

Supplementary information:

**Homoleptic, Heteroleptic and Mixed-Valent Thallium and Indium Complexes of
Multidentate Chalcogen-Centered PCP-Bridged Ligands**

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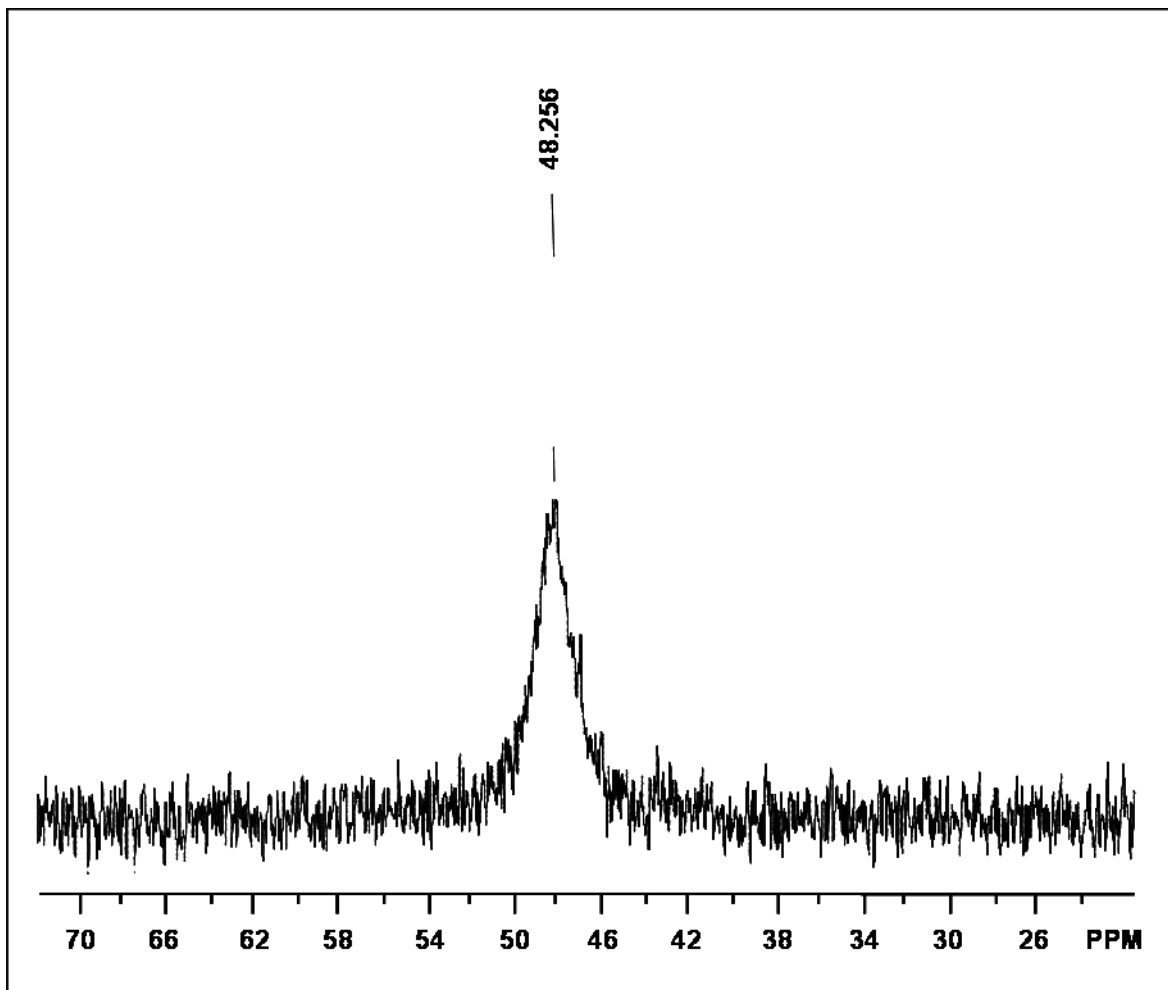


Figure S1. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Tl}_2[(\text{SPh}_2\text{P})_2\text{CSSC}(\text{PPh}_2\text{S})_2]$ (**9b**) recorded in CD_2Cl_2 at 23 °C.

