# Supporting Online Material for:

## Stoichiometric and Catalytic Sn-Mediated Dehydrocoupling of Primary Phosphines

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### Materials and Methods

**General Methods**: THF was distilled from sodium-benzophenone. All synthetic work was carried out under an inert argon atmosphere using standard Schlenk and glove box techniques. $^{31}$P NMR and $^{31}$P{$^{1}$H} NMR spectra were recorded on a Bruker DRX 500 FTNMR spectrometer at 25°C and were referenced with respect to an 85% solution of $H_3PO_4$ in $D_2O$. Mass spectra were recorded on a Waters Quattro LC (ESI) and a Bruker BioApex II 4.7e FTICR (EI). X-ray structure analysis data for **5**, **6** and **7** were collected on a Nonius KappaCCD diffractometer, and was solved by direct methods and refined by full-matrix least squares on $F^2$ (G. M. Sheldrick, SHELX-97, Göttingen, **1997**). CCDC 768905, 768906 and 768907 contain the supplementary crystallographic data for **5**, **6** and **7**, respectively. Data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from The Cambridge Crystallography Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax 441223 316033). $CyPH_2$ was obtained commercially from Strem and used without any further purification. $Cp^*_2Sn$, $Cp^*_2SnCl_2$, $^{t}BuPH_2$, $FcPH_2$ and $FcCH_2PH_2$ were prepared according to literature procedures.(*S1-S5*)

**General stoichometric procedure:** A PTFE-valved NMR tube was charged with $Cp^*_2Sn$ (10.0 mg, 0.025 mmol), phosphine (10 equivalents) and THF (0.5 mL) under nitrogen. A sealed capillary of triphenylphosphine in $D_6$-acetone (0.1 mL) was added as an integration standard. The NMR tube was then sealed and heated to 60°C (14 hrs). All products were analysed using $^{31}$P NMR, $^{31}$P{$^{1}$H} NMR spectroscopy, showing the distinct AA′BB′ splitting pattern in the $^{31}$P NMR spectrum for the diphosphanes RP(H)P(H)R. Some of the phosphines produced [CyP(H)P(H)Cy, $^{t}$BuP(H)P(H)$^{t}$Bu] are known in the literature and their identities were confirmed by comparison to literature data (see Figures S1 and S2).(*S6,S7*) For the compounds FcP(H)P(H)Fc and $FcCH_2P(H)P(H)FcCH_2$ see following $^{31}$P NMR and $^{31}$P{$^{1}$H} NMR spectra (Figures S3-S6).

