(2-Pyridyloxy)arsines as Ligands in Transition Metal Chemistry: A Stepwise As(III)→ As(II)→ As(I) Reduction

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Supporting Information:

Content:

- NMR spectra of compound **1**, **2**, **3**, **5**, **6**, and **7**
- Transition states of the interconversion of $\mathbf{1}^{II}$ into $\mathbf{1}^{I}$
- NMR spectra of the reaction mixture of the reaction of **2** with $[RuCl_2(PPh_3)_3]$
- Single-crystal X-ray structure overlay of $[PhP(\mu\text{-}PyO)_2RuCl_2(PPh_3)]$ and $[PhAs(\mu\text{-}PyO)_2RuCl_2(PPh_3)]$ (**3**)
- Parameters of single-crystal X-ray diffraction data collection and structure refinement
- Additional NBO/NLMO representations
- Atomic coordinates of gas phase optimized molecular structures

- NMR spectra of compound **1**, **2**, **3**, **5**, **6**, and **7**

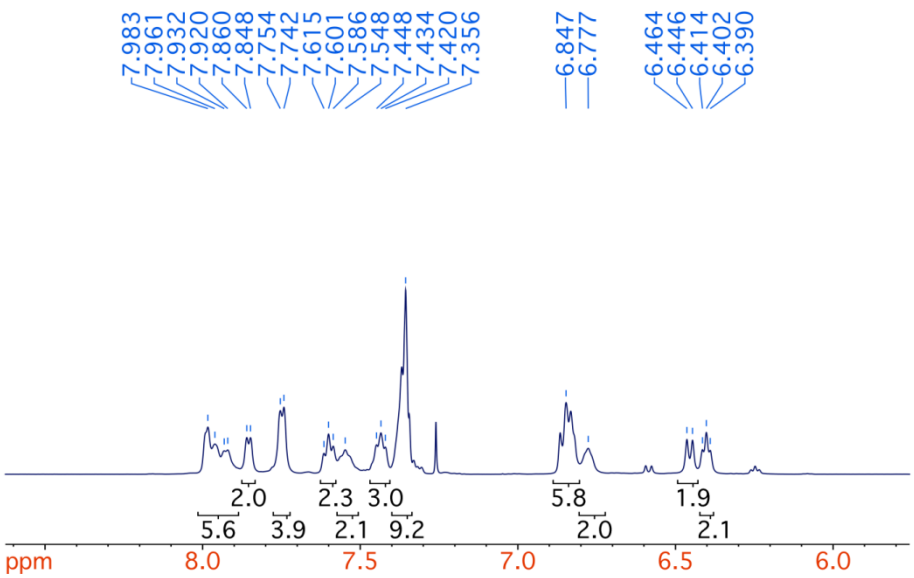

Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$.

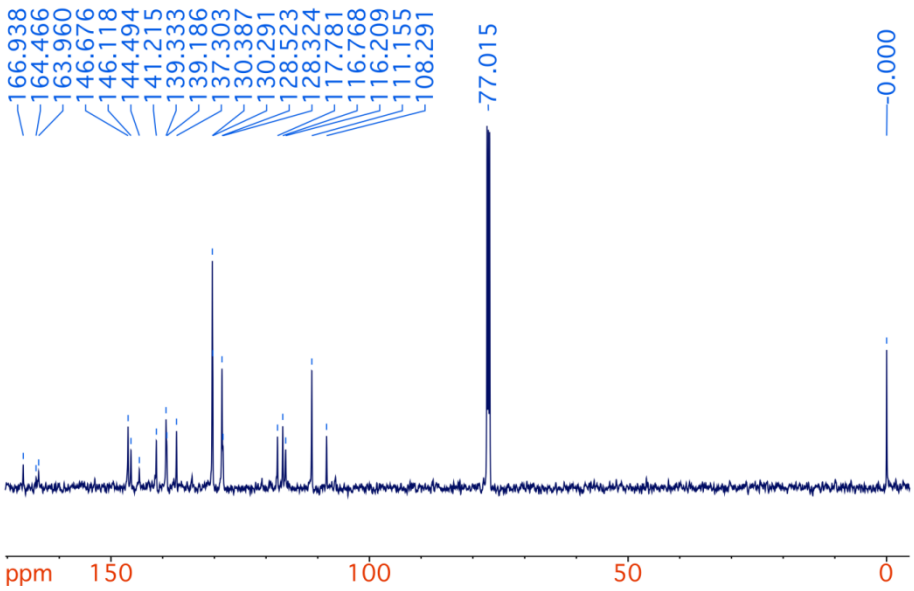

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$.

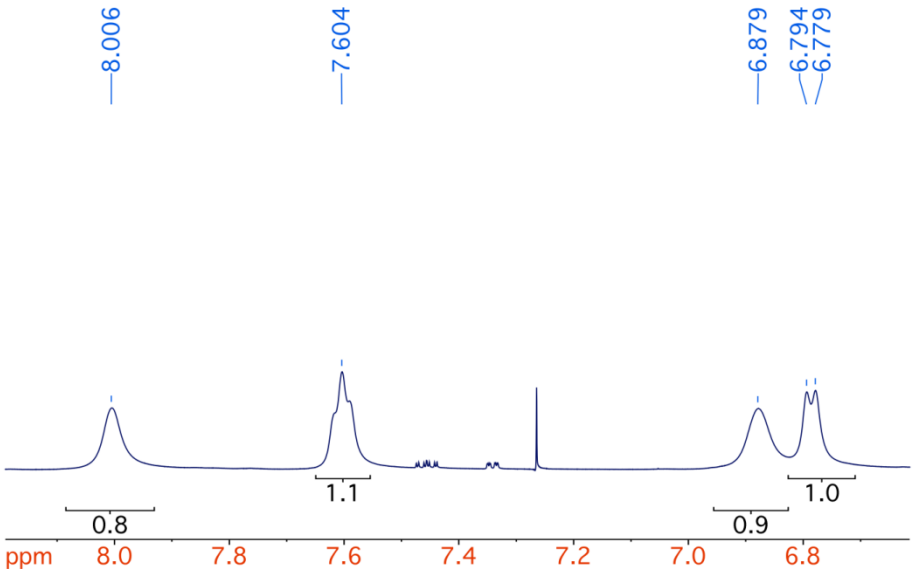

Figure S3. ^{1}H NMR spectrum of **2** in $CDCl_3$.

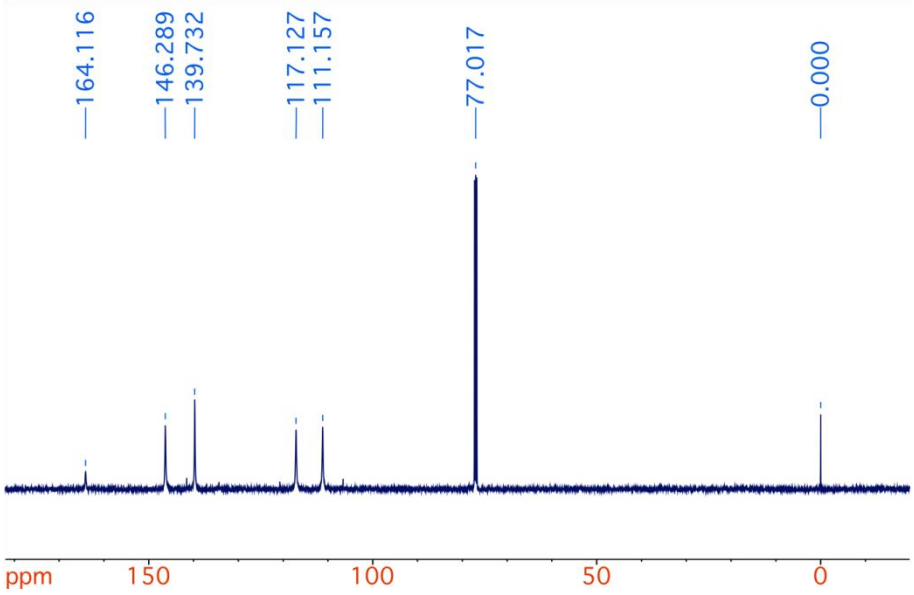

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$.

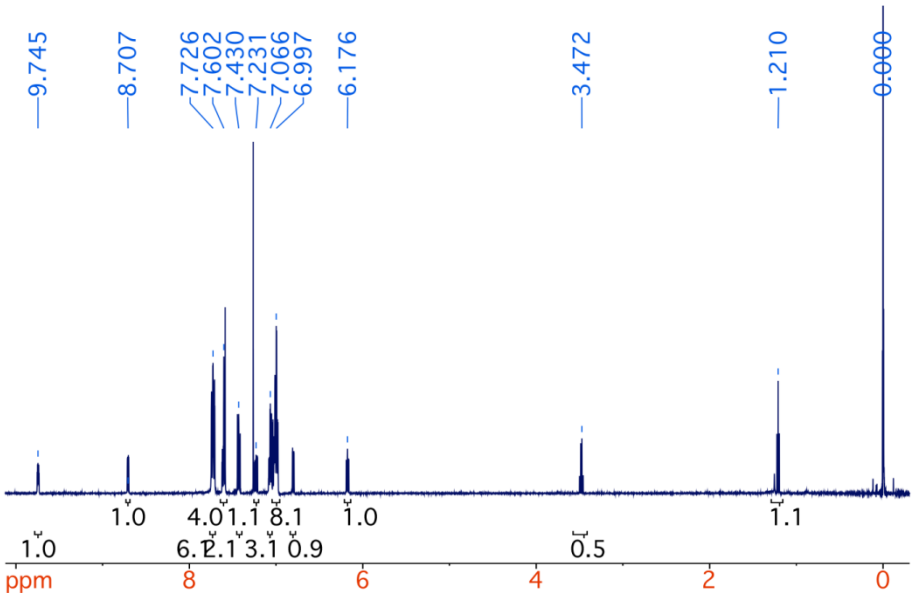

Figure S5. ^{1}H NMR spectrum of **3** in $CDCl_3$.

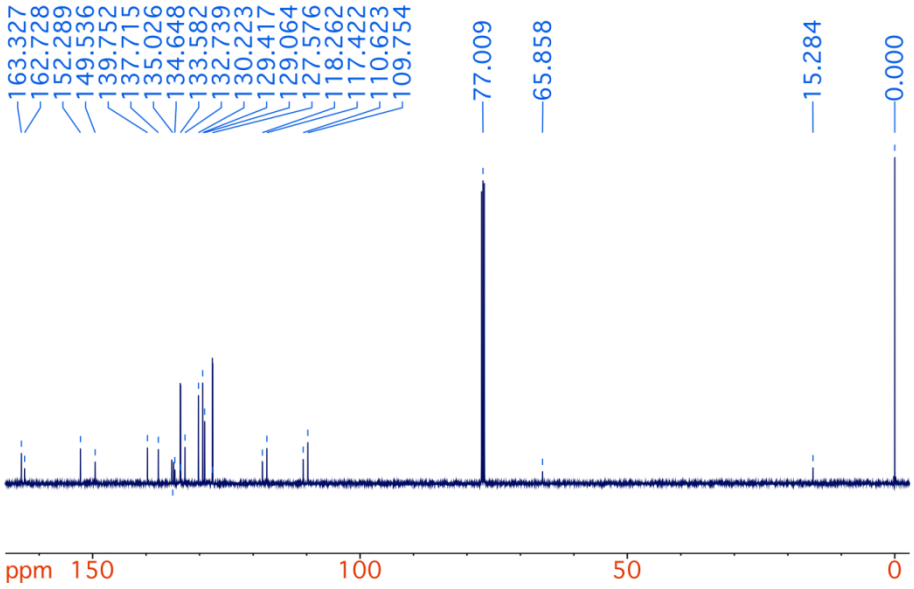

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

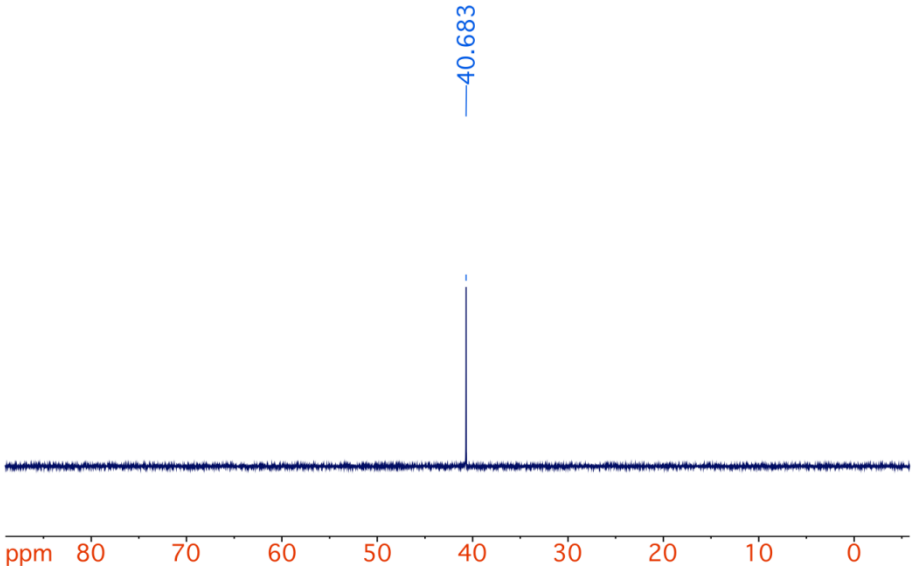

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

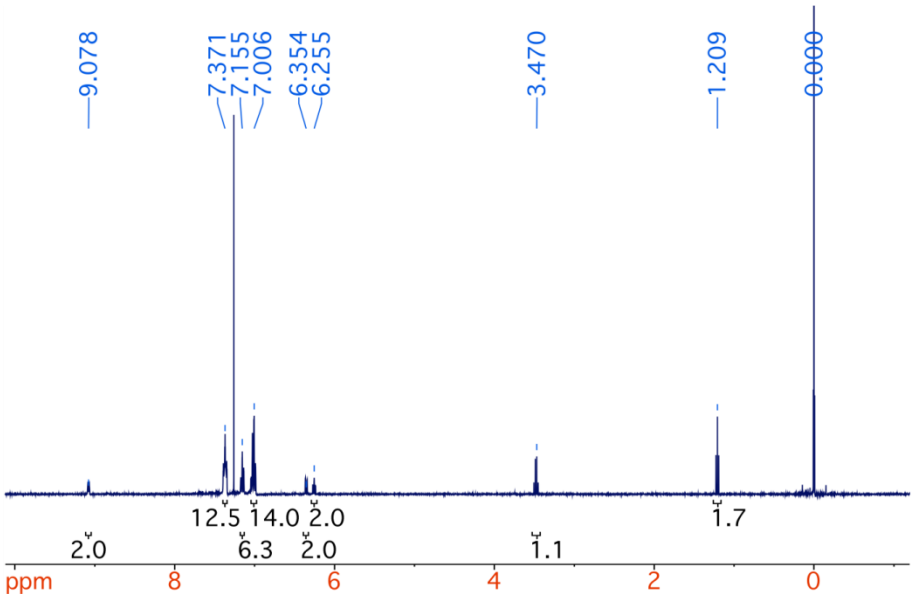

Figure S8. ^{1}H NMR spectrum of **5** in $CDCl_3$.