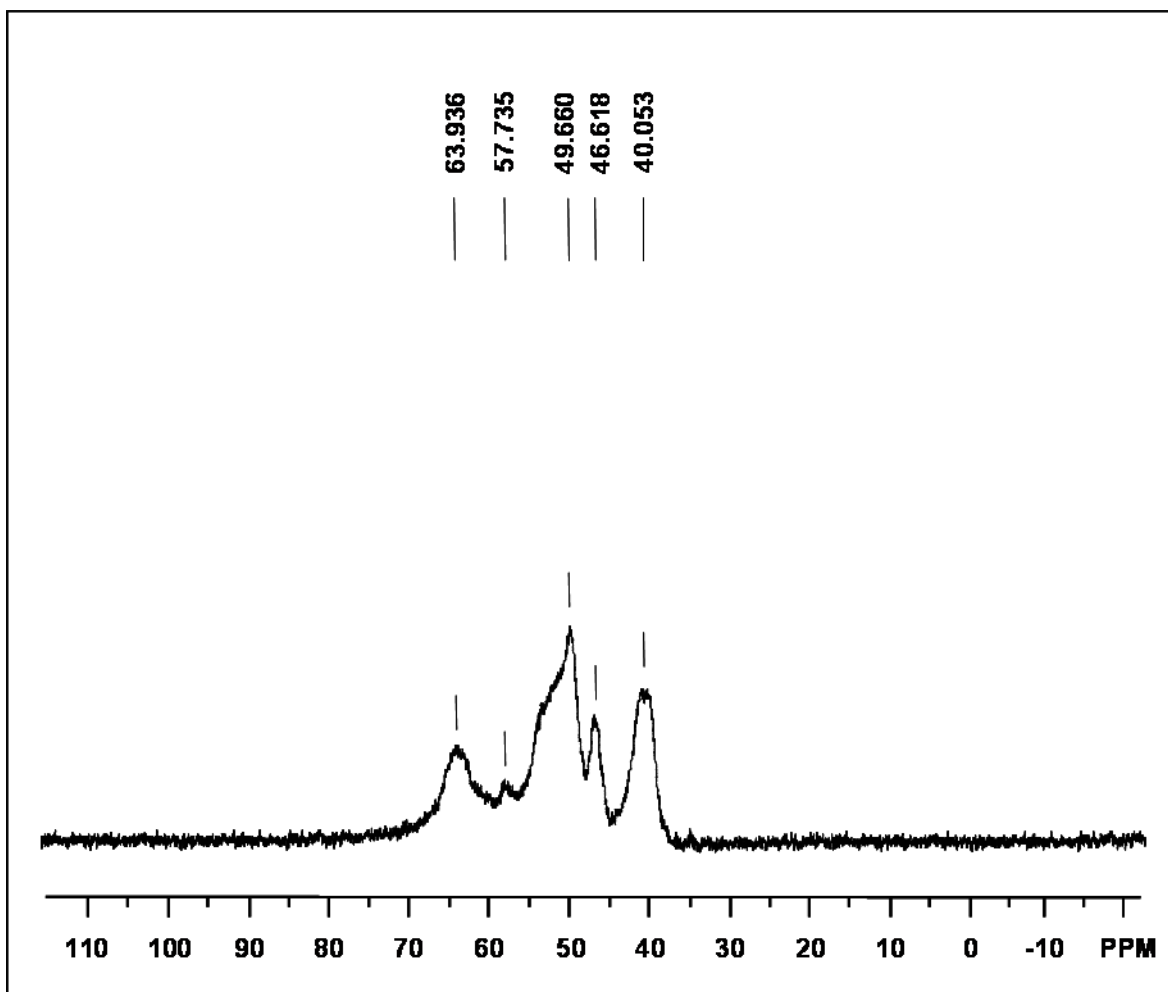


Figure S2. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Tl}_2[(\text{SPh}_2\text{P})_2\text{CSSC}(\text{PPh}_2\text{S})_2]$ (**9b**) recorded in CD_2Cl_2 at $-80\text{ }^\circ\text{C}$.