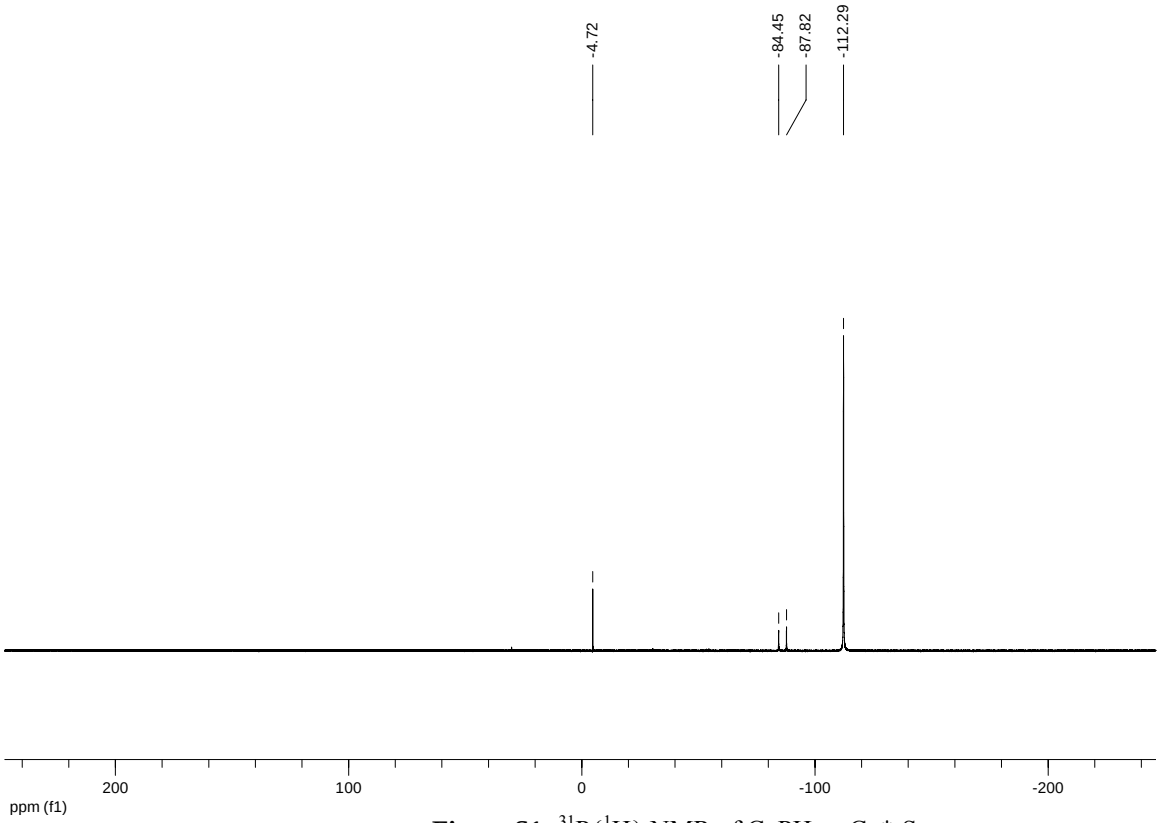



**Figure S1:** $^{31}P\{^{1}H\}$ NMR of $CyPH_2$ + $Cp^*_2Sn$.

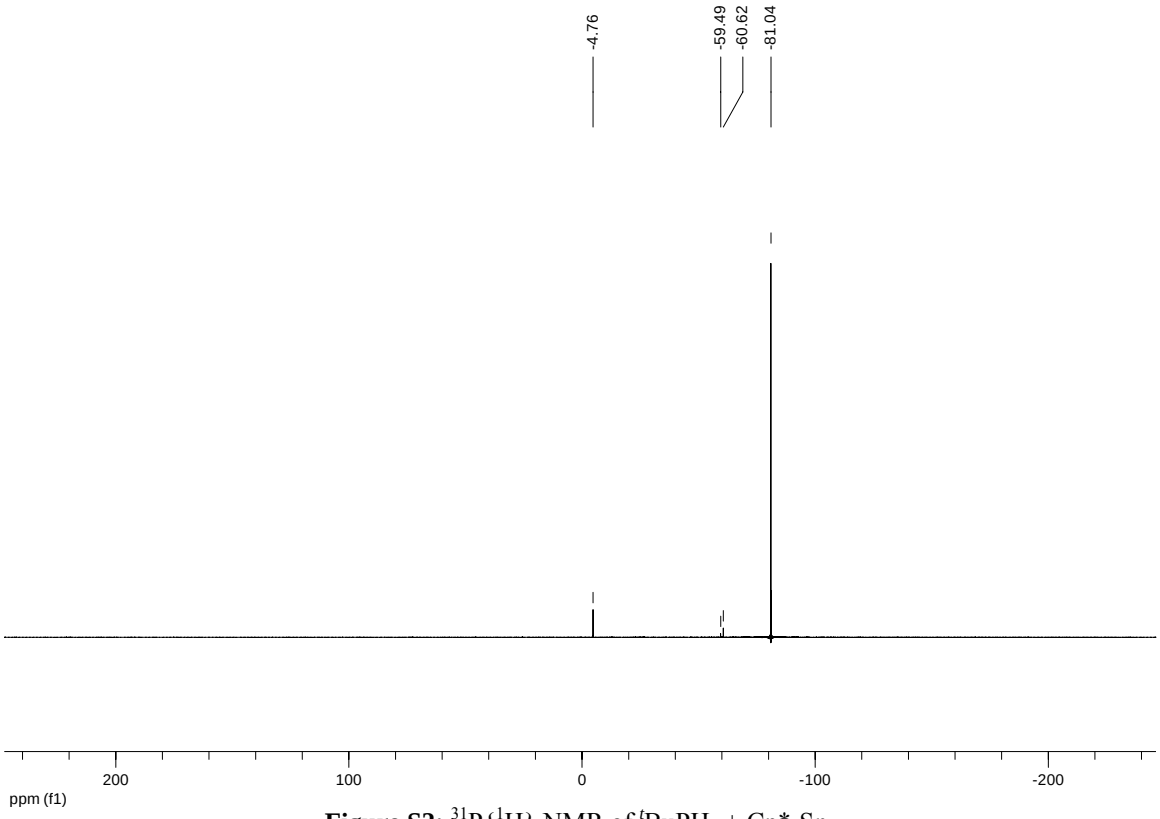



**Figure S2:** $^{31}P\{^{1}H\}$ NMR of $^{t}BuPH_2$ + $Cp^*_2Sn$.

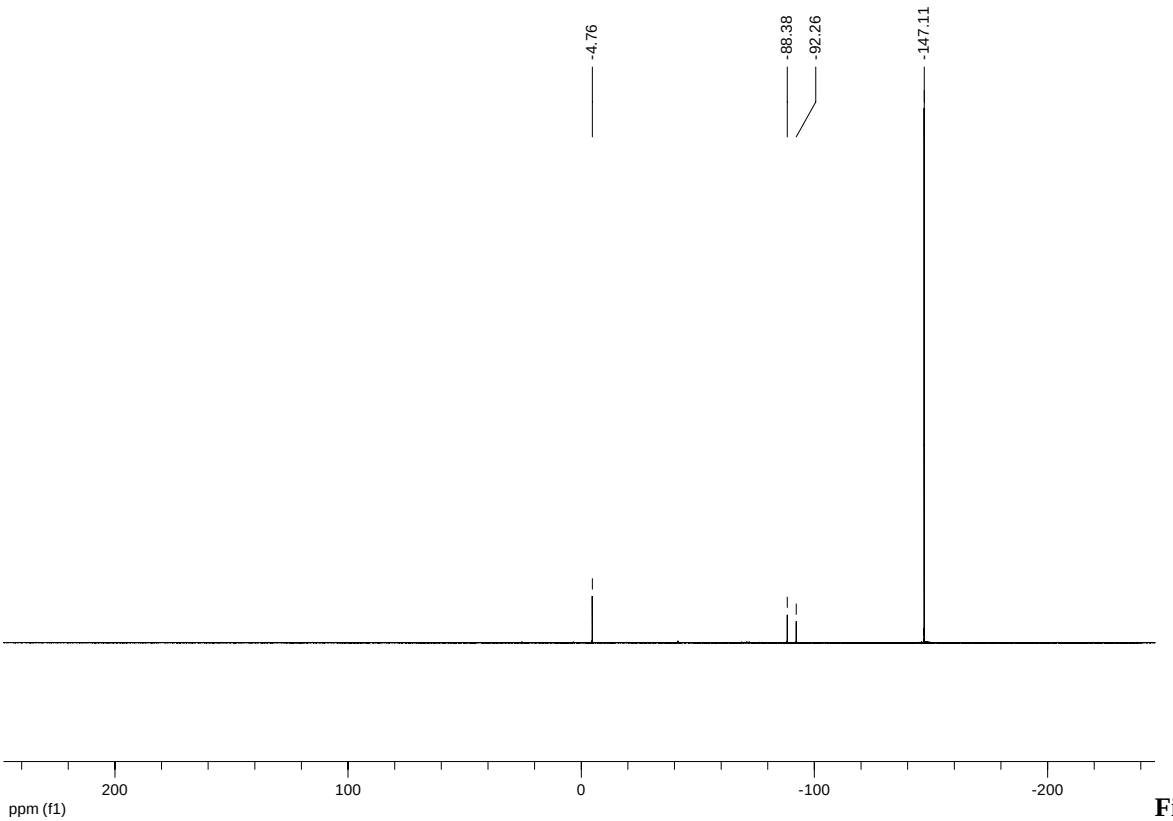



**Figure S3:** $^{31}P\{^{1}H\}$ NMR of $FcPH_2$ + $Cp^*_2Sn$.

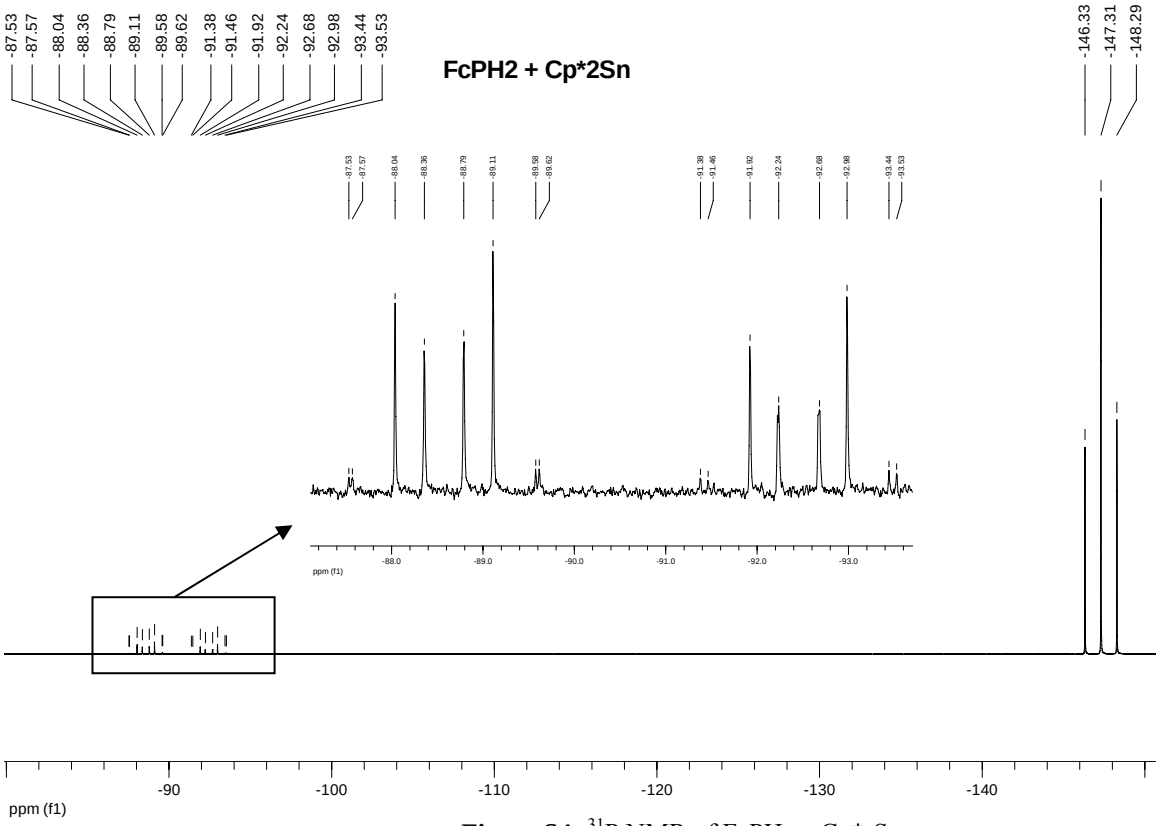



**Figure S4:** $^{31}P$ NMR of $FcPH_2$ + $Cp^*_2Sn$.

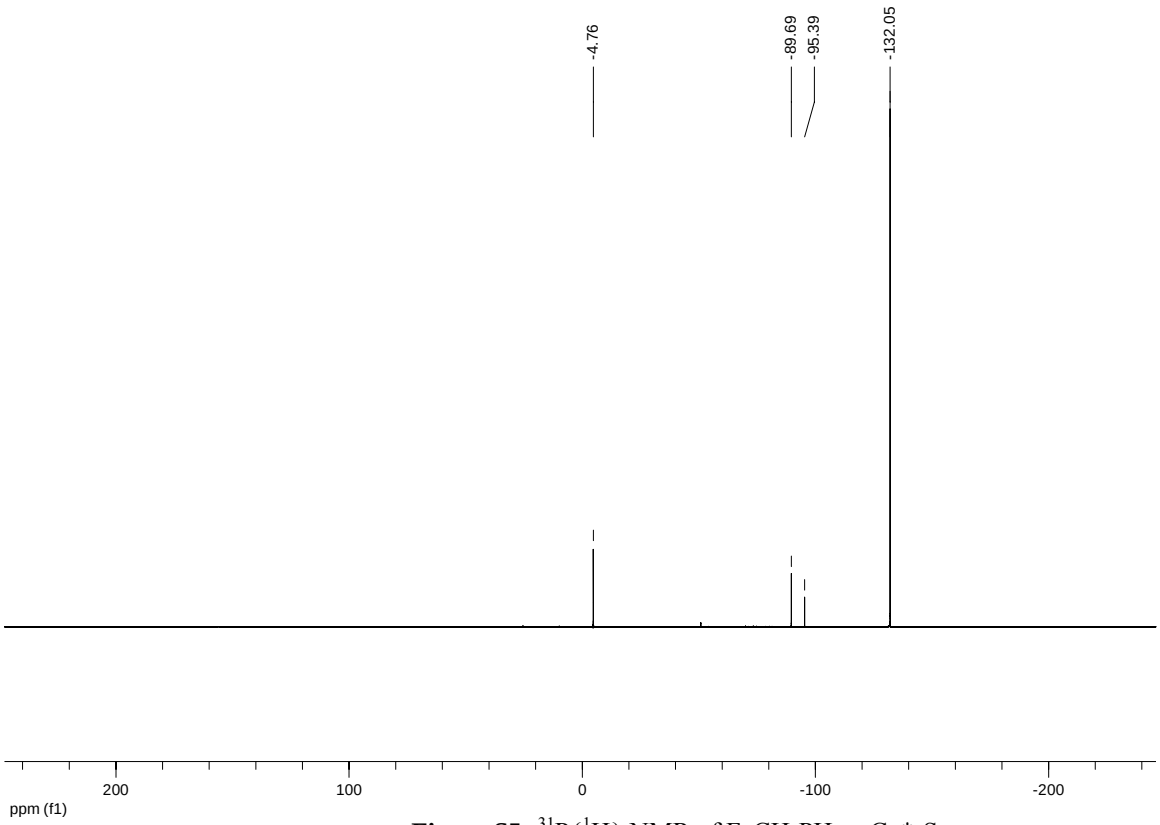



**Figure S5:** $^{31}P\{^{1}H\}$ NMR of $FcCH_2PH_2$ + $Cp^*_2Sn$.

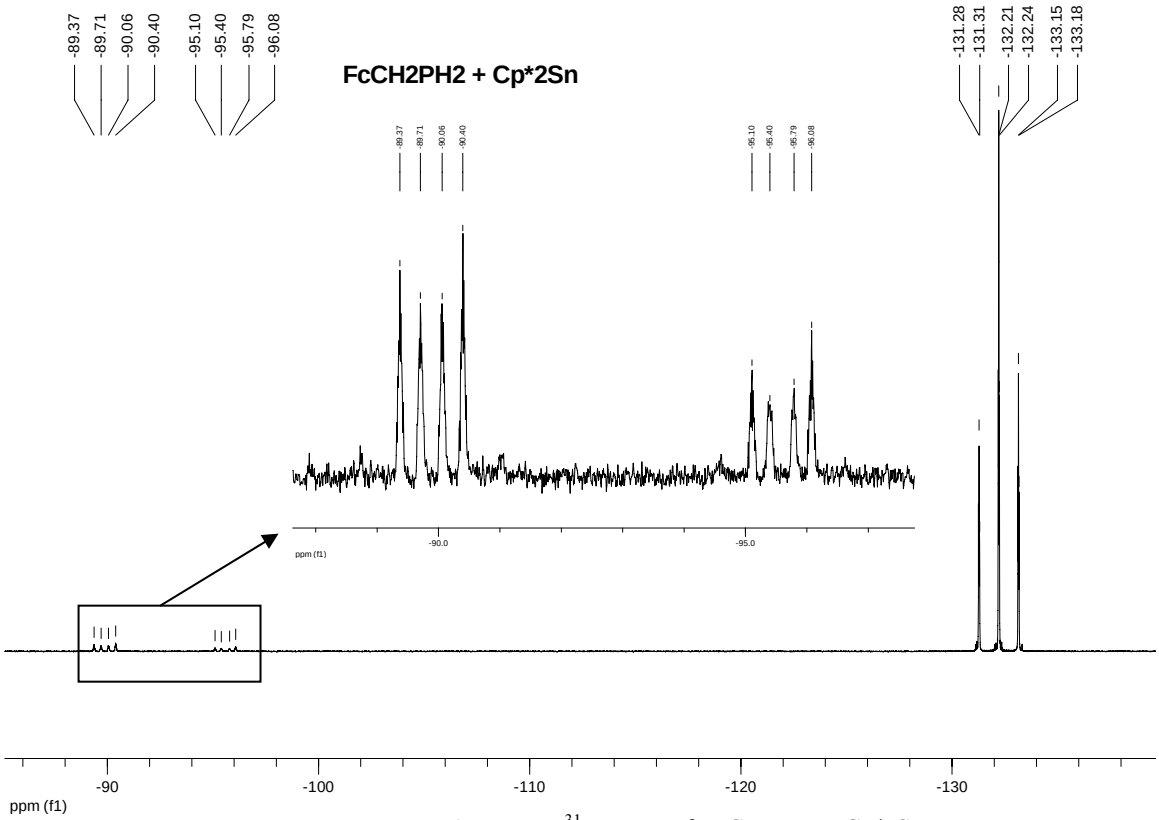



**Figure S6:** $^{31}P$ NMR of $FcCH_2PH_2$ + $Cp^*_2Sn$.

**General catalytic procedure:** A PTFE-valved NMR tube was charged with $Cp^*_2SnCl_2$ (6.9 - 11.5 mg, 0.015 - 0.025 mmol), phosphine (10 equivalents) and THF (0.5 mL). A sealed capillary of triphenylphosphine in $D_6$-acetone (0.1 mL) was added as an integration standard. The NMR tube was then sealed and heated to 60°C (4 days). At regular intervals, $^{31}P\{^{1}H\}$-NMR and

$^{31}$P-NMR spectra were recorded. The reaction was monitored until no more phosphine was consumed. All products were analysed using $^{31}$P and $^{31}$P{$^{1}$H} NMR spectroscopy and mass spectroscopy (ESI and EI). Many of the products produced [CyP(H)P(H)Cy, $^{t}$BuP(H)P(H)$^{t}$Bu, $[CyP]_4$, $[^{t}BuP]_4$] are known in the literature and their identities were confirmed by comparison to literature data.(*S6*,*S7*) Novel products **5**, **6** and **7** were further analysed using X-ray structure analysis.

