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Supporting Information

Synthesis and reactivity of titanium‐ and zirconium‐dinitrogen complexes bearing anionic pyrrole-based PNP-type pincer ligands

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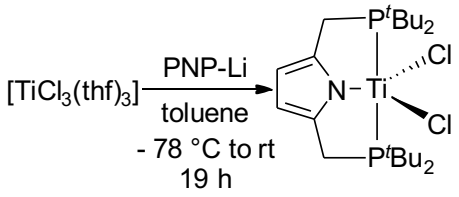
General Methods.

^{1}H NMR (400 MHz), and ^{31}P{^{1}H} NMR (162 MHz) spectra were recorded on a JEOL ECS-400 spectrometer in suitable solvent, and spectra were referenced to residual solvent (^{1}H) or external standard (^{31}P{^{1}H}: H_3PO_4). IR spectra were recorded on a JASCO FT/IR 4100 Fourier Transform infrared spectrometer. Magnetic susceptibility was measured in solution by using Evans' method.[S1] Absorption spectra were recorded on a Shimadzu MultiSpec-1500. Evolved dihydrogen was quantified by a gas chromatography using a Shimadzu GC-8A with a TCD detector and a SHINCARBON ST (6 m × 3 mm). Elemental analyses were performed at Microanalytical Center of The University of Tokyo.

All manipulations were carried out under an atmosphere of nitrogen by using standard Schlenk techniques or glovebox techniques unless otherwise stated. Solvents were dried by general methods, and degassed before use. lithium 2,5-bis(di-*tert*-butylphosphinomethyl)pyrrolide (PNP-Li),[S2] KC_8,[S3] Cp^*_2Co (Cp^* = 1,2,3,4,5-pentamethylcyclopentadienyl),[S4] $[H(OEt_2)_2]BAr^F_4$ (Ar^F = 3,5-$(CF_3)_2C_6H_3$),[S5] and $[Ph_2NH_2]OTf$ (OTf = OSO_2CF_3)[S6] were prepared according to literature methods. All the other reagents were commercially available.

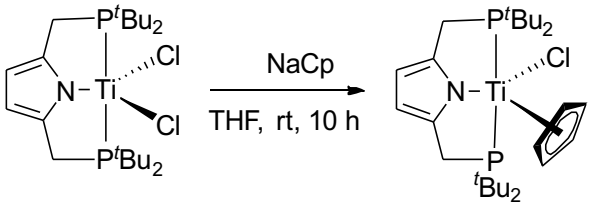
Preparation of [$TiCl_2$(PNP)] (1a)



1a, 91%

To a suspension of [$TiCl_3(thf)_3$] (438 mg, 1.18 mmol) in toluene (40 mL) was added a suspension of PNP-Li (460 mg, 1.18 mmol) in toluene (20 mL) at -78 °C. The resultant green solution was stirred at room temperature for 19 h. The solution was filtered through Celite, and the solvent was removed and dried *in vacuo* to afford a green solid (536 mg, 1.07 mmol, 91%). Green crystals of **1a** suitable for X-ray crystallography were obtained by recrystallization from hexane at -30 °C. ^{1}H NMR (C_6D_6): No characteristic peak was observed. Magnetic susceptibility (Evans' method): μ_{eff} = 1.6±0.1 μ_B in C_6D_6 at 296 K. Anal. Calcd. for $C_{22}H_{42}Cl_2NP_2Ti$: C, 52.71; H, 8.45; N, 2.79. Found: C, 52.54; H, 8.25; N, 3.18.

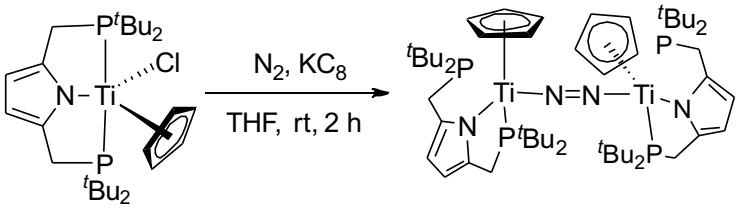
Preparation of [TiCl(PNP)Cp] (1b)



1a **1b**, 58 %

To a suspension of **1a** (536 mg, 1.07 mmol) in THF (10 mL) was added a suspension of sodium cyclopentadienide (94.2 mg, 1.07 mmol) in THF (5 mL). The resultant purple solution was stirred at room temperature for 10 h, and the solvent was removed and dried *in vacuo*. After the addition of Et_2O (30 mL) to the purple residue, the solution was filtered through Celite, and the filtrate was concentrated to *ca.* 20 mL. The solution was kept at -30 ℃ to give **1b** as golden yellow crystals, which were collected by decantation and dried *in vacuo* (322 mg, 0.63 mmol, 58%). Magnetic susceptibility (Evans' method): μ_{eff} = 1.6±0.1 μB in C_6D_6 at 296 K. ^{1}H NMR (C_6D_6): No characteristic peak was observed. Anal. Calcd. for $C_{27}H_{47}ClNP_2Ti$: C, 61.08; H, 8.92; N, 2.64. Found: C, 60.79; H, 8.63; N, 2.92.

