.51467000
H	4.41984100	10.84445200	-1.31660600
H	6.90256600	6.15020000	3.24636900
C	8.83493300	6.71712800	2.48150800
C	8.95429600	8.84363700	1.34380300
H	7.08941400	9.91997300	1.17239600
H	3.86589100	7.42771100	5.01669400
C	3.35550500	5.34454600	4.69035200
C	3.86742500	4.48733300	2.48658300
H	4.78425600	5.88314900	1.11371800
H	5.65166300	7.31828900	6.15715600

Supporting Information

C	7.65592900	6.55605300	6.20263500
C	9.38426200	8.06078100	5.45657500
H	8.75202300	10.00094300	4.79918700
H	7.66321700	11.06771000	3.26139700
C	8.15260500	13.05515100	3.94111300
C	6.89996300	13.85461900	5.84600900
H	5.45392300	12.48767100	6.68157000
H	2.92723700	9.56324400	5.78857100
C	2.82668900	9.53061600	7.95679400
C	4.92128300	9.94052900	9.09645400
H	6.64622000	10.23805800	7.83430100
H	9.31823200	5.81063700	2.85351800
C	9.58113900	7.68445200	1.80885700
H	9.52850300	9.60141300	0.80425900
H	2.93595400	5.20638700	5.69009700
C	3.34644300	4.29547600	3.77105600
H	3.85024800	3.66910700	1.76209900
H	7.34432200	5.59141200	6.61074600
C	9.00578400	6.81810700	5.96160700
H	10.43776400	8.27968500	5.26738500
H	8.89009800	13.22016700	3.15196100
C	7.87273600	14.06245000	4.86750600
H	6.65232600	14.65239800	6.55037400
H	1.75378400	9.32640700	7.98830200
C	3.54812700	9.67817400	9.14134000
H	5.48968100	10.05126500	10.02336700
H	10.65111500	7.53465500	1.64275300
H	2.92495500	3.32624700	4.04999700
H	9.76092300	6.05687900	6.17335100
H	8.39814600	15.01905300	4.81159100
H	3.04189300	9.58652400	10.10589400

YUCICp₂

Atom	x	y	z
C	4.63890700	9.68788200	3.69122600
U	2.80325200	10.91411200	2.50777400
P	4.98951100	8.43971400	2.57076200
P	5.60865200	9.98862600	5.06627000
Cl	2.78567400	12.15533600	4.82261600
S	4.09619200	8.99311200	0.81899300
C	0.78501900	9.30965200	3.62725000
C	0.20363700	10.60432400	3.52089700
C	0.03095000	10.89914300	2.14535100
C	0.57607200	9.81830800	1.38835500
C	1.00988200	8.81957600	2.31287000
C	2.16256700	12.90407300	0.43653800
C	2.46150700	13.56054800	1.66109000
C	3.83479300	13.30846900	1.96457800
C	4.35535100	12.45018300	0.95690900
C	3.30764900	12.17426600	0.02845200
C	6.76505000	8.08419000	2.24226100

