Supplementary Material (ESI) for New Journal of Chemistry

Supporting Information Document to Accompany:

Radical Synthesis of Trialkyl, Triaryl, Trisilyl, and Tristannyl Phosphines from P_4

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General Experimental Considerations:

All manipulations were performed in a Vacuum Atmospheres model MO-40M glovebox under an inert atmosphere of purified N_2. All solvents were obtained anhydrous and oxygen-free by bubble degassing (N_2) and purification using a Glass Contours Solvent Purification System built by SG Water. Deuterated solvents were purchased from Cambridge Isotope Labs. Benzene-d_6 was degassed and stored over molecular sieves for at least 2 d prior to use. Celite 435 (EM Science) were dried by heating above 200 °C under a dynamic vacuum for at least 24 h prior to use. Ti(N[^{t}Bu]Ar)$_3$ (Ar = 3,5-$Me_2C_6H_3$),[1] V(N[Np]Ar)$_3$ (Np = $CH_2{}^t$Bu),[2] Cp*$_2$Sm,[3] and Cp_2TiCl[4] were prepared by literature methods. All other reagents were purchased from Aldrich chemical company and were used without further purification. All glassware was oven-dried at temperatures greater than 170 °C prior to use. NMR spectra were obtained on Varian Inova 500 instruments equipped with Oxford Instruments superconducting magnets and referenced to residual C_6H_5D (^{1}H = 7.16 ppm, ^{13}C = 128.06 ppm). ^{31}P NMR spectra were referenced externally to 85% H_3PO_4 (0 ppm). GC-MS data were collected using an Agilent 6890N network GC system with an Agilent 5973 Network mass selective detector and an RTX-1 column from Restek.

Abbreviations:

Ph = C_6H_5
Mes = 2,4,6-$Me_3C_6H_2$
Cy = C_6H_{11}
Dmp = 2,6-$Mes_2C_6H_3$
Ar = 3,5-$Me_2C_6H_3$
Np = $CH_2{}^t$Bu

Representative protocol for reaction between Ti(N[^{t}Bu]Ar)$_3$, RX (RX = PhBr, MesBr, DmpI, CyBr, Me_3SiI, and Ph_3SnCl), and P_4: Synthesis of PPh_3

Ti(N[^{t}Bu]Ar)$_3$ (279 mg, 0.484 mmol) was added to a 0.04 M solution of P_4 in benzene (5 mg total P_4, 0.040 mmol). BrC_6H_5 (76 mg, 0.484 mmol) was then added to the reaction mixture at room temperature by microliter syringe. Over the course of a minute, the originally green reaction mixture took on a bright orange color. The reaction mixture was analyzed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies. Using $OPPh_3$ (26 ppm) as an internal standard, a single pulse ^{31}P NMR experiment showed 71% conversion to PPh_3 (s, −4.9 ppm) with the balance made up by P_2Ph_4 (−14 ppm). GC-MS analysis confirmed that assignment. A solvent screening (benzene, toluene, THF, Et_2O, n-hexane) and concentration screening (0.01 M P_4, 0.02 M P_4, 0.03 M P_4,

0.04 M P_4, and 0.05 M P_4) indicated these conditions as optimal for conversion of 0.25 equiv P_4 to 1 equiv PPh_3 using 3 equiv Ti(N[^{t}Bu]Ar)$_3$ and 3 equiv PhBr.

In order to convert all of the P_4 to PPh_3, the reaction was repeated using a 0.04 M solution of P_4 (5 mg total P_4, 0.040 mmol, 0.25 equiv), 5 equiv (465 mg, 0.807 mmol) of Ti(N[^{t}Bu]Ar)$_3$, and 5 equiv (126 mg, 0.807 mmol) of BrC_6H_5. Again, over the course of a minute, the originally green reaction mixture took on a bright orange color. The reaction mixture was analyzed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies. Using $OPPh_3$ (26 ppm) as an internal standard, a single pulse ^{31}P NMR experiment showed 98% conversion to PPh_3 (s, −4.9 ppm). GC-MS analysis confirmed that assignment. A screening of reaction stoichiometry showed 5 equiv of Ti(N[^{t}Bu]Ar)$_3$ and 5 equiv BrC_6H_5 was necessary for the complete conversion of P_4 to PPh_3; when fewer equivalents were used, small amounts of P_2Ph_4 were still observed. When the optimized conditions are scaled up 10-fold, PPh_3 was isolated by repeated crystallizations at −35 ºC in Et_2O in 72% yield (304 mg).