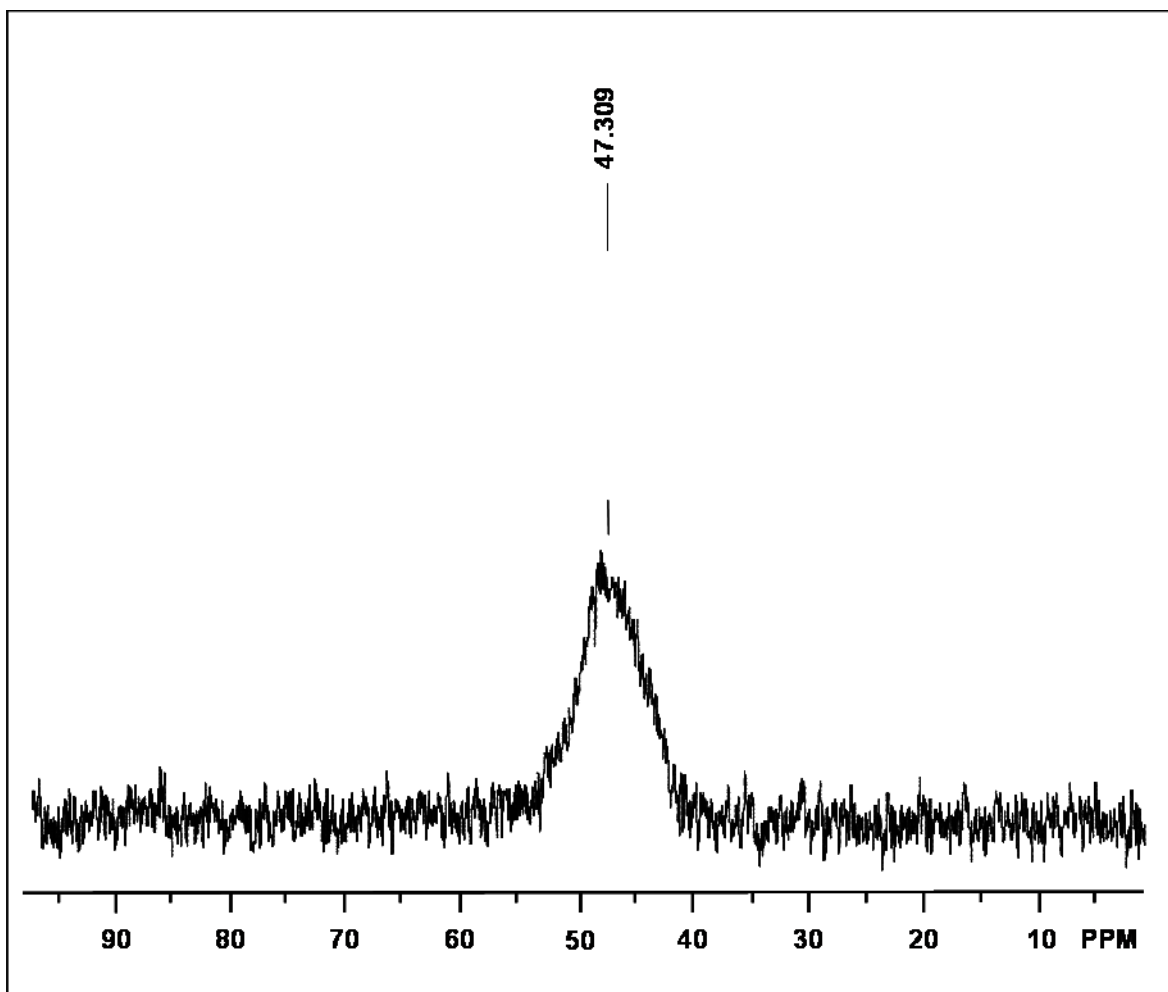


Figure S3. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Tl}_2[(\text{SPh}_2\text{P})_2\text{CSeSeC}(\text{PPh}_2\text{S})_2]$ (**9c**) recorded in CD_2Cl_2 at 23 °C.

