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[′Bu]Ar)$_3$ (Ar = 3,5-Me$_2$C$_6$H$_3$), V(N[Np]Ar)$_3$ (Np = CH$_2$tBu),$^1$ Cp*$_2$Sm,$^3$ and Cp$_2$TiCl$_4$ 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$_6$H$_5$D (1H = 7.16 ppm, 13C = 128.06 ppm).$^{31}$P NMR spectra were referenced externally to 85% H$_3$PO$_4$ (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$_6$H$_5$
Mes = 2,4,6-Me$_3$C$_6$H$_2$
Cy = C$_6$H$_{11}$
Dmp = 2,6-Mes$_2$C$_6$H$_3$
Ar = 3,5-Me$_2$C$_6$H$_3$
Np = CH$_2$tBu

Representative protocol for reaction between Ti(N[′Bu]Ar)$_3$, RX (RX = PhBr, MesBr, DmpI, CyBr, Me$_3$SiI, and Ph$_3$SnCl), and $P_4$: Synthesis of PPh$_3$

Ti(N[′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$_6$H$_5$ (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$_2$Ph$_4$ (−14 ppm). GC-MS analysis confirmed that assignment. A solvent screening (benzene, toluene, THF, Et$_2$O, n-hexane) and concentration screening (0.01 M $P_4$, 0.02 M $P_4$, 0.03 M $P_4$, 0.04 M $P_4$, etc.)
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[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[Bu]Ar]$_3$, and 5 equiv (126 mg, 0.807 mmol) of BrC$_6$H$_5$. 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[Bu]Ar]$_3$ and 5 equiv BrC$_6$H$_5$ 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 $-35$ °C in Et$_2$O 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[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[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$_2$O. For the synthesis of $P_3$Mes$_3$ and cis,trans-DmpP$_4$Dmp, the same conditions are used but with only 1.5 equiv of RX/Ti[N[Bu]Ar]$_3$. $P_3$Mes$_3$ was isolated by repeated crystallization from Et$_2$O in 61% yield starting with 50 mg of $P_4$. cis,trans-DmpP$_4$Dmp was isolated by repeated crystallization from Et$_2$O 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[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$_3$SnCl, 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, $^1J_{119Sn/P} = 715$ Hz, $^1J_{117Sn/P} = 682$ Hz), respectively, each in greater than 95% yield.
Characterization Data:

**PPh₃:**
$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C₆D₆, 20 °C): $\delta = -4.9$ ppm (s, 1P). GC-MS = 262 m/z.

**P₂Ph₄:**
$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C₆D₆, 20 °C): $\delta = -14.4$ ppm (s, 1P). GC-MS = 370 m/z.

**PCy₃:**
$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C₆D₆, 20 °C): $\delta = 10.5$ ppm (s, 1P). GC-MS = 280 m/z.

**P(Ph₂)Mes:**
$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C₆D₆, 20 °C): $\delta = -16.0$ ppm (s, 1P). GC-MS = 304 m/z.

**P(Ph₂)Cy:**
$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C₆D₆, 20 °C): $\delta = -3.4$ ppm (s, 1P). GC-MS = 268 m/z.

**P(Ph₂)SnPh₃:**
$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C₆D₆, 20 °C): $\delta = -56.2$ ppm (s, 1P), $^1J_{119\text{Sn/P}} = 715$ Hz, $^1J_{117\text{Sn/P}} = 682$ Hz.)
P(SiMe$_3$)$_3$: 
$^1$H NMR (500 MHz, C$_6$D$_6$, 20 °C): $\delta = 0.27$ ppm (d, $^3$J$_{H,P} = 4$ Hz, 27H, SiMe$_3$); $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$, 20 °C): $\delta = -251.9$ ppm

\[ \text{PPM: -140 to -340} \]

P(SnPh$_3$)$_3$: 
$^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$, 20 °C): $\delta = -324.7$ ppm ( $^1$J$_{119\text{Sn,P}} = 442$ Hz, $^1$J$_{117\text{Sn,P}} = 425$ Hz)
**P₃Mes₃:**

$^1$H NMR (500 MHz, C₆D₆, 20 °C): $\delta = 1.92$ (s, 6 H, $p$-CH₃ of cis-oriented 2,4,6-Me₃C₆H₂), 2.07 (s, 3 H, $p$-CH₃, of trans-oriented 2,4,6-Me₃C₆H₂), 2.49 (s, 12 H, $o$-CH₃ of cis-oriented 2,4,6-Me₃C₆H₂), 2.79 (s, 6 H, $o$-CH₃ of trans-oriented 2,4,6-Me₃C₆H₂ group), 6.5 (s, 4 H, $m$-H of cis-oriented 2,4,6-Me₃C₆H₂ groups), 6.69 (s, 2 H, $m$-H of trans-oriented 2,4,6-Me₃C₆H₂ group).