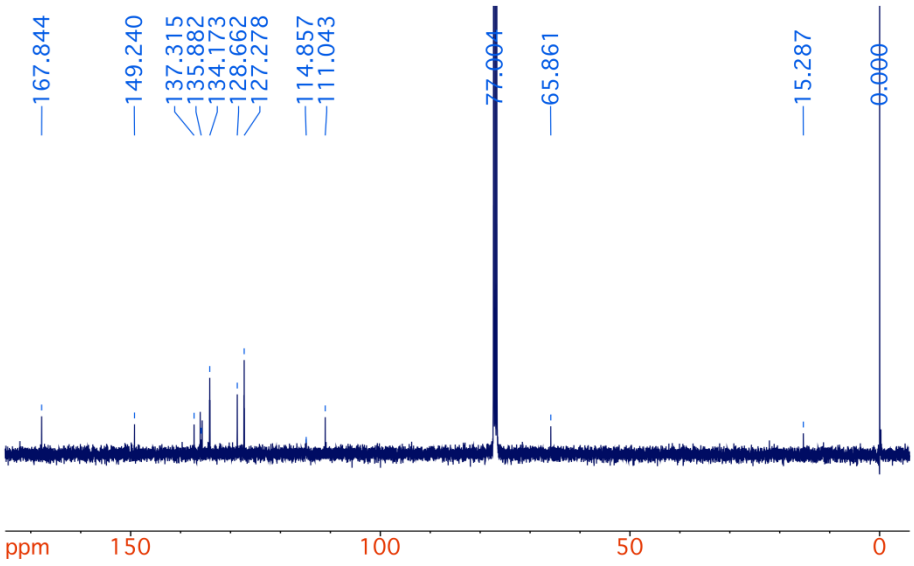

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

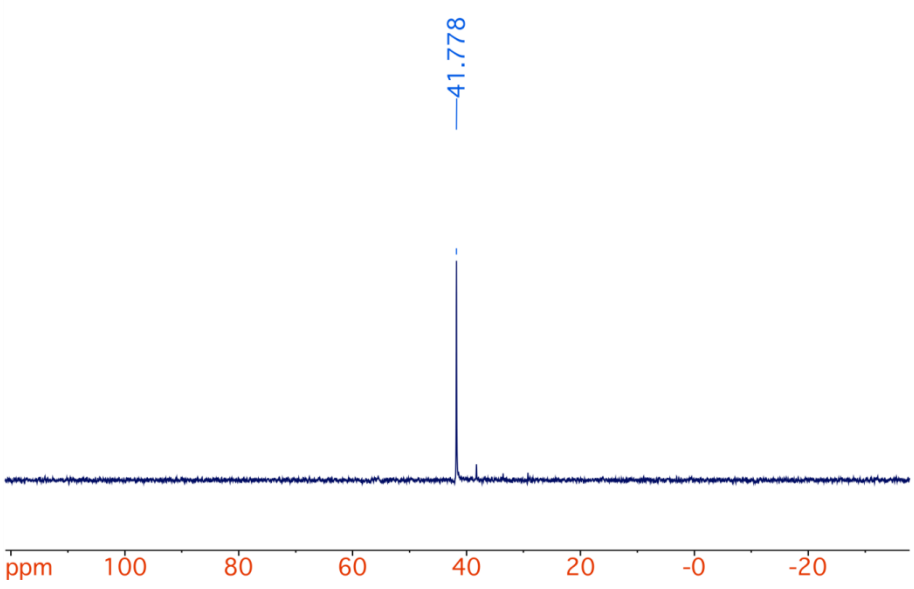

Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

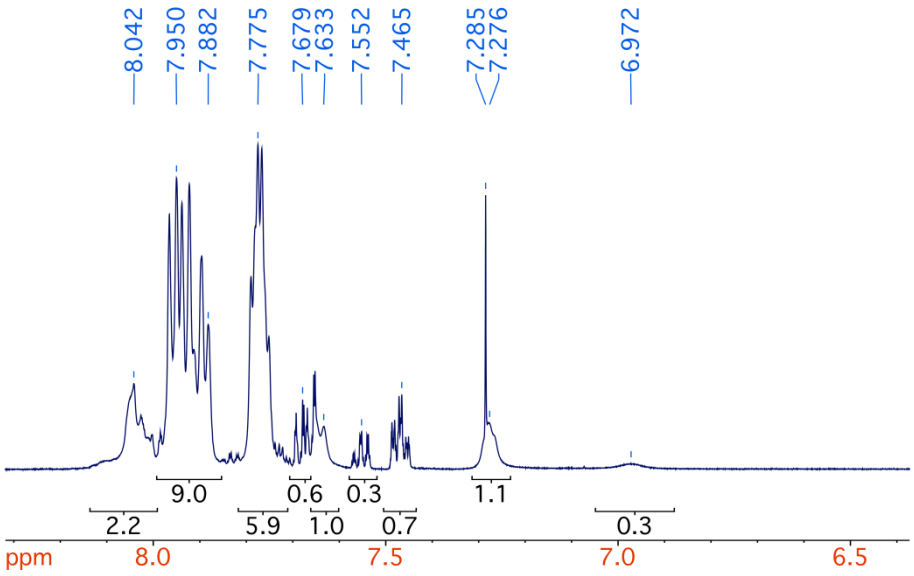

Figure S11. ^{1}H NMR spectrum of **6** in $CDCl_3$.

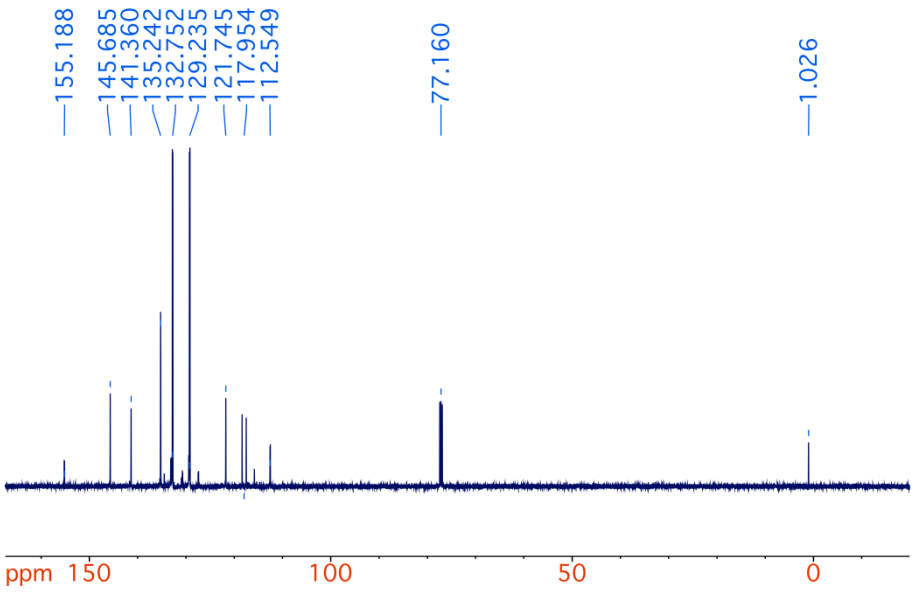

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$.

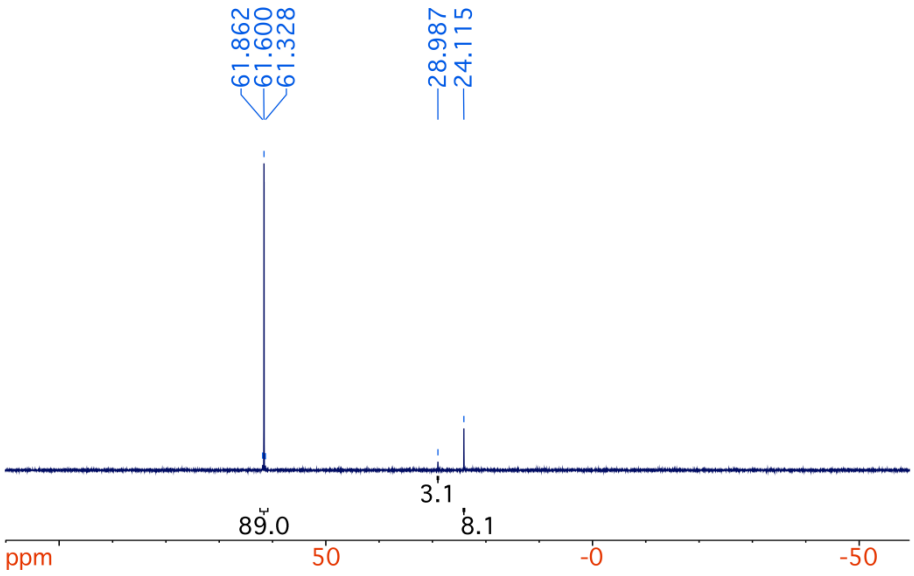

Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$.

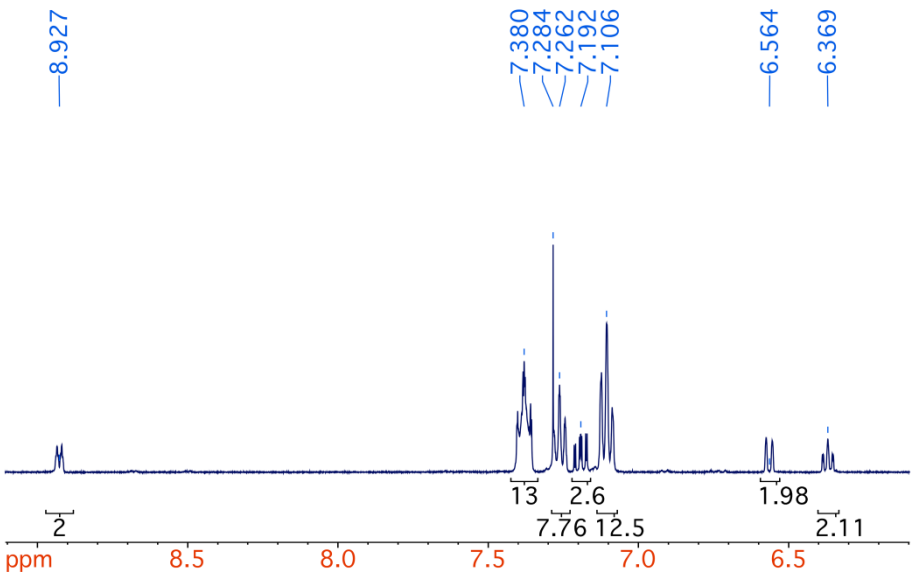

Figure S14. ^{1}H NMR spectrum of **7** in $CDCl_3$.

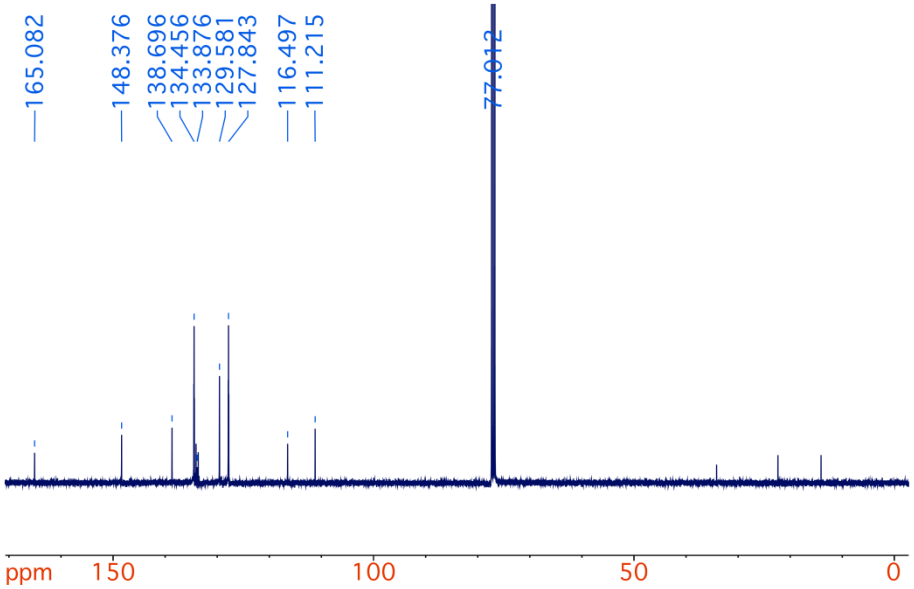

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$.

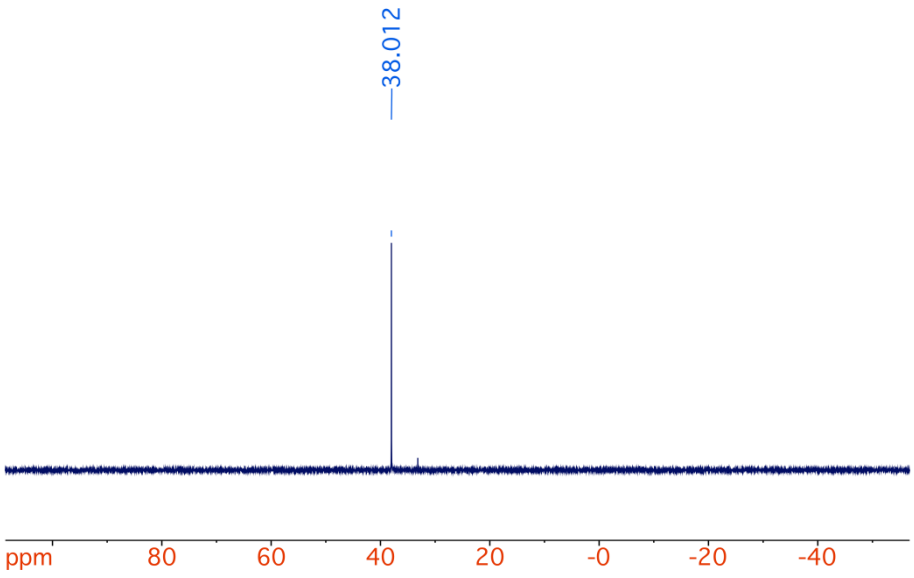

Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$.

