Supplementary Information for:

Isolation of Uranium(III) Primary Phosphido Complexes Diana Perales^a, Rina Bhowmick^b, Matthias Zeller^a, Pere Miro^b, Bess Vlaisavljevich^{*b}, and Suzanne C. Bart^{*a}

^a H. C. Brown Laboratory, Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, United States

^b Department of Chemistry, University of South Dakota, Vermillion, South Dakota 57069, United States

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General Considerations.

All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques or using an MBraun inert atmosphere drybox with an atmosphere of purified nitrogen. The MBraun drybox was equipped with a cold well used for freezing samples in liquid nitrogen, making dry ice and acetone baths, as well as two -35 °C freezers for cooling samples and crystallizing compounds. Solvents for sensitive manipulations were dried and deoxygenated using literature procedures with a Seca solvent purification system. Benzene-d₆ was purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by three freeze–pump–thaw cycles. H₂PPh was purchased from Alpha Aesar, 1M MesMgBr in THF, 2.5M n-butyllithium in hexanes, and 1-bromo-2,4,6-tri-tert-butylbenzene (BrMes*) was purchased from Sigma Aldrich and used as received. KTp*,¹ **1-Bn**,² and KTSA³ were synthesized using literature procedures described below.

Caution! U-238 is a weak α -emitter with a half-life of $t_{1/2} = 4 \times 10^9$ years. All manipulations were performed in an inert-atmosphere glovebox in a laboratory equipped with proper detection equipment.

¹H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at a frequency of 300 MHz. All chemical shifts are reported relative to the peak for SiMe₄, using ¹H residual chemical shifts of the solvent as a secondary standard. Spectra for paramagnetic molecules were obtained using an acquisition time of 0.5 s; thus, the peak widths reported have an error of ± 2 Hz. ¹¹B NMR spectra were recorded on a Varian Inova 300 spectrometer operating at a frequency of 96.24 MHz. ¹¹B chemical shifts are reported relative to the peak for BF₃·Et₂O. For paramagnetic molecules, the ¹H NMR data are reported with the chemical shift, followed by the peak width at half height in Hertz, the integration value, and, where possible, the peak assignment. ³¹P NMR spectra were recorded on a Bruker AV-III-400-HD spectrometer operating at 161.98 MHz. Elemental analyses were performed by Microanalysis Laboratory - University of Illinois at Urbana-Champaign. Solid state infrared spectra were recorded using a Thermo Nicolet 6700 spectrophotometer; samples were made by using salt plates or by crushing the solids, mixing with dry KBr, and pressing into a pellet. Electronic absorption spectroscopic measurements were recorded at 294 K in sealed 1 cm quartz cuvettes with a Cary 6000i UV–vis-NIR spectrophotometer.

Single crystals suitable for X-ray diffraction for **2-PPh** were coated with poly(isobutylene) oil in the glovebox and quickly transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, a Photon II area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Mo K α radiation ($\lambda = 0.71073$ Å) at 150 K. Single crystals suitable for X-ray diffraction for **2-PMes**, **2-PMes**^{*}, and **3-PMes**^{*} were coated with poly(isobutylene) oil in the glovebox and quickly transferred to the goniometer head of a Bruker Quest diffractometer with kappa geometry, an I- μ -S microsource X-ray tube, laterally graded multilayer (Goebel) mirror single crystal for monochromatization, a Photon-III C14 area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Cu K α radiation ($\lambda = 1.54184$ Å) at 150 K.

Synthesis of Tp*₂U(III) Compounds

For 2-PPh and 2-PMes: A 20-mL scintillation vial was charged with 1-Bn (0.100 g, 0.108 mmol), 5 mL of THF, and a stir bar. This green solution was cooled to -35 °C. To this green solution H₂R (R = PPh, PMes) (PPh = 0.109 mmol, 12 mg; PMes = 0.105 mmol, 16 mg) was added, and the reaction mixture was stirred for 1 hour at room temperature, resulting in little to no color change. The volatiles were removed *in vacuo*. Crude product of uranium(III) mixture, 2-PPh or 2-PMes, were washed with pentane (3 x 5mL) to afford blue/green powders assigned as 2-PPh (100 mg, 0.106 mmol, 98% yield) or 2-PMes (54 mg, 0.055 mmol, 51% yield). Single blue/green crystals of 2-PPh were grown from a concentrated solution of THF at -35 °C. Single blue/green crystals of 2-PMes were grown from a concentrated solution of 1:1 toluene and pentane at -35 °C.

For **2-PMes***:

Method A: A bomb flask was charged with **1-Bn** (0.100 g, 0.108 mmol), 10 mL of toluene, and a stir bar. To this green solution H_2PMes^* (0.115 mmol 32 mg) was added, and the reaction mixture was stirred for 3 hours at 70 °C resulting in a green solution. The volatiles were removed *in vacuo* which results in a green powder assigned as **2-PMes**^{*} (0.110 g, 0.103 mmol, 95% yield). Single green crystals of **2-PMes**^{*} were grown from a diffusion of pentane into a concentrated solution of toluene at -35 °C.

Method B: A 20-mL scintillation vial was charged with **1-Bn** (0.100 g, 0.108 mmol), 15 mL of diethyl ether, 1 mL of tetrahydrothiophene, and a stir bar. To this green solution H₂PMes* (0.115 mmol 32 mg) was added, and the reaction mixture was stirred for 3 hours at room temperature, resulting in a green solution. The volatiles were removed *in vacuo* which results in a green powder assigned as **2-PMes*** (0.116 g, 0.105 mmol, 97% yield).

For **3-OMes**^{*}: A 20-mL scintillation vial was charged with **1-Bn** (0.150 g, 0.162 mmol), 5 mL of THF, and a stir bar. To this green solution HOMes^{*} (43 mg, 0.162 mmol) was added, and the reaction mixture was stirred for 1 hour at room temperature, resulting in a slightly darker green solution. The volatiles were removed *in vacuo*. Crude product of the uranium(III) alkoxide was washed with cold pentane (2 x 5mL) to afford green powder assigned as **3-OMes**^{*} (144 mg, 0.137 mmol, 87% yield). Green crystals of **3-OMes**^{*} were grown from a concentrated solution of dimethyl ether at -35 °C.

For **3-PMes***: A 20-mL scintillation vial was charged with **1-Bn** (0.100 g, 0.108 mmol), 5 mL of THF, and a stir bar. To this green solution H_2PMes^* (0.108 mmol 30 mg) was added, and the reaction mixture was stirred for 1 hour at room temperature, resulting in a brown/green solution. The volatiles were removed *in vacuo*. Crude product of uranium(III) phosphido mixtures **3-PMes*** were extracted from excess **1-Bn** using pentane (3 x 5mL) to afford green powder assigned as **3-PMes*** (0.122 g, 0.102 mmol, 94% yield). Single green crystals of **3-PMes*** were grown from a concentrated solution of diethyl ether at -35 °C.



