Supporting Information

Heterobimetallic Single-Source Precursors: A Springboard to the Synthesis of Binary Intermetallics

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Figure S1. Expanded version of Figure 1. Powder XRD patterns of solids obtained after thermolysis of (a) [ClNi(o-Ph2P-C6H4)3As]Cl (600 °C), (b) ClNi(o-Ph2P-C6H4)3SbCl (600 °C), (c) [ClPd(o-Ph2P-C6H4)3As]Cl (475 °C), (d) [(CyNC)Pd(o-Ph2P-C6H4)2SbCl2][SbF6] (600 °C, * = Pd), (e) ClPd(o-Ph2P-C6H4)2SbCl2 (450 °C), (f) ClPt(o-Ph2P-C6H4)3SbCl (340 °C), and (g) ClAu(o-iPr2P-C6H4)2BiCl (600 °C, ‡ = Bi). Standard patterns are shown in red.
Figure S2. (a) Reaction scheme, (b) visual appearance of the precursor (photograph courtesy of Carena L. Daniels. Copyright 2018), (c) optical micrograph of the intermetallic product (courtesy of Deyny Mendivelso-Perez. Copyright 2018), (d) TGA-DSC, (e) powder XRD (600 °C), (f) IR and (g) MS of evolved gases for the thermolysis of [ClNi(o-Ph2P-C6H4)3As]Cl (SSP).
Figure S3. (a) Reaction scheme, (b) visual appearance of the precursor (photograph courtesy of Carena L. Daniels. Copyright 2018), (c) optical micrograph of the intermetallic product (courtesy of Deyny Mendivelso-Perez. Copyright 2018), (d) TGA-DSC, (e) powder XRD (600 °C), (f) IR and (g) MS of evolved gases for the thermolysis of ClNi(\(\sigma\)-Ph\(_2\)P-C\(_6\)H\(_4\))\(_3\)SbCl (SSP).
Figure S4. (a) Reaction scheme, (b) initial appearance, (b) visual appearance of the precursor (photograph courtesy of Carena L. Daniels. Copyright 2018), (c) optical micrograph of the intermetallic product (courtesy of Deyny Mendivelso-Perez. Copyright 2018), (d) TGA-DSC, (e) powder XRD (475 °C), (f) IR and (g) MS of evolved gases for the thermolysis of [ClPd(o-Ph₂P-C₆H₄)₃As]Cl (SSP).
Figure S5. (a) Reaction scheme, (b) visual appearance of the precursor (photograph courtesy of Carena L. Daniels. Copyright 2018), (c) optical micrograph of the intermetallic product (courtesy of Deyny Mendivelso-Perez. Copyright 2018), (d) TGA-DSC, (e) powder XRD (600 °C), (f) IR and (g) MS of evolved gases for the thermolysis of [(CyNC)Pd(o-Ph2P-C6H4)2SbCl2][SbF6] (SSP).
Figure S6. (a) Reaction scheme, (b) visual appearance of the precursor (photograph courtesy of Carena L. Daniels. Copyright 2018), (c) TGA-DSC, (d) powder XRD (450 °C), (e) IR and (f) MS of evolved gases for the thermolysis of ClPd(o-Ph2P-C6H4)2SbCl2 (SSP).
Figure S7. (a) Reaction scheme, (b) visual appearance of the precursor (photograph courtesy of Carena L. Daniels. Copyright 2018), (c) optical micrograph of the intermetallic product (courtesy of Deyny Mendivelso-Perez. Copyright 2018), (d) TGA-DSC, (e) powder XRD (340 °C), (f) IR and (g) MS of evolved gases for the thermolysis of ClPt(\(\sigma\)-Ph\(_2\)P-C\(_6\)H\(_4\))\(_3\)SbCl (SSP).
Figure S8. (a) Reaction scheme, (b) visual appearance of the precursor (photograph courtesy of Carena L. Daniels. Copyright 2018), (c) optical micrograph of the intermetallic product (courtesy of Deyny Mendivelso-Perez. Copyright 2018), (d) TGA-DSC, (e) powder XRD (600 °C), (f) IR and (g) MS of evolved gases for the thermolysis of ClAu(o-Ph2P-C6H4)2BiCl (SSP).
Figure S9. Raman spectra of intermetallic compounds produced by thermolysis of heterobimetallic single source precursors. The excess mass difference between the % mass left after TGA analysis and the theoretical mass of the inorganic binary is denoted by $\Delta$, where $\Delta = TGA_{m}^{f} - theo_{m}^{inor}$. $\lambda_{max} = 532$ nm, 3 µm diameter, 0.3 mW. The 532 nm excitation laser (diameter: 3 µm, Power: 0.3 mW) was used for the analysis of PtSb, NiSb, Pd$_2$As, PdSb, and Au$_2$Bi samples, whereas the 785 nm (diameter: 3 µm, Power: 0.9 mW) excitation laser was used for the NiAs sample.
Figure S10. Representative TEM of NiSb produced by thermolysis of ClNi(o-Ph2P-C6H4)3SbCl (600°C) (Courtesy of Bryan A. Rosales. Copyright 2018).
Figure S11. Powder XRD of the solids produced by thermolysis of ClNi(o-Ph₂P-C₆H₄)₃SbCl (SSP) vs. equimolar mixtures of Ni(cod)₂ and Ph₃Sb, or NiCl₂ and Ph₃Sb (all cases were heated to 600 °C) (impurity marked with * corresponds to an Ni₅Sb₂ byproduct).
Figure S12. Powder XRD of Pd$_2$As before and after plasma cleaning for 72 h.
Figure S13. Powder XRD of the solids produced by thermolysis of ClPt(o-Ph$_2$P-C$_6$H$_4$)$_3$SbCl at different temperatures.
Figure S14. Powder XRD of the solids produced by thermolysis of ClPd(o-Ph₂P-C₆H₄)₃AsCl at different temperatures.
Figure S15. Powder XRD of the solids produced by thermolysis of ClPd(o-Ph2P-C6H4)2SbCl2 at different temperatures.
Figure S16. $^1$H NMR spectrum of [(CyNC)Pd(o-Ph$_2$P-C$_6$H$_4$)$_2$SbCl$_2$][SbF$_6$] in CD$_2$Cl$_2$.