Preparation of [Ti(PNP)Cp]$_2$(μ-N$_2$) (1c)

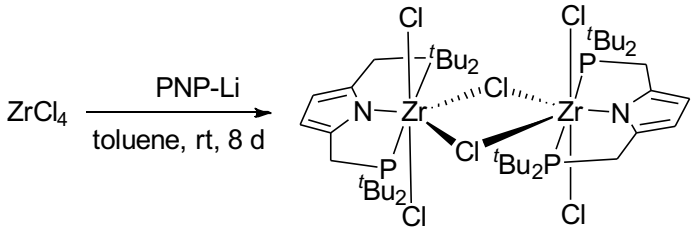


1b **1c**, 31%

To a solution of **1b** (19.6 mg, 0.037 mmol) in THF (8 mL) was added a suspension of KC_8 (7.5 mg, 0.055 mmol) in THF (1 mL). The mixture was stirred at room temperature for 2 h, and the solvent was removed and dried *in vacuo*. After the addition of hexane (5 mL) to the purple residue, the solution was filtered through Celite, and the filtrate was concentrated to *ca.* 1 mL. The solution was slowly evaporated to give **1c**·C_6H_{14} as purple crystals, which were collected by decantation and dried *in vacuo* to give a powder of **1c** (5.8 mg, 0.0057 mmol, 31%). Anal. Calcd. for $C_{54}H_{94}N_4P_4Ti_2$: C, 63.65;

H, 9.30; N, 5.50. Found: C, 63.26; H, 9.72; N, 4.27.

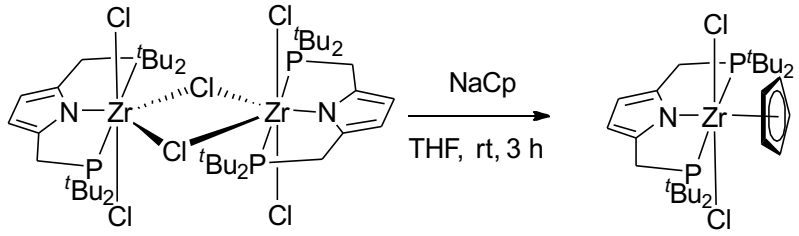
Preparation of $[ZrCl_2(PNP)(\mu\text{-}Cl)]_2$ (2a)



2a, 69%

PNP-Li (2.00 g, 5.14 mmol) and $ZrCl_4$ (1.20 g, 5.15 mmol) were stirred in toluene (130 mL) at room temperature for 8 days, and the solvent was removed and dried *in vacuo*. After the addition of dichrolomethane (100 mL) to the orange residue, the solution was filtered through Celite, and the solvent was removed and dried *in vacuo*. The resultant orange solid was dissolved in THF (5 mL) and then hexane (30 mL) was added. The precipitate was collected by filteration (2.05 g, 1.76 mmol, 69%). Orange crystals of **2a** suitable for X-ray crystallography were obtained by recrystallization from THF/hexane at -30 °C. ^{1}H NMR (THF-d_8): 5.65 (s, Ar*H*, 4H), 3.31-3.30 (m, CH_2P^{t}Bu$_2$, 8H), 1.34-1.31 (m, CH$_2$P^t*Bu*$_2$, 72H). ^{31}P{^{1}H} NMR (THF-d_8): 46.5 (s). Anal. Calcd. for $C_{44}H_{84}Cl_6N_2P_4Zr_2$: C, 45.55; H, 7.30; N, 2.41. Found: C, 45.95; H, 7.22; N, 2.43.

Preparation of $[ZrCl_2(PNP)Cp]$ (2b)

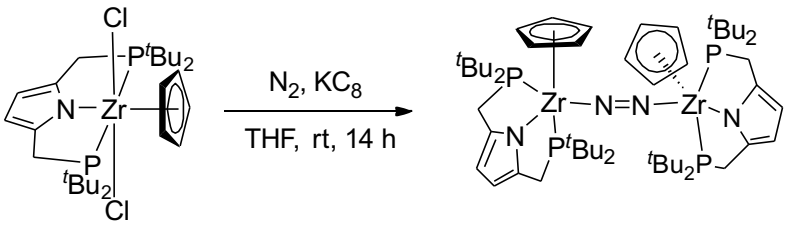


2a **2b**, 60 %

To a solution of **2a** (300 mg, 0.259 mmol) in THF (30 mL) was added a suspension of sodium cyclopentadienide (47.8 mg, 0.543 mmol) in THF (4 mL). The resultant purple solution was stirred at room temperature for 3 h, and the solvent was removed and dried *in vacuo*. After the addition of dichrolomethane (20 mL) to the purple residue, the solution was filtered through Celite. After the filtrate was concentrated to *ca.* 1 mL, addition of hexane (10 mL) afforded the purple solid **2b**, which was collected by

decantation (190 mg, 0.311 mmol, 60%). Purple crystals of **2b** suitable for X-ray crystallography were obtained by slow evaporation of THF solution. ^{1}H NMR (C_6D_6): 6.78 (s, Ar*H*, 5H), 6.18 (s, Ar*H*, 2H), 3.27-3.25 (s, C*H*$_2$P^{t}Bu$_2$, 4H), 1.15-1.12 (m, CH$_2$P^t*Bu*$_2$, 36H). ^{31}P {^{1}H} NMR (C_6D_6): δ 53.4 (s). Anal. Calcd. for $C_{27}H_{47}Cl_2NP_2Zr$: C, 53.17; H, 7.77; N, 2.30. Found: C, 53.40; H, 7.59; N, 2.77.