Supporting Information

C	4.34081900	6.79264000	3.04440700
C	6.97598900	8.78360900	5.39487100
C	6.43162500	11.62039000	5.03247200
C	4.75599000	9.90375900	6.68271900
C	0.79102600	8.48109500	4.87297400
C	-0.36523200	11.41702500	4.64000700
C	-0.90076400	11.96920400	1.67002000
C	0.45977600	9.56171500	-0.08136300
C	1.26823700	7.39336400	1.94005700
C	1.03264300	13.21604500	-0.49320700
C	1.61413800	14.54756800	2.40423200
C	4.64714600	14.06589500	2.96515100
C	5.80273100	12.14227700	0.75419900
C	3.45108400	11.50070900	-1.30041200
C	7.39195000	6.91814400	2.69785400
C	7.51887200	9.04333800	1.55351500
C	3.81070100	6.59513100	4.31927100
C	4.32749500	5.74125400	2.11775600
C	6.61112600	7.53596600	5.92680900
C	8.33334100	9.04507200	5.17108100
C	7.37579500	11.86020100	4.02270600
C	6.12865100	12.63679400	5.94537900
C	3.39435400	9.61558900	6.73403900
C	5.48774000	10.04036200	7.87211500
H	-0.11108700	7.84436300	4.89766600
H	0.76417800	9.10552300	5.77501800
H	1.65459400	7.80937900	4.93769500
H	-0.30695900	12.49315300	4.42450800
H	0.17770600	11.25307700	5.58032400
H	-1.42811200	11.16256600	4.80374500
H	-1.02607000	11.95496900	0.58260300
H	-0.58942100	12.97764700	1.97024400
H	-1.89727100	11.79846400	2.11264600
H	0.25391200	10.47675500	-0.64942700
H	-0.35862700	8.85046900	-0.29373600
H	1.38400800	9.11775500	-0.48228100
H	0.32621100	6.93056100	1.59488900
H	1.63129700	6.80225900	2.78924600
H	2.00339200	7.29878900	1.12954800
H	1.42827900	13.81451800	-1.33288400
H	0.24212500	13.80882700	-0.01980700
H	0.57310900	12.32464800	-0.94028000
H	2.05888400	15.55653500	2.35986300
H	1.52542400	14.27589800	3.46728200
H	0.60145500	14.62145200	1.98569000
H	5.08661300	14.96401900	2.49458600
H	5.47423100	13.46495300	3.35447700
H	4.04508000	14.38480900	3.82447300
H	5.93403800	11.26897700	0.10186000
H	6.30749200	11.94324800	1.70730500
H	6.31872900	12.99904200	0.28521200
H	3.60832100	12.24860000	-2.09882700
H	2.55474300	10.92407300	-1.56942600

Supporting Information

H	4.30507500	10.80980600	-1.32080900
H	6.82305200	6.16413000	3.24368900
C	8.75628600	6.72468600	2.47769500
C	8.88305300	8.85230400	1.34339600
H	7.02198200	9.93411500	1.17108400
H	3.78792300	7.43604500	5.01500700
C	3.27841400	5.35558200	4.68007600
C	3.79649700	4.50426300	2.47552100
H	4.71843600	5.90303100	1.10950800
H	5.56703300	7.32316000	6.15577200
C	7.57239800	6.56503200	6.19564800
C	9.29608100	8.07299000	5.44596000
H	8.65920400	10.01071000	4.78781900
H	7.57557700	11.08964400	3.27480200
C	8.04985500	13.07822400	3.96049300
C	6.79262300	13.86223500	5.86904000
H	5.35614400	12.48264800	6.70014300
H	2.84737000	9.53026900	5.79730700
C	2.75571100	9.46499600	7.96558800
C	4.84701900	9.90220500	9.10134300
H	6.56123300	10.24573800	7.83625200
H	9.23609900	5.81546600	2.84753100
C	9.50591300	7.69030000	1.80629100
H	9.45943800	9.60858800	0.80412000
H	2.85544200	5.21513700	5.67802600
C	3.27111100	4.30925800	3.75763700
H	3.78056400	3.68839900	1.74838700
H	7.26339300	5.60023100	6.60529800
C	8.92120600	6.82980100	5.95249200
H	10.34876500	8.29434500	5.25526400
H	8.78508900	13.25143900	3.17105800
C	7.76199900	14.08075700	4.88946400
H	6.53981600	14.65591500	6.57616300
H	1.68716500	9.23888900	7.99827800
C	3.47945300	9.61217700	9.14880800
H	5.41711300	10.01302300	10.02718200
H	10.57517000	7.53660700	1.63915800
H	2.84741800	3.33978200	4.03228500
H	9.67837200	6.07053300	6.16395300
H	8.27922800	15.04190700	4.83543900
H	2.97960900	9.49874500	10.11437400

YK

Atom	x	y	z
S	8.82732400	7.86332700	6.94564900
P	7.55863500	6.31731900	6.57925000
K	5.59551300	9.25880200	6.05216100
C	6.39173600	6.45527400	5.35959700
C	6.60948400	5.98260100	8.13929000
C	8.55737200	4.76108000	6.45273100
O	5.79542500	9.90383000	8.88928400
O	3.31734400	8.86443400	7.98666700

