Supporting Information for the Paper Entitled **"Phosphinidene Group-Transfer with the Phospha-Wittig Reagent $Me_3P{=}PAr$ (Ar = 2,4,6-$^tBu_3C_6H_2$ and 2,6-$Mes_2C_6H_3$). New Entry Way to Transition Metal Phosphorus Multiple Bonds."**

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Experimental Section

General Considerations.

Unless otherwise stated, all operations were performed in a M. Braun Lab Master double drybox under an atmosphere of purified N_2 or using high-vacuum standard Schlenk techniques under an Ar atmosphere.[1] Anhydrous *n*-hexane, pentane, toluene, and benzene were purchased from Aldrich in sure-seal reservoirs (18 L) and dried by passage through two columns of activated alumina and a Q-5 column. Diethyl ether and CH_2Cl_2 were dried by passage through two columns of activated alumina.[1] Tetrahydrofuran (THF) was distilled, under N_2, from purple sodium benzophenone ketyl and stored under Na metal. Distilled THF was transferred under vacuum into bombs before being pumped into a drybox. C_6D_6 was purchased from Cambridge Isotope Laboratory, degassed and dried over CaH_2, and then vacuum transferred to 4-Å molecular sieves. Celite, alumina, and 4-Å molecular sieves were activated under vacuum overnight at 200 °C. Compounds $Me_3P{=}PAr$ (Ar = 2,4,6-$^tBu_3C_6H_2$ and 2,6-$Mes_2C_6H_3$),[2] $Cp_2Zr(PMe_3)_2$,[3] (PNP)V($CH_2{}^tBu)_2$,[4] $Cp^*{}_2Ti(\eta^2\text{-}CH_2CH_2)$,[5] V{$N(CH_2CH_2NSiMe_3)_3$}[6] were prepared according to literature procedures. ^1H, ^{13}C, ^{51}V, ^{15}N and ^{31}P-NMR spectra were recorded

on Varian 500, 400 or 300 MHz NMR spectrometers. ^{1}H and ^{13}C-NMR are reported with reference to residual solvent resonances: for ^{1}H-NMR residual C_6H_6 in C_6D_6 at 7.16 ppm, for ^{13}C-NMR C_6D_6 at 128 ppm. ^{31}P NMR chemical shifts are reported with respect to external H_3PO_4 (0.0 ppm). ^{51}V NMR chemical shifts are reported with respect to $VOCl_3$ (0.0 ppm). Values of $\nu_{1/2}$ in ^{51}V spectra are reported with the line broadening parameter set to 20. X-ray diffraction data were collected on a Bruker APEX Kappa DUO using Mo radiation under a stream of N_2 (g) at low temperatures. CI mass spectra were collected with a MAT-95 XP mass spectrometer. Peak matching was done with CMASS and LIST subroutines of XCalibur.

Synthesis of $Cp_2Zr{=}P\{2,6\text{-}Mes_2C_6H_3\}(PMe_3)$ (1) from $Cp_2Zr(PMe_3)_2$ + $Me_3P{=}P\{2,6\text{-}Mes_2C_6H_3\}$. $Me_3P{=}P\{2,6\text{-}Mes_2C_6H_3\}$ (0.013 g, 0.032 mmol) was mixed with 0.012 g (0.032 mmol) of $Cp_2Zr(PMe_3)_2$ in *ca.* 0.5 mL C_6D_6 in an NMR tube. No formation of $Cp_2Zr{=}P\{2,6\text{-}Mes_2C_6H_3\}(PMe_3)$ was observed by ^{31}P NMR spectroscopy after keeping the reaction mixture at room temperature overnight. In a separate reaction, a mixture of 0.014 g (0.037 mmol) of $Cp_2Zr(PMe_3)_2$ and 0.017 g (0.037 mmol) of $Me_3P{=}P\{2,6\text{-}Mes_2C_6H_3\}$ were dissolved in *ca.* 0.5 mL of toluene in an NMR tube. The NMR tube was flame-sealed under vacuum and brought up to room temperature. The NMR tube was then heated at 45°C overnight. Analysis of mixture by ^{31}P NMR spectroscopy revealed the major products as $Cp_2Zr{=}P\{2,6\text{-}Mes_2C_6H_3\}(PMe_3)$ (**1**) and PMe_3. The presence of unreacted $Cp_2Zr(PMe_3)_2$ and $DmpP{=}PMe_3$ was also noted, but prolonged heating for an additional 24 h did not notably increase the yield of **1**. Some starting material and the formation of other unidentified compounds in minor amounts was also observed.