These optimized conditions of 0.04 M P_4 (0.25 equiv), benzene, and 5 equiv of RX/Ti(N[^{t}Bu]Ar)$_3$ are effective for both PPh_3 and PCy_3 syntheses. For $P(SiMe_3)_3$ and $P(SnPh_3)_3$ the same conditions are used but with only 3 equiv (stoichiometric) RX/Ti(N[^{t}Bu]Ar)$_3$. Starting with 50 mg of P_4, $P(SiMe_3)_3$ was isolated by vacuum transfer in 86% yield (348 mg) and $P(SnPh_3)_3$ was isolated in 75% yield (1.30 g) by repeated recrystallization from Et_2O. For the synthesis of P_3Mes_3 and *cis*,*trans*-DmpP$_4$Dmp, the same conditions are used but with only 1.5 equiv of RX/Ti(N[^{t}Bu]Ar)$_3$. P_3Mes_3 was isolated by repeated crystallization from Et_2O in 61% yield starting with 50 mg of P_4. *cis*,*trans*-DmpP$_4$Dmp was isolated by repeated crystallization from Et_2O in 78% yield starting with 50 mg of P_4.

In order to use P_2Ph_4 as the starting material for PPh_3 synthesis, the same reaction protocol and conditions can be used. Treatment of a 0.04 M solution of P_2Ph_4 (5 mg, 0.014 mmol, 0.5 equiv) with Ti(N[^{t}Bu]Ar)$_3$ (93 mg, 0.16 mmol, 1 equiv) followed by BrPh (60 mg, 0.16 mmol, 1 equiv) resulted in a rapid color change from green to orange upon stirring. The reaction mixture was analyzed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies. Using $OPPh_3$ (26 ppm) as an internal standard, a single pulse ^{31}P NMR experiment showed 97% conversion to PPh_3 (s, −4.9 ppm). Similar results were found when 0.5 equiv P_2Ph_4 was treated with 1 equiv of MesBr, CyBr, or Ph_3SnCl, which produced 1 equiv of $P(Ph_2)Mes$ (−16.0 ppm), $P(Ph_2)Cy$ (−3.4 ppm), or $P(Ph_2)SnPh_3$ (−56.2 ppm, $^1J_{^{119}Sn/P}$ = 715 Hz, $^1J_{^{117}Sn/P}$ = 682 Hz) , respectively, each in greater than 95% yield.

Characterization Data:

PPh_3:
$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 20 °C): δ = −4.9 ppm (s, 1P). GC-MS = 262 m/z.

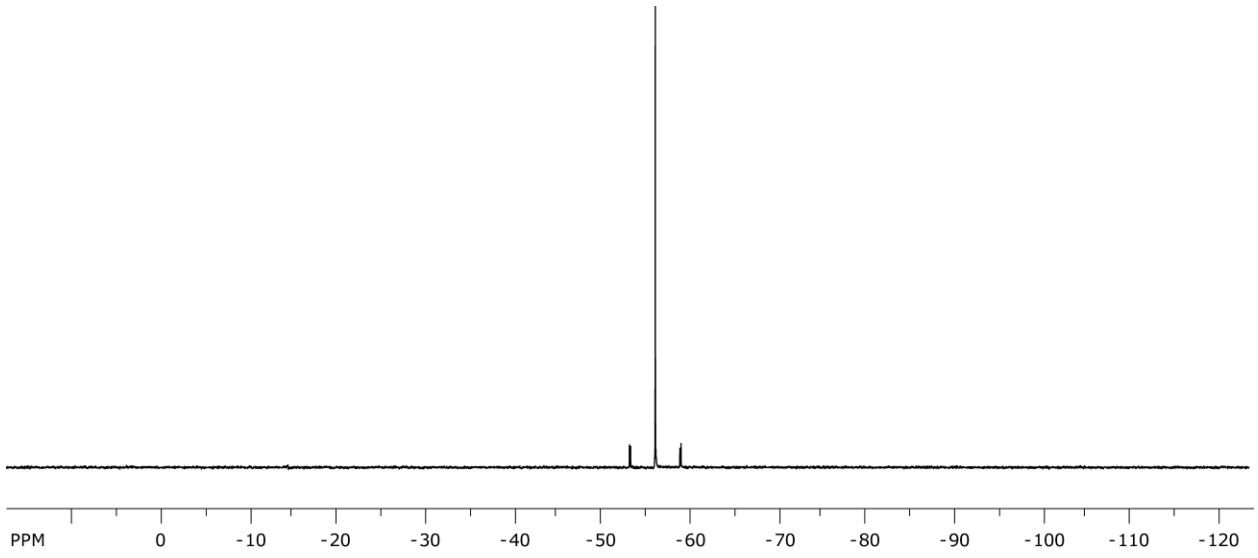
P_2Ph_4:
$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 20 °C): δ = −14.4 ppm (s, 1P). GC-MS = 370 m/z.