- Transition state of the interconversion of $\mathbf{1}^{II}$ and $\mathbf{1}^{I}$

To find the transition state of the conversion of $\mathbf{1}^{II}$ into $\mathbf{1}^{I}$ the calculation was started from the optimized structure of $\mathbf{1}^{II}$ at DFT-PBEPBE cc-pVTZ/SDD(As)-D3BJ level of theory in the gas phase. A 360°-scan (in 10° steps) of the dihedral angle O-As-N-C_2 (i.e., rotation of the pyridyloxy ligand about the As-N-bond) was performed. The energy profile is depicted in figure S17 and shows the lowest energy as well as shortest As•••O separation of the non-bonding O atom of the pyridyloxy ligand to be at an O-As-N-C_2 dihedral angle of ≈180° (thermodynamically stable form of $\mathbf{1}^{II}$). A scan of the As•••O separation of the non-bonding O atom of the pyridyloxy ligand starting at O-As-N-C_2 dihedral angle of ≈180° in the range 2.6-1.7 Å shows only a chelating coordination of the PyO ligand rather than a switch of the As-N toward an As-O bonding mode (Figure 18). Therefore, a scan of the As•••N separation of the bonding N atom of the pyridyloxy ligand at O-As-N-C_2 dihedral angle of ≈180° in the range 2.0-2.8 Å was performed (Figure S19). At an As-N separation between 2.3-2.4 Å a switch from As-N to As-O bonding was detected. The optimization of the transition state starting from this geometry (As•••N: 2.3 Å) was performed. Frequency calculation at the optimized transition state shows one negative mode assigned to the As-N vs. As-O bonding mode (TS1: $\Delta G^{‡}$ = 25.03 kcal mol^{-1}).

The nudged elastic band (NEB) method,[1] as implemented in ORCA, was used to verify if TS1 is the lowest transition state. Starting and end point were set as $\mathbf{1}^{II}$ and $\mathbf{1}^{I}$, respectively and the minimum energy path was optimized with 10 steps. It was found, that a switch between As-N and As-O bonding occurs at an O-As-N-C_2 dihedral angle between 72.6° and 96.0° (Figure S20). Starting from the NEB results, the optimization of the transition state was performed. Frequency calculation at the optimized transition state shows one negative mode assigned to the As-N vs. As-O bonding mode (TS2: $\Delta G^{‡}$ = 23.44 kcal mol^{-1}). The Gibbs free energy profile regarding TS2 of the interconversion of $\mathbf{1}^{II}$ into $\mathbf{1}^{I}$ is given in figure S21 and compared with is phosphorus analogue, which was treated in a similar manner.

Additional for PhAs(PyO)$_2$, geometry optimization followed by frequency calculation of $\mathbf{1}^{I}$, $\mathbf{1}^{II}$ and the transition state TS2 of the isomerization were performed at DFT-B3LYP cc-pVTZ/SDD(As)-D3BJ level of theory in the gas phase (red, figure S22) and including solvent effects (chloroform) using the Conductor like Screening Model (COSMO; blue, figure S22).[2] Atomic radii[3] have been used as reported (1.350 (H), 1.700 (C), 1.608 (N), 1.517 (O), and 1.967 Å (As)). A dielectric constant of 4.8 and solvent probe radius of 3.17 Å was used for chloroform. The f(ε) scaling was set to 0.9057 as described by Klamt et al..[4]

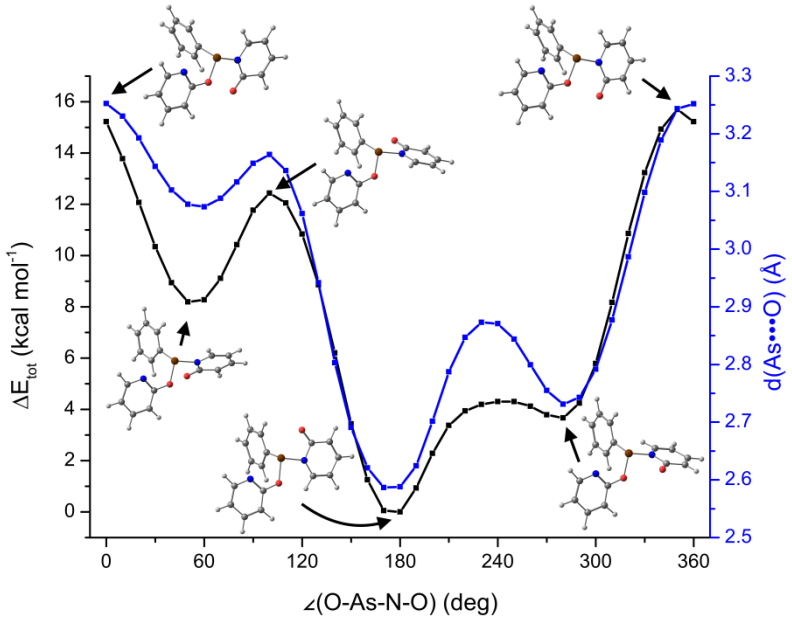

Figure S17. The dihedral angle O-As-N-C_2 was scanned in 10° steps of rotation about the As-N bond from 0-360°. The total energy profile (black) and As•••O separation of the non-bonding O atom (blue) is depicted.

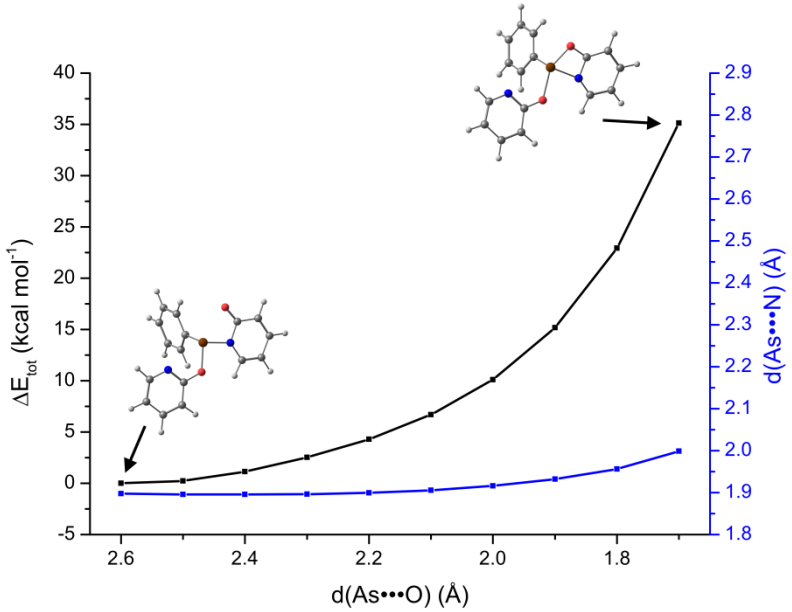

Figure S18. Energy surface scan of the As•••O separation of the non-bonding O atom.

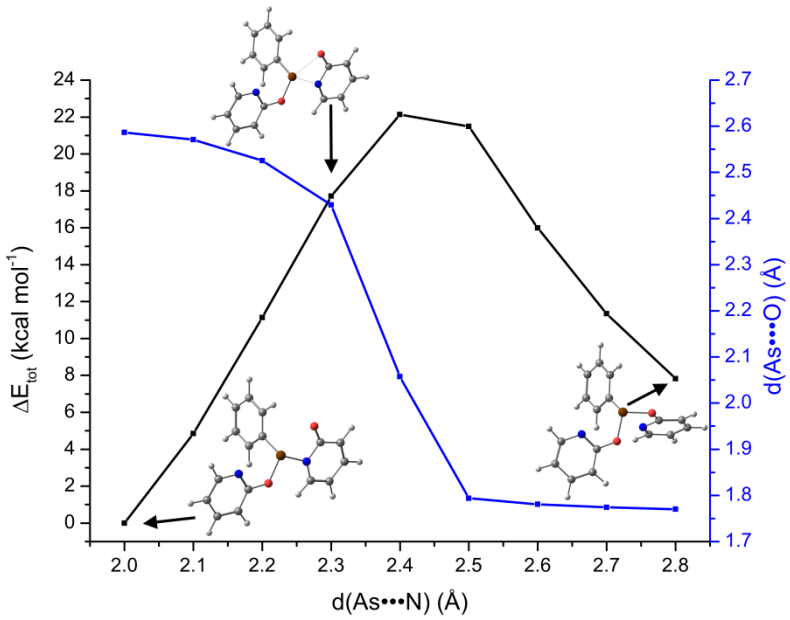

Figure S19. Energy surface scan of the As•••N separation of the As-N bound PyO.

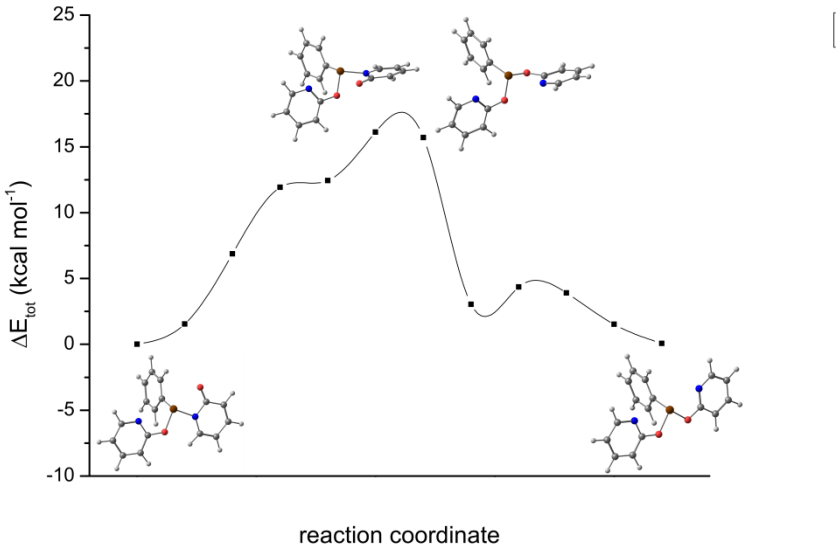

Figure S20. Energy profile of the NEB calculation of the isomerization of isomer $\mathbf{1}^{II}$ into isomer $\mathbf{1}^{I}$ for $PhAs(PyO)_2$.

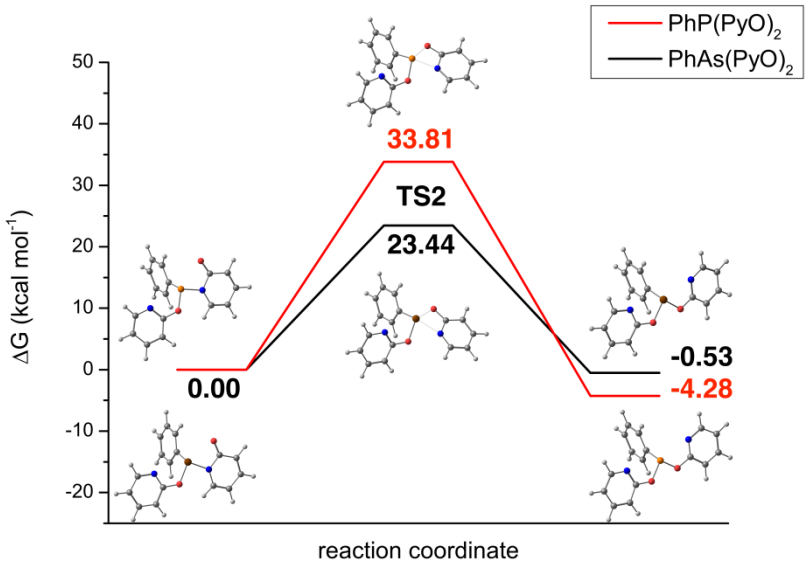

Figure S21. Gibbs free energy plots for the transition state TS2 of the isomerization of isomer $\mathbf{1}^{II}$ into isomer $\mathbf{1}^{I}$ for $PhP(PyO)_2$ (red) and $PhAs(PyO)_2$ (black). ΔG is referenced to $\mathbf{P1}^{II}$ (0.00 kcal mol^{-1}) or $\mathbf{As1}^{II}$ (0.00 kcal mol^{-1}), respectively. G is obtained from frequency calculations at 293.15 K and values are given in kcal mol^{-1}.

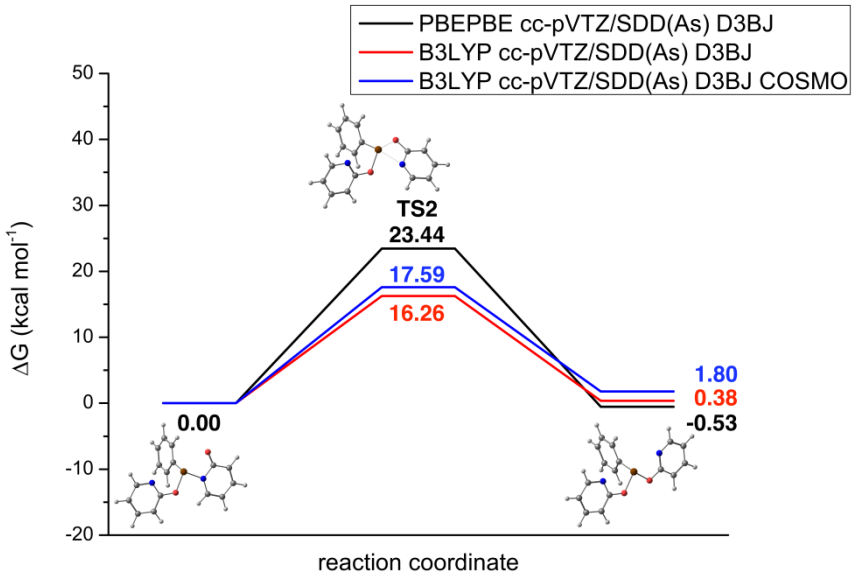

Figure S22. Gibbs free energy plots for the transition state TS2 of the isomerization of isomer $\mathbf{1}^{II}$ into isomer $\mathbf{1}^{I}$ for $PhAs(PyO)_2$ at different level of theory. ΔG is referenced to $\mathbf{As1}^{II}$ (0.00 kcal mol^{-1}), respectively. G is obtained from frequency calculations at 293.15 K and values are given in kcal mol^{-1}.