Scheme S1. Synthesis of 3-PMes*.

2-PPh: ¹H NMR (C₆D₆, 25 °C): δ (ppm) = +19.5 (13, s, 2H, *o*-C*H*), +14.8 (7, s, 2H, *m*-C*H*), +9.8 (4, s, 1H, *p*-C*H*), +7.1 (5, s, 2H, Tp*-B*H*), +7.2 (5, s, 6H, Tp*-C*H*), +0.5 (5, s, 18H, Tp*-C*H*₃), –12.9 (12, s, 18H, Tp*-C*H*₃), –29.3 (106, s, 1H, -P*H*). ¹¹B NMR (C₆D₆, 25 °C): δ –2.9 ppm. ³¹P NMR (C₆D₆, 25 °C): δ = 2345 ppm. IR (salt plate): v_{P-H} = 2267 cm⁻¹; v_{B-H} = 2477, 2548 cm⁻¹. Elemental analysis of C₃₆H₅₀B₂N₁₂PU, Calculated, C, 45.93; H, 5.35; N, 17.85. Found, C, 44.75; H, 5.28; N, 16.86. Combustion aid was used for the prevention of carbides. The weight of the samples was very not stable on the balance.

2-PMes: ¹H NMR (C₆D₆, 25 °C): δ (ppm) = +12.7 (5, s, 2H, *m*-C*H*), +10.9 (8, s, 3H, *p*-C*H*₃), +8.1 (4, s, 6H, *o*-C*H*₃), +7.5 (6, s, 6H, Tp*-C*H*), +0.4 (5, s, 18H, Tp*-C*H*₃), -11.6 (18, s, 18H, Tp*-C*H*₃), -31.3 (107, s, 1H, -P*H*). ¹¹B NMR (C₆D₆, 25 °C): δ -0.6 ppm. IR (KBr): *v*_{P-H} = 2322 cm⁻¹; *v*_{B-H} = 2551, 2486 cm⁻¹. ³¹P NMR (C₆D₆, 25 °C): δ = 2802 ppm. Elemental analysis of C₃₉H₅₆B₂N₁₂PU, Calculated, C, 47.62; H, 5.74; N, 17.09. Found, C, 43.51; H, 5.20; N, 15.75. Combustion aid was used for the prevention of carbides. The weight of the samples were not very stable on the balance.

2-PMes*: ¹H NMR (C₆D₆, 25 °C): δ (ppm) = +12.1 (3, s, 2H, *m*-C*H*), +3.5 (6, s, 18H, *o*-(C*H*₃)₃), +2.9 (3, s, 9H, *p*-C*H*₃), -23.9 (299, s, 1H, -P*H*). ¹¹B NMR (C₆D₆, 25 °C): δ +1.2 ppm. ³¹P NMR (C₆D₆, 25 °C): δ = 2910 ppm. IR (salt plate): v_{P-H} = 2364 cm⁻¹; v_{B-H} = 2555, 2527 cm⁻¹. Elemental analysis of C₄₈H₇₄B₂N₁₂PU, Calculated, C, 51.95; H, 6.72; N, 15.15. Sample is too unstable to be shipped for elemental analysis.

3-PMes*: ¹H NMR (C₆D₆, 25 °C): δ (ppm) = +42.8 (46, s, 2H, THF-CH₂), +23.8 (52, s, 2H, THF-CH₂), +13.8 (28, s, 2H, THF-CH₂), +9.1 (5, s, 2H, THF-CH₂), +6.9 (6, s, 6H, Tp*-CH), +4.2 (5, s, 18H, *o*-(CH₃)₃), +2.9 (4, s, 2H, *m*-CH), +1.8 (4, s, 9H, *p*-CH₃), -1.9 (5, s, 18H, Tp*-CH₃), -11.5 (27, s, 18H, Tp*-CH₃). ¹¹B NMR (C₆D₆, 25 °C): δ -5.9 ppm. ³¹P NMR (C₆D₆, 25 °C): δ -64.0 ppm. IR (salt plate): v_{P-H} = 2390 cm⁻¹; v_{B-H} = 2554, 2527 cm⁻¹. Elemental analysis of C₅₂H₈₂B₂N₁₂OPU, Calculated, C, 52.84; H, 6.99; N, 14.22. Found, C,47.18; H, 4.76; N, 16.83. Sample is too unstable to be shipped for elemental analysis.

3-OMes^{*: 1}H NMR (C₆D₆, 25 °C): δ (ppm) = +23.1 (15, s, 18H, *o*-(CH₃)₃), +21.8 (5, s, 2H, *m*-CH), +6.5 (5, s, 3H, Tp*-CH), +4.5 (5, s, 3H, Tp*-CH), +2.4 (22, s, 18H, Tp*-CH₃), -4.8 (5, s, 8H, Tp*-CH₃), -8.7 (5, s, 18H, *p*-CH₃), -9.4 (5, s, 8H, Tp*-CH₃), -56.5 (17, s, 6H, Tp*-CH₃). ¹¹B NMR (C₆D₆, 25 °C): δ -14.9 ppm. IR (salt plate): v_{B-H} = 2560, 2531 cm⁻¹. Elemental analysis of C₄₈H₇₃B₂N₁₂OU, Calculated, C, 52.71; H, 6.73; N, 15.37. Found, C, 50.53; H, 6.19; N, 15.33. Combustion aid was used for the prevention of carbides.

Attempted Synthesis of Tp*₂U(III) THF Ring-Opened Compounds with 2-PPh and 2-PMes

A bomb flask was charged with **2-PPh** (50 mg, 0.053 mmol) or **2-PMes** (50 mg, 0.051 mmol), 10 mL of THF, and a stir bar. The reaction mixture was stirred for 3 hours at 70 °C resulting in little to no color change. The volatiles were removed *in vacuo* which identified **2-PPh** and **2-PPMes**, respectively, via ¹H NMR spectroscopy.

Attempted Synthesis of Tp*₂U(III) THT Ring-Opened Compounds with **2-PPh**, **2-PMes**, and **2-PMes***

A bomb flask was charged with **2-PPh** (50 mg, 0.053 mmol), **2-PMes** (50 mg, 0.051 mmol), or **2-PMes*** (50 mg, 0.023 mmol) and 1 mL of THT, 10 mL toluene, and a stir bar. The reaction mixture was stirred for 3 hours at 70 °C resulting in little to no color change. The volatiles were removed *in vacuo* which identified **2-PPh**, **2-PPMes**, and **2-PMes*** respectively, via ¹H NMR spectroscopy.