PCy_3:
$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 20 °C): δ = 10.5 ppm (s, 1P). GC-MS = 280 m/z.

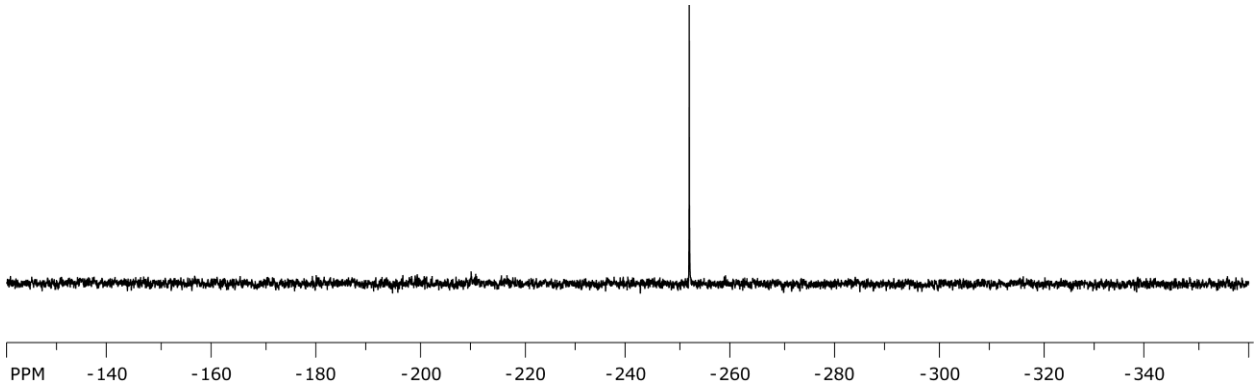
$P(Ph_2)Mes$:
$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 20 °C): δ = −16.0 ppm (s, 1P). GC-MS = 304 m/z.

$P(Ph_2)Cy$:
$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 20 °C): δ = −3.4 ppm (s, 1P). GC-MS = 268 m/z.

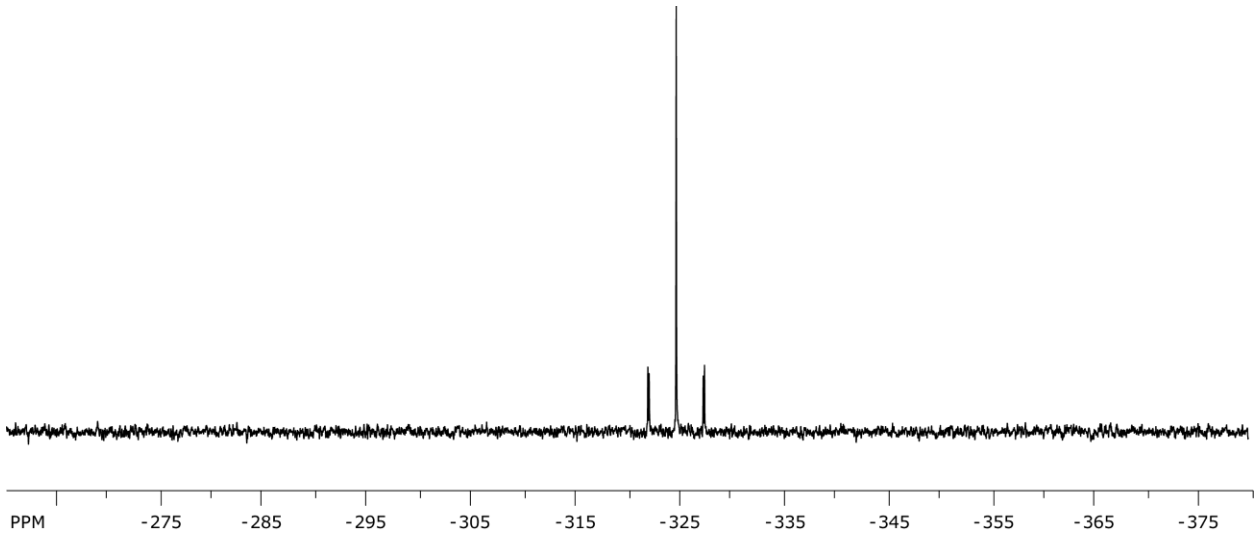
$P(Ph_2)SnPh_3$:
$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 20 °C): δ = −56.2 ppm (s, 1P, $^1J_{^{119}Sn/P}$ = 715 Hz, $^1J_{^{117}Sn/P}$ = 682 Hz).