Compound **1** was prepared independently from $Cp_2Zr(Me)Cl$ and $Li(OEt_2)(PHAr)$ in the presence of PMe_3.[7]

Synthesis of (PNP)V=P{2,4,6-^{t}Bu$_3$C$_6$H$_2$}(CH^{t}Bu) (2) from (PNP)V(CH$_2{}^t$Bu)$_2$ + Me$_3$P=P{2,4,6-^{t}Bu$_3$C$_6$H$_2$}. To a C_6D_6 solution of (PNP)V($CH_2{}^t$Bu)$_2$ (50 mg, 0.0804 mmol) in an NMR tube with a J. Young screw top valve was added Me_3P=P{2,4,6-^{t}Bu$_3$C$_6$H$_2$} (29 mg, 0.0822 mmol) in C_6D_6. This solution was heated to 50 °C overnight over the course of which time the green solution went brown. Through the course of heating, formation of neopentane and PMe_3 was observed by ^{1}H-NMR spectroscopy along with other resonances corresponding to (PNP)V=P{2,4,6-^{t}Bu$_3$C$_6$H$_2$}(CH^{t}Bu) (**2**). Formation of **2** was clean and high yield (90% conversion to **2**) when judged by ^{31}P and ^{1}H NMR spectroscopy using 1,4-dioxane as an internal standard. To isolate pure product the solution was then dried, and taken up into pentane and filtered. The filtrate was dried and taken up into diethyl ether. X-ray diffraction quality crystals were grown from this solution at room temperature over several days (15 mg, 0.0181 mmol, two crops, 22 % yield based on vanadium precursor). The reaction can be up scaled to 200 mg of (PNP)V($CH_2{}^t$Bu)$_2$, and isolation of pure brown microcrystalline material, **2**, can be increased to ~40% yield.

^{1}H-NMR (25 °C, 400.1 MHz, C_6D_6): 7.52 (s, 1H, Ar*H*); 7.33(s, 1H, Ar*H*); 7.26(broad, 2H, Ar*H*); 6.96 (s, 1H, Ar*H*); 6.84 (m, 3H, Ar*H*); 2.53 (septet, 1H, C*H*Me$_2$); 2.44 (septet, 1H, C*H*Me$_2$); 2.35 (septet, 1H, C*H*Me$_2$, partially obscured by C*Me$_3$* resonance); 2.27 (s, 9H, C*Me$_3$*); 2.18 (s, 3H, C*H$_3$*); 2.16 (s, 3H, C*H$_3$*) ; 2.10 (septet, 1H, C*H*Me$_2$, partially obscured by C*H$_3$* resonance); 1.56 (s, 9H, C*Me$_3$*); 1.56 (m, 3H, CH*Me$_2$*, obscured by