Preparation of [Zr(PNP)Cp]$_2$(μ- N$_2$) (2c)



2b **2c**, 23%

To a solution of **2b** (78.6 mg, 0.129 mmol) in THF (30 mL) was added KC_8 (73.3 mg, 0.542 mmol). The resultant black suspension was stirred at room temperature for 14 h, and the solvent was removed and dried *in vacuo*. After the addition of dichrolomethane (10 mL) to the residue, the solution was filtered through Celite. After the filtrate was concentrated to *ca.* 1 mL, addition of hexane (5mL) afforded the brown solid **2c**, which was collected by decantation 16.6 mg, 0.015 mmol, 23%). Orange crystals of **2c**·2C$_7$H$_8$ suitable for X-ray crystallography were obtained as orange crystals by recrystallization from toluene/hexane at -30 °C. ^{1}H NMR (C_6D_6): 6.42 (s, *Cp*, 10H), 6.20 (d, *J* = 12.4 Hz, *pyrrole,* 4H), 3.53-3.50 (m, C*H*$_2$P^{t}Bu$_2$, 2H), 3.02-3.73 (m, C*H*$_2$P^{t}Bu$_2$, 6H), 1.29 (m, CH$_2$P^t*Bu*$_2$, 54H). 0.88 (d, $J_{P\text{-}H}$ = 10.5 Hz, CH$_2$P^t*Bu*$_2$, 18H). ^{31}P {^{1}H} NMR (C_6D_6): δ 57.3 (d, *J* = 21.8 Hz), 50.5 (d, *J* = 26.2 Hz). Anal. Calcd. for $C_{54}H_{94}N_4P_4Zr_2$: C, 58.66; H, 8.57; N, 5.07. Found: C, 58.98; H, 8.37; N, 4.58.

X-ray crystallography.

Crystallographic data of **1a**, **1b**, **1c**, **2a**, **2b**, and **2c**·$2C_7H_8$ are summarized in Tables S1-S2. The ORTEP drawings are shown in Figures S1-S6, and selected bond lengths and angles are summarized in Tables S3-S8. Diffraction data were collected for 2θ range of 4° to 55° at temperatures ranging from –90 °C to –100 °C on a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated Mo *K*α radiation (λ = 0.71075 Å) with VariMax optics. Intensity data were corrected for Lorenz-polarization effects and for empirical absorption (ABSCOR). The structure solution and refinements were carried out by using the *CrystalStructure* crystallographic software package.[S7] The positions of the non-hydrogen atoms were determined by direct methods (SIR 97[S8] for **1a**, **1c**, and **2b**; SHELXT Version 2014/5[S9] for **1b** and **2c**·$2C_7H_8$; SHELXS Version 2013/1[S9] for **2a**) and subsequent Fourier syntheses (SHELXL Version 2016/6[S9]), and were refined on Fo^2 using all unique reflections by full-matrix least-squares with anisotropic thermal parameters with some following exceptions. Two methyl carbon atoms of a *tert*-butyl group in **1b** are disordered among two positions in a ratio of 0.5:0.5 (C(17A) and C(17B), C(18A) and C(18B), respectively) with both pairs solved anisotropically, where six hydrogen atoms of these two disordered methyl groups could not be located. Five cyclopentadienyl carbon atoms in **2b** are disordered among two positions in a ratio of 0.7:0.3 (C(23A)–C(24A)–C(25A)–C(26A)–C(27A) and C(23B)–C(24B)–C(25B)–C(26B)–C(27B), respectively) with the major pair solved anisotropically and the minor pair solved isotropically, where five hydrogen atoms of the disordered cyclopentadienyl group could not be located. All the other hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. Although the crystal of **1c** contains one molar amount of hexane per **1c** as **1c**·C_6H_{14}, the diffused electron density associated with these solvent molecules were removed by SQUEEZE routine in PLATON[S10] because of heavy disorders of hexane molecules.

Table S1 | X-ray crystallographic data for **1a, 1b** and **1c**.