Synthesis of PCl₂Mes

The synthesis was adapted from a previously reported procedure.⁴ The synthesis is done in an inert atmosphere. A solution of MesMgBr (1 M in THF, 5 mL, 5 mmol) in THF (5 mL) was cooled to -78 °C for 15 minutes. Once cooled, PCl₃ (8.7 mL, 99.5 mmol) is added quickly to the cooled MesMgBr solution. The solution is stirred at -78 °C for 15 minutes then the cold bath is removed, and the reaction is warmed to room temperature and allowed to stir at room temperature overnight at which point the solution becomes cloudy and light yellow. After stirring overnight, the solvent and excess PCl₃ are removed *in vacuo*. The resulting yellow solid is filtered in diethyl ether to remove salts. The diethyl ether is removed *in vacuo* yielding the yellow oil PCl₂Mes (687 mg, 3.11 mmol, 62%). ³¹P NMR (C₆D₆, 25 °C): δ (ppm) = 168.8. ¹H NMR (C₆D₆, 25 °C): δ (ppm) = 6.46 (s, 2H, *p*-CH), 2.51 (s, 6H, *o*-CH₃), 1.89 (s, 3H, *p*-CH₃). Note: A small quantity of PClBrMes might be detected due to halogen competition which can be solved by adding more PCl₃, stirring longer, or heating the reaction. PClBrMes ³¹P NMR (C₆D₆, 25 °C): δ (ppm) = 162.8.

Synthesis of PCl₂Mes*

The synthesis was adapted from a previously reported procedure.⁵ The synthesis is done in an inert atmosphere. Mes*Br (1 g, 3.1 mmol) is dissolved in THF (5 mL) and cooled to -78°C. Once cool, a solution of n-butyllithium (2.5 M in hexanes, 1.47 mL, 3.68 mmol) is added dropwise and allowed to stir for 1h at -78 °C. After stirring, PCl₃ (0.54 mL, 6.1 mmol) is added while cold, whereupon the solution turns yellow. The reaction is warmed to room temperature and stirred overnight. After stirring overnight, the solvent and excess PCl₃ are removed *in vacuo*. The resulting yellow solid is filtered in diethyl ether to remove salts. The diethyl ether is removed *in vacuo* yielding the solid of PCl₂Mes* (1.076 g, 3.1 mmol, 99%).

³¹P NMR (C₆D₆, 25 °C): δ (ppm) = 153.6. ¹H NMR (C₆D₆, 25 °C): δ (ppm) 7.48 (s, 2H, *-m*-C*H*), 1.60 (s, 12H, *-o*-(C*H*₃)₃), 1.16 (s, 6H, *-p*-(C*H*₃)₃).

Synthesis of PH₂Mes and PH₂Mes*

The synthesis was adapted from a previously reported procedure.⁵ The synthesis is done in an inert atmosphere. LiAlH₄ (4.56 g, 120 mmol) was suspended in 5mL of diethyl ether and cooled to -78 °C. Once cooled, a solution of PCl₂Mes (1 g, 4.5 mmol) or PCl₂Mes* (1 g, 3.1 mmol) in 5mL of diethyl ether was added to the cooled LiAlH₄ suspension. The reaction mixture was stirred at -78 °C for 15 minutes then the cool bath was removed, and the mixture was stirred overnight at room temperature. The next morning, the solution had grey precipitants and a colorless solution. The solution was cooled to -78 °C and any excess LiAlH₄ is quenched by slowly adding 4mL of aqueous 1M HCl followed by 2mL of distilled water. *Caution: Vigorous* H_2 gas evolution is possible! The organic layer is separated from the aqueous layer and washed several times with diethyl ether. The diethyl ether is removed *in vacuo* yielding the oil of PH₂Mes (0.850 g, 5.6 mol, 85%) or PH₂Mes* (0.819 g, 2.9 mol, 96%).

PH₂Mes: ³¹P NMR (C₆D₆, 25 °C): δ (ppm) = -154.9. ¹H NMR (C₆D₆, 25 °C): δ (ppm) 6.71 (s, 2H, -*m*-C*H*), 3.61 (d, 2H, -PH₂), 2.21 (s, 6H, -*o*-C*H*₃), 2.09 (s, 6H, -*p*-C*H*₃).

PH₂Mes*: ³¹P NMR (C₆D₆, 25 °C): δ (ppm) = -129.9. ¹H NMR (C₆D₆, 25 °C): δ (ppm) 7.55 (s, 2H, -*m*-CH), 4.26 (d, 2H, -PH₂), 1.57 (s, 12H, -*o*-(CH₃)₃), 1.30 (s, 6H, -*p*-(CH₃)₃).



Figure S1. ¹H NMR spectrum (C_6D_6 , 25 °C) of 2-PPh



Figure S2. ¹¹B NMR spectrum (C_6D_6 , 25 °C) of 2-PPh



Figure S3. ³¹P NMR spectrum (C_6D_6 , 25 °C) of 2-PPh



Figure S4. IR spectrum (salt plate) of 2-PPh



Figure S5. ¹H NMR spectrum (C_6D_6 , 25 °C) of **2-PMes**



Figure S6. ¹¹B NMR spectrum (C_6D_6 , 25 °C) of 2-PMes



Figure S7. ³¹P NMR spectrum (C_6D_6 , 25 °C) of 2-PMes



Figure S8. IR spectrum (KBr) of 2-PMes



Figure S9. ¹H NMR spectrum (C_6D_6 , 25 °C) of 2-PMes*



Figure S10. ¹¹B NMR spectrum (C₆D₆, 25 °C) of 2-PMes*



Figure S11. ³¹P NMR spectrum (C₆D₆, 25 °C) of 2-PMes*



Figure S12. IR spectrum (salt plate) of 2-PMes*



Figure S13. ¹H NMR spectrum (C_6D_6 , 25 °C) of 3-PMes*



Figure S14. ¹¹B NMR spectrum (C_6D_6 , 25 °C) of 3-PMes*



Figure S15. ³¹P NMR spectrum decoupled (top) and nondecoupled (bottom) (C_6D_6 , 25 °C) of 3-PMes*



Figure S16. IR spectrum (salt plate) of 3-PMes*



Figure S17. ¹H NMR spectrum (C₆D₆, 25 °C) of 3-OMes*



Figure S18. ¹¹B NMR spectrum (C_6D_6 , 25 °C) of 3-OMes*



Figure S19. IR spectrum (salt plate) of 3-OMes*



Figure S20. Electronic absorption spectra of **2-PPh** (black), **2-PMes** (red), and **2-PMes*** (blue) recorded from 350 to 1600 nm in toluene at 25 °C.



Figure S21. Electronic absorption spectra of **2-PPh** (black) and **2-PMes** (red) recorded from 350 to 1600 nm in THF at 25 °C.



Figure S22. Electronic absorption spectra of **3-PMes*** recorded from 350 to 1600 nm in THF at 25 °C.



Figure S23. Electronic absorption spectra of **3-OMes*** recorded from 350 to 1600 nm in THF at 25 °C.



Figure S24. Molecular structure of **3-PMes*** displayed with 30% probability ellipsoids. Selected hydrogen atoms and co-crystallized solvent molecules have been omitted for clarity.