- NMR spectra of the reaction mixture of the reaction of **2** with $[RuCl_2(PPh_3)_3]$**]**

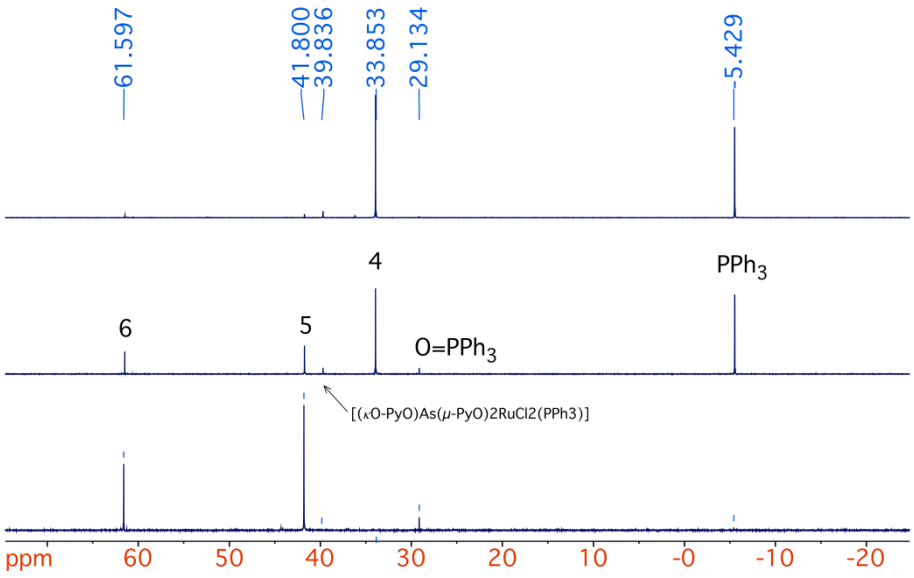

Figure S23. $^{31}P\{^1H\}$ NMR spectra of the reaction mixture of **2** with $[RuCl_2(PPh_3)_3]$ in $CDCl_3$ (after few minutes – top; after 2 h – middle; after 7 h – bottom).

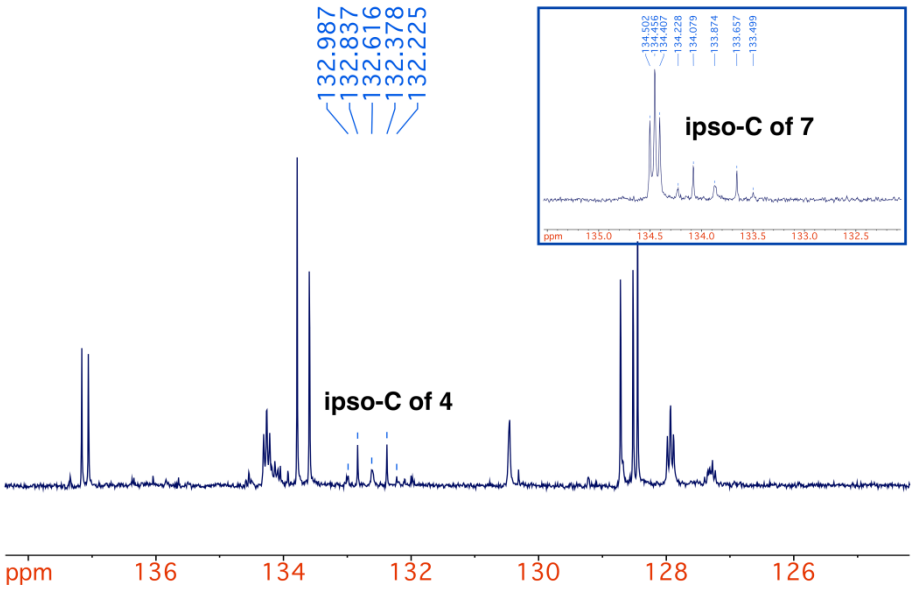

Figure S24. $^{13}C\{^1H\}$ NMR spectra of the reaction mixture of **2** with $[RuCl_2(PPh_3)_3]$ in $CDCl_3$ after few minutes. The characteristic signal of the *ipso*-C atoms of the phenyl groups in a *cis*-Ph_3P-Ru-PPh_3 arrangement is highlighted. The inset shows the NMR signal of the *ipso*-C atoms of the phenyl groups in the *cis*-Ph_3P-Ru-PPh_3 moiety in compound **7** for comparison.

- Single-crystal X-ray structure overlay of $[PhP(\mu\text{-}PyO)_2RuCl_2(PPh_3)]$ and $[PhAs(\mu\text{-}PyO)_2RuCl_2(PPh_3)]$ (**3**)

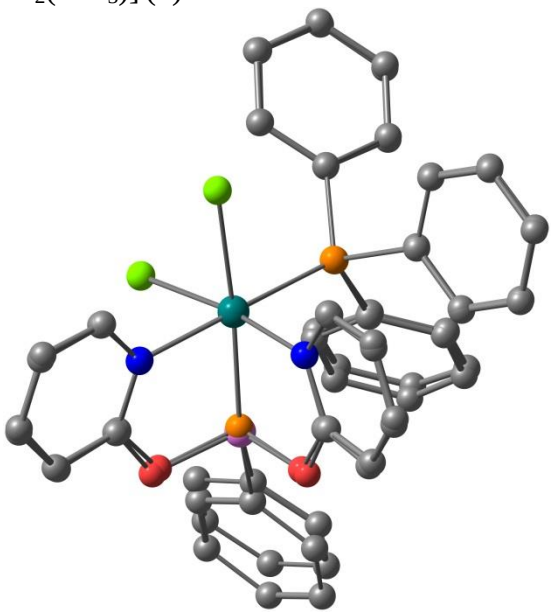

Figure S25. Overlay was generated by root-mean-square distances of the $RuCl_2N_2P$ unit with equal weights on each atom (RMSD = 0.0228 Å). Hydrogen atoms are omitted for clarity.

- Parameters of single-crystal X-ray diffraction data collection and structure refinement

Table S1. Parameters of data collection and structure refinement for **1**, **2** and **3**·1.5$CHCl_3$.

Data sets were collected at 200 K with Mo K_α radiation using a Stoe IPDS-2T diffractometer. Absorption correction: Integration (*X-SHAPE)*. H-atoms were included in the refinement in idealized positions (riding model).

	$PhAs(PyO)_2$ (**1**)	$As(PyO)_3$ (**2**)	**3**·1.5$CHCl_3$
Crystal data			
Chemical formula	$C_{16}H_{13}AsN_2O_2$	$C_{15}H_{12}AsN_3O_3$	$C_{34}H_{28}AsCl_2N_2O_2PRu$·1.5($CHCl_3$)
M_r	340.20	357.20	953.49
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, *C*2/*c*	Triclinic, $P\bar{1}$
a, *b*, *c* (Å)	8.3588(4), 9.2389(4), 10.3537(5)	32.4502(12), 7.2230(3), 13.5042(5)	11.7469(5), 12.8872(6), 16.5916(7)
α, β, γ (°)	85.179(4), 73.420(3), 70.026(3)	90, 108.146(3), 90	107.717(3), 105.382(3), 115.059(3)
V (Å^3)	720.16(6)	3007.8(2)	1928.07(16)
Z	2	8	2
μ (mm^{-1})	2.37	2.28	1.79
Crystal size (mm)	0.45 × 0.38 × 0.15	0.40 × 0.35 × 0.30	0.30 × 0.18 × 0.15
T_{min}, T_{max}	0.466, 0.740	0.542, 0.658	0.721, 0.849
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18924, 3465, 3298	19975, 3338, 3005	22790, 9315, 7827
R_{int}	0.058	0.043	0.038
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.661	0.643	0.660
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.026, 0.067, 1.11	0.047, 0.095, 1.26	0.040, 0.097, 1.09
No. of reflections	3465	3338	9315
No. of parameters	191	296	501
No. of restraints	0	36	104
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.39, -0.70	0.22, -0.37	0.56, -0.78

Table S2. Parameters of data collection and structure refinement for **5**·2$CHCl_3$, **6** and **7**·$CHCl_3$.

Data sets were collected at 200 K with Mo K_α radiation using a Stoe IPDS-2T diffractometer. Absorption correction: Integration (*X-SHAPE)*. H-atoms were included in the refinement in idealized positions (riding model).

	5·2$CHCl_3$	**6**	**7**·$CHCl_3$
Crystal data			
Chemical formula	$C_{46}H_{38}AsClN_2O_2P_2Ru$·2($CHCl_3$)	$C_{23}H_{19}NOP$·Cl	$C_{46}H_{38}AsAuCl_2N_2O_2P_2Ru$·$CHCl_3$
M_r	1162.90	391.81	1275.95
Crystal system, space group	Triclinic, $P\bar{1}$	Hexagonal, $P6_1$	Triclinic, $P\bar{1}$
a, *b*, *c* (Å)	16.0117(5), 17.9816(5), 20.4442(6)	9.3905(2), 9.3905(2), 40.1802(17)	12.3889(6), 12.8306(6), 15.0564(7)
α, β, γ (°)	114.483(2), 109.348(2), 96.110(2)	90, 90, 120	97.133(4), 102.510(4), 94.659(4)
V (Å^3)	4846.5(3)	3068.46(18)	2303.93(19)
Z	4	6	2
μ (mm^{-1})	1.49	0.28	4.62
Crystal size (mm)	0.50 × 0.35 × 0.25	0.50 × 0.25 × 0.25	0.42 × 0.20 × 0.02
T_{min}, T_{max}	0.543, 0.718	0.873, 0.964	0.355, 0.924
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	100356, 28253, 23541	10175, 3833, 3630	48246, 11109, 9248
R_{int}	0.037	0.035	0.050
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.703	0.617	0.661
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.034, 0.084, 1.03	0.033, 0.081, 1.08	0.033, 0.085, 1.07
No. of reflections	28253	3833	11109
No. of parameters	1299	244	514
No. of restraints	239	1	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.74, -0.74	0.24, -0.20	1.27, -1.21
Absolute structure	–	χ(Flack) determined using 1573 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).	–
Absolute structure parameter	–	-0.06 (5)	–

- Additional NBO/NLMO representations

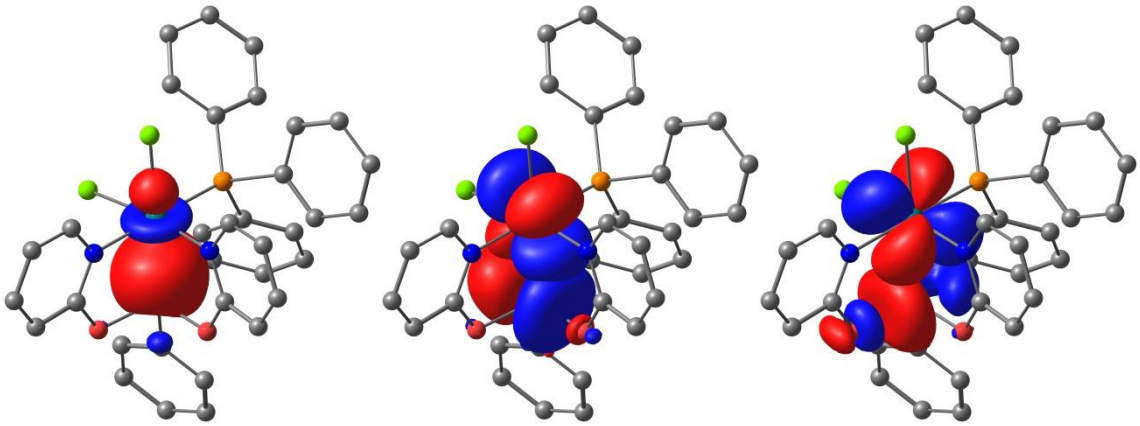

Figure S26. NLMO representation of σ-(As→Ru) bond in **3** (left) and NBO representations of π-(As←Ru) backbonding in **3** (middle, right) shown at an isosurface value of 0.06. H-atoms are omitted for clarity.

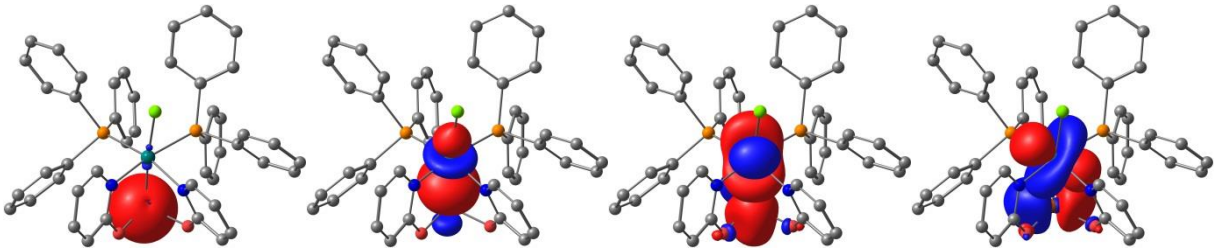

Figure S27. NLMO representation of As lone pair (left) and σ-(As→Ru) bond in **5** (middle left) and NBO representations of π-(As←Ru) backbonding in **5** (middle right, right) shown at an isosurface value of 0.06. H-atoms are omitted for clarity.

- Atomic coordinates of gas phase optimized molecular structures

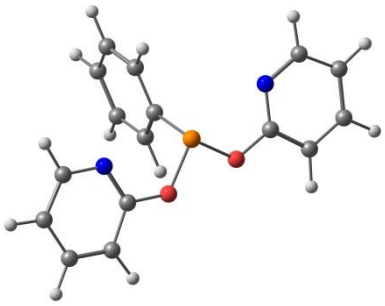

Figure S28. Optimized molecular structure of **P1**^{I}.

Total energy at DFT-PBEPBE cc-pVTZ (for C H N O P) D3BJ level of theory: -1213.49753598913 au.
Gibbs free energy: -1213.26245435 kcal mol^{-1}

Table S3. Atomic coordinates of optimized structure of **P1**^{I}.