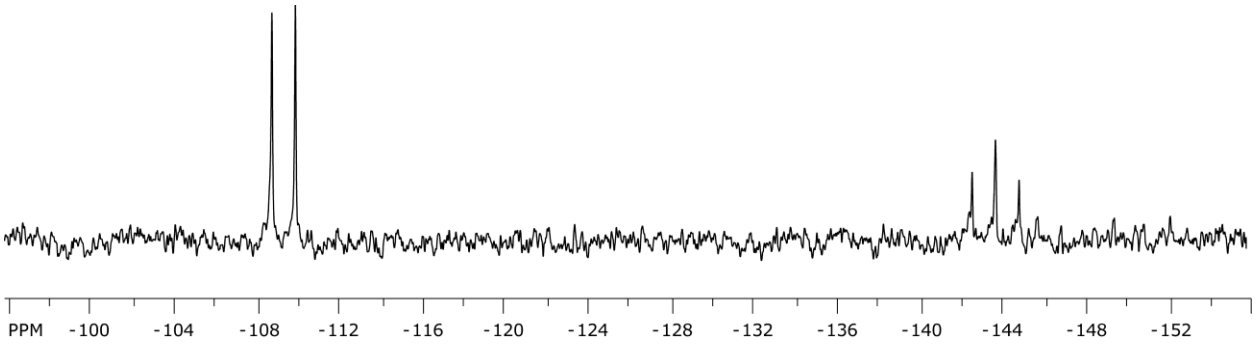
$P(SiMe_3)_3$:
^1H NMR (500 MHz, C_6D_6, 20 °C): δ = 0.27 ppm (d, $^3J_{H,P}$ = 4 Hz, 27H, $SiMe_3$); $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 20 °C): δ = −251.9 ppm



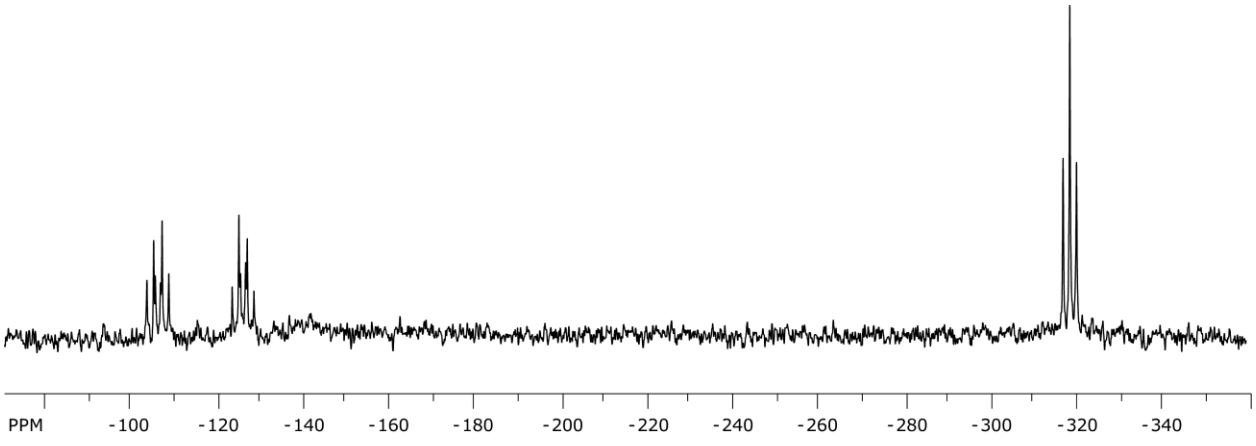
$P(SnPh_3)_3$:
$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 20 °C): δ = −324.7 ppm ($^1J_{^{119}Sn,P}$ = 442 Hz, $^1J_{^{117}Sn,P}$ = 425 Hz)