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Table S1. Select Angles (°) and Distances (Å) for 2-PPh , 2-PMes , and 2-PMes* .
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	2-PPh	2-PMes	2-PMes*
U-N _{anilido} (Å)	3.0456(8)	3.016(4)	2.9815(16)
U-N _{pyrazole} (Å)	2.518(3) - 2.841(3)	2.487(10) - 2.667(10)	2.542(4) - 2.788(4)
U-N _{anilido} -C (°)	112.11(10)	129.5(5)	134.34(17)

Compound: 2-PPh

Local Name: DP_3_92_2_0m

CCDC number: 2162659

 Table S2. Crystallographic details for Tp*₂UPH(phenyl)

Crystal data		
Chemical formula	$C_{36}H_{50}B_2N_{12}PU \cdot 2(C_4H_8O)$	
M _r	1085.70	
Crystal system, space group	Monoclinic, $P2_1/n$	
Temperature (K)	150	
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.1859 (4), 19.3077 (7), 24.7773 (10)	
β (°)	92.876 (2)	

$V(Å^3)$	4866.7 (3)
Ζ	4
Radiation type	Μο Κα
μ (mm ⁻¹)	3.42
Crystal size (mm)	0.17 imes 0.13 imes 0.02
Data collection	
Diffractometer	Bruker AXS D8 Quest diffractometer with PhotonII charge-integrating pixel array detector (CPAD)
Absorption correction	Multi-scan, SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D. (2015). J. Appl. Cryst. 48, 3-10.
T_{\min}, T_{\max}	0.325, 0.381
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	171405, 14904, 11165
R _{int}	0.089
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.716
Refinement	
$R[F^2 > 2\sigma(F^2)],$ $wR(F^2), S$	0.031, 0.070, 1.03
No. of reflections	14904
No. of parameters	658
No. of restraints	320
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	2.49, -1.07

Refinement notes: Two tetrahydrofuran molecules are disordered over two positions. The two disordered moieties were restrained to have similar bond distances and angles. In addition C39 and C39A were constrained to have identical positions and thermal parameters (EADP and EXYZ). The phosphorous bound H atom was found in a difference electron density Fourier map and its position is freely refined.

Computer programs: Apex3 v2019.11-0 (Bruker, 2020), SAINT V8.40B (Bruker, 2020),

SHELXT (Sheldrick, 2015), SHELXL2018/3 (Sheldrick, 2015a, 2018), SHELXLE Rev1117

(Hübschle et al., 2011).

Compound: 2-PMes

Local Name: dp5167_0m_final

CCDC number: 2162662

Table S3. Crystallographic details for Tp*₂UPH(2,4,6-trimethylphenyl)

Crystal data	
Chemical formula	C ₃₉ H ₅₅ B ₂ N ₁₂ PU
M _r	982.57
Crystal system, space group	Triclinic, P ¹
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.9713 (8), 11.9909 (11), 17.0052 (12)
α, β, γ (°)	78.759 (5), 75.724 (4), 86.939 (5)
$V(Å^3)$	2126.4 (3)
Ζ	2
Radiation type	Cu Κα
μ (mm ⁻¹)	11.44
Crystal size (mm)	$0.15 \times 0.04 \times 0.03$
Data collection	
Diffractometer	Bruker AXS D8 Quest diffractometer with PhotonIII_C14 charge-integrating pixel array detector (CPAD)
Absorption correction	Multi-scan, SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{\min}, T_{\max}	0.034, 0.144
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	27587, 8734, 6047
R _{int}	0.086
$(\sin \theta / \lambda)_{max} (\text{Å}^{-1})$	0.639

Refinement	
$R[F^2 > 2\sigma(F^2)],$ $wR(F^2), S$	0.065, 0.195, 1.04
No. of reflections	8734
No. of parameters	515
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	3.25, -0.86

Refinement notes: The PH hydrogen was located in the electron density map and refined

without restraints or constraints. The BH hydrogen atoms were located using HFIX 14 command and refined.

Computer programs: Apex3 v2019.11-0 (Bruker, 2020), SAINT V8.40B (Bruker, 2020),

SHELXT (Sheldrick, 2015), SHELXL2018/3 (Sheldrick, 2015a, 2018), SHELXLE Rev1117

(Hübschle et al., 2011).

Compound: 2-PMes*

Local Name: dp4184_a_0m_a - final

CCDC number: 2162661

Table S4.	Crystallographic	details for Tp*	$_{2}$ UPH(2,4,6-tri- ^{<i>t</i>}]	Bu-phenyl) 2-PMes*
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Crystal data	
Chemical formula	$C_{48}H_{74}B_2N_{12}PU$
$M_{ m r}$	1109.81
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	23.1916 (8), 10.9114 (3), 23.5679 (8)
β (°)	118.915 (1)
$V(Å^3)$	5220.4 (3)
Ζ	4
Radiation type	Cu Kα
μ (mm ⁻¹)	9.38
Crystal size (mm)	0.10 imes 0.06 imes 0.03

Data collection	
Diffractometer	Bruker AXS D8 Quest diffractometer with PhotonIII_C14 charge-integrating pixel array detector (CPAD)
Absorption correction	Multi-scan, SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D. (2015). J. Appl. Cryst. 48, 3-10.
T_{\min}, T_{\max}	0.517, 0.754
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	31924, 10132, 8488
$R_{\rm int}$	0.065
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)],$ $wR(F^2), S$	0.040, 0.078, 1.10
No. of reflections	10132
No. of parameters	603
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	1.26, -1.24

Computer programs: Apex3 v2019.11-0 (Bruker, 2020), SAINT V8.40B (Bruker, 2020),

SHELXT (Sheldrick, 2015), SHELXL2018/3 (Sheldrick, 2015a, 2018), SHELXLE Rev1117

(Hübschle et al., 2011).

Compound: 3-PMes*

Local Name: dp56_0m_final

CCDC number: 2162660

Table S5. Crystallographic details for Tp*2UO(CH2)4PH(2,4,6-tri-'Bu-phenyl) 3-PMes*

Crystal data					
Chemical formula	$C_{56}H_{92}B_2N_{12}O_2PU$				
M _r	1256.03				
Crystal system, space group	Triclinic, P^{1}				
Temperature (K)	150				
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.1649 (4), 13.9998 (4), 18.9583 (6)				

α, β, γ (°)	97.820 (2), 94.859 (2), 116.996 (1)
$V(Å^3)$	3041.69 (16)
Ζ	2
Radiation type	Cu Kα
μ (mm ⁻¹)	8.14
Crystal size (mm)	0.16 imes 0.14 imes 0.02
Data collection	
Diffractometer	Bruker AXS D8 Quest diffractometer with PhotonIII_C14 charge-integrating pixel array detector (CPAD)
Absorption correction	Multi-scan, SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D. (2015). J. Appl. Cryst. 48, 3-10.
T_{\min}, T_{\max}	0.526, 0.754
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	132642, 11974, 10825
R _{int}	0.075
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)],$ $wR(F^2), S$	0.029, 0.060, 1.09
No. of reflections	11974
No. of parameters	693
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta \rho_{max}$, $\Delta \rho_{min}$ (e Å ⁻³)	1.79, -0.98

Refinement notes: The P-bound H atom H1D was located in a difference Fourier map and its position was refined. To avoid a close contact between the P-bound atom H1D and tert-Bu H47B the distance between the two H-atoms was restrained to be at least 2.00(2) Å.