C*Me*$_3$ resonance); 1.42 (s, 9H, C*Me*$_3$); 1.32 (m, 6H, CH*Me*$_2$); 1.29 (s, 9H, C*Me*$_3$); 1.09 (m, 6H, CH*Me*$_2$); 0.95 (m, 3H, CH*Me*$_2$); 0.71 (m, 3H, CH*Me*$_2$). The alkylidene CH resonance could not be located. ^{51}V-NMR (25 °C, 131.5 MHz, C_6D_6): 168.5 ($\Delta\nu_{1/2}$ = 1620 hz). ^{31}P-NMR (25 °C, 121.5 MHz, C_6D_6): 339.9 (V=*P*-Mes*); 63.8 (*PNP*). ^{13}C{^{1}H, ^{31}P}-NMR (25 °C, 100.6 MHz, C_6D_6): δ 296.5 (V=*C*^{t}Bu), 160.8 (*Ar*), 155.2 (*Ar*), 153.7 (*Ar*), 151.1 (*Ar*), 149.8 (*Ar*), 132.3 (*Ar*), 131.6 (*Ar*), 131.4 (*Ar*), 130.9 (*Ar*), 125.3 (*Ar*), 125.0 (*Ar*), 123.2 (*Ar*), 121.9 (*Ar*), 120.6 (*Ar*), 116.4 (*Ar*), 115.9 (*Ar*), 48.9 (*C*Me$_3$), 39.0 (*C*Me$_3$), 38.4 (*C*Me$_3$), 35.0 (*C*Me$_3$), 34.5 (C*Me*$_3$), 33.9 (C*Me*$_3$), 33.2 (C*Me*$_3$), 31.3 (C*Me*$_3$), 27.3 (CHMe$_2$), 26.7 (CHMe$_2$), 21.0 (CHMe$_2$), 20.8 (Ar*Me*), 20.4 (CHMe$_2$), 20.1 (CHMe$_2$), 19.4 (CHMe$_2$), 19.1 (CHMe$_2$), 18.7 (CHMe$_2$), 18.2 (CHMe$_2$), 18.2 (CHMe$_2$), 17.1 (CHMe$_2$), 16.4 (CHMe$_2$). Resonances for Ar*Me* (*PNP* ligand tolyl groups) are thought to be accidentally degenerate. MS-CI for formula $C_{49}H_{79}NP_3V$: Theoretical $[M]^+$, 825.4860; Experimental $[M]^+$, 825.4835.

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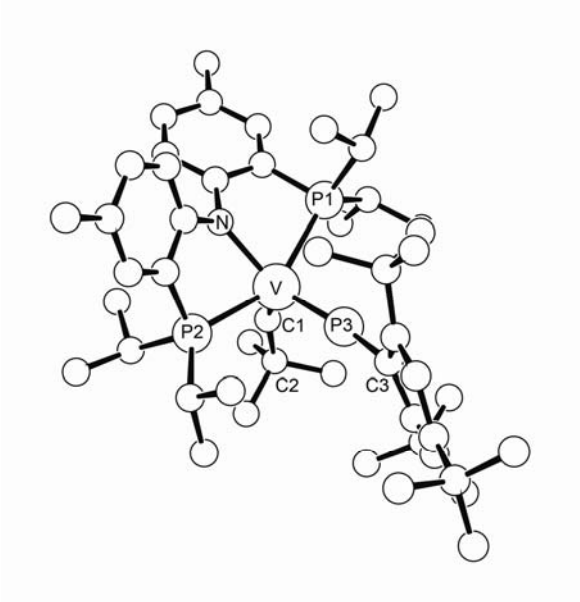
Computational Details. All calculations were carried out using Density Functional Theory as implemented in the Jaguar 6.0 suite[8] of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP[9-12] and the 6-31G** basis set with no symmetry restrictions. Transition metals were represented using the Los Alamos LACVP basis[13-15]. The NMR chemical shift calculation was computed by additional single-point calculations on each optimized geometry using Dunning's correlation-consistent triple-ζ basis set cc-pVTZ(-f) that includes a double set of polarization functions. For all transition metals, we used a modified version of LACVP, designated as

LACV3P, in which the exponents were decontracted to match the effective core potential with the triple-ζ quality basis.