**Catalytic procedure using $CyPH_2$** (17.5 mg, 0.15 mmol): Yield: 80%. $^{31}$P{$^{1}$H} NMR: $\delta$/ppm = -4.7 (s, $Ph_3P$), -31.4 – -39.8 (CyP(H){CyP}$_n$P(H)Cy), -68.6 (s, $[CyP]_4$), -85.1 (s, CyP(H)P(H)Cy), -88.5 (s, CyP(H)P(H)Cy), -122.9 (s, $CyPH_2$). MS (ESI, 10 V): *m/z* = 253 (CyP(H)P(H)Cy + $Na^+$). MS (EI): *m/z* = 456 ($[CyP]_4$), 570 ($[CyP]_5$).

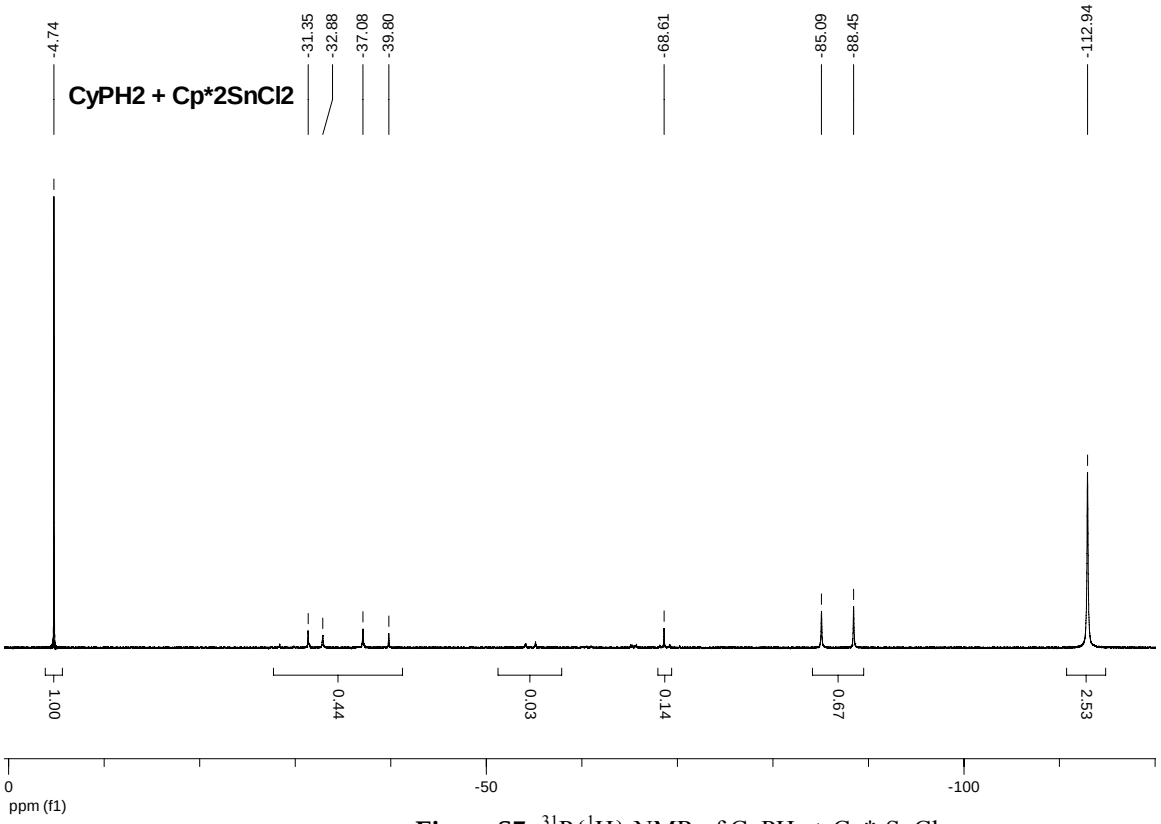



**Figure S7:** $^{31}$P{$^{1}$H} NMR of $CyPH_2$ + $Cp^*_2SnCl_2$.

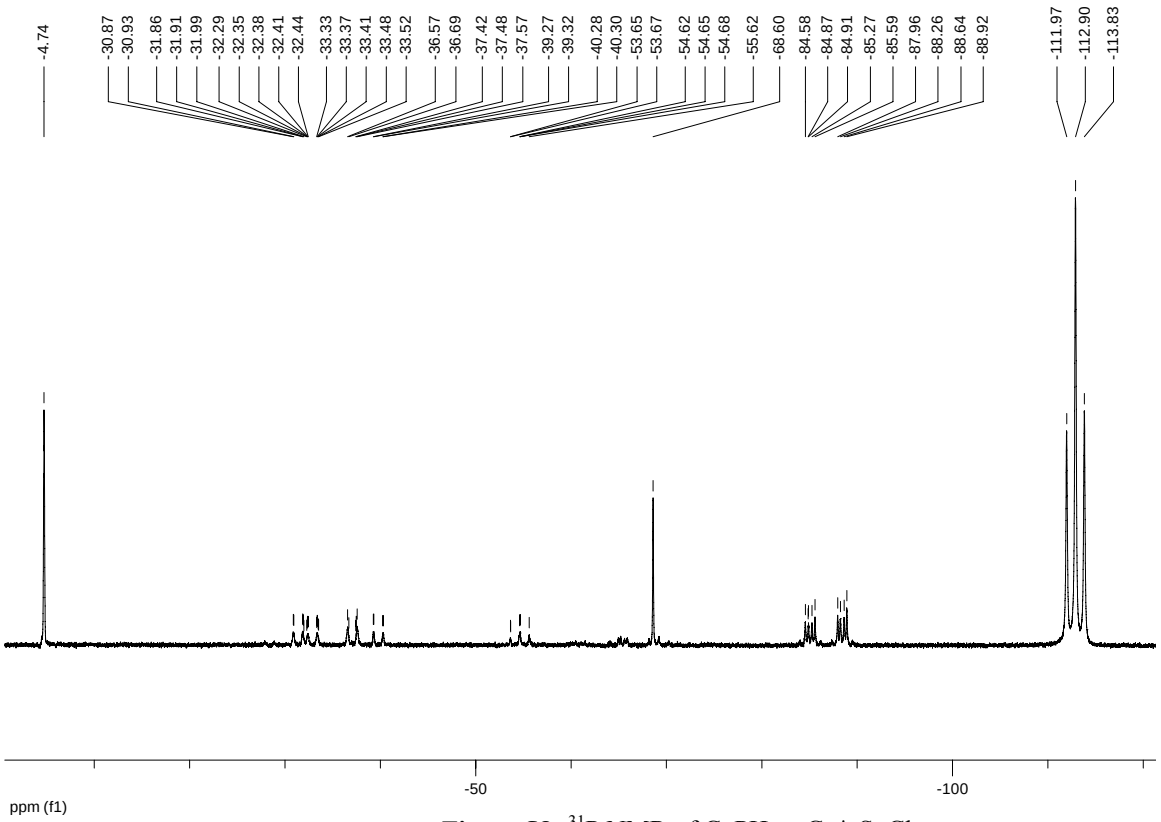



**Figure S8:** $^{31}P$ NMR of $CyPH_2$ + $Cp^*_2SnCl_2$.

**Catalytic procedure using $^t$BuPH$_2$** (22.5 mg, 0.25 mmol): Yield: 68%. $^{31}P\{^1H\}$ NMR: $\delta$/ppm = -4.7 (s, $Ph_3P$), -23.1 – -26.8 ($^t$BuP(H)$\{^t$BuP$\}_n$P(H)$^t$Bu), -59.5 (s, $^t$BuP(H)P(H)$^t$Bu), -60.6 (s, $^t$BuP(H)P(H)$^t$Bu), -81.1 (s, $^t$BuPH$_2$). MS (ESI, 10 V): *m/z* = 179 ($^t$BuP(H)P(H)$^t$Bu + $H^+$), 353 ([$^t$BuP]$_4$ + $H^+$), 441 ([$^t$BuP]$_5$ + $H^+$).