Computer programs: Apex3 v2019.11-0 (Bruker, 2020), SAINT V8.40B (Bruker, 2020),

SHELXT (Sheldrick, 2015), SHELXL2018/3 (Sheldrick, 2015a, 2018), SHELXLE Rev1117

(Hübschle et al., 2011).

Extended Computational Details

Density functional theory (DFT) calculations were performed for complexes **2-PPh**, **2-NPh**, **2-PMes**, **2-NMes**, **2-PMes**^{*}, and **2-NMes**^{*}. Geometry optimizations using the M06-L⁶ functional were performed for the quartet spin state, and the structures were confirmed as minima by means of harmonic vibrational analysis as implemented in the Turbomole program package V7.3.14.⁷ Note that no more than two small imaginary frequencies of i35 or less are observed for the complexes corresponding to methyl rotations. The def-TZVPP basis set was used for uranium, def2-TZVPP was used for N and P, and the def2-TZVP basis set was used on boron, carbon, and hydrogen.^{8–13} The corresponding ECP was employed for uranium to account for scalar relativistic effects. The resolution of identity (RI) approximation was included to speed up integral evaluation.¹⁴ Single point calculations were performed on the quartet structure for the doublet and sextet states confirming that the quartet is the ground state. These results were further analyzed by computing CM5 charges, atomic contributions to the molecular orbitals calculated using the Hirshfeld method, and the topological analysis of the electron density with Bader's Atoms in Molecules (QTAIM) as implemented in the MultiWFN 3.8 software package.^{15–17}

To calculate Mayer, Gopinathan-Jug (G-J), and Nalewajski-Mrozek (N-M) bond orders, DFT single-point calculations were performed on the optimized ground state structures using the M06-L functional as implemented in the Amsterdam Density Functional (ADF) program package.¹⁸ The TZP all-electron basis set was used with no frozen core. Scalar relativistic effects were included using the zero-order regular approximation (ZORA). Subsequent energy decomposition analysis (EDA) combined with the natural orbitals for chemical valence (NOCV) analysis was also performed in ADF at the same level of theory. The species were divided into two fragments: one containing the anilido or phosphido ligand and the other containing the remainder of the molecule. A single-point calculation was performed on each fragment. The anilido/phosphido ligands were taken to be formally -1 and closed-shell singlets, while the remainder of the basis for the calculation on the full molecule (quartet spin, neutral charge). Mayer, Gopinathan-Jug, and Nalewajski-Mrozek bond order analysis was also performed.

In addition to the DFT calculations, the electronic structure was studied by the complete active space self-consistent field (CASSCF) method along with second-order energy corrections $(CASPT2)^{19,20}$ for **2-NPh** and **2-PPh**. CASPT2 calculations were performed using the OpenMolcas 18.094 program package²¹ on the geometries obtained from the DFT ground state. The ANO-RCC basis set of triple- ζ quality was used for uranium, nitrogen, and phosphorus atoms. A minimal basis set was used for peripheral carbon, boron, and hydrogen atoms.^{22,23} The specific contractions used were 9s8p6d4f2g1h for U, 4s3p2d1f for N, 5s4p2d1f for P, 2s1p for C, 2s1p for B, and 1s for H. Scalar relativistic effects are included through the use of the second-order Douglas-Kroll-Hess (DKH) Hamiltonian.^{24,25} The computation of the three-centered integrals was expedited through the use of Cholesky decomposition and local exchange screening.^{26–29} The CASPT2 zeroth-order Hamiltonian included an IPEA shift of 0.25 and an imaginary shift 0.2 a.u. An active space of nine electrons in thirteen orbitals, denoted (9*e*,13*o*),

was employed. This includes the seven 5*f* orbitals and three sets of π bonding and antibonding orbitals in the anilido or phosphido ligands, respectively. The active orbitals are for all of the calculations are reported (**Figures S32 to S37**). The doublet, quartet, and sextet spin states are computed.

Density Functional Theory Results Computed in Turbomole

Table S6. DFT optimized uranium-pnictogen bond distances (in Angstroms) and angles (in degree).

Ligand	Bond Distance	U-P _n -C Angle
2-NPh	2.366	141.4
2-NMes	2.340	151.5
2-NMes*	2.350	162.3
2-PPh	3.043	110.1
2-PMes	2.961	126.4
2-PMes*	2.9896	126.2

Table S7. M06-L relative energies in kcal/mol computed on the ground state quartet (S=3/2) geometry. The * indicates that the $\langle S^2 \rangle$ value is large (1.75 for the doublet states).

Spin	2-NPh	2-NMes	2-NMes*	2-PPh	2-PMes	2-PMes*
doublet	22.8*	21.9*	22.8*	23.0*	23.0*	22.5*
quartet	0.0	0.0	0.0	0.0	0.0	0.0
sextet	74.1	70.5	69.4	55.3	55.3	53.7

Table S8. Relative energy of the two different coordinations of the six complexes.

complexes	Starting Geom	Final Geom	Kcal/mol
2-NPh	7	7	0.0
	8	8	2.6
2-PPh	8	8	0.0
	7	7ª	2.2
2-NMes	7	7	0.0

	8	7 ^b	2.9
2-PMes	7	7	0.0
	8	8	-2.6
2-NMes*	7	7	0.0
	8	8ª	6.5
2-PMes*	7	7	0.0
	8	8	-0.3

a =constraint optimization b=did not fully converged to optimization

Atomic Charges. Atomic charges can give us the insight about the extent to which charge transfer has occurred from the pnictogen to uranium. A lower charge is observed on N (-0.70) in the HNPh⁻ fragment compared to the charge on P (-0.54) in the HPPh⁻ fragment. As such, we attribute these differences to the nature of the pnictogen within the ligand. However, a higher charge is observed on the U center for the anilido complexes compared to the phosphide complexes consistent with nitrogen groups being stronger donors. We note that the uranium center has a higher charge of 1.21 was observed for **2-PPh** compared to the charge in **2-PMes** and **2-PMes*** which could be a result of the side on interaction of the pyrazole nitrogen atom with uranium in this species.

Table S9. CM5 charges computed at the M06-L/def2-TZVPP, def2-TZVPP, def2-TZVP level of theory. The charges on the $N_{pyrazole}$ atoms are averaged.