Figure S17. $^{13}$C{$^1$H} NMR spectrum of [(CyNC)Pd(o-Ph$_2$P-C$_6$H$_4$)$_2$SbCl$_2$][SbF$_6$] in CD$_2$Cl$_2$. 
Figure S18. $^{31}$P{$^1$H} NMR spectrum of [(CyNC)Pd($\sigma$-Ph$_2$P-C$_6$H$_4$)$_2$SbCl$_2$][SbF$_6$] in CD$_2$Cl$_2$.

Figure S19. $^1$H NMR spectrum of [ClPd($\sigma$-Ph$_2$P-C$_6$H$_4$)$_3$As]Cl in CDCl$_3$. 
Figure S20. $^{13}$C$\{^1\text{H}\}$ NMR spectrum of [ClPd(o-Ph$_2$P-C$_6$H$_4$)$_3$As]Cl in CDCl$_3$.

Figure S21. $^{31}$P$\{^1\text{H}\}$ NMR spectrum of [ClPd(o-Ph$_2$P-C$_6$H$_4$)$_3$As]Cl in CDCl$_3$. 
Figure S22. The asymmetric unit of [(CyNC)Pd(o-Ph₂P-C₆H₄)₂SbCl₂][SbF₆] contains two independent molecules which display very similar geometries. A displacement ellipsoid plot of one of the two independent molecules in the solid state structure is shown. Thermal ellipsoids were drawn at 50% probability level. H-atoms and SbF₆⁻ counter-ion were omitted for clarity.

Figure S23. Displacement ellipsoid plot of [ClPd(o-Ph₂P-C₆H₄)₃As]Cl. Thermal ellipsoids were drawn at 50% probability level. H-atoms, CHCl₃ and Cl⁻ counter-ion were omitted for clarity.
Table S1. Selected bond lengths (Å) and angles (°) for complex \([(\text{CyNC})\text{Pd}(\sigma-\text{Ph}_2\text{P-C}_6\text{H}_4)_2\text{SbCl}_2)][\text{SbF}_6]\) determined crystallographically.

| Parameter       | \([(\text{CyNC})\text{Pd}(\sigma-\text{Ph}_2\text{P-C}_6\text{H}_4)_2\text{SbCl}_2)][\text{SbF}_6]\) |
|-----------------|--------------------------------------------------|
| Sb-Pd           | 2.4535(2)                                        |
| Pd-C37          | 2.025(1)                                         |
| Sb-Cl1          | 2.459(1)                                         |
| Sb-Cl2          | 2.524(1)                                         |
| Pd-P1           | 2.332(1)                                         |
| Pd-P2           | 2.322(1)                                         |
| Cl1-Sb-Cl2      | 171.1(5)                                         |
| Sb-Pd-C37       | 168.2(2)                                         |
| P1-Pd-P2        | 164.8(5)                                         |

Table S2. Selected bond lengths (Å) and angles (°) for complex \([\text{ClPd}(\sigma-\text{Ph}_2\text{P-C}_6\text{H}_4)_3\text{As}]\text{Cl}\) determined crystallographically.

| Parameter       | \([\text{ClPd}(\sigma-\text{Ph}_2\text{P-C}_6\text{H}_4)_3\text{As}]\text{Cl}\) |
|-----------------|----------------------------------------------------------------------------------|
| As-Pd           | 2.2806(3)                                                                        |
| Pd-Cl1          | 2.354(6)                                                                         |
| Pd-P1           | 2.402(6)                                                                         |
| Pd-P2           | 2.479(6)                                                                         |
| As-Pd-Cl1       | 177.3(2)                                                                         |
| P1-Pd-P2        | 116.4(2)                                                                         |
| P1-Pd-P3        | 124.4(2)                                                                         |
| P2-Pd-P3        | 116.6(2)                                                                         |