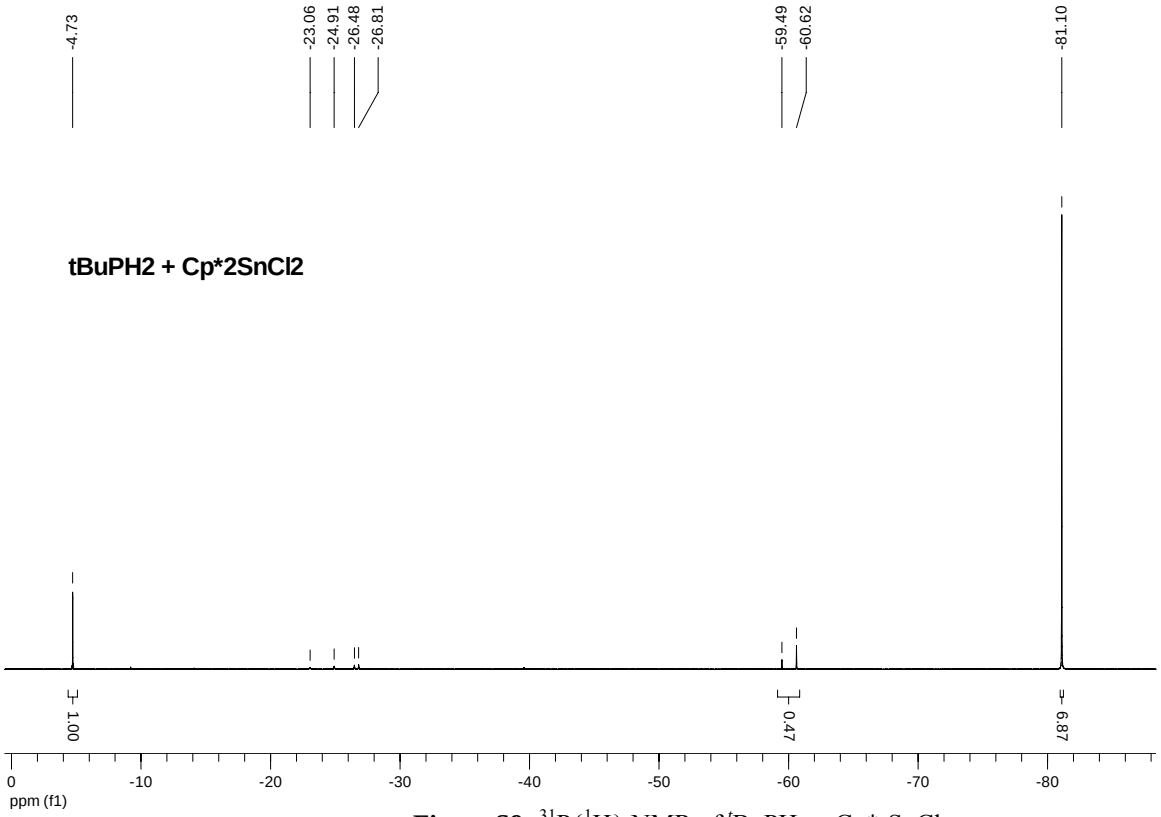



**Figure S9:** $^{31}P\{^1H\}$ NMR of $^t$BuPH$_2$ + $Cp^*_2SnCl_2$.

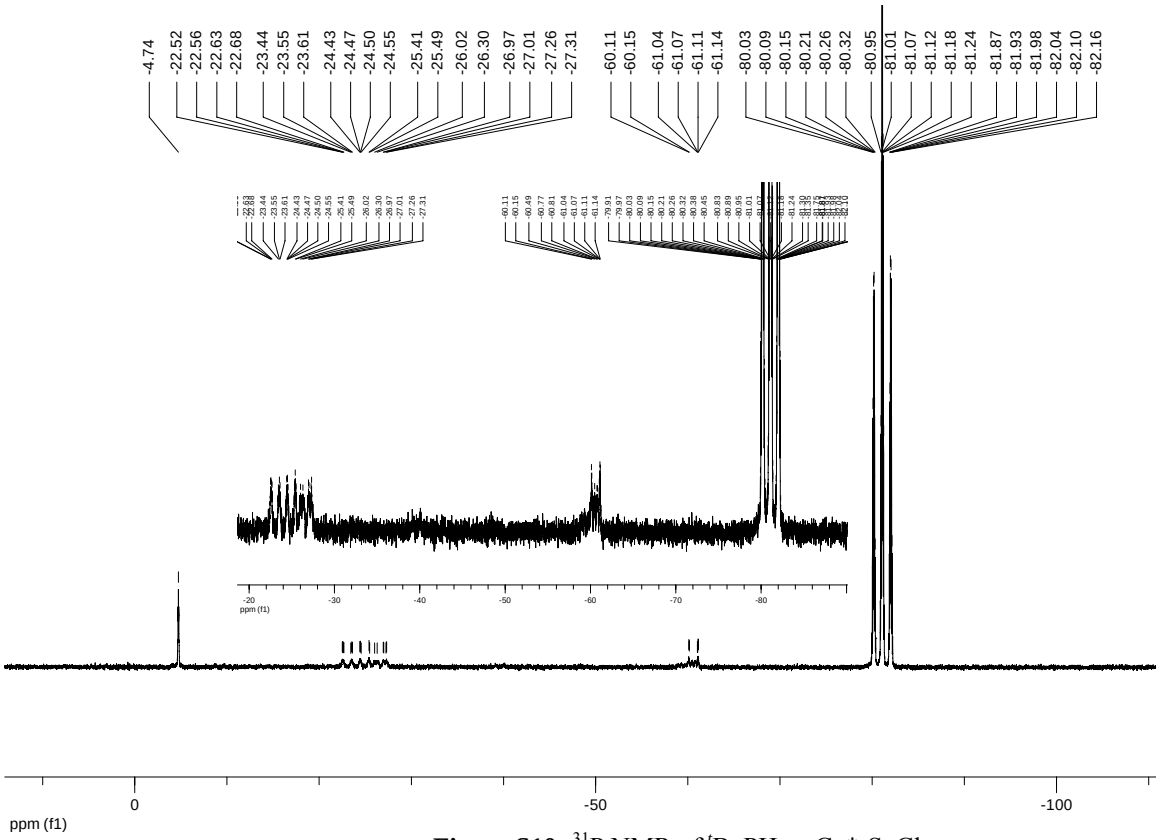



**Figure S10:** $^{31}P$ NMR of $^{t}BuPH_2$ + $Cp^*_2SnCl_2$.

**Catalytic procedure using $FcPH_2$** (54.5 mg, 0.25 mmol): Yield: 82%. $^{31}P\{^{1}H\}$ NMR: $\delta$ppm = -4.7 (s, $Ph_3P$), -42.1 – -66.0 (FcP(H){FcP}$_n$P(H)Fc), -88.3 (s, FcP(H)P(H)Fc), -92.2 (s, FcP(H)P(H)Fc), -147.1 (s, $FcPH_2$). MS (ESI, 10 V): *m/z* = 457 (FcP(H)P(H)Fc + $Na^+$). MS (ESI, 60 V): *m/z* = 903 ($[FcP]_4 + K^+$), 1119 ($[FcP]_5 + K^+$).