The models used in this study consist of up to ~100 atoms, which represent the non-truncated molecules that were also used in the related experimental work. These calculations challenge the current state of computational capabilities, and the numerical efficiency of the Jaguar program allows us to accomplish this task in a bearable time frame.

S1. Geometry, bond order and and frontier orbitals.

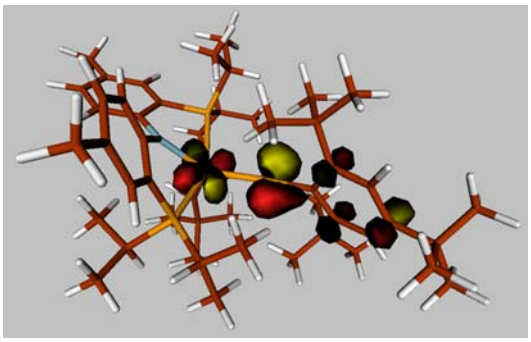


Select bond lengths (Å) and bond angles (°).

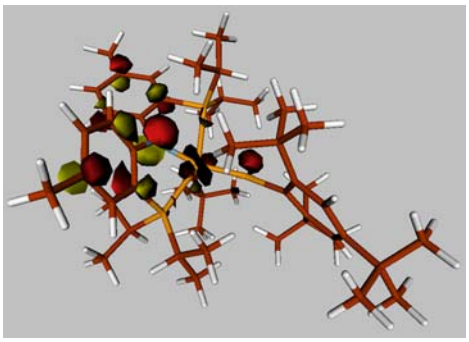
V-P3	2.140
V-P2	2.568
V-P1	2.540
V-C1	1.804
V-N	2.083
V-P3-C3	162.1

V-C1-C2	157.2
P1-V-P2	149.8
N-V-C1	114.4
N-V-P3	135.6
C1-V-P3	110.0
P2-V-C1	96.6
P1-V-C1	97.4

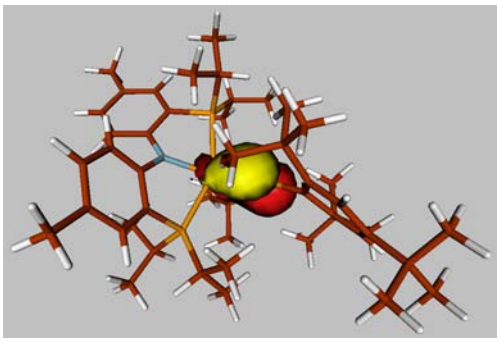
Mayer bond order: V-P3 1.75, V-P1 0.57, V-P2 0.61, V-C1 1.70, V-N 0.51.



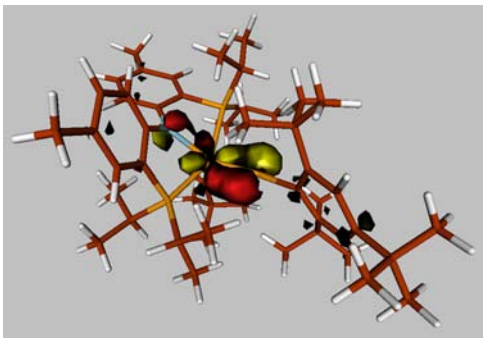
LUMO(-1.567 eV)



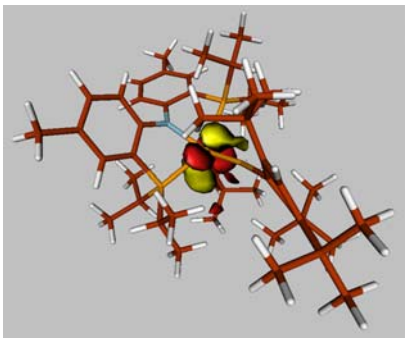
HOMO(-4.237 eV)



HOMO-1(-4.708 eV)



HOMO-2(-4.999 eV)



HOMO-3(-5.273 eV)

S2. *Optimized Structures*

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