	1a	**1b**	**1c**
chemical formula	$C_{22}H_{42}Cl_2N_1P_2Ti_1$	$C_{27}H_{47}Cl_1N_1P_2Ti_1$	$C_{54}H_{94}N_4P_4Ti_2$
CCDC number	1847681	1847685	1847686
formula weight	501.33	530.98	1019.06
dimensions of crystals	0.11 × 0.08 × 0.08	0.22 × 0.20 × 0.02	0.48 × 0.23 × 0.19
crystal color, habit	Green, chunk	Yellow, platelet	Black, prism
crystal system	Orthorhombic	Monoclinic	Orthorhombic
space group	$P2_12_12_1$	$C2/c$	$P2_12_12_1$
a, Å	12.5443(3)	47.9405(19)	12.9662(3)
b, Å	14.5948(4)	8.5955(3)	22.1194(4)
c, Å	15.2113(4)	13.8464(6)	22.1259(4)
α, deg	90	90	90
β, deg	90	97.655(7)	90
γ, deg	90	90	90
V, Å^3	2784.91(13)	5654.9(4)	6345.8(2)
Z	4	8	4
ρ_{calcd}, g cm^{-3}	1.196	1.274	1.067
F(000)	1068.00	2280.00	2200.00
μ, cm^{-1}	6.224	5.258	3.86
trans. factors range	0.769 - 0.951	0.519 - 0.990	0.291 - 0.851
no. reflections measured	27304	26064	62392
no. unique reflections	6384 (R_{int} = 0.0422)	6457 (R_{int} = 0.0932)	14499 (R_{int} = 0.0546)
no. parameters refined	265	317	602
$R1$ ($I > 2\ \sigma(I)$)[a]	0.0341	0.0635	0.0375
$wR2$ (all data)[b]	0.0555	0.1373	0.0715
GOF (all data)[c]	1.000	1.000	1.022
max diff peak / hole, e Å^{-3}	+0.26 / –0.27	+1.23 / –0.53	+0.27 / -0.17

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (qP)^2 + rP]$, $P = (\mathrm{Max}(F_o^2, 0) + 2\ F_c^2)/3$ [q = 0 (**1a**), 0 (**1b**), 0.0364 (**1c**); r = 1.3750 (**1a**), 36.2000 (**1b**), 0 (**1c**)]. [c] $\mathrm{GOF} = [\Sigma w(F_o^2-F_c^2)^2/(N_o-N_{params})]^{1/2}$.

Table S2 | X-ray crystallographic data for **2a, 2b** and **2c**·$2C_7H_8$.

	2a	**2b**	**2c**·$2C_7H_8$
chemical formula	$C_{44}H_{84}Cl_6N_2P_4Zr_2$	$C_{27}H_{47}Cl_2N_1P_2Zr_1$	$C_{68}H_{110}N_4P_4Zr_2$
CCDC number	1847682	1847683	1847684
formula weight	1160.21	609.75	1289.98
dimensions of crystals	0.41 × 0.20 × 0.20	0.18 × 0.15 × 0.10	0.10 × 0.06 × 0.06
crystal color, habit	Yellow, block	Purple, block	Brown, prism
crystal system	Orthorhombic	Monoclinic	Monoclinic
space group	*Aea*2	*I*2/*a*	*C*2/*c*
a, Å	14.8731(10)	21.3223(6)	27.0349(9)
b, Å	14.7823(9)	9.88221(3)	14.8663(4)
c, Å	25.3833(15))	28.558(3)	17.7670(6)
α, deg	90	90	90
β, deg	90	104.499(7)	107.262(8)
γ, deg	90	90	90
V, Å^3	5580.7(6)	5825.7(7)	6819.1(5)
Z	4	8	4
ρ_{calcd}, g cm^{-3}	1.381	1.390	1.256
F(000)	2416.00	2560.00	2744,00
μ, cm^{-1}	8.054	6.868	4.403
trans. factors range	0.291 - 0.851	0.615 - 0.933	0.580 - 0.974
no. reflections measured	24238	27118	31974
no. unique reflections	6357 (R_{int} = 0.0550)	6664 (R_{int} = 0.0794)	7781(R_{int} = 0.0853)
no. parameters refined	276	330	330
*R*1 ($I > 2\ \sigma(I)$)[a]	0.0568	0.0489	0.0592
*wR*2 (all data)[b]	0.1168	0.1084	0.1313
GOF (all data)[c]	1.000	1.000	1.000
max diff peak / hole, e Å^{-3}	+1.35 / –0.65	+0.56 / –0.43	+0.99 / -0.59

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (qP)^2 + rP]$, $P = (\mathrm{Max}(F_o^2, 0) + 2\ F_c^2)/3$ [q = 0 (**2a**), 0 (**2b**), 0 (**2c**); r = 31.5000 (**2a**), 0 (**2b**), 39.2000 (**2c**·$2C_7H_8$)]. [c] $\mathrm{GOF} = [\Sigma w(F_o^2-F_c^2)^2/(N_o-N_{params})]^{1/2}$.