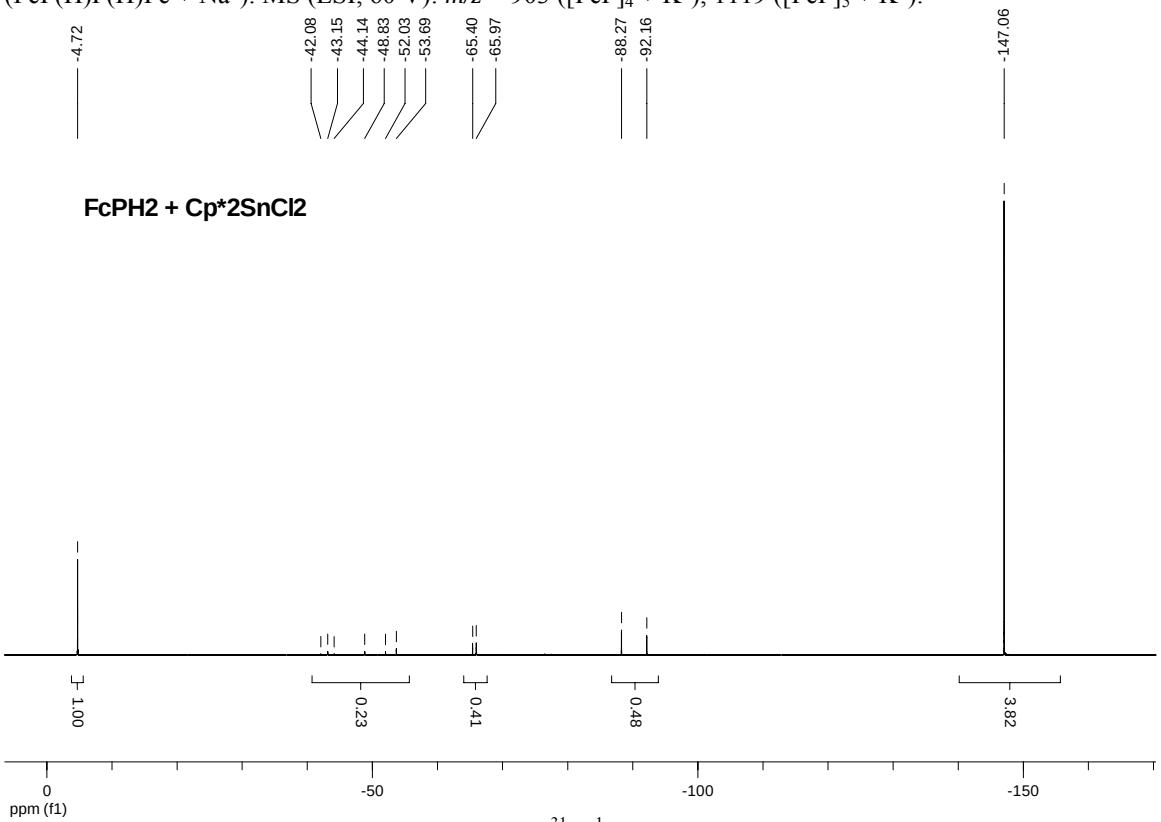



**Figure S11:** $^{31}P\{^{1}H\}$ NMR of $FcPH_2$ + $Cp^*_2SnCl_2$.

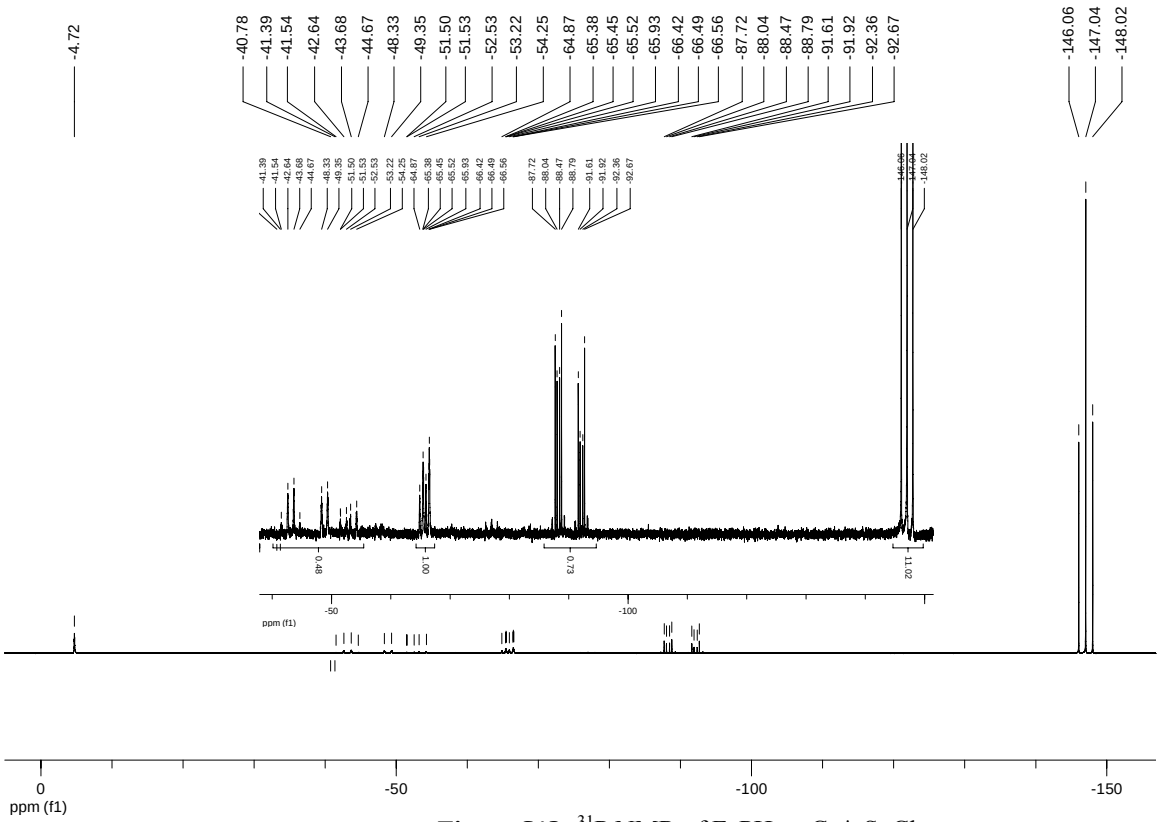



**Figure S12:** $^{31}P$ NMR of $FcPH_2$ + $Cp^*_2SnCl_2$.

**Catalytic procedure using $FcCH_2PH_2$** (58.0 mg, 0.25 mmol): Yield: 65%.(*S8*) $^{31}P\{^1H\}$ NMR: $\delta$/ppm = -4.7 (s, $Ph_3P$), -53.2 (s, $[FcCH_2P]_4$), -42.9 – -57.8 ($FcCH_2P(H)\{FcCH_2P\}_nP(H)FcCH_2$), -89.0 (s, $FcCH_2P(H)P(H)FcCH_2$), -94.7 (s, $FcCH_2P(H)P(H)FcCH_2$), -131.4 (s, $FcCH_2PH_2$). MS (ESI, 40 V): *m/z* = 501 ($FcCH_2P(H)P(H)FcCH_2$ + $K^+$), 693 ($FcCH_2P(H)\{FcCH_2P\}P(H)FcCH_2$ + $H^+$), 731 ($FcCH_2P(H)\{FcCH_2P\}P(H)FcCH_2$ + $K^+$), 921 ($[FcCH_2P]_4$ + $H^+$), 1151 ($[FcCH_2P]_5$ + $H^+$). MS (EI): *m/z* = 462 ($FcCH_2P(H)P(H)FcCH_2$).