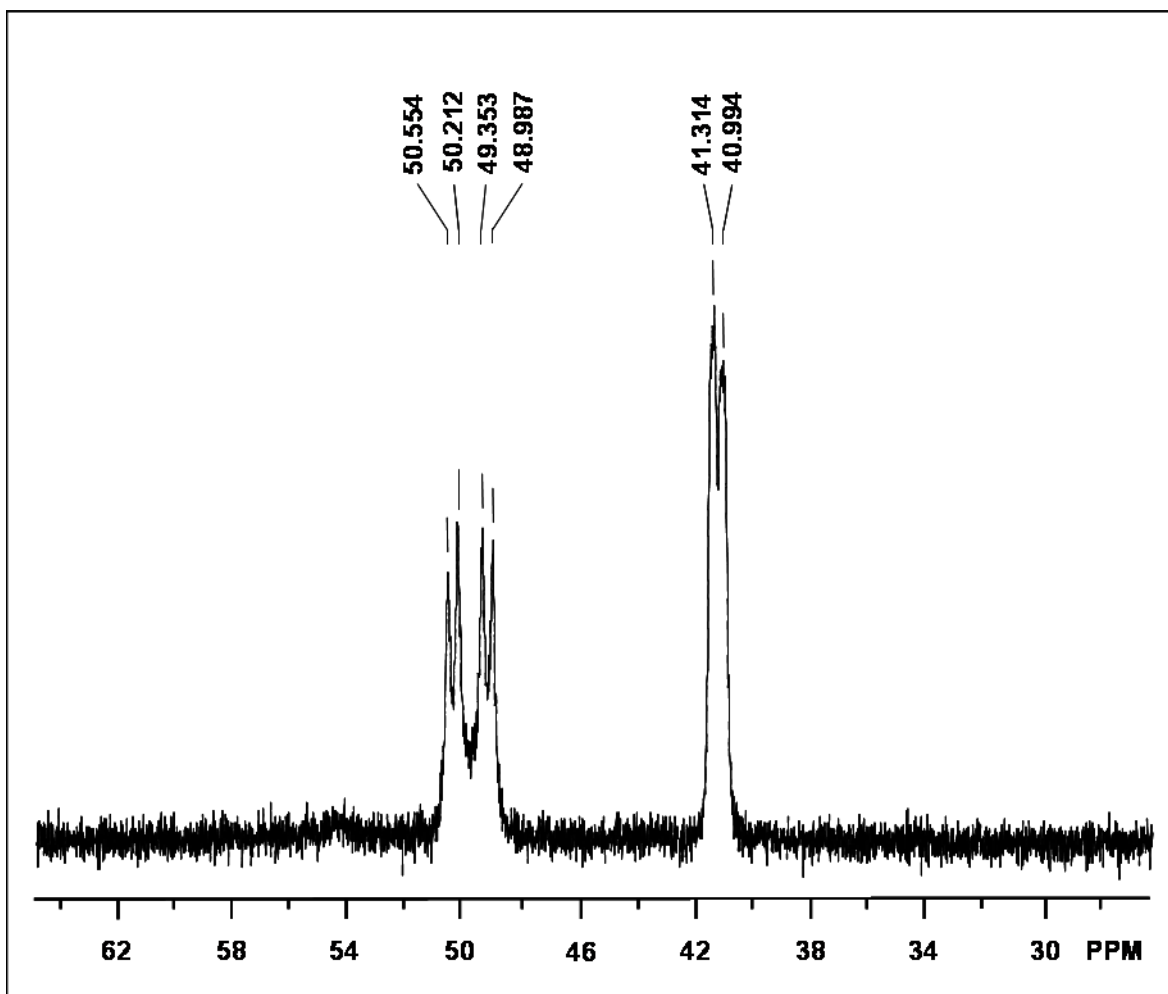


Figure S4. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Tl}_2[(\text{SPh}_2\text{P})_2\text{CSeSeC}(\text{PPh}_2\text{S})_2]$ (**9c**) recorded in CD_2Cl_2 at $-60\text{ }^\circ\text{C}$.