Supporting Information

O	2.85943900	8.74767900	5.18646400
O	4.41692700	10.36947400	3.45812300
O	7.01564300	11.07973700	4.30650400
O	7.40118000	11.44370700	7.10646600
P	6.58566400	6.09888800	3.75840100
C	5.39868100	5.28069700	8.06413700
C	7.09530000	6.37526500	9.39126700
C	9.95373500	4.79087800	6.39896800
C	7.89311700	3.52993300	6.34702800
C	6.62325200	10.96052600	9.30283500
C	4.71016100	9.65514800	9.74179200
C	3.91982700	8.49140400	9.20536300
C	2.59680400	7.83035600	7.36604600
C	1.90363400	8.38921500	6.14848900
C	2.32472000	9.39509800	4.06025600
C	3.38657300	9.52876000	2.99988000
C	5.50774400	10.43893300	2.57124400
C	6.48890000	11.47102900	3.06538500
C	7.91191700	12.01183200	4.85713400
C	7.82140400	11.04847600	8.39358500
C	8.44899600	11.49815500	6.16866900
C	7.22197400	4.43858800	3.26596600
C	4.91411000	6.15211800	2.96655800
C	7.66739200	7.20009000	2.72444100
H	5.01789000	5.01641300	7.07277800
C	4.69609300	4.95154000	9.22530000
C	6.38562700	6.05939600	10.55236200
H	8.02933700	6.94325200	9.43251900
C	10.67800100	3.60546700	6.24754100
H	10.45942000	5.75767500	6.48149600
H	6.80143200	3.50051200	6.35648000
C	8.61604700	2.34837500	6.20572700
H	6.98106000	10.79275400	10.33922400
H	6.06637100	11.92029400	9.28994800
H	5.06238400	9.40031200	10.76211700
H	4.05705600	10.54869700	9.82059400
H	4.59358600	7.62978200	9.06642000
H	3.15073900	8.19909500	9.94880100
H	1.83101800	7.41428800	8.05269100
H	3.26902600	6.99931000	7.07473900
H	1.20768000	7.62687200	5.74225500
H	1.30054000	9.26895800	6.45079100
H	1.93508700	10.39562800	4.33811800
H	1.48776500	8.80815400	3.63257300
H	3.77831600	8.52860200	2.74825400
H	2.92000100	9.94466000	2.08288700
H	5.17240300	10.73828100	1.55699400
H	6.00667500	9.45548200	2.47901500
H	7.29746600	11.57397800	2.31359900
H	5.97697700	12.45069900	3.15482300
H	7.40564200	12.98491500	5.02015700
H	8.76290500	12.18770800	4.16730500
H	8.53236600	11.79040000	8.81327700

Supporting Information

H	8.31987500	10.06119700	8.35320600
H	9.24675400	12.18936100	6.51214000
H	8.90089300	10.49657400	6.02963200
C	8.60379000	4.22532200	3.15587700
C	6.35111000	3.34627500	3.16050800
C	3.81443200	6.03102100	3.82530200
C	4.68917200	6.26407400	1.58770500
C	7.96582900	6.95719800	1.37316400
C	8.25568700	8.29718400	3.36234000
H	3.75528100	4.39794400	9.15607400
C	5.19010100	5.33927100	10.47369100
H	6.77075200	6.37322000	11.52678400
C	10.01242800	2.38283900	6.15651200
H	11.77046200	3.63929600	6.20543100
H	8.08698900	1.39657300	6.11392100
H	9.29493500	5.06497100	3.26231400
C	9.10255000	2.94389400	2.93102300
C	6.85208300	2.06467300	2.92862200
H	5.27284200	3.49980300	3.25919300
H	4.02373200	5.97972100	4.89785600
C	2.51589300	6.00905100	3.31740500
C	3.38793800	6.26113700	1.08006800
H	5.52573300	6.36985900	0.89685100
H	7.59001500	6.05550000	0.88235500
C	8.78064800	7.83479700	0.65888500
C	9.08545000	9.16660700	2.65094500
H	8.09634100	8.44469500	4.43390700
H	4.63988200	5.08729700	11.38453800
H	10.57924600	1.45529400	6.03808600
H	10.18189500	2.78787600	2.86662900
C	8.22837300	1.86173700	2.81147200
H	6.16364100	1.21979600	2.83961600
H	1.66721100	5.90560200	3.99889400
C	2.29763600	6.12863100	1.94300800
H	3.22612800	6.35984800	0.00340700
H	9.00061500	7.63912200	-0.39417400
C	9.33523500	8.94982900	1.29617400
H	9.54640500	10.01074300	3.16939100
H	8.62167800	0.85665900	2.63791600
H	1.27993800	6.11820000	1.54326500
H	9.98296600	9.63205800	0.73855200