Atom Center	2-NPh	2-NMes	2-NMes*	2-PPh	2-PMes	2-PMes*
P/N	-0.72	-0.73	-0.73	-0.34	-0.34	-0.32
U	1.27	1.25	1.23	1.21	1.16	1.18
N _{pyrazole}	-0.30	-0.30	-0.29	-0.29	-0.30	-0.30

Quantum Theory of Atoms in Molecules (QTAIM). In order to further understand the nature of the chemical bonding in the six complexes, we performed a topological analysis of the electron density using the quantum theory of atoms in molecules (QTAIM) developed by Bader. In QTAIM, a chemical bond is present if a line of locally maximum electron density joins neighboring atoms. A bond critical point (BCP) is a point along the bond path where the electron density reaches a minimum. At a BCP, the gradient (ρ) of the electron density is zero and the Laplacian of the electron density, $\nabla^2(\rho)$, could be positive or negative. A positive Laplacian means a local depletion of charge while a negative value corresponds to a local concentration of charge. In a covalent bond, the Laplacian should be negative since it is a sign of shared interaction of electron density between two linked atoms. A closed-shell interaction is associated with a positive Laplacian and these types of bonds generally are not considered covalent due to depletion of charge at the location of the BCP. The total electronic energy density, E(r), at the

BCP is defined as the sum of the Lagrangian kinetic energy, G(r), and the potential energy density, V(r). In clear cases, when E(r) and the Laplacian electron density are both negative, the bond is covalent. In less clear cases, the Laplacian is positive and E(r) is negative then the bond is considered to be dative. On the other hand, if E(r) is close to zero, then the bond is metallic. Finally, if E(r) is positive, the bond would be identified as ionic or Van der Waals. We also report the bond degree (BD), defined as $E(r)/\rho$, that gives a measure of the degree of covalency in these bonds. More negative values of BD suggest a greater covalent interaction.

Compound	Bond	∇ ² (ρ)	G(r)	V(r)	E(r)	ρ
2-PPh	U-P	0.04960	0.02276	-0.03312	-0.01036	0.04686
	U-N4	0.15357	0.04903	-0.05966	-0.01064	0.06068
	U-N5	0.15643	0.04991	-0.06071	-0.01080	0.06146
	U-N6	0.10673	0.03097	-0.03526	-0.00429	0.04128
	U-N10	0.10772	0.03014	-0.03335	-0.00321	0.03731
	U-N11	0.14524	0.04545	-0.05459	-0.00914	0.05650
	U-N12	0.13382	0.04104	-0.04862	-0.00758	0.05188
2-NPh	U-N	0.20801	0.07395	-0.09590	-0.02195	0.08576
	U-N3	0.15282	0.04728	-0.05634	-0.00907	0.05690
	U-N4	0.13361	0.04022	-0.04703	-0.00681	0.05033
	U-N5	0.11221	0.03214	-0.03623	-0.00409	0.04116
	U-N9	0.10264	0.02929	-0.03291	-0.00363	0.03859
	U-N10	0.12711	0.03838	-0.04498	-0.00660	0.04920
	U-N11	0.13781	0.04233	-0.05020	-0.00788	0.05292

Table S10. Properties at the bond critical points for **2-PPh** and **2-NPh**. All values are expressed in atomic units. Atom numbers are labeled in Figure S38.

Table S11. Properties at the bond critical points for **2-PMes** and **2-NMes.** All values are expressed in atomic units. Atom numbers are labeled in Figure S38.

Compounds	Bonds	∇ ² (ρ)	G(r)	V(r)	E(r)	ρ
2-PMes	U-P	0.06060	0.02302	-0.03089	-0.00787	0.04264
	U-N2	0.16640	0.04821	-0.05481	-0.00661	0.05452

	LI NA	0 12053	0.03445	0.03878	0.00432	0.04405
	0-114	0.12033	0.03443	-0.03878	-0.00432	0.04403
	U-N6	0.10659	0.02846	-0.03028	-0.00182	0.03551
	U-N8	0.10159	0.02691	-0.02843	-0.00151	0.03344
	U-N10	0.13702	0.03808	-0.04191	-0.00383	0.04454
	U-N12	0.14907	0.04219	-0.04712	-0.00493	0.04859
2-NMes	U-N	0.23541	0.07644	-0.09403	-0.01759	0.08138
	U-N2	0.15574	0.04439	-0.04985	-0.00546	0.05086
	U-N4	0.10492	0.02876	-0.03128	-0.00253	0.03682
	U-N6	0.12012	0.03285	-0.03567	-0.00282	0.04018
	U-N8	0.11648	0.03077	-0.03241	-0.00165	0.03615
	U-N10	0.11408	0.03000	-0.03147	-0.00147	0.03530
	U-N12	0.16103	0.04538	-0.05051	-0.00513	0.05046

Table S12. Properties at the bond critical points for **2-PMes*** and **2-NMes***. All values are expressed in atomic units. Atom numbers are labeled in Figure S38.

Compounds	Bonds	∇ ² (ρ)	G(r)	V(r)	E(r)	ρ
2-PMes*	U-P	0.05643	0.02150	-0.02889	-0.00739	0.04080
	U-N4	0.14063	0.03960	-0.04403	-0.00444	0.04676
	U-N2	0.10244	0.02722	-0.02882	-0.00161	0.03420
	U-N9	0.14054	0.03996	-0.04479	-0.00483	0.04749
	U-N8	0.08849	0.02262	-0.02311	-0.00050	0.02759
	U-N10	0.13859	0.03955	-0.04446	-0.00491	0.04769
	U-N3	0.16690	0.04898	-0.05623	-0.00725	0.05601
2-NMes*	U-N	0.23714	0.07506	-0.09083	-0.01578	0.07795
	U-N15	0.15826	0.04432	-0.04907	-0.00475	0.04935
	U-N8	0.11069	0.02992	-0.03216	-0.00224	0.03684
	U-N14	0.10297	0.02733	-0.02892	-0.00159	0.03417
	U-N10	0.10121	0.02674	-0.02818	-0.00144	0.03345
	U-N12	0.11203	0.02975	-0.03148	-0.00174	0.03566
	U-N4	0.16653	0.04674	-0.05186	-0.00511	0.05079

	Bonds	∇ ² (ρ)	G(r)	V(r)	E(r)	ρ	BD = E(r)/ρ	V(r) /G(r)
2-PPh	U-P	0.0496	0.0228	-0.0331	-0.0104	0.0469	-0.2211	1.4552
2-NPh	U-N	0.2080	0.0740	-0.0959	-0.0220	0.0858	-0.2559	1.2968
2-PMes	U-P	0.0606	0.0230	-0.0309	-0.0079	0.0426	-0.1846	1.3419
2-NMes	U-N	0.2354	0.0764	-0.0940	-0.0176	0.0814	-0.2161	1.2301
2-PMes*	U-P	0.0564	0.0215	-0.0289	-0.0074	0.0408	-0.1811	1.3437
2-NMes*	U-N	0.2371	0.0751	-0.0908	-0.0158	0.0780	-0.2024	1.2101

Table S13. A summary of the properties at the bond critical points for all structures. All values are expressed in atomic units.