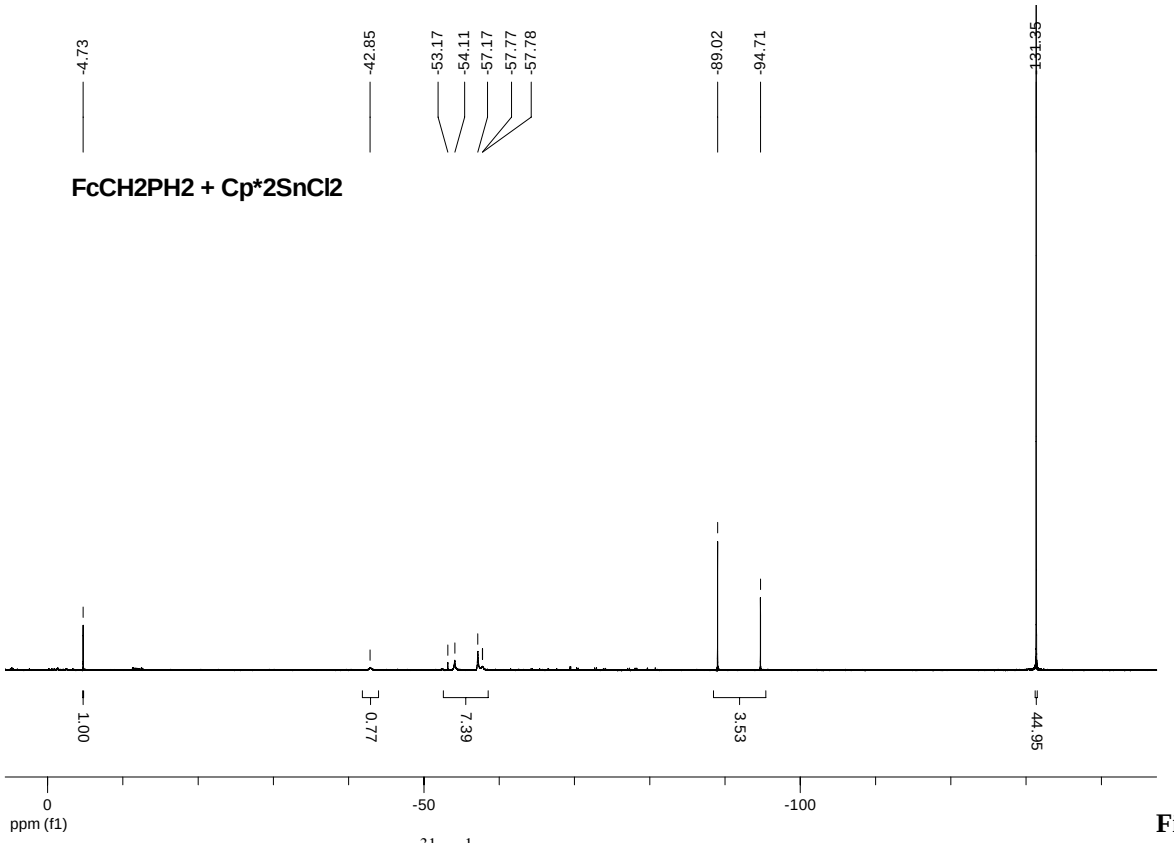



**Figure S13:** $^{31}P\{^{1}H\}$ NMR of $FcCH_2PH_2$ + $Cp^*_2SnCl_2$.

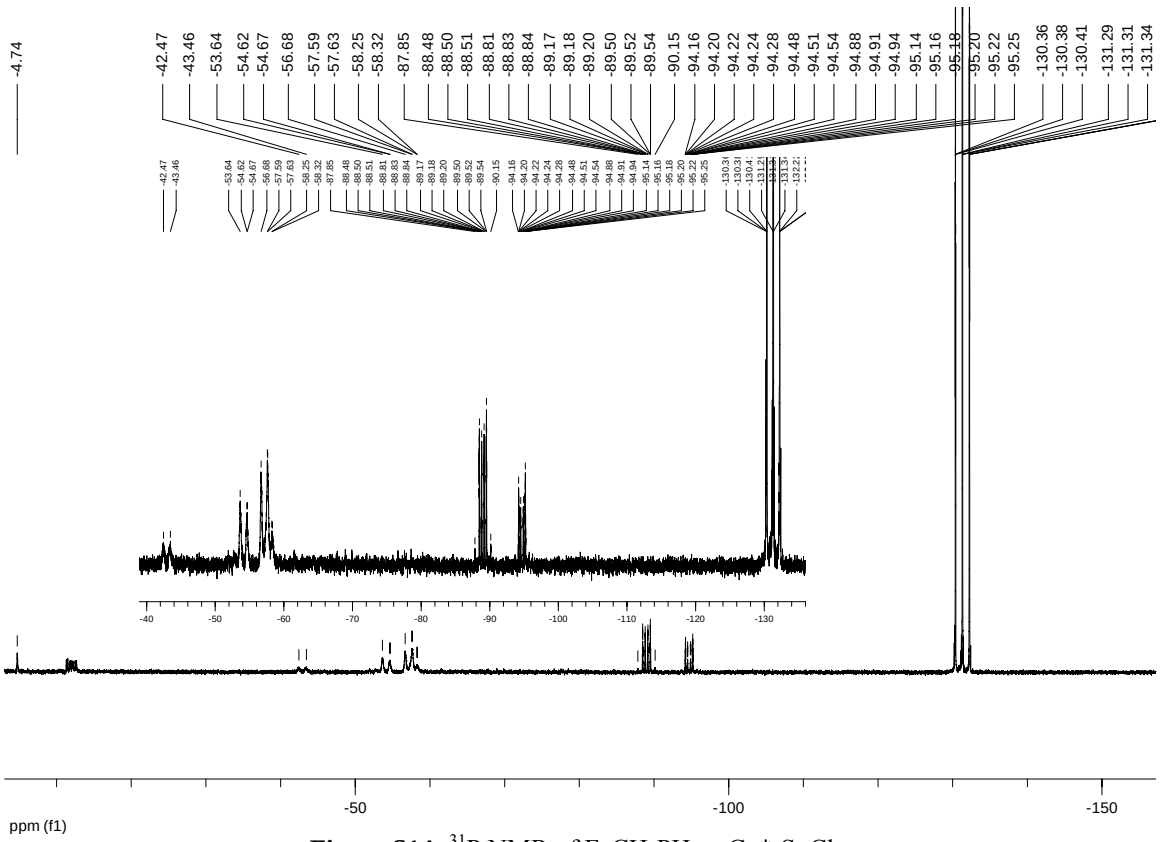



**Figure S14:** $^{31}P$ NMR of $FcCH_2PH_2$ + $Cp^*_2SnCl_2$.

**Synthesis of $[FcP]_4$ (5), $[FcP]_5$ (6) and $[(ClSn)_4(FcPPFc)_2]$ (7)**: $Cp^*_2SnCl_2$ (23.0 mg, 0.05 mmol) and ferrocenylphosphine (110 mg, 0.50 mmol) were dissolved in benzene (1.0 mL) and stirred at room temperature for 5 min. Storage of the reaction

mixture at room temperature without stirring (2 days) gave orange crystals of **5**. The mother liquor was stored at room temperature for a further 2 days, giving red crystals of **6** (together with more of **5**). Further storage of the solution for 1 day gave dark red crystals of **7**.

**5**: MS (ESI, 60 V): *m/z* = 903 ($[FcP]_4 + K^+$).

Crystal data for **5**; Molecular formula $C_{40}H_{36}Fe_4P_4$, *FW* = 863.96, *T* = 153(2)K, Crystal system *tetragonal*, space group *P*-4, *a* = *b* = 11.6520(16), *c* = 6.2473(12), *V* = 848.2(2)Å$^3$, *Z* = 1, $\rho_{calcd}$ = 1.691 Mg m$^{-3}$, $\mu$(Mo-K$_\alpha$) = 1.896 mm$^{-1}$, reflections collected 11580, independent reflections 1499 [$R_{int}$ = 0.053]. *R*1 = 0.041 ($I > 2\sigma I$), *wR*2 = 0.1078 (all data). The crystal is a 50:50 merohedral twin, and additionally there is a 70:30% disorder of the $P_4$ unit.

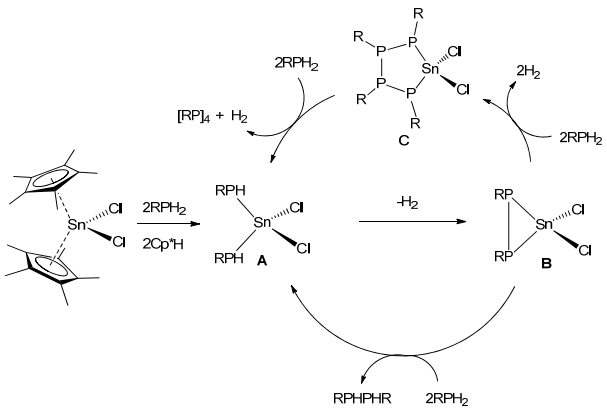
**6**: MS (ESI, 60 V): *m/z* = 1119 ($[FcP]_5 + K^+$).

Crystal data for **6**·($C_6H_6$); molecular formula $C_{56}H_{51}Fe_5P_5$, *FW* = 1158.07, *T* = 180(2)K, crystal system *orthorhombic*, space group *Pbca*, *a* = 10.85880(10), *b* = 24.6233(2), *c* = 36.4979(3)Å, *V* = 9758.79(14)Å$^3$, *Z* = 8, $\rho_{calcd}$ = 1.576 Mg m$^{-3}$, $\mu$(Mo-K$_\alpha$) = 1.654 mm$^{-1}$, reflections collected 88631, independent reflections 9973 [$R_{int}$ = 0.1023]. *R*1 = 0.0453 ($I > 2\sigma I$), *wR*2 = 0.0897 (all data).

**7**: Crystal data for **7**·2($C_6H_6$); molecular formula $C_{52}H_{48}Cl_4Fe_4P_4Sn_4$, *FW* = 1636.74, *T* = 260(2)K, Crystal system orthogonal, space group *Cmcm*, *a* = 18.245(4), *b* = 15.165(3), c = 19.997(4) Å, *V* = 5532.8(19)Å$^3$, Z = 4, $\rho_{calcd}$ = 1.965 Mg m$^{-3}$, $\mu$(Mo-K$_\alpha$) = 3.136 mm$^{-1}$, reflections collected 19629, independent reflections 2892 [$R_{int}$ = 0.056]. *R*1 = 0.0363 ($I > 2\sigma I$), *wR*2 = 0.1002 (all data). There is a 50:50 disorder across the mirror plane defined by the unique Sn atoms; additionally three residual peaks of *ca.