P	2.61799291086423	-0.83831663984043	-4.92646840684194
O	3.53042119222041	-0.77833998467142	-3.54755922738452
N	4.26532987173569	-2.87253758425551	-3.93998153264738
N	1.07238066178568	0.73876205541125	-6.64354955555102
O	2.18746087141838	0.74086010744699	-4.68485576850466
C	4.93452228648384	-1.25717206760829	-8.21923475769610
C	3.94994657655036	-1.41499445587449	-7.26830493785496
C	3.92491836726977	-0.60441233057822	-6.15640919336792
C	4.89004133603910	0.36962896646650	-5.99469461242462
C	5.87317234226246	0.52941964907317	-6.94140188348369
C	5.89469876667633	-0.28544940920050	-8.05474708386461
H	4.95269427013567	-1.88848297758659	-9.08355198473383
H	3.19791854434796	-2.16804130098517	-7.38655249675821
H	4.86271096914008	0.99517049079670	-5.12716260500205
H	6.62180489211938	1.28452583178494	-6.81652388754313
H	6.66081618421439	-0.16080664832680	-8.79223335110466
C	0.95681403535873	2.64434955741097	-5.23998026048581
C	0.14955573710355	3.26918289184408	-6.14586232879782
C	-0.20201581484030	2.61587555032910	-7.31740056332123
C	0.28562275752393	1.35534151845004	-7.51260294627568
C	1.39278855457811	1.36301602966044	-5.54824556843150
H	1.25628543261702	3.10035586901355	-4.32211813559474
H	-0.20942327360831	4.25852348648522	-5.94948036095682
H	-0.83138732357646	3.07725788725954	-8.04708242997657
H	0.04581625639111	0.80601476801648	-8.40038920068522
C	4.22503207114955	-1.83876902391987	-3.15150617338100
C	4.87513507331090	-1.78274362532009	-1.92627643716636
C	5.59145785771902	-2.87954391049200	-1.54339652172694
C	5.64257869269885	-3.98981859174473	-2.37261208596865
C	4.96141902576066	-3.93152038907167	-3.55476674125156
H	4.80086633119067	-0.90293142310513	-1.32584545767270
H	6.10952264157794	-2.87971535476757	-0.60646516637860

H	6.19478582784380	-4.86370222348056	-2.10278195371560
H	4.96796787393747	-4.76074273861993	-4.23283657344993

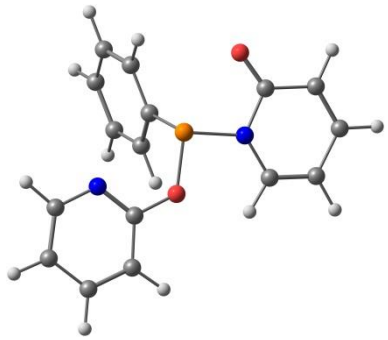

Figure S29. Optimized molecular structure of **P1**^{II}.

Total energy at DFT-PBEPBE cc-pVTZ (for C H N O P) D3BJ level of theory: -1213.49182461239 au.
Gibbs free energy: -1213.25564167 kcal mol^{-1}

Table S4. Atomic coordinates of optimized structure of **P1**^{II}.

P	2.55941897799513	1.57596655910030	-4.02094451835511
O	2.49330190804220	2.60823155326803	-2.72260415621269
N	4.17510221040441	1.47890629462574	-1.73523367767447
N	1.30711216108210	2.47529241477957	-4.88138913681195
O	1.74823004815135	0.99581036641137	-6.46854582420129
C	5.84380516316569	1.90569762818210	-6.35539564227142
C	4.72229004790026	1.43144909511350	-5.71207831194929
C	4.01809606442027	2.25084090170668	-4.85662980066685
C	4.44103393192270	3.54772119024973	-4.64666877396436
C	5.56066432282855	4.02192712425374	-5.28785483879110
C	6.26309039065489	3.19917462047279	-6.14265132529290
H	6.38625447894779	1.26878626550861	-7.02293854216759
H	4.37755221149832	0.43418962487736	-5.88471424795948
H	3.89738954689618	4.18140433187422	-3.97850782292525
H	5.88758411330395	5.02778108307534	-5.12211939261783
H	7.13545764635865	3.56781270452398	-6.64193148291439
C	0.02513074341961	2.54398795657242	-6.89601520899055
C	-0.63633446924353	3.60328196008552	-6.42149671079464
C	-0.33074324891144	4.14070553339167	-5.14054320029701
C	0.62845843964889	3.55583228356388	-4.42024950742594
C	1.06953137920028	1.92963824623169	-6.12219646789966
H	-0.17448628184940	2.11711272533151	-7.85417867799042
H	-1.40684328240817	4.05825259244735	-7.01008377979678
H	-0.85289212285545	4.98766938394275	-4.75493654565958
H	0.90931992924962	3.89702189312418	-3.45324840583216
C	3.26567946159707	2.40249584470646	-1.65524929124736
C	3.06510154199822	3.19037802468534	-0.53275067897529
C	3.87928160109544	2.96980221537093	0.54229915108935
C	4.85261782168910	1.98648194995877	0.47401182959994
C	4.95517751008662	1.27093353359438	-0.68595847568744
H	2.29777713858847	3.93323821900900	-0.52907994119477

H	3.76161341338704	3.55458052747034	1.43117625068864
H	5.50534610237475	1.78932217271200	1.29639132860537
H	5.69038092936046	0.49968956977878	-0.79290040341575

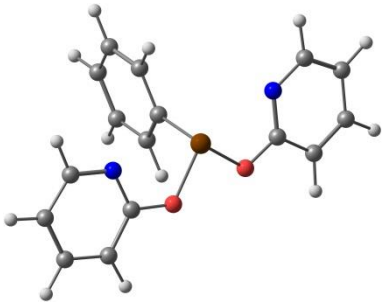

Figure S30. Optimized molecular structure of $\mathbf{1}^{I}$.

Total energy at DFT-PBEPBE cc-pVTZ (for C H N O) and SDD (for As) D3BJ level of theory: -878.73251089777 au.
Gibbs free energy: -878.49947445 kcal mol^{-1}

Table S5. Atomic coordinates of optimized structure of $\mathbf{1}^{I}$.

C	4.96038601995928	-1.17994436276758	-8.16199148598400
C	3.95293530449838	-1.39070094911661	-7.24671587232110
C	3.87260388538639	-0.61556798602207	-6.11349421474904
C	4.80314575985031	0.37631416893417	-5.89169519227111
C	5.81070509723073	0.59014150416839	-6.80303013526076
C	5.88878590389059	-0.18867050644112	-7.93844273838231
H	5.02180904742581	-1.78401022475680	-9.04367150563810
H	3.22835775180642	-2.16151432926231	-7.41742860173359
H	4.72977198725102	0.97219313522016	-5.00673640964980
H	6.53448637485038	1.36038414349865	-6.63218999870725
H	6.67346810759195	-0.02158678203348	-8.64740500087589
C	0.94846655194510	2.72336422600186	-5.32416884160855
C	0.20437332963265	3.29456317300254	-6.31431681527929
C	-0.14647154059554	2.55081542510830	-7.43258779947266
C	0.27858685935031	1.25506681285950	-7.48952072040737
C	1.32946942012666	1.39582563434847	-5.48827279558457
H	1.24281413420727	3.25360955450482	-4.44537435685515
H	-0.10725421955619	4.31525314723131	-6.22649494096964
H	-0.72702234270298	2.97130115827570	-8.22459264261946
H	0.03736460452893	0.63548903413982	-8.32962189228694
C	4.20738315454710	-1.84587596420090	-3.06737835980407
C	4.99421928878639	-1.83420446629613	-1.92055588183103
C	5.74212216866924	-2.94362439362481	-1.65566746043441
C	5.69638890354586	-4.03069151653065	-2.51763505596803
C	4.88748031210098	-3.93610580705499	-3.61289669484617
H	4.99516186489799	-0.97382219275840	-1.28824177431644
H	6.36260504744244	-2.97320606078368	-0.78345391041116
H	6.27185530940740	-4.91240178061664	-2.33723588625844
H	4.81437070926102	-4.74486047640869	-4.31175768680164
As	2.45306230485126	-0.93315333072390	-4.85113202044792
O	3.47366085639224	-0.79765447530469	-3.37203331421893

N	4.15729767290728	-2.86511342655719	-3.88405448194512
N	1.00297188682167	0.68762878434395	-6.53715419827485
O	2.05429028369161	0.80100310962299	-4.56593150378521

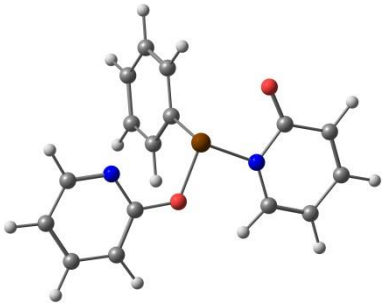

Figure S31. Optimized molecular structure of $\mathbf{1}^{II}$.

Total energy at DFT-PBEPBE cc-pVTZ (for C H N O) and SDD (for As) D3BJ level of theory: -878.732627032363 au.
Gibbs free energy: -878.49862734 kcal mol^{-1}

Table S6. Atomic coordinates of optimized structure of $\mathbf{1}^{II}$.

C	5.84188577944534	1.95516385505162	-6.37608931660693
C	4.72650726489254	1.44187364424177	-5.75243324401599
C	4.03131375163838	2.20367270490639	-4.83967094043820
C	4.45622116336455	3.48218159252890	-4.55004133674064
C	5.56837122830506	3.99774747868316	-5.17367255429807
C	6.26281485859931	3.23293446720100	-6.08601585337531
H	6.37687137349102	1.36215891111608	-7.08873737726182
H	4.38347652309984	0.45743655197102	-5.99147792455875
H	3.91828358498989	4.07128680822438	-3.83914164981321
H	5.89553690041987	4.99202217190684	-4.94862116823987
H	7.12903664673113	3.63428977675321	-6.57051519796980
C	0.04016125241021	2.52996696373988	-6.96285075215665
C	-0.62907132264135	3.60568340844481	-6.52311285753610
C	-0.39233138578974	4.14345634135190	-5.23206823255690
C	0.52062859688195	3.54328844108865	-4.45754387078523
C	1.01752421064444	1.91098800647974	-6.12098626335514
H	-0.11595455057761	2.10713099999311	-7.93080686237142
H	-1.35647045809880	4.07164136347956	-7.15653036338202
H	-0.92283340207720	5.00044896115524	-4.88185355021862
H	0.76256280278710	3.87809945280032	-3.47595122818456
C	3.22113386781341	2.43353511935318	-1.59836066991512
C	3.15181784015111	3.26745273983137	-0.48947293938160
C	4.02697137282298	3.03431005184116	0.53251265680146
C	4.93729864804601	1.99287126902314	0.43705784637862
C	4.91525541110750	1.23352158550171	-0.69831763471100
H	2.43229245526430	4.05614889408600	-0.45948687021478
H	4.00724214555445	3.65554978372124	1.40434567418912
H	5.63478756161849	1.78648097841368	1.21929789631973
H	5.59614634360863	0.41657009235259	-0.82583955353227
As	2.49488024169608	1.41962226269905	-3.97511597404801
O	2.40709663339213	2.62466075152535	-2.61887188160378

N	4.07482431200854	1.45120666341710	-1.69738785855102
N	1.19704790760753	2.46058221071894	-4.88685935553590
O	1.70917027079291	0.94743208639792	-6.39059702233025

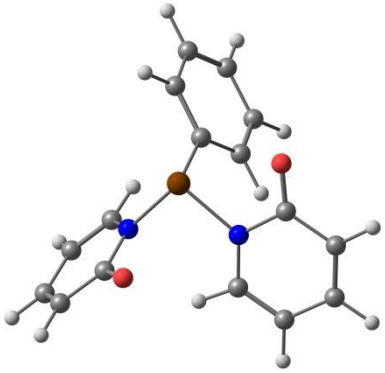

Figure S32. Optimized molecular structure of $\mathbf{1}^{III}$.

Total energy at DFT-PBEPBE cc-pVTZ (for C H N O) and SDD (for As) D3BJ level of theory: -878.727182408373 au.

Table S7. Atomic coordinates of optimized structure of $\mathbf{1}^{III}$.

C	-2.45273966923720	4.81511220243795	0.02849588159679
C	-1.44636738444658	3.96003641680170	-0.16619317495542
C	-0.60794698920200	5.18676840127590	-2.03723485212456
C	-1.70148640806303	6.10229660471698	-1.85302200122500
C	-2.57595809069071	5.91993484671296	-0.85852474778608
H	-3.14433114078875	4.66301163786845	0.82661335232681
H	-1.29670828838158	3.10721200661391	0.45393660375889
H	-1.76234160525490	6.92155572762374	-2.53515896315437
H	-3.38124176652387	6.61309035474116	-0.72331830188046
C	-0.50719348969916	-0.27838019429453	0.65409202645743
C	0.00834072687674	-0.03182777636735	1.90471816655352
C	0.79115034910228	1.08374129590208	2.11988916416769
C	1.05056563758777	1.95362112202837	1.08801814783573
C	0.52723841188551	1.71824731417647	-0.16622535125346
C	-0.24030998580246	0.59449514277997	-0.37919858940991
H	-1.10669515912860	-1.14785139738901	0.48095312874704
H	-0.19125701613641	-0.70846485995130	2.70956771644176
H	1.19994181354235	1.27031303079760	3.09141160179210
H	1.65698146744022	2.81638811836508	1.26024809885237
H	-0.63481446101751	0.39597576615198	-1.35626424651343
C	3.35811820065913	3.16132544640453	-1.03005678678067
C	4.54187353208142	3.78797259658883	-0.51849114433392
C	4.46778449226602	5.00647793942085	0.03170300017488
C	3.23172185490020	5.70229619135686	0.11652449345317
C	2.14052767911967	5.10944978821257	-0.37678838183960
H	5.45570616866623	3.24124457436309	-0.59563196014457
H	5.35382314880707	5.46948808434641	0.41608843848709
H	3.17117649866787	6.67660029701270	0.54677774833802
H	1.18147775409960	5.56921162813445	-0.35521572350759
As	0.79877623216131	2.88322896836902	-1.68637391081807
O	3.27871871030773	2.05971394981224	-1.52646863232891

N	2.19780235951356	3.87847682393264	-0.92526685861773
N	-0.54662062855264	4.12359606246981	-1.16763826367293
O	0.26175180524074	5.29403739858389	-2.86621960863661

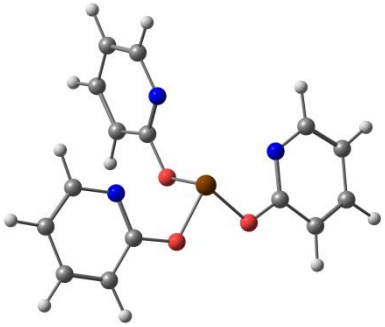

Figure S33. Optimized molecular structure of $\mathbf{2}^{I}$.

Total energy at DFT-PBEPBE cc-pVTZ (for C H N O) and SDD (for As) D3BJ level of theory: -969.649991768985au.

Table S8. Atomic coordinates of optimized structure of $\mathbf{2}^{I}$.