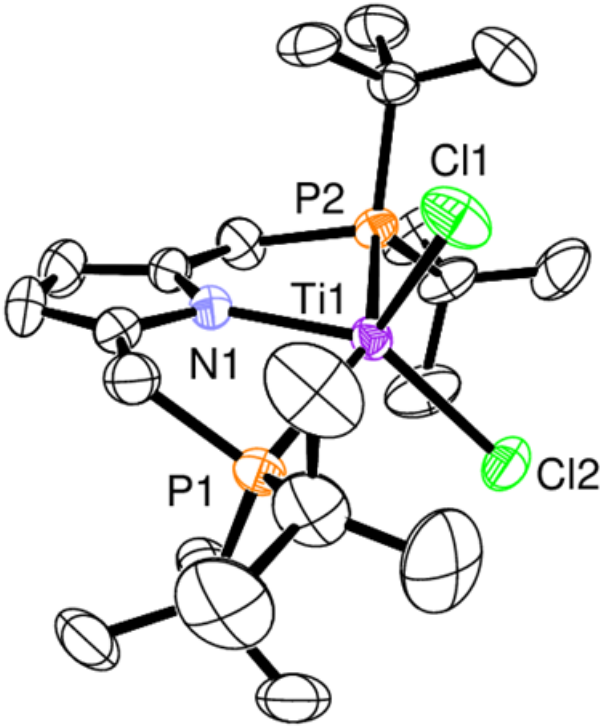


Figure S1. ORTEP drawing of **1a**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S3. Selected Bond Lengths (Å) and Angles (deg) for **1a**.

Ti(1)-Cl(1)	2.2762(9)	Ti(1)-Cl(2)	2.2997(9)
Ti(1)-P(1)	2.6000(9)	Ti(1)-P(2)	2.6462(9)
Ti(1)-N(1)	2.042(2)		
Cl(1)-Ti(1)-Cl(2)	103.50(4)	Cl(1)-Ti(1)-P(1)	99.22(3)
Cl(1)-Ti(1)-P(2)	102.60(3)	Cl(1)-Ti(1)-N(1)	115.19(7)
Cl(2)-Ti(1)-P(1)	94.81(3)	Cl(2)-Ti(1)-P(2)	100.24(3)
Cl(2)-Ti(1)-N(1)	141.08(7)	P(1)-Ti(1)-P(2)	149.68(3)
P(1)-Ti(1)-N(1)	75.57(7)	P(2)-Ti(1)-N(1)	76.20(7)

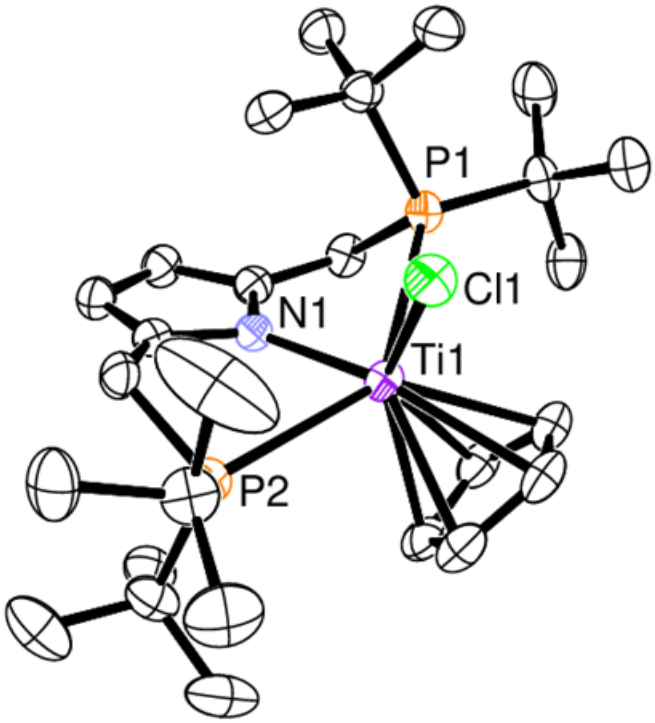


Figure S2. ORTEP drawing of **1b**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S4. Selected Bond Lengths (Å) and Angles (deg) for **1b**.

Ti(1)-Cl(1)	2.3766(12)	Ti(1)-P(1)	2.7565(13)
Ti(1)-P(2)	2.8352(13)	Ti(1)-N(1)	2.099(3)
Cl(1)-Ti(1)-P(1)	87.18(4)	Cl(1)-Ti(1)-P(2)	92.35(4)
Cl(1)-Ti(1)-N(1)	114.60(9)	P(1)-Ti(1)-N(1)	70.50(8)
P(1)-Ti(1)-P(2)	139.25(4)	P(2)-Ti(1)-N(1)	72.84(8)
Cl(1)-Ti(1)-P(1)	87.18(4)	Cl(1)-Ti(1)-P(2)	92.35(4)