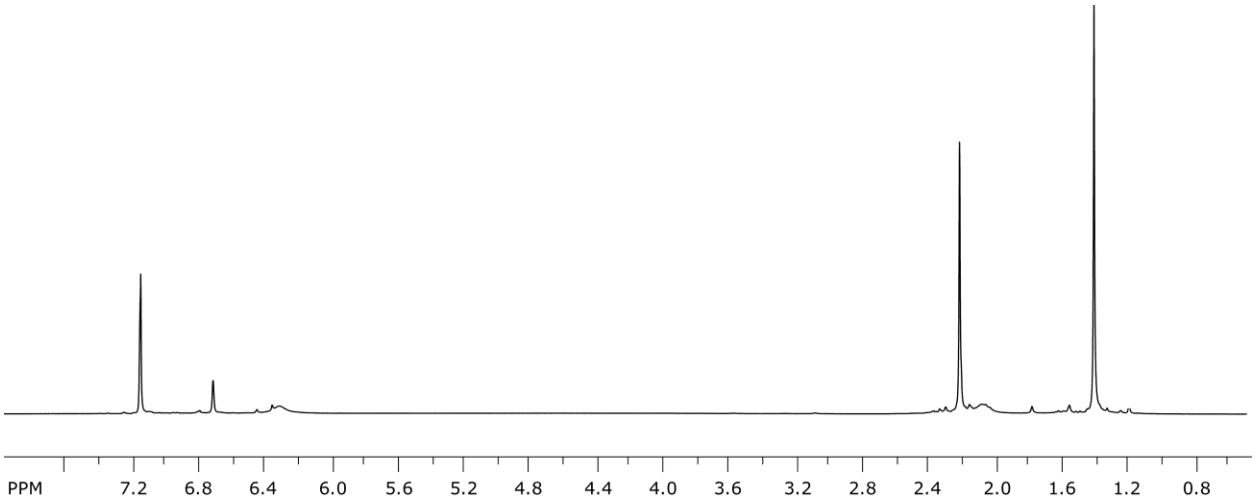
P_3Mes_3:
^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ = 1.92 (s, 6 H, *p*-CH_3 of *cis*-oriented 2,4,6-$Me_3C_6H_2$), 2.07 (s, 3 H, *p*-CH_3, of *trans*-oriented 2,4,6-$Me_3C_6H_2$), 2.49 (s, 12 H, *o*-CH_3 of *cis*-oriented 2,4,6-$Me_3C_6H_2$), 2.79 (s, 6 H, *o*-CH_3 of *trans*-oriented 2,4,6-Me3C6H2 group), 6.5 (s, 4 H, *m*-H of *cis*-oriented 2,4,6-$Me_3C_6H_2$ groups), 6.69 (s, 2 H, *m*-H of trans-oriented 2,4,6-$Me_3C_6H_2$ group). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 20 °C): −109.3 (d,2P, $^1J_{P,P}$ = 185 Hz), −143.8 (t, 1P, $^1J_{P,P}$ = 185 Hz).



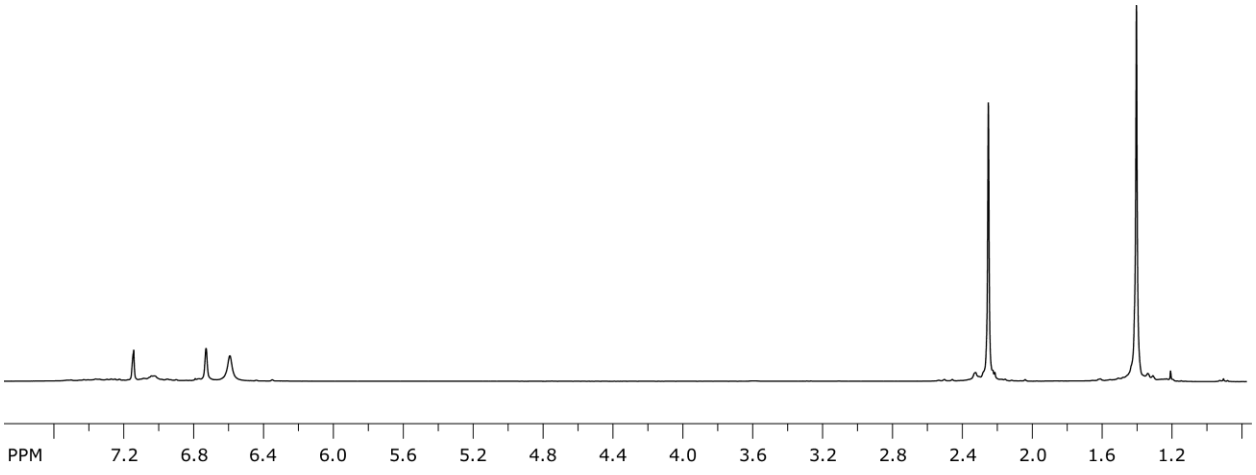
***cis*,*trans*-DmpP$_4$Dmp:**
^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ = 2.216 (s, 12H, *o*-CH_3), 2.222 (s, 12H, *o*-CH_3), 2.303 (s, 6H, *p*-CH_3), 2.335 (s, 6H, *p*-CH_3), 6.8 – 7.2 (multiple overlapping signals, 14H); ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 20 °C): δ = −104 ppm (apparent q, 1P, $^1J_{P,P}$ = 193 Hz), −123 ppm (apparent q, 1P, $^1J_{P,P}$ = 191 Hz), −318 ppm (t, 2P, $^1J_{P,P}$ = 190 Hz).