DFT Frontier Molecular Orbitals. DFT molecular orbitals are plotted in **Figures S26 to S28.** The three unpaired electrons are distributed in uranium 5*f* orbitals labeled as SOMO 1, SOMO 2 and SOMO 3. This is consistent with a trivalent uranium 5*f*³ configuration. In the three anilido complexes, one σ and one π interaction were observed along the U-N bond. Specifically, in **2**-**NPh**, the uranium contribution is 9.9% and the N contribution is 45.8% in the π interaction (HOMO) while the U contribution is higher in σ bond (HOMO-1) at 37.5% with a P contribution of 42.3% (**Figure S26**). On the other hand, in **2-PPh**, no π interaction is observed. The HOMO orbital has a much larger contribution (53.8%) from the P with only 15.2 % from uranium (**Figure S26**). These differences between the pnictogen centers are consistent with phosphorus being a weaker Lewis base The σ and π interactions in **2-NPh**, in addition to the other analyses of the DFT results, suggest higher orbital contributions arise in part from the " π -like" mixing resulting in stronger U-N bonds compared to U-P bonds. A similar trend is observed for the other anilido and phosphido complexes (**Figures S27 to S28**).



Figure S26. DFT frontier orbitals for **2-NPh** (top row) and **2-PPh** (bottom row). The Hirshfeld atomic contributions to the MOs are also shown. The orbitals are plotted using an isovalue of 0.04.



Figure S27. DFT frontier orbitals for **2-NMes** (top row) and **2-PMes** (bottom row). The Hirshfeld atomic contributions to the MOs are also shown. The orbitals are plotted using an isovalue of 0.04.



Figure S28. DFT frontier orbitals for **2-NMes*** (top row) and **2-PMes*** (bottom row). The Hirshfeld atomic contributions to the MOs are also shown. The orbitals are plotted using an isovalue of 0.04.

Density Functional Theory Results Computed in ADF

Bond Orders. Three types of bond orders are available in the ADF software package: Mayer, Gopinathan-Jug (G-J), and Nalewajski-Mrozek (N-M).^{30–32} Mayer and Gopinathan-Jug bond order indices use a set of basis functions to identify the atom based on Widberg's earlier work. These bond indices recover the covalent portion of the bond. For highly polarized bonds such as those in this work, the values of a single bond are often much lower than one due to important electrostatic contributions to bonding and is observed in both the U-N and U-P bond orders reported in Table S14. On the other hand, the Nalewajski-Mrozek (N-M) valence indices comprise both, covalent and ionic contributions as they take a different approach in their formalism by starting from a well-defined atomic referenced frame related to two-electron probabilities. There are three alternative NM bond order indices are calculated from each set of the valence indices and differ slightly due to arbitrariness in the way of splitting the one-center terms between bonds. We focus our discussion on the N-M (3) bond orders, those calculated from valence indices based on partitioning Tr(P Δ P), since these include all contributions and are the default set in ADF.

The highly-polarized uranium-nitrogen bonds are predicted to be slightly stronger than single Sbonds by Nalewajski-Mrozek bond orders, while the phosporhous analogues are predicted to be closer to single bonds. On the other hand, Mayer and Gopinathan-Jug bond orders correspond to polarized single bonds for both complexes. Both Nalewajski-Mrozek and Gopinathan-Jug bond orders predict a stronger bond for the anilido bonds compared to the phosphido bonds consistent with nitrogen being a stronger donor. Mayer bond orders predict the opposite trend. Given the sensitivity of Mayer bond orders to basis set choice and that these bonds are highly polarized, we argue that the N-M (3) bond orders are more reliable for analysis.

Table S14. DFT bond orders for the uranium-pnictogen bond distances computed at the M06-L/TZP in the ADF program package. Mayer, Gopinathan-Jug (G-J), and Nalewajski-Mrozek (N-M) bond orders are included. The three alternative NM bond order indices are included for completeness, but NM3 values are discussed.

Ligand	Mayer	G-J	N-M (1)	N-M (2)	N-M (3)
2-NPh	0.539	0.773	1.264	1.703	1.234
2-NMes	0.485	0.806	1.312	1.738	1.284
2-NMes*	0.525	0.780	1.263	1.683	1.237
Avg.	0.516	0.786	1.279	1.708	1.252
2-PPh	0.787	0.617	1.013	1.105	0.955
2-PMes	0.916	0.707	1.161	1.234	1.090
2-PMes*	1.058	0.659	1.074	1.149	1.009
Avg.	0.920	0.661	1.083	1.163	1.018

Energy decomposition analysis (EDA) based on natural orbitals for chemical valence (NOCV). In order to understand the contributions to the uranium-prictogen bonds, we performed an energy decomposition analysis (EDA) as implemented in ADF. Computations were performed using the previously noted level of theory on two fragments. The first consists of the phosphido (or anilido) ligand and was computed for the singlet state with a charge of -1. The second fragment consists of the remainder of the molecule having a charge of +1 in the quartet spin state. Then, the two fragments were used as the basis for the computation of the molecular orbitals of the whole molecule. This allows the interaction of the two fragments along the uranium-pnictogen bond to be decomposed into the contributions in Table S15 where ΔE_{int} is the total interaction energy. ΔE_{int} is the sum of the electrostatic interaction (ΔE_{elstat}), the Pauli repulsion (ΔE_{Pauli}), and the orbital interactions (ΔE_{oi}). The sum of the ΔE_{elstat} and ΔE_{Pauli} is referred to as the total steric interaction (ΔE_{steric}). In addition to EDA, the nature of metal-ligand bonds can be further analyzed using the so-called natural orbitals for chemical valence (NOCV) approach by decomposing the deformation density into different components along the chemical bond. Each NOCV pair has a corresponding orbital interaction energy to quantify the strength of that specific redistribution of electron density.

Table S15. Ener	gy decompositior	1 analysis (EDA) in kcal/mol at the	M06-L/TZP	level of theory
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Spin	2-NPh	2-NMes	2-NMes*	2-PPh	2-PMes	2-PMes*
ΔE_{int}	-138.9	-137.1	-139.8	-114.0	-113.9	-118.1
ΔE_{oi}	-79.2	-80.9	-86.2	-48.3	-52.2	-52.9

ΔE_{Pauli}	118.9	123.3	114.8	66.3	73.0	60.1
ΔE_{elstat}	-178.6	-179.5	-168.4	-131.9	-134.7	-125.3
ΔE_{steric}	-58.7	-56.2	-53.6	-65.7	-61.7	-65.2
% orb	57.0	59.0	61.6	42.4	45.8	44.8
% steric	43.0	41.0	38.4	57.6	54.2	55.2

Table S16. Orbital interaction energy contributions from each NOCV pair in kcal/mol. Only those with interaction energies larger than 5 kcal/mol are included.

	2-NPh	2-NMes	2-NMes*	2-PPh	2-PMes	2-PMes*
1	-11.9	-16.9	-10.5	-12.9	-13.3	-11.8
2	-8.9	-10.7	-10.1		-5.6	
3	-7.0		-5.6			



Figure S29. EDA-NOCV results for the nitrogen containing species. The shape of the deformation densities and corresponding orbital interaction energy contributions (kcal/moL) that gives the size of the charge migration from the yellow region to the blue region are shown.