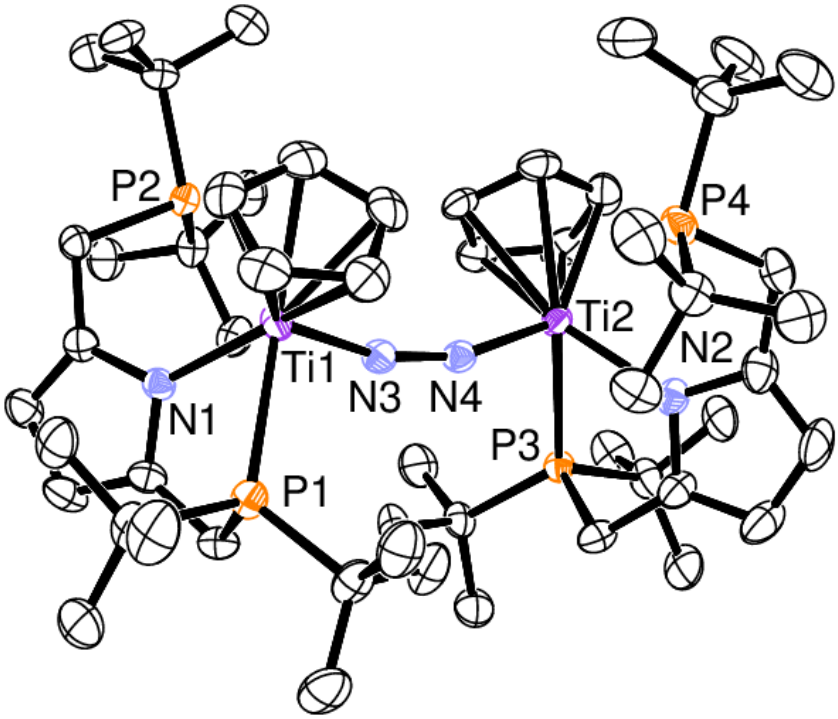


Figure S3. ORTEP drawing of **1c**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S5. Selected Bond Lengths (Å) and Angles (deg) for **1c**.

Ti(1)-P(1)	2.7234(8)	Ti(1)-N(1)	2.138(2)
Ti(1)-N(3)	1.816(2)	Ti(2)-N(2)	2.140(2)
Ti(2)-P(3)	2.6928(8)	Ti(2)-N(4)	1.808(2)
N(3)-N(4)	1.247(3)		
P(1)-Ti(1)-N(1)	71.43(5)	P(1)-Ti(1)-N(3)	94.26(7)
P(3)-Ti(2)-N(2)	72.69(6)	P(3)-Ti(2)-N(4)	93.57(7)
N(2)-Ti(2)-N(4)	109.14(9)	N(1)-Ti(1)-N(3)	108.88(8)
P(3)-Ti(2)-N(2)	72.69(6)	P(3)-Ti(2)-N(4)	93.57(7)
Ti(1)-N(3)-N(4)	158.91(18)	Ti(2)-N(4)-N(3)	159.63(18)

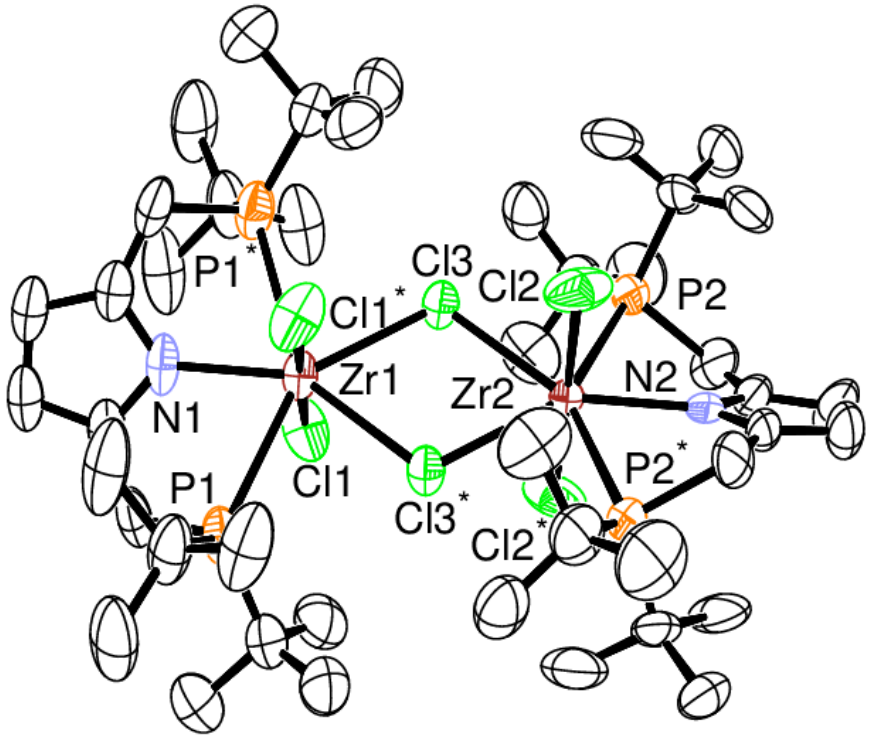


Figure S4. ORTEP drawing of **2a**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S6. Selected Bond Lengths (Å) and Angles (deg) for **2a**.

Zr(1)-Cl(1)	2.407(2)	Zr(1)-Cl(3)	2.627(3)
Zr(1)-Cl(1)*	2.407(2)	Zr(1)-Cl(3)*	2.627(3)
Zr(1)-P(1)	2.866(3)	Zr(1)-N(1)	2.189(10)
Zr(2)-Cl(2)	2.400(2)	Zr(2)-Cl(3)	2.629(3)
Zr(2)-P(2)	2.861(3)	Zr(2)-N(2)	2.200(13)
Cl(1)-Zr(1)-Cl(1)*	178.99(10)	Cl(1)-Zr(1)-Cl(3)	83.22(8)
Cl(1)*-Zr(1)-Cl(3)	95.96(8)	Cl(1)-Zr(1)-P(1)	84.54(8)
Cl(1)*-Zr(1)-P(1)	95.81(8)	Cl(1)-Zr(1)-N(1)	90.51(7)
Cl(1)*-Zr(1)-N(1)	90.51(7)	Cl(3)-Zr(1)-Cl(3)*	72.66(7)
Cl(3)-Zr(1)-P(1)	144.03(7)	Cl(3)-Zr(1)-P(1)*	75.17(7)
Cl(3)-Zr(1)-N(1)	143.67(5)	P(1)-Zr(1)-N(1)	69.91(5)
P(1)-Zr(1)-P(1)*	139.82(8)		