4 Nomenclature and Detailed Bonding Analysis

Nomenclature. “In this article, we compare different types of ligands, which are structurally related but differ in their overall charge. These ligands are methandiides (**A**) and yldiides (**B**), which furthermore are related to bisylides (**C**). The following figure compares the structure of these ligands and their differences in the overall charge. While methandiides are dianionic, the negative charges are equalized in bisylides by two onium moieties. The herein discussed yldiides are intermediate structures between both types of compounds with only one onium moiety, thus resulting in an overall monoanionic system. Formally, methandiides thus serve as X_2 -type ligands, while yldiides are X,L and bisylides neutral L_2 -type ligands. This is a simple formalism based on the overall charge of the different ligands according to Green’s classification of covalent compounds.^[14] Thus, depending on the substitution pattern also a bisylide ligand may displace an anionic ligand in a complex and thus exhibit X -type ligand character. Because of the different overall charge, the compounds also exhibit different reactivities for example towards metal halides. The interested reader is referred to references 15-17, which discuss the reaction of methandiides, yldiides and carbodiphosporanes towards $GeCl_2$.dioxane, all giving different types of products.

We also would like to point out that the stabilizing effects of phosphonio moieties are different compared to phosphinoyl moieties. This becomes evident from the different P-C distances in **1** and **2**. As a result of metal coordination or alkylation of the sulfur atom, this difference becomes blurred and an yldiide or methanediide can be converted into a bisylide.

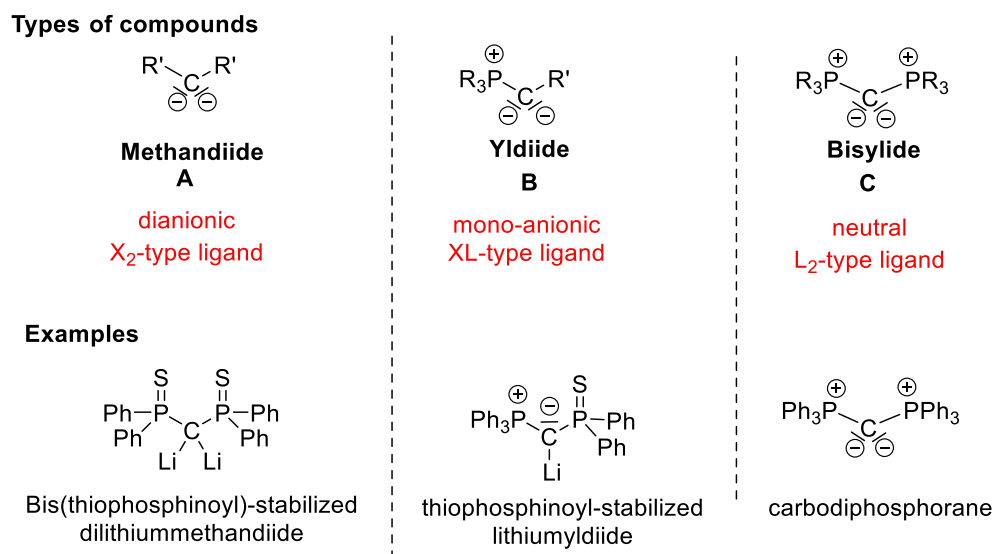


Figure S29. Comparison between divalent carbon ligands.

In the text, we use the terms ylides and metalated ylides. Both terms essentially describe the same type of compounds. However, the term ylide only focusses on the carbanionic ligand, while metalated ylide also includes the metal cation, which of course is always present. These terms are comparable to “methyl anion” or „methanide“ and “methyl lithium”.