$^{31}$P{¹H} NMR (202 MHz, C₆D₆, 20 °C): $-109.3$ (d, 2P, $^1J_{P,P} = 185$ Hz), $-143.8$ (t, 1P, $^1J_{P,P} = 185$ Hz).

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**cis,trans-DmpP₄Dmp:**

$^1$H NMR (500 MHz, C₆D₆, 20 °C): $\delta = 2.216$ (s, 12H, $o$-CH₃), 2.222 (s, 12H, $o$-CH₃), 2.303 (s, 6H, $p$-CH₃), 2.335 (s, 6H, $p$-CH₃), 6.8 – 7.2 (multiple overlapping signals, 14H); $^{31}$P{¹H} NMR (202 MHz, C₆D₆, 20 °C): $\delta = -104$ 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).
$\text{ClTi(N}^\text{tBu}\text{Ar)}_3$:  
$^1H$ NMR (500 MHz, C$_6$D$_6$, 20 $^\circ$C): $\delta = 1.3973$ (s, 27H, $^\text{tBu}$), 2.2103 (s, 18H, Ar-Me), 6.3219 (br s, 6H, $m$-Ar), 6.7259 (s, 3H, $p$-Ar) ppm.

$\text{BrTi(N}^\text{tBu}\text{Ar)}_3$:  
$^1H$ NMR (500 MHz, C$_6$D$_6$, 20 $^\circ$C): $\delta = 1.3772$ (s, 27H, $^\text{tBu}$), 2.2285 (s, 18H, Ar-Me), 6.6045 (br s, 6H, $m$-Ar), 6.7379 (s, 3H, $p$-Ar) ppm.
ITi(N\textsuperscript{[Bu]}Ar)\textsubscript{3}:
\textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}, 20 °C): \( \delta = 1.3789 \) (s, 27H, \textsuperscript{1}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\textsubscript{3} Synthesis:

Using the same protocol as outlined above for the generation of PPh\textsubscript{3} and PCy\textsubscript{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\textsubscript{2}, Fe\textsuperscript{0} at 100 °C, Zn\textsuperscript{0} at 100 °C, Cp\textsubscript{2}TiCl, ClCo(PPh\textsubscript{3})\textsubscript{3}, Cp*\textsubscript{2}Sm, CrCl\textsubscript{2}, and V(N[Np]Ar)\textsubscript{3}) with 1 equiv of P\textsubscript{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 \textsuperscript{31}P NMR spectroscopy.

Following the control runs with P\textsubscript{4} only, the reactions with the two different RBr sources (PhBr, CyBr) were carried out as follows:

For SmI\textsubscript{2}, ClCo(PPh\textsubscript{3})\textsubscript{3}, and Cp*\textsubscript{2}Sm, 12 equiv of reagent were combined with 3.7 mg of P\textsubscript{4} as a stock solution in benzene. For ClCo(PPh\textsubscript{3})\textsubscript{3}, 1 additional mL of benzene was added and for the Cp*\textsubscript{2}Sm and SmI\textsubscript{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\textsubscript{2} reactions, however the ClCo(PPh\textsubscript{3})\textsubscript{3} reaction darkened from light green to a dark green-brown. Following the reaction time the \textsuperscript{31}P NMR spectra of all samples were obtained. It is of note that SmI\textsubscript{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\textsubscript{2} with maximum reducing power.\textsuperscript{5-8} It is therefore quite conceivable that using SmI\textsubscript{2} in a mixture of HMPA/THF would allow for a synthesis of
trisubstituted phosphines from P₄. As a first test of this possibility, 5 mg of P₄ (0.04 mmol) were combined with SmI₂ (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 P₄ 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 SmI₃ was formed, but no PPh₃ was generated during the process. It is possible that other RX substrates might be more amenable here.

For Fe powder, Zn dust, and CrCl₂, 12 equiv of reagent were placed in thick walled tubes along with 3.7 mg of P₄ 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 ³¹P NMR analysis.

Cp₂TiCl was first prepared by treatment of 89 mg of Cp₂TiCl₂ 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 P₄ 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 ³¹P NMR spectroscopy.

The results of all experiments are summarized in the table below (along with the Ti(N[tBu]Ar)₃ results):

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<th>Reagent</th>
<th>12 equiv Reacts with P₄?</th>
<th>Formation of PPh₃?</th>
<th>12 equiv Reacts with BrPh at all?</th>
<th>Formation of PCy₃?</th>
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<td>ClCo(PPh₃)₃</td>
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<td>Cp*₂Sm</td>
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<td>- -</td>
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<td>CrCl₂, 70 °C</td>
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Effect of stoichiometry on reaction of V(N[Np]Ar)₃ with P₄ and CyBr:

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References