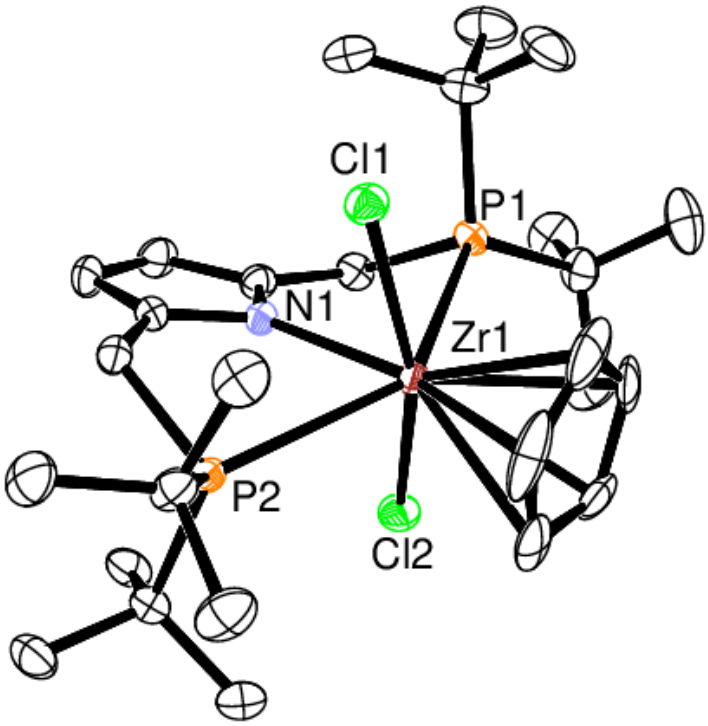


Figure S5. ORTEP drawing of **2b**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms as well as minor disordered Cp carben atoms (A : B = 7 : 3) are omitted for clarity.

Table S7. Selected Bond Lengths (Å) and Angles (deg) for **2b**.

Zr(1)-Cl(1)	2.4902(10)	Zr(1)-Cl(2)	2.4928(10)
Zr(1)-P(1)	2.9068(9)	Zr(1)-P(2)	2.8963(9)
Zr(1)-N(1)	2.247(3)		
Cl(1)-Zr(1)-Cl(2)	159.96(3)	Cl(1)-Zr(1)-P(1)	90.25(3)
Cl(1)-Zr(1)-P(2)	82.49(3)	Cl(1)-Zr(1)-N(1)	80.29(7)
Cl(2)-Zr(1)-P(1)	82.46(3)	Cl(2)-Zr(1)-P(2)	91.47(3)
Cl(2)-Zr(1)-N(1)	79.68(7)		

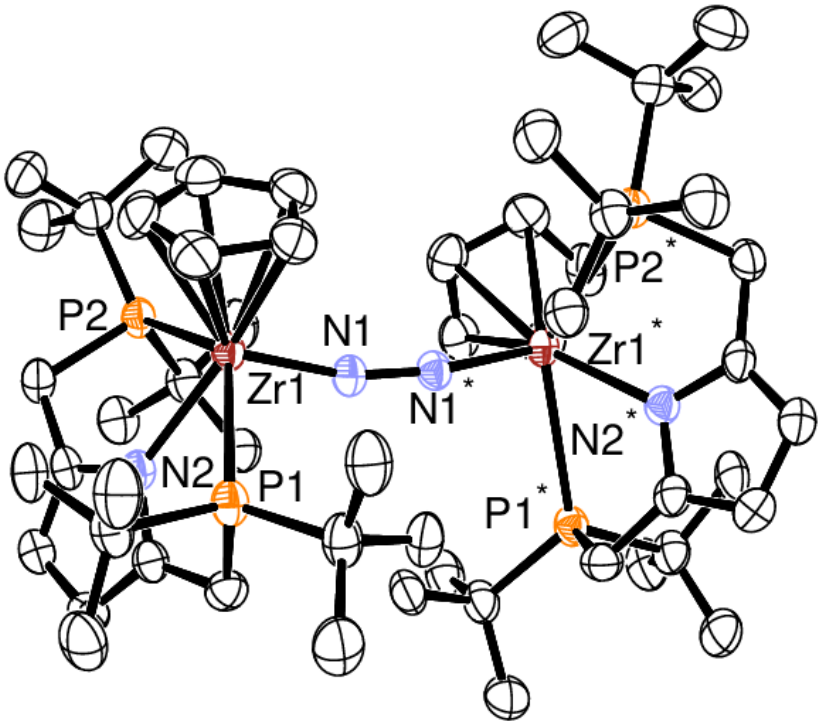
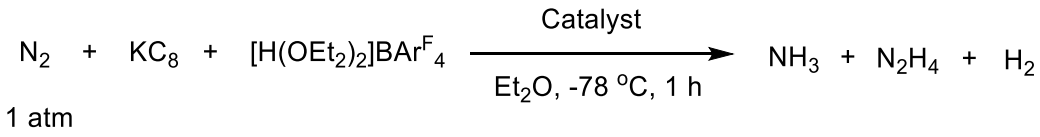


Figure S6. ORTEP drawing of **2c**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S8. Selected Bond Lengths (Å) and Angles (deg) for **2c**.