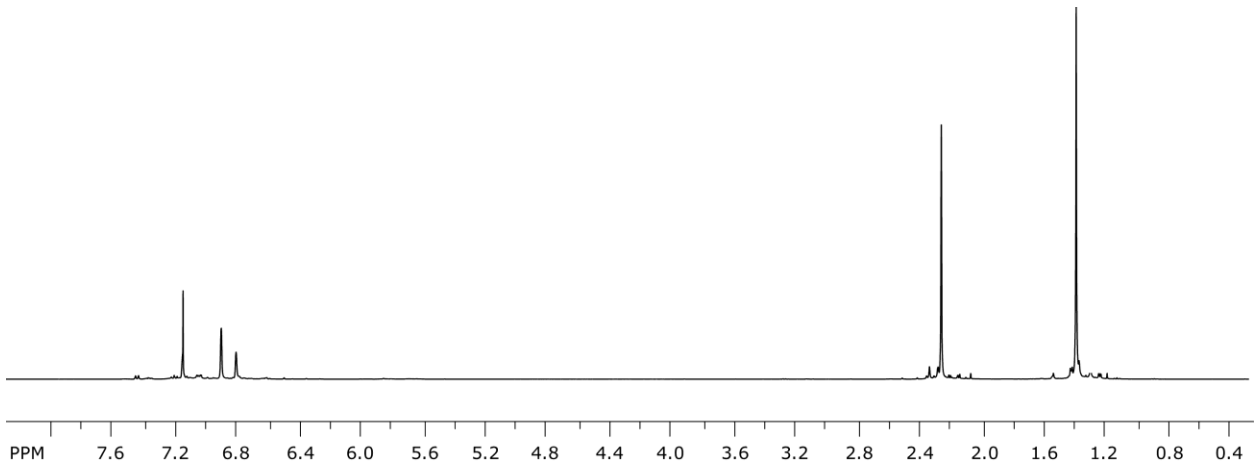
ClTi(N[^{t}Bu]Ar)$_3$:
^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ = 1.3973 (s, 27H, ^{t}Bu), 2.2103 (s, 18H, Ar-Me), 6.3219 (br s, 6H, *m*-Ar), 6.7259 (s, 3H, *p*-Ar) ppm.



BrTi(N[^{t}Bu]Ar)$_3$:
^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ = 1.3772 (s, 27H, ^{t}Bu), 2.2285 (s, 18H, Ar-Me), 6.6045 (br s, 6H, *m*-Ar), 6.7379 (s, 3H, *p*-Ar) ppm.



$ITi(N[^tBu]Ar)_3$:
^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ = 1.3789 (s, 27H, ^{t}Bu), 2.2530 (s, 18H, Ar-Me), 6.8146 (s, 6H, *m*-Ar), 6.9121 (s, 3H, *p*-Ar) ppm.