N	8.07417620375816	1.74481977477825	12.36390354761620
N	10.92415255401970	5.01657239642641	9.17576391667346
N	8.58820618979280	2.27632580427564	8.83746478403818
O	9.86499531367208	3.01627654446810	12.78588902948437
O	11.16104360953122	4.49360474985890	11.33744380681811
O	10.26440583342787	2.29503734426864	10.34808393126537
C	9.01652469401744	2.09449007157153	13.19844217606115
C	9.14741528678446	1.54435828579747	14.46713818255505
H	9.93877049779150	1.86806584016085	15.10649977402212
C	8.23961783793194	0.59509251694117	14.83867568025851
H	8.30590175781449	0.14410652242362	15.80756788776920
C	7.23410927081567	0.21752938317486	13.96059316515347
H	6.51089390856304	-0.52316309112216	14.22400226951187
C	7.19873503166101	0.82582599540660	12.73819104592812
H	6.44603458531716	0.57353683509748	12.01899460266942
C	11.64096450419223	5.09376362820932	10.26530501658012
C	12.85371201818055	5.76775339204557	10.32806895951214
H	13.39748552073259	5.79787877855846	11.24631732151325
C	13.30079418961900	6.36751444566561	9.18614052063899
H	14.23231102732049	6.89552525995143	9.19082831187848
C	12.54774360886886	6.29110494014653	8.02361611055274
H	12.87357688461235	6.74931516166524	7.11536894994608
C	11.36809036084155	5.60453077154637	8.07666086001871
H	10.74537378051995	5.51196668054251	7.20997446112947
C	9.69097069614665	1.74863774030371	9.28905259503218
C	10.29351276711955	0.63897324758795	8.70984339179409
H	11.19749530874131	0.25210731194250	9.12585530989117
C	9.69051373457461	0.08608966820221	7.61729616255596
H	10.12457641886470	-0.77020043625911	7.14304317437092
C	8.51712780378415	0.63858595823063	7.12817076362097
H	8.01880356376413	0.23142356230049	6.27530147994051
C	8.01417911225299	1.73046212842030	7.77776880731275
H	7.10988249455667	2.19715551311775	7.44191434446636

As 9.57163563040913 3.70012127429519 11.16298765942044

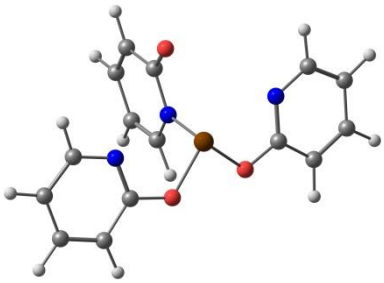

Figure S34. Optimized molecular structure of $\mathbf{2}^{II}$.

Total energy at DFT-PBEPBE cc-pVTZ (for C H N O) and SDD (for As) D3BJ level of theory: -969.650697007676 au.

Table S9. Atomic coordinates of optimized structure of $\mathbf{2}^{II}$.

N	6.98905511960453	4.34323081864293	9.58034781733799
N	11.78151449548090	2.80691517795832	11.39066967179243
N	9.18937415343058	2.23095161105775	9.85813410307403
O	7.60414717771286	3.52039472692319	11.56182138359209
O	9.78259524153025	2.81950070271306	12.38352277253049
O	10.17890357151473	3.43708298618444	8.27179194944255
C	6.63004379166509	3.91188392967665	10.75915446783481
C	5.30733070194860	3.84848758108171	11.17388264874649
H	5.07080967141649	3.48820230449292	12.15075517628613
C	4.35219214167143	4.26105632683535	10.28837737390562
H	3.31860504874296	4.22818135700830	10.56600835546433
C	4.72276804173880	4.72163804459461	9.03398620422794
H	3.99651612955978	5.04930756482452	8.32252244332341
C	6.05551807517680	4.74327185183947	8.73260929648042
H	6.40234258014864	5.08822806791813	7.77995222512287
C	11.06164899918333	2.49113892965658	12.43309613913248
C	11.57928840071240	1.84116951146494	13.54452600727149
H	10.94433951826286	1.60880502476071	14.37088921568245
C	12.90813291462665	1.52454274288701	13.52325758070600
H	13.34935122602073	1.02145349510139	14.35913415306785
C	13.68190484836825	1.85578103887477	12.42118099136962
H	14.72269829805442	1.61933691491306	12.37832754753891
C	13.06802219738914	2.49841500930334	11.38310493743697
H	13.61361510119898	2.77959354539174	10.50554937388958
C	9.71347376920013	2.37787276571614	8.59741457999023
C	9.65017962412587	1.20344867560703	7.76045575831959
H	10.05249362685059	1.29717450396191	6.77567644805654
C	9.11210606840713	0.07067538090744	8.21601730683934
H	9.07262494834766	-0.79221319541342	7.58244424866994
C	8.58459078184390	-0.01526514172100	9.53934770804952
H	8.15374224033925	-0.91935613495418	9.90761749292399
C	8.64568455938777	1.07132454717316	10.30659046632091
H	8.27826344431848	1.10397917941477	11.30758972662017
As	9.27265656202007	3.74221913520326	10.92598209895283

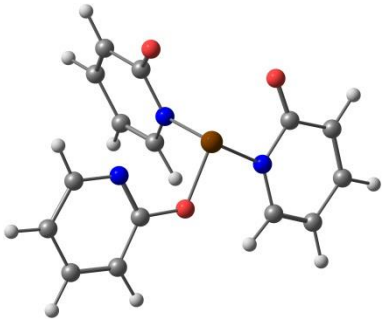

Figure S35. Optimized molecular structure of $\mathbf{2}^{III}$.

Total energy at DFT-PBEPBE cc-pVTZ (for C H N O) and SDD (for As) D3BJ level of theory: -969.645030251708 au.

Table S10. Atomic coordinates of optimized structure of $\mathbf{2}^{III}$.

N	9.04330552852556	5.91349170042813	9.06525809755889
N	10.86638995358709	3.08607527414214	11.82723225408266
N	8.40902025326606	4.25388416489764	11.55556674203067
O	10.63791040133035	5.22357573474282	10.46469872658418
O	9.38244121635748	1.47281927745404	11.76599579583571
O	6.96899256178691	3.37998100794445	10.10194738368379
C	10.14749947337916	6.18878407617505	9.70217445182262
C	10.79048061334618	7.41410639979819	9.61266148800188
H	11.69391331892400	7.58823389810661	10.15486396439338
C	10.21966834610017	8.36447681512028	8.81230664979086
H	10.68138747490862	9.32548108817205	8.71427017908533
C	9.04672454028695	8.08179415587596	8.13078172831105
H	8.57938202788762	8.80619033554928	7.50010388297380
C	8.50075569493054	6.83847669817923	8.29156695351696
H	7.59528360954261	6.56087106103404	7.79194441082905
C	10.39630430343062	1.88640484954150	12.28452052667958
C	11.15095580352206	1.25571789895611	13.32803772821996
H	10.79247120253276	0.31976335131366	13.69606563634285
C	12.25486943388505	1.84815937847745	13.79975453259263
H	12.81658992207229	1.37725847413290	14.58069329193571
C	12.70161516070579	3.09576801019833	13.28302553806864
H	13.58450500354177	3.56480899748520	13.65582313568878
C	11.98788464192723	3.66805249834754	12.30893873054602
H	12.24952848602764	4.60028657892378	11.86585621082950
C	7.13041004743021	3.96238128602432	11.13805250527944
C	6.07430731389259	4.41156214537563	12.01554643954473
H	5.07627699601375	4.18100328684945	11.71386609216425
C	6.35492469897093	5.07755325110432	13.13549730552018
H	5.56044587953875	5.40538505083056	13.77464780340511
C	7.70543881488442	5.36501087284740	13.50198006593817
H	7.93613793850888	5.90217753785655	14.39464725908197
C	8.67480225396420	4.93907250437685	12.69670729913389
H	9.70740368903251	5.11408606927744	12.89668663081248
As	9.73381759595919	3.64832228046105	10.41664064971527

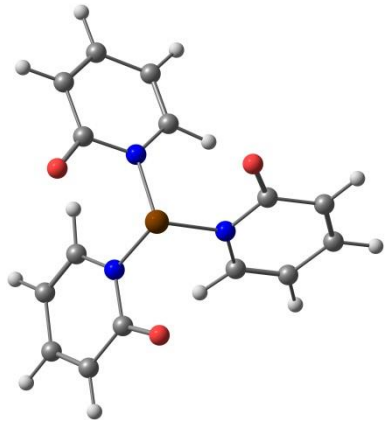

Figure S36. Optimized molecular structure of $\mathbf{2}^{IV}$.

Total energy at DFT-PBEPBE cc-pVTZ (for C H N O) and SDD (for As) D3BJ level of theory: -969.645485209008 au.

Table S11. Atomic coordinates of optimized structure of $\mathbf{2}^{IV}$.

N	0.14387157402032	-1.58135617730681	-0.03436492967953
N	-1.43819203560498	0.65988128567051	-0.01865967802792
N	1.29393217631790	0.90954618356137	-0.03233744823282
O	-1.58480950696787	-2.10699637995250	-1.29177474708915
O	-1.04239357841376	2.42034848704520	-1.27946184059967
O	2.60732968500110	-0.31283075425212	-1.30772516650589
C	-0.77195037186649	-2.49607904223605	-0.48316180861420
C	-0.69374027575356	-3.81173994542807	0.08104812840482
H	-1.39635816376922	-4.53512732418439	-0.26951623084271
C	0.22759474982784	-4.08446658736770	1.01312649112733
H	0.27830956902457	-5.06638331081950	1.43765951295014
C	1.14584690393632	-3.09211192230741	1.45288612880438
H	1.88445050651950	-3.30836291363878	2.19156852000888
C	1.07482267031871	-1.87909744619117	0.90058690748590
H	1.73507842880846	-1.09029447165042	1.17181407085223
C	-1.77723973806736	1.91057726330739	-0.46327150122544
C	-2.94977230601471	2.50026507293932	0.11357708302211
H	-3.22853107730043	3.47074240106249	-0.23329612133295
C	-3.63702620781952	1.83789110711603	1.05219857745126
H	-4.50833125128549	2.28457576158665	1.48609045448848
C	-3.23230613993464	0.54612209304758	1.48673287180325
H	-3.78138167684864	0.01392568996169	2.23053002011815
C	-2.15191426644445	0.00163293742007	0.92299259293903
H	-1.79610256809625	-0.96479116562472	1.18975735149326
C	2.54184962523339	0.57768493744134	-0.49002738022010
C	3.64494901301268	1.29718134901763	0.07648693182018
H	4.62106641129081	1.05340365759728	-0.28076060252782
C	3.42503235342145	2.22228337034173	1.01873111179451
H	4.25217759315165	2.75252766628354	1.44491316128160
C	2.10858893529784	2.51766308099059	1.46715631369902
H	1.93016781940045	3.25833482428045	2.21382892453083
C	1.09085552498333	1.85558192541659	0.91275757308718
H	0.07884438785775	2.03089136225602	1.18997101071539
As	-0.00547076323669	-0.00053101538386	-1.05600528297971

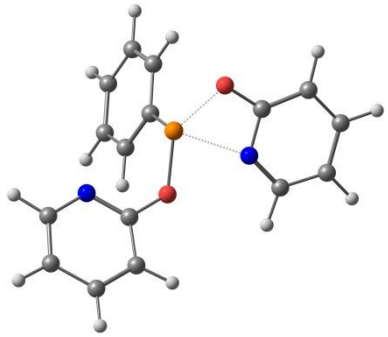

Figure S37. Transition state TS2 molecular structure of $PhP(PyO)_2$.

Total energy at DFT-PBEPBE cc-pVTZ (for C H N O P) D3BJ level of theory: -1213.43766429196 au.
Gibbs free energy: -1213.2017545 kcal mol^{-1}

Table S12. Atomic coordinates of transition state structure of $PhP(PyO)_2$.

P	-0.42036380152162	-0.88593950818298	-0.49697089671028
O	-0.50578372039323	0.08013035515396	0.90725925448934
N	1.08846964376506	-1.17896876523905	1.89991280345840
N	-2.32136245647907	-0.11364472999366	-0.68015979879053
O	-0.95228267171409	-0.43915951508817	-2.22267669174855
C	3.23872315364954	-0.56240331450284	-2.19918776737207
C	2.00099604096898	-0.99733121323935	-1.78637884599950
C	1.20665693320694	-0.19923043208328	-0.98802519003644
C	1.66463460581418	1.04501159627014	-0.61543906144514
C	2.90004436171772	1.48708041154961	-1.03446045586337
C	3.69093459728459	0.68389960691307	-1.82383156100721
H	3.85077278144032	-1.19315462825857	-2.81083950540062
H	1.64798044835983	-1.96545511849216	-2.07980178025431
H	1.05996849031511	1.66817479582373	0.00680670270379
H	3.24637171862059	2.45683480381994	-0.74043722659200
H	4.65418772435566	1.02478219911510	-2.14333546859835
C	-3.22544776761770	0.12864874092472	-2.84573439058434
C	-4.42050150001357	0.42011731225647	-2.25868784826900
C	-4.56853806792211	0.43991172834409	-0.86901494364793
C	-3.47852838179416	0.15902377204016	-0.10564408110911
C	-2.17023144935151	-0.13663491465146	-1.97928443817312
H	-3.08811256001385	0.10261131297605	-3.90352861745036
H	-5.26802295033665	0.63773236438631	-2.87609018569251
H	-5.50746415148152	0.67296311107314	-0.41777345004463
H	-3.49891141150012	0.15406459987574	0.96370118605457
C	0.33281049529476	-0.11882814682698	1.91401400911148
C	0.35755184237545	0.81685334153643	2.94168354552168
C	1.22196431993414	0.60300213824362	3.97633646923010
C	2.03445037407842	-0.51969612755825	3.96872104847131
C	1.92454517217582	-1.37292215770449	2.90686318206123
H	-0.28482877908921	1.66920683103543	2.89708505946576
H	1.27185356454029	1.30234231810467	4.78573519430450
H	2.72524963259240	-0.71635528121566	4.75970507102652
H	2.53001526873853	-2.25506769640551	2.84981519889073

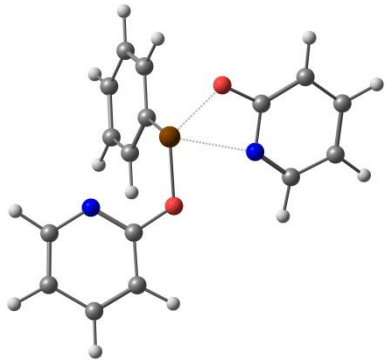

Figure S38. Transition state TS1 molecular structure of $PhAs(PyO)_2$.

Total energy at DFT-PBEPBE cc-pVTZ (for C H N O) and SDD (for As) D3BJ level of theory: -878.691966775811 au.
Gibbs free energy: -878.45873675 kcal mol^{-1}

Table S13. Atomic coordinates of transition state structure of $PhAs(PyO)_2$.