* 2 eÅ$^{-3}$ were refined as unique Sn atoms from a very small disorder component (*ca.* 2%). No allowance was made for the lighter atoms of the 2% disorder component, the lighter atoms of the main component being refined at full occupancy.

**Mechnistic suggestion**

As mentioned in the manuscrips there are a number of mechanisms can account for the experimental observations with $Cp^*_2SnCl_2$. However, although the formation of RP(H)P(H)R can be explained by a simple $\sigma$-bond metathesis reaction alone, related to that proposed for Group 4 metals, the formation of *cyclo*-tetraphosphanes $[RP]_4$ as products is more difficult to account for. Although a radical mechanism cannot be discounted, it appears most likely that a stepwise mechanism akin to that proposed by Stephan and coworkers and identified in other non-catalytic main group reactions is operating here. Scheme S1 shows one plausible cycle. It can be noted that this explains directly the formation of RP(H)P(H)R (from **B**) and $[RP]_4$ (from **C**), with the *cyclo*-pentaphosphane $[RP]_5$ resulting either from further insertion of $RPH_2$ into the five-membered ring of **C** or from thermal equilibriation of RP(H)P(H)R.(*S9*) In addition, irreversible reductive elimination of P-P bonded products (like RP(H)P(H)R from **A**, or $[RP]_4$ from **C**) would give $SnCl_2$ and result in deactivation (as seen in the structure of **7**).




**Scheme S1**

**References and Notes**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[S2] P. Jutzi, F. Kohl, P. Hoffman, C. Krüger, Y. H. Tsay, Chem. Ber. **113**, 757 (1980).
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[S5] N. J. Goodwin, W. Henderson, B. K. Nicholson, J. Fawcett, D. R. Russell, J. Chem. Soc., Dalton Trans. 1785 (1999).
[S6] S. Blaurock, E. Hey-Hawkins, Z. Anorg. Allg. Chem. **628**, 37 (2002).
[S7] M. Baudler, C. Gruner, H. Tschaebunin, J. Hahn, Chem. Ber. **115**, 1739 (1982).
[S8] Note $C_{(reference\ capillary)}$ = 0.425 mol/L, therefore the integral of $RPH_2$ seems relatively large compared to the other spectra shown.
[S9] The greater reaction times necessary for reactions involving $Cp^*_2SnCl_2$ compared to $Cp^*_2Sn$ may account for the formation of $[RP]_5$ via the known equilibrium 5[RP(H)P(H)R] ↔ 5$RPH_2$ + $[RP]_5$; J. P. Albrand, D. Gagnaire, J. Am. Chem. Soc. **94**, 8630 (1972).