Electronic structure of ylide **1**.

The conclusions discussed here are based on the computational results given in Table S3.

The bonding situation in the ylide is characterized by ylidic bonding situations (Figure S26), which can be described by several canonical structures. According to the charge distribution within the ylide, structure **1'** with a maximum of formal charges would be the best representation. Yet, phosphine sulfides (like phosphine oxides) are usually depicted with a P=S double bond. Thus, we also selected this representation to facilitate the understanding of the structures and to emphasize that our primary focus in our investigation was the bonding arising from the ylidic carbon atom. The ylene structures **1''** and **1'''** don't agree with the true electron distribution, the bent geometry and the reactivity of the compounds.

We would also like to point out that ChemDraw structures are often simplified representations, which not necessarily describe the true electron distribution in a molecule. This is particularly true for compounds with delocalized or non-classical multi-center covalent bonds. However, also in simple molecules formal and natural charges do often not match each other and should also not be confused with each other. For example, the ammonium cation NH_4^+ is often depicted with a positive formal charge at nitrogen, yet it bears a negative partial charge.

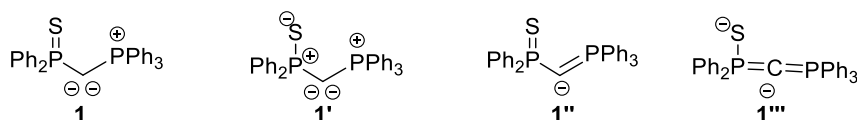


Figure S30. Possible resonance forms of ylide **1**.

Bonding situation in compounds **1-4**.

The bonding situation in complexes **1-4** are likewise characterized by ylidic bonding situations and highly ionic metal carbon interactions (Figure S27). We opted for the description of the potassium compound **1** as a ionic salt like structure because of the very low covalent character of the C-K bond. This conclusion is based on our computational studies, which yielded a very low Wiberg bond index of the C-K bond (WBI = 0.018), a very low charge density at the bond critical point of only 0.014 and an overall charge of almost -1 on the ylide ($q = -0.954$). These parameters clearly argue for an ionic bonding situation as expected for an organopotassium compound and is different compared to complexes **2** and **3**.

In comparison to **1**, the Hg-C bond features a more than twenty times higher WBI and a decreased charge on the ligand, which let us to depict this compound by a covalent bond, albeit the bond still has a significant ionic character as expressed by the low charge density at the BCP. Since the

WBI further increases to the actinides we kept the same description for the actinide complexes, albeit structure 3' certainly also contributes to the true electronic structure of the complexes as mentioned in the main text. The phosphoniocarbene structure 3'' however, does not contribute to the bonding situation since no π -interaction is observed as for example suggested by the NBO analysis.

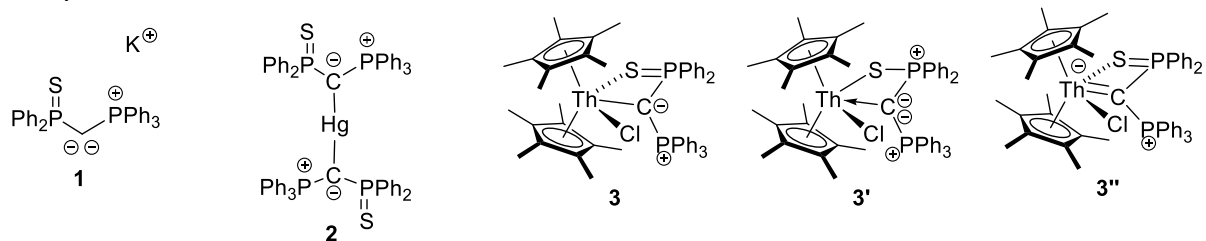


Figure S31. Structures of compounds 1-3.

5 Author Contributions

M. J. and A. J. G. carried out the synthetic work and standard analytical characterization. D. K. performed the computational, S. P. K. the crystallographic studies. V. H. G. and J. R. W. supervised the work and wrote the manuscript with contributions from all authors.

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Supporting Information

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