Screening other Potential Halogen Atom Abstractors for PR_3 Synthesis:

Using the same protocol as outlined above for the generation of PPh_3 and PCy_3, other halogen atom abstractors were tested for competency. The first experiments performed here were with 12 equiv of reagent (halogen atom abstractors include: SmI_2, Fe^0 at 100 °C, Zn^0 at 100 °C, Cp_2TiCl, $ClCo(PPh_3)_3$, Cp^*_2Sm, $CrCl_2$, and $V(N[Np]Ar)_3$) with 1 equiv of P_4 to ensure that no reaction takes place. All reactions were carried out at 20 °C except for the reactions with Fe and Zn, which were carried out at 100 ºC. All experiments were analyzed by ^{31}P NMR spectroscopy.

Following the control runs with P_4 only, the reactions with the two different RBr sources (PhBr, CyBr) were carried out as follows:

For SmI_2, $ClCo(PPh_3)_3$, and Cp^*_2Sm, 12 equiv of reagent were combined with 3.7 mg of P_4 as a stock solution in benzene. For $ClCo(PPh_3)_3$, 1 additional mL of benzene was added and for the Cp^*_2Sm and SmI_2 reactions, THF was used as the solvent. Upon mixing, 12 equiv of the RBr source was added. The reaction mixtures were allowed to stir for 5 h during which time no observable change took place for the SmX_2 reactions, however the $ClCo(PPh_3)_3$ reaction darkened from light green to a dark green-brown. Following the reaction time the ^{31}P NMR spectra of all samples were obtained. It is of note that SmI_2 is known to be competent for abstracting halogen atoms from aryl iodides and aryl bromides, however in these cases HMPA is necessary as an additive to produce SmI_2 with maximum reducing power.[5-8] It is therefore quite conceivable that using SmI_2 in a mixture of HMPA/THF would allow for a synthesis of

trisubstituted phosphines from P_4. As a first test of this possibility, 5 mg of P_4 (0.04 mmol) were combined with SmI_2 (4.46 g of 0.1 M solution in THF, 0.484 mmol, 12 equiv) and HMPA (867 mg, 4.84 mmol, 120 equiv). When the P_4 had fully dissolved, PhI (54 μL, 0.484 mmol, 12 equiv) was added to the reaction mixture. No immediate color change was observed. Over the next 17 h the PhI was consumed and SmI_3 was formed, but no PPh_3 was generated during the process. It is possible that other RX substrates might be more amenable here.

For Fe powder, Zn dust, and $CrCl_2$, 12 equiv of reagent were placed in thick walled tubes along with 3.7 mg of P_4 and 12 equiv of RBr in THF. The reaction mixtures were refluxed for 5 h with stirring during which time no consumption of the respective metals was observed. After the reaction time had elapsed, the solutions were taken for ^{31}P NMR analysis.

Cp_2TiCl was first prepared by treatment of 89 mg of Cp_2TiCl_2 with 30 mg of Zn (1.2 equiv) in benzene. The bright red reaction mixtures were allowed to stir for 1.5 h during which time the color slowly progressed to bright emerald-turquoise green. Following the reaction time, 3.7 mg of P_4 was added followed by 12 equiv of RBr. The reaction mixtures were allowed to stir 4 h during which time there was no observable color change. Following the reaction time the reaction mixtures were assessed by ^{31}P NMR spectroscopy.

The results of all experiments are summarized in the table below (along with the $Ti(N[tBu]Ar)_3$ results):

Reagent	12 equiv Reacts with P_4?	Formation of PPh_3?	12 equiv Reacts with BrPh at all?	Formation of PCy_3?	12 equiv Reacts with PCy_3 at all?
$Ti(N[tBu]Ar)_3$	Weak equilibrium	Yes	Yes	Yes	Yes
SmI_2	No	No	No	No	No
Fe^0, 100 ºC	No	No	No	No	No
Zn^0, 100 ºC	No	No	No	No	No
Cp_2TiCl	No	No	No	No	No
$ClCo(PPh_3)_3$	Yes, no soluble products	No	- -	No	- -
Cp^*_2Sm	Yes, as reported[9]	No	- -	No	- -
$CrCl_2$, 70 ºC	No	No	No	No	No
$V(N[Np]Ar)_3$	No	No	No	Yes	Yes

Effect of stoichiometry on reaction of $V(N[Np]Ar)_3$ with P_4 and CyBr:

Equiv CyBr and $V(N[Np]Ar)_3$	$[P_4]$	Yield PCy_3	$PCy_3 : P_2Cy_4$
12	0.02 M	40%	2.5:1
15	0.02 M	61%	3.2:1
15	0.04 M	75%	5:1
20	0.04 M	90%	10.2:1

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