As	2.76612201053320	1.24613344554403	-3.82721928518560
O	2.62446158311834	2.58661782296214	-2.54572143573027
N	4.36823071544493	1.56751853033633	-1.57898948464059
N	1.10371565328930	2.87628346476877	-4.66458095809418
O	1.69473766897406	0.93730715428944	-5.40553851829698
C	5.43431255905754	2.22483925302505	-6.85561909518332
C	4.43569166270139	1.64529039770198	-6.10628720507212
C	4.09808650491190	2.16458831676439	-4.87194583949456
C	4.77558185363422	3.26479546247171	-4.39002784734067
C	5.76811292950331	3.84930902621395	-5.14183211632509
C	6.09953360866117	3.32933972498533	-6.37382255321667
H	5.68846137121085	1.81905137560261	-7.81301520436888
H	3.90505948266091	0.79950171643180	-6.48721850034873
H	4.51908484277468	3.66770758345114	-3.43740257060538
H	6.28365282477893	4.70955296804314	-4.76730401880045
H	6.87357437901758	3.78493911746040	-6.95650456385471
C	0.14575682919060	2.19919800613544	-6.71815671155825
C	-0.52901472054284	3.38569408027599	-6.76664421905278
C	-0.38331661448365	4.32831195521861	-5.75468664889456
C	0.45215742802127	4.02219302425904	-4.71865860296553
C	0.97359331044159	1.98962397482262	-5.61982413212590
H	0.05997999705831	1.45651534462727	-7.48025980865841
H	-1.17522940824729	3.59224183003191	-7.59542406378879
H	-0.90470107637980	5.25990577351716	-5.78219620291861
H	0.61424025533761	4.69882492947990	-3.90458111937782
C	3.35248590519650	2.38755168329415	-1.47213209496915
C	3.04268438259254	3.04668780949393	-0.28406024221827
C	3.84339872472077	2.82317495993553	0.79658384379815
C	4.91871746742441	1.95114392269056	0.69095394150408
C	5.12833871680487	1.34973273098194	-0.51605453012761
H	2.19923219176029	3.70086952909722	-0.24896903139103
H	3.63845384274453	3.31638251122455	1.72483256413883
H	5.56288072608884	1.75398032083837	1.52008014602814
H	5.94242239199914	0.66660825402359	-0.65299189086430

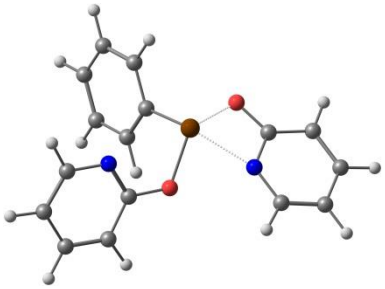

Figure S39. Transition state TS2 molecular structure of $PhAs(PyO)_2$.

Total energy at DFT-PBEPBE cc-pVTZ (for C H N O) and SDD (for As) D3BJ level of theory: -878.694712972797 au.
Gibbs free energy: -878.461278 kcal mol^{-1}

Table S14. Atomic coordinates of transition state structure of $PhAs(PyO)_2$.

As	-0.40783083181757	-1.07004308012623	-0.41592973254620
O	-0.53526294133198	0.08902470374752	1.01472770314567
N	1.05742524198010	-1.17986473659029	1.95188883017637
N	-2.42901306367904	-0.17987589443119	-0.66625791456593
O	-1.03429091618564	-0.57763084287523	-2.22403871594964
C	3.30615473447841	-0.53378896386404	-2.19398737217917
C	2.09762087958378	-1.02723696061035	-1.75671368205672
C	1.26459123603130	-0.25389176285399	-0.97807174507955
C	1.64875645932500	1.02446121078929	-0.64139396377244
C	2.85282613739958	1.52480363709289	-1.08240973052918
C	3.68468780406978	0.74600982099792	-1.85627248672502
H	3.94956354540037	-1.14388240167486	-2.79419808502690
H	1.80391933495506	-2.02311298522968	-2.02527745616057
H	1.00838785174554	1.62618824832584	-0.03427224489474
H	3.14492904029248	2.52105588345825	-0.81988131525681
H	4.62334617976598	1.13478315925646	-2.19376573107830
C	-3.24718420306035	0.11488838186519	-2.86276282596638
C	-4.44387188140646	0.48288037107334	-2.32682018195415
C	-4.63829499959758	0.51966348854034	-0.94439071184161
C	-3.59148435708947	0.17444037274107	-0.14722784385145
C	-2.23245558597726	-0.21343076289570	-1.96419050869848
H	-3.07107638039500	0.07793225965337	-3.91475670498586
H	-5.25163350318492	0.74946511425827	-2.97765829932976
H	-5.57446400100367	0.81370151166973	-0.52376873816132
H	-3.65553618049152	0.18111627036039	0.92099838732016
C	0.31851795871819	-0.10176081627989	1.99505313264775
C	0.40873956550480	0.82953813976506	3.02558688442077
C	1.31219804024561	0.59320005653719	4.02028813075889
C	2.10283971546651	-0.54591991825900	3.97802346158937
C	1.93229364441457	-1.39397166487887	2.92104121937203
H	-0.21739164728126	1.69482217953659	3.01197763068075
H	1.41088250448291	1.28866578951707	4.82870193181955
H	2.82192229940863	-0.75730132344639	4.73924487714433
H	2.51798981923308	-2.28732869517006	2.83685032153455

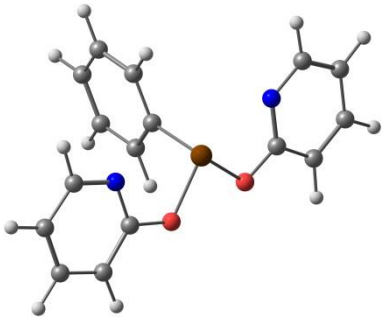

Figure S40. Optimized molecular structure of $\mathbf{1}^{I}$.

Total energy at DFT-B3LYP cc-pVTZ (for C H N O) and SDD (for As) D3BJ level of theory: -884.072801288045 au.
Gibbs free energy: -883.85994507 kcal mol^{-1}

Table S15. Atomic coordinates of optimized structure of $\mathbf{1}^{I}$.

C	4.96801126036032	-1.14943531183142	-8.15568458222212
C	3.96715025315196	-1.34313074607965	-7.21196526534522
C	3.91189982524558	-0.54575185863591	-6.07459959910076
C	4.86326799321141	0.44994875301045	-5.88119449432017
C	5.86545321786715	0.64515288674251	-6.82338960392687
C	5.91842652041195	-0.15371404496274	-7.96075065643707
H	5.00749960546741	-1.77124799146719	-9.04004807976066
H	3.22842118525070	-2.11994223193406	-7.36674588495905
H	4.81516821203149	1.06623604779366	-4.99454132295068
H	6.60509462041766	1.42023981077846	-6.67169963991324
H	6.69927896375805	0.00025677204257	-8.69357729884536
C	0.91591493853446	2.79776757737039	-5.37132901830378
C	0.13801672926957	3.27020543412199	-6.40894588755081
C	-0.19846087426551	2.42404434016076	-7.46772131369825
C	0.27027464201838	1.12392292967961	-7.43368672509258
C	1.34427451776604	1.46560751078329	-5.43087830627680
H	1.19962569648645	3.41446117119588	-4.53219850048146
H	-0.20940645797957	4.29442732151000	-6.39887237521610
H	-0.80501629683797	2.76703882862662	-8.29257689824745
H	0.04016134546524	0.42528841892906	-8.22880402940457
C	4.24637086199771	-1.78874121411834	-2.99763854314627
C	5.06799455885740	-1.88225557610028	-1.86730315597413
C	5.76042856200531	-3.05996481993241	-1.67113816120826
C	5.62317724790879	-4.10787451138239	-2.58381841568094
C	4.78420702998826	-3.92025677176591	-3.66638078142869
H	5.14037468556690	-1.04661000460714	-1.18780788792770
H	6.40637280568845	-3.16823353453304	-0.81009668802072
H	6.15363909117965	-5.03944935856212	-2.45587574209069
H	4.64145881463000	-4.69947809980075	-4.40524927447241
As	2.48028985371567	-0.85785420195838	-4.76886793776475
O	3.55816326460017	-0.67825147771270	-3.25064861168639
N	4.11064094208252	-2.78521763193674	-3.87222574560956
N	1.02767942573820	0.65324573086603	-6.43898047158645
O	2.10379875841014	0.94980983370988	-4.46763929135002

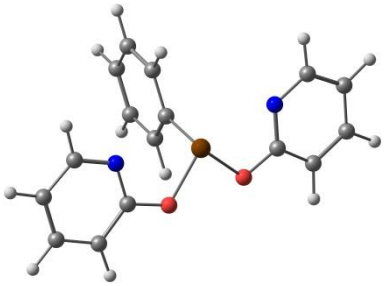

Figure S41. Optimized molecular structure of $\mathbf{1}^{I}$.

Total energy at DFT-B3LYP cc-pVTZ (for C H N O) and SDD (for As) D3BJ COSMO level of theory: -884.081491281782 au.
Gibbs free energy: -883.86915122 kcal mol^{-1}

Table S16. Atomic coordinates of optimized structure of $\mathbf{1}^{I}$.

C	4.96133062775113	-1.15024832248384	-8.14699782125778
C	3.95866939899059	-1.34862964949534	-7.20503614447722
C	3.89855338519439	-0.55259658627527	-6.06619760180713
C	4.84689086122668	0.44621509042386	-5.86961834808162
C	5.85106279484644	0.64654476827190	-6.80965394511964
C	5.90872684862119	-0.15103514084583	-7.94887080025450
H	5.00404481924858	-1.77083737331261	-9.03187593819965
H	3.22324527267066	-2.12757482969223	-7.36266304698489
H	4.79782401009884	1.06274300306692	-4.98328210179741
H	6.58746142989195	1.42387174712927	-6.65494789721578
H	6.69035516071772	0.00663282175830	-8.67992597806318
C	0.92424196717189	2.79708344729388	-5.37516812441733
C	0.16077964305592	3.27785195277030	-6.42096804831265
C	-0.17905911785631	2.43269728484495	-7.47994205916444
C	0.26935196156258	1.12545333544142	-7.43907095020940
C	1.33256743344094	1.45936109828189	-5.42837884163839
H	1.20965393696061	3.41476799117876	-4.53722320274380
H	-0.17140224743880	4.30675874986790	-6.41681633704774
H	-0.77384014583021	2.78205498896720	-8.31055021659277
H	0.03441176883336	0.42831565715075	-8.23350051321612
C	4.23589231412397	-1.79708247304381	-2.99203734007773
C	5.07069941394520	-1.88017924058185	-1.87178514022015
C	5.77901548604022	-3.05092064989814	-1.68388830338439
C	5.64268094678466	-4.10004317493147	-2.59587957691525
C	4.78875546543018	-3.92323078188798	-3.66870105421912
H	5.14412917603322	-1.04491792947698	-1.19180656369479
H	6.43624225731614	-3.15179887120895	-0.83099164506587
H	6.18507399315940	-5.02546655411464	-2.47416983030144
H	4.64583491877414	-4.70442906165567	-4.40483675722751
As	2.46102413496543	-0.87643595477055	-4.76916538362160
O	3.53215994057761	-0.69135318908490	-3.24120782773965
N	4.09940070889404	-2.79388151947075	-3.86541919979068
N	1.01245791231559	0.64710623179786	-6.43476462515118
O	2.08141532248198	0.93344711398564	-4.45753902598915

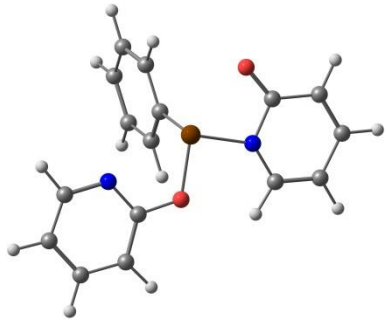

Figure S42. Optimized molecular structure of $\mathbf{1}^{II}$.

Total energy at DFT-B3LYP cc-pVTZ (for C H N O) and SDD (for As) D3BJ level of theory: -884.073982164335 au.
Gibbs free energy: -883.86055649 kcal mol^{-1}

Table S17. Atomic coordinates of optimized structure of $\mathbf{1}^{II}$.

C	5.88790088215515	1.95798901340592	-6.34222252757080
C	4.76029427527622	1.44844313052772	-5.71082625759675
C	4.03343438287211	2.24239153198894	-4.82896659648814
C	4.44050207400552	3.54900068105797	-4.58125314869798
C	5.56557853708981	4.05991822424910	-5.21556403970969
C	6.29183388345919	3.26431284780924	-6.09451145107499
H	6.44725098869806	1.33778667565142	-7.02969266899239
H	4.43570686478328	0.43946705915877	-5.92254480238325
H	3.88094291393549	4.16657582979906	-3.89320511163874
H	5.87674003741313	5.07775898527495	-5.02265158117679
H	7.16917462356474	3.66244249101618	-6.58581121821104
C	0.01426471103873	2.44137413083155	-6.96514519862194
C	-0.67371923601359	3.56577961100249	-6.60205055624369
C	-0.45082275947461	4.19189089852158	-5.35579225902878
C	0.47166651886307	3.64539029581376	-4.50874070053332
C	0.98364789686242	1.89038765346063	-6.07542468030195
H	-0.13951083051734	1.94941165098721	-7.91312362181452
H	-1.40321128561626	3.98657419224248	-7.28197976903320
H	-0.98990629882161	5.08063426581481	-5.06911455303882
H	0.70693942844627	4.05082029151372	-3.53757248267520
C	3.20726355156712	2.47804139486575	-1.55062564078473
C	3.19677606004957	3.26827484815582	-0.39451005217606
C	4.09913631008744	2.96025863362340	0.60417321109609
C	4.97684678647734	1.88761904463695	0.43994493238498
C	4.90531820669529	1.16459403094674	-0.73700216443638
H	2.49772356306335	4.08645737487552	-0.30792221194289
H	4.12181406739199	3.54969747906441	1.51095017058309
H	5.69295847097909	1.62333244146416	1.20367616180904
H	5.56155899142581	0.32193659596054	-0.91649804193318
As	2.47656747783656	1.44030750657263	-3.93637005940565
O	2.36915559450593	2.73185915441850	-2.55662708278942
N	4.04213614987071	1.45454080967336	-1.71449186343881
N	1.15260617061390	2.53763850630643	-4.86553264058270
O	1.71193082141612	0.88850910930828	-6.24818772355140

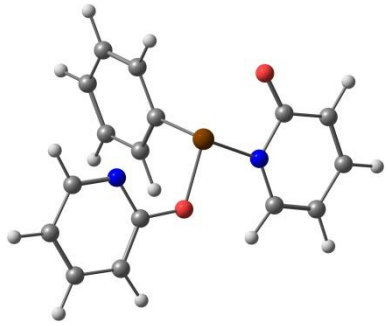

Figure S43. Optimized molecular structure of $\mathbf{1}^{II}$.