Surfaces are plotted with an isovalue of 0.002 a.u. Interactions larger than 5 kcal/mol are included.



Figure S30. EDA-NOCV results for the phosphorus containing species. The shape of the deformation densities and corresponding orbital interaction energy contributions (kcal/moL) that gives the size of the charge migration from the yellow region to the blue region are shown. Surfaces are plotted with an isovalue of 0.002 a.u. Interactions larger than 5 kcal/mol are included.



Figure S31. Comparison of the largest orbital interaction energies from EDA-NOCV for all six complexes. Surfaces are plotted with an isovalue of 0.002 a.u. Interactions larger than 6 kcal/mol are included.

Table S17. CASPT2 relative energies in kcal/mol computed using the (9e,13o) active space on the DFT ground state quartet (S=3/2) geometry.

Spin	2-NPh	2-PPh
doublet	17.1	17.5
quartet	0.0	0.0
sextet	98.6	96.5



Figure S32. CASSCF natural orbitals of 2-NPh for doublet spin state with occupation numbers in parentheses. An isovalue of 0.04 was used.



Figure S33. CASSCF natural orbitals of **2-NPh** for quartet spin state with occupation numbers in parentheses. An isovalue of 0.04 was used.



Figure S34. CASSCF natural orbitals of **2-NPh** for sextet spin state with occupation numbers in parentheses. An isovalue of 0.04 was used.



Figure S35. CASSCF natural orbitals of **2-PPh** for doublet spin state with occupation numbers in parentheses. An isovalue of 0.04 was used.



Figure S36. CASSCF natural orbitals of **2-PPh** for quartet spin state with occupation numbers in parentheses. An isovalue of 0.04 was used.



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Figure S37. CASSCF natural orbitals of 2-PPh for sextet spin state with occupation numbers in parentheses. An isovalue of 0.04 was used.



Figure S38. Optimized structures of 2-NPh, 2-NMes, 2-NMes*, 2-PPh, 2-PMes and 2-PMes* in the quartet ground state.

References

- J. D. Woollins, *Inorganic Experiments*, Wiley-VCH, Weinheim, 3rd, rev. ed. edn., 2010.
- 2 E. M. Matson, W. P. Forrest, P. E. Fanwick and S. C. Bart, *JACS*, 2011, **133**, 4948–4954.
- 3 D. Perales, S. A. Ford, S. R. Salpage, T. S. Collins, M. Zeller, K. Hanson and S. C. Bart, *Inorg. Chem.*, 2020, **59**, 11910–11914.
- 4 F. Nief and F. Mathey, *Tetrahedron*, 1991, **47**, 6673–6680.
- 5 J. Bresien, A. Hinz, A. Schulz, T. Suhrbier, M. Thomas and A. Villinger, *Chem. Eur. J.*, 2017, **23**, 14738–14742.

- 6 Y. Zhao and D. G. Truhlar, J. Chem. Phys., 2008, **128**, 184109–8.
- 7 TURBMOLE V7.3 2018, a development of the University of Karlsruhe and Forschungszentrum Karlsruhe GmBH, 1989-2007, TURBMOLE GmbH, since 2007
- 8 A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829–5835.
- 9 W. Küchle, M. Dolg, H. Stoll and H. Preuss, J. Chem. Phys., 1994, **100**, 7535–7542.
- 10 X. Cao, M. Dolg and H. Stoll, J. Chem. Phys., 2003, **118**, 487–496.
- 11 F. Weigend, M. Häser, H. Patzelt and R. Ahlrichs, *Chem. Phys. Lett.*, 1998, **294**, 143–152.
- 12 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
- 13 F. Weigend, M. Häser, H. Patzelt and R. Ahlrichs, *Chem. Phys. Lett.*, 1998, **294**, 143–152.
- 14 K. Eichkorn, O. Treutler, H. Ohm, M. Haser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **242**, 652–660.
- 15 T. Lu and C. Fei-Wu, *Acta Chimica Sinica*, 2011, **69**, 2393–2406.
- 16 R. F. W. Bader, *Chem. Rev.*, 1991, **91**, 893–928.
- 17 T. Lu and F. Chen, J. Comput. Chem., 2012, **33**, 580–592.
- 18 G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931–967.
- 19 K. Andersson, P. A. Malmqvist, B. O. Roos, A. J. Sadlej and K. Wolinski, *J. Phys. Chem.*, 1990, **94**, 5483–5488.
- 20 K. Andersson, P. A. Malmqvist, B. O. Roos, J. Chem. Phys., 1992, 96, 1218–1226.
- F. Aquilante, J. Autschbach, R. K. Carlson, L. F. Chibotaru, M. G. Delcey, L. de Vico, I. Fdez. Galván, N. Ferré, L. M. Frutos, L. Gagliardi, M. Garavelli, A. Giussani, C. E. Hoyer, G. Li Manni, H. Lischka, D. Ma, P. Å. Malmqvist, T. Müller, A. Nenov, M. Olivucci, T. B. Pedersen, D. Peng, F. Plasser, B. Pritchard, M. Reiher, I. Rivalta, I. Schapiro, J. Segarra-Martí, M. Stenrup, D. G. Truhlar, L. Ungur, A. Valentini, S. Vancoillie, V. Veryazov, V. P. Vysotskiy, O. Weingart, F. Zapata and R. Lindh, *J. Comput. Chem.*, 2016, **37**, 506–541.
- 22 B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov and P.-O. Widmark, *Chem. Phys. Lett.*, 2005, **409**, 295–299.
- B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov and P.-O. Widmark, *J. Phys. Chem. A*, 2004, 108, 2851–2858.
- 24 B. A. Hess, *Phys. Rev. A Gen. Phys.*, 1986, **33**, 3742–3748.
- 25 M. Douglas and N. M. Kroll, Ann. Phys. (N.Y.), 1974, **82**, 89–155.
- 26 F. Aquilante, L. Gagliardi, T. B. Pedersen and R. Lindh, J. Chem. Phys., 2009, 130, 154107–9.
- 27 F. Aquilante, R. Lindh and T. B. Pedersen, J. Chem. Phys., 2008, **129**, 034106–034106.

- 28 F. Aquilante, P.-Å. Malmqvist, T. B. Pedersen, A. Ghosh and B. O. Roos, *J. Chem. Theory Comput.*, 2008, **4**, 694–702.
- 29 F. Aquilante, T. B. Pedersen and R. Lindh, *J. Chem. Phys.*, 2007, **126**, 194106–194106.
- 30 A. Michalak, R. L. DeKock and T. Ziegler, *J. Phys. Chem. A*, 2008, **112**, 7256–7263.
- 31 M. S. Gopinathan and K. Jug, *Theoretica. Chimica. Acta.*, 1983, **63**, 497–509.
- 32 I. Mayer, Chem. Phys. Lett., 1983, 97, 270–274.