Total energy at DFT-B3LYP cc-pVTZ (for C H N O) and SDD (for As) D3BJ COSMO level of theory: -884.084596362769 au.
Gibbs free energy: -883.8720163 kcal mol^{-1}

Table S18. Atomic coordinates of optimized structure of $\mathbf{1}^{II}$.

C	6.00420465266310	1.91032017767667	-6.13097426602554
C	4.87110644218977	1.38946268913157	-5.51702429104844
C	4.00944203868203	2.22431849797427	-4.81295942489589
C	4.28620681696510	3.58471990037054	-4.72253839859329
C	5.41766708276792	4.10762029243033	-5.33687643232784
C	6.27806275311489	3.27069189530626	-6.04082215894704
H	6.67032735585257	1.25751842456369	-6.67857054519837
H	4.65745014313476	0.33166773867677	-5.59612540421168
H	3.62334982923162	4.23511854825951	-4.16898966455856
H	5.62878813993027	5.16623990627079	-5.26596562103867
H	7.15899027985613	3.67852671943047	-6.51735841194065
C	0.00886781472289	2.52166504709814	-6.98407360817586
C	-0.67217474700914	3.64063476292149	-6.58867563741655
C	-0.44964001810411	4.21845553332393	-5.32039318023807
C	0.46335788507431	3.63379931760561	-4.48873060519369
C	0.96380811384895	1.92940163297417	-6.10868776343440
H	-0.14526869136885	2.06517737145978	-7.94978724998727
H	-1.39296371603666	4.09143951718874	-7.25775008294536
H	-0.98118871508695	5.10150641262651	-5.00377238664345
H	0.69472071191273	4.00576048942880	-3.50418951400135
C	3.20333042905359	2.43685422071267	-1.56754004452076
C	3.23674904848535	3.24876180981196	-0.42794046790491
C	4.16345437043012	2.94521427696406	0.55058637970843
C	5.02156898913712	1.85683171743926	0.38044697717240
C	4.90756946219729	1.11329773062946	-0.78015661460336
H	2.55395561186600	4.07992778040024	-0.33638757166537
H	4.22102408793814	3.55061679044227	1.44475502273783
H	5.75556699285431	1.59626487923320	1.12816609938108
H	5.54704087265890	0.25877887589647	-0.96168758804457
As	2.44267532980288	1.41689670584037	-3.94563776439755
O	2.33774526307664	2.68515391296389	-2.55460872644114
N	4.01813800734798	1.39828966593198	-1.73832505065044
N	1.13908392237273	2.53176205821854	-4.87962563041714
O	1.67748327043760	0.91872109079759	-6.32299660353254

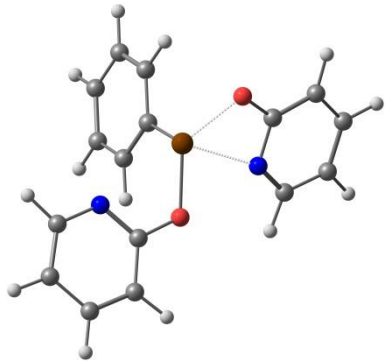

Figure S44. Transition state TS1 molecular structure of $PhAs(PyO)_2$.

Total energy at DFT-B3LYP cc-pVTZ (for C H N O) and SDD (for As) D3BJ level of theory: -884.045153002596 au.
Gibbs free energy: -883.83217237 kcal mol^{-1}

Table S19. Atomic coordinates of transition state structure of $PhAs(PyO)_2$.

As	2.73838984354684	1.21742756476864	-3.71884128622456
O	2.50374852960306	2.60405793186177	-2.41058950650238
N	4.31568049037217	1.53806604103277	-1.55939948057668
N	1.12101341231947	2.95415930036602	-4.70649953691454
O	1.56611225302986	0.86487233297416	-5.28480884515724
C	5.41973250150465	2.18989690537454	-6.80393725964196
C	4.44021414802926	1.59397892392225	-6.01951636699076
C	4.05694093458499	2.17339402441245	-4.81081410410348
C	4.66812415193230	3.35134256471613	-4.39105420998645
C	5.64325756975343	3.94900713885783	-5.17730346599221
C	6.02256797854827	3.36844424483056	-6.38300484949698
H	5.70874800197006	1.73682555098332	-7.74240826482090
H	3.96055260214150	0.68647289316127	-6.35953932886482
H	4.36799782185338	3.80880094987221	-3.46120445829438
H	6.10757926663968	4.86964303770480	-4.85076473916439
H	6.78398118709575	3.83552600775791	-6.99305682478264
C	0.11199381388299	2.14139442791458	-6.71582932990579
C	-0.48104560414001	3.37673307476204	-6.89500816721509
C	-0.26529863722050	4.40512892663346	-5.97423247524064
C	0.55089602756831	4.14348797063997	-4.88766270109564
C	0.92561913527765	1.97176172643614	-5.58739582659110
H	-0.02652006519489	1.32752572558918	-7.41097580080102
H	-1.11258775468467	3.54722254768629	-7.75686969788351
H	-0.72090530779222	5.37572706359837	-6.09843908126113
H	0.76018294283862	4.89285900780020	-4.13465759478671
C	3.29815552115583	2.38036954044998	-1.36586658418832
C	3.06882245943696	3.01625977311734	-0.13723051677060
C	3.94654544727609	2.76023745012373	0.89625841806901
C	5.00941102893693	1.87513332439750	0.70165427774825
C	5.14361849904893	1.28473908779490	-0.54116497596500
H	2.22449232155842	3.68029963107946	-0.02932143590781
H	3.80495973302234	3.23952181996927	1.85565773437391

H	5.70995952583250	1.65355941077473	1.49300884626536
H	5.94756022027202	0.58754007863622	-0.74440056132982

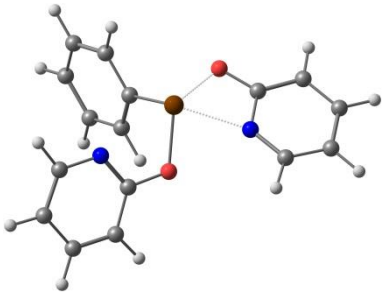

Figure S45. Transition state TS2 molecular structure of $PhAs(PyO)_2$.

Total energy at DFT-B3LYP cc-pVTZ (for C H N O) and SDD (for As) D3BJ level of theory: -884.047806635603 au.
Gibbs free energy: -883.83464963 kcal mol^{-1}

Table S20. Atomic coordinates of transition state structure of $PhAs(PyO)_2$.

As	-0.38510824011027	-1.03369558224456	-0.34986543324734
O	-0.53681524596991	0.23578552382928	1.06565564770786
N	1.03281939205243	-1.14460172017108	1.94710831290685
N	-2.48753641626025	-0.13943621503543	-0.65028295331056
O	-1.04400133421725	-0.56440307079280	-2.23567225353079
C	3.38614741172365	-0.55930916214194	-2.14919023664968
C	2.17099156778296	-1.04485841174469	-1.68133083115787
C	1.30494729728338	-0.21809095723094	-0.97218272305973
C	1.66303521526211	1.10513682388389	-0.73891360815252
C	2.87445473110737	1.59518733170541	-1.21002043693040
C	3.73921003026337	0.76375742077165	-1.91310326753856
H	4.05618487205539	-1.21176556164410	-2.69320231977192
H	1.90409201272310	-2.07781404363826	-1.87109628976434
H	0.99469427755365	1.75156777173203	-0.18848337237590
H	3.14544679848815	2.62658021607475	-1.02732708403080
H	4.68428079077425	1.14547226449215	-2.27461495446163
C	-3.28934803571390	0.07163359283411	-2.88976867802463
C	-4.51885617644280	0.43571871921986	-2.38063967763641
C	-4.73231841012820	0.50777488746121	-0.99746187473810
C	-3.67886935470199	0.20413672876456	-0.15901277986781
C	-2.26502279309878	-0.21148330776853	-1.97072921517688
H	-3.09754994542340	0.00359615258094	-3.94957348266334
H	-5.32882691602840	0.66773208551215	-3.05939197064229
H	-5.68912004102546	0.79886380270773	-0.59208573824279
H	-3.76262495782552	0.24091531169775	0.91916902821436
C	0.32212015856205	-0.02195900572997	2.04968275606356
C	0.45413420228762	0.85831974550853	3.13231400224115
C	1.36033613215638	0.53259924338625	4.12135815826426
C	2.11010201654067	-0.64062173294969	4.01794185305003
C	1.90927416004812	-1.44325595965025	2.90944265550307
H	-0.14212053389285	1.75761932419389	3.16687985466245
H	1.48946051150141	1.18875820809397	4.97194973463191
H	2.82798405535362	-0.91930113954793	4.77489543167468

H	2.46620426731925	-2.36295949415995	2.77788826605405

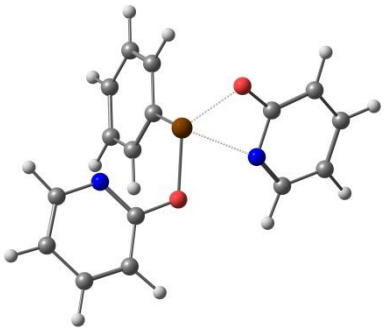

Figure S46. Transition state TS1 molecular structure of $PhAs(PyO)_2$.

Total energy at DFT-B3LYP cc-pVTZ (for C H N O) and SDD (for As) D3BJ COSMO level of theory: -884.053557073856 au.
Gibbs free energy: -883.84120383 kcal mol^{-1}

Table S21. Atomic coordinates of transition state structure of $PhAs(PyO)_2$.

As	2.72103467438131	1.19515068789472	-3.70603397420912
O	2.48056116336684	2.57745096468591	-2.39242377248865
N	4.30870367483280	1.52060232581996	-1.56297166554725
N	1.11281703509054	2.94473266898300	-4.70074043854028
O	1.53435102369313	0.84833512379912	-5.27609871923348
C	5.42445154035749	2.17140219259804	-6.77001522445864
C	4.45168248709441	1.56481216278714	-5.98378280464809
C	4.03262354368250	2.16299273318349	-4.79627009661850
C	4.60086634724318	3.36976610240798	-4.39758780586891
C	5.57010639264001	3.97785440453479	-5.18430638790365
C	5.98484816712386	3.37892579857351	-6.37034313573773
H	5.74171255605720	1.70391824230806	-7.69201715912213
H	4.00904052956364	0.63251955527292	-6.30590717715122
H	4.27222364623231	3.84138313299753	-3.48438614587764
H	6.00137552385379	4.91985185328187	-4.87443354001167
H	6.74055563097584	3.85386833257304	-6.98118441550715
C	0.12296920340025	2.15175383076065	-6.72807248123005
C	-0.44410224257692	3.39869935243049	-6.91760835857325
C	-0.22346301150759	4.42294165253698	-5.99281853346054
C	0.56916517284475	4.14654503961498	-4.89226954186833
C	0.91380621739133	1.96786144888542	-5.58637838226376
H	-0.01961543929879	1.34229164319354	-7.42772315293474
H	-1.05722968664683	3.58078732439091	-7.78984509376489
H	-0.65763501498344	5.40224817379610	-6.12452051625071
H	0.77973001687865	4.89390531713806	-4.13797711653429
C	3.29303013964157	2.36226200458440	-1.35719971742631
C	3.08248622044711	3.00648508711643	-0.13020083406482
C	3.97770717237114	2.75895249989812	0.89118042862239
C	5.03948113905078	1.87433632382934	0.68463769483975
C	5.15559212495875	1.27537972831719	-0.55587721196130
H	2.24004517465036	3.67109504910856	-0.01081381994843
H	3.85086330439075	3.24442193806337	1.84913306205783
H	5.75327414733771	1.65944651556412	1.46582881678142

H	5.95744142546156	0.57843678907026	-0.76619077909589

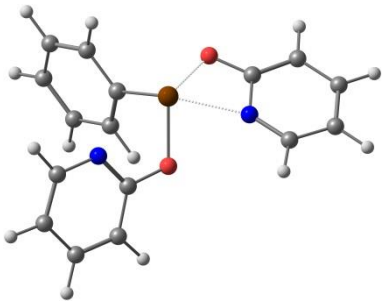

Figure S47. Transition state TS2 molecular structure of $PhAs(PyO)_2$.

Total energy at DFT-B3LYP cc-pVTZ (for C H N O) and SDD (for As) D3BJ COSMO level of theory: -884.056677270052 au.
Gibbs free energy: -883.84398295 kcal mol^{-1}

Table S22. Atomic coordinates of transition state structure of $PhAs(PyO)_2$.

As	-0.40768721890044	-1.03286073604630	-0.36859750628611
O	-0.55342152515335	0.22195534152241	1.05802453660303
N	1.00129838372062	-1.17242079589871	1.94922200115913
N	-2.50351605665851	-0.15171929799255	-0.66092200107590
O	-1.04416048603816	-0.49511348812571	-2.25047428630497
C	3.41131663747310	-0.57401166323570	-2.08475596874450
C	2.18755375789229	-1.05821950381922	-1.63432634537177
C	1.30036568009372	-0.22258958122091	-0.96167481453446
C	1.64630231606159	1.10792260356268	-0.74694550596467
C	2.86574870320116	1.59687502623315	-1.20000513104256
C	3.75160318974819	0.75635552987739	-1.86741979275022
H	4.09751377356408	-1.23323596377535	-2.59945494488764
H	1.93200968592304	-2.09696430529157	-1.80652511690633
H	0.96347758763896	1.76244253557837	-0.22425540472648
H	3.12661757404923	2.63326039023384	-1.03161722640211
H	4.70230147666976	1.13679787688398	-2.21494771699753
C	-3.29960783486909	0.13084027465135	-2.89369923948794
C	-4.53875345316684	0.45328436146484	-2.37642478465489
C	-4.75811007327857	0.46692902299560	-0.99249737386745
C	-3.70367239056131	0.15004326680584	-0.15991022849520
C	-2.27789413653655	-0.16946829039622	-1.98061943232378
H	-3.10467380297386	0.10737100616426	-3.95491756877186
H	-5.34977262367560	0.69642498903385	-3.04926277288531
H	-5.72193394721800	0.72349648177410	-0.58073131897192
H	-3.79496052965973	0.14105168621492	0.91774466843453
C	0.31860072887886	-0.03080255552794	2.03450892273998
C	0.49030873100065	0.87538958628936	3.08908650276502
C	1.40842443909899	0.55714496328762	4.07044754430208
C	2.13135056639909	-0.63486615358572	3.98446952037650
C	1.89212989552890	-1.46369967913499	2.90324556551105
H	-0.08349634892422	1.78949884590230	3.11103206926061
H	1.56818032940855	1.23331437018414	4.89935848806455
H	2.85790704452659	-0.90839353955595	4.73494480381193
H	2.42645292673685	-2.39843060505315	2.78823785842518

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