Zr(1)-P(1)	2.8473(11)	Zr(1)-P(2)	2.9518(11)
Zr(1)-N(1)	1.914(3)	Zr(1)-N(2)	2.295(3)
N(1)-N(1)*	1.287(4)		
P(1)-Zr(1)-P(2)	135.77(3)	P(1)-Zr(1)-N(1)	93.45(9)
P(1)-Zr(1)-N(2)	68.36(8)	P(2)-Zr(1)-N(2)	67.46(8)
P(2)-Zr(1)-N(1)	101.70(9)	Zr(1)-N(1)-N(1)	163.7(2)

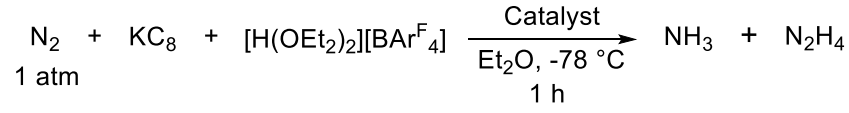
Catalytic Reduction of Dinitrogen to Ammonia and Hydrazine under N_2 (1 atm).



Catalytic reduction of dinitrogen into ammonia and hydrazine was carried out according to a method similar to the Peters' procedure.[S11] A typical experimental procedure using **2c** is described below.

In a 50 mL Schlenk flask were placed **2c** (5.5 mg, 0.0050 mmol), KC_8 (54.4 mg, 0.400 mmol), and $[H(OEt_2)_2]BAr^F{}_4$ (384.1 mg, 0.380 mmol). After the mixture was cooled to -78 °C, Et_2O (5 mL) was added to the mixture. After stirring at -78 °C for 1 h, the mixture was warmed to room temperature and further stirred at room temperature for 20 min. The amount of dihydrogen evolved in the reaction was determined by GC analysis. The reaction mixture was evaporated under reduced pressure, and the distillate was trapped in dilute H_2SO_4 solution (0.5 M, 10 mL). Aqueous solution of potassium hydroxide (30 wt%, 5 mL) was added to the residue, and the mixture was distilled into another dilute H_2SO_4 solution (0.5 M, 10 mL). The amount of NH_3 present in each of the H_2SO_4 solutions was determined by the indophenol method.[S12] The amount of NH_2NH_2 present in each of the H_2SO_4 solutions was determined by the *p*-(dimethylamino)benzaldehyde method.[S13]

Table S9. Titanium- and zirconium-catalyzed reduction of dinitrogen to ammonia and hydrazine[a]



Entry	Catalyst	KC_8 (equiv)[b]	$[H(OEt_2)_2][BAr^F{}_4]$ (equiv)[b]	NH_3 (equiv)[b]	N_2H_4 (equiv)[b]	Fixed N atom (equiv)[b]	H_2 (equiv)[b]
1	**1c**	40	38	1.0	0	1.0	5.3
2	**1b**	40	38	0.13	0	0.1	2.9
3	**2c**	40	38	1.3	0.31	1.9	7.6
4	**2c**	80	76	1.3	0	1.3	17
5[c]	**2c**	36	48	0.52	0.45	1.4	0.81
6	**2a**	40	38	0.31	0	0.3	5.9

[a]To a mixture of the catalysts, KC_8, and $[H(OEt_2)_2][BAr^F{}_4]$ was added Et_2O at -78 °C, and then the resultant mixture was stirred at -78 °C for 1 h. [b]Equiv based on the metal atom. [c]$CoCp^*{}_2$ and $[Ph_2NH_2]OTf$ were used as reductant and proton source, respectively.

Computational Details. DFT calculations were performed with the Gaussian 09 program (Rev. E01).[S14] Geometry optimizations of dinitrogen-bridged bimetallic Ti and Zr complexes **1c** and **2c** were carried out with the B3LYP functional with the Grimme's dispersion correction (B3LYP-D3).[S15-S19] The SDD (Stuttgart/Dresden pseudopotentials) basis set[S20,S21] and 6-31G(d) basis set[S22–S25] were employed for metal atoms and the other atoms, respectively. Optimized structures were confirmed to have no imaginary frequencies by vibrational analysis. For all calculations in the present study, solvation effects of tetrahydrofuran were taken into account by using the polarizable continuum model (PCM).[S26] Figure S7 presents the optimized structures of **1c** and **2c** in the closed-shell singlet state. Selected bond distances, angles, and the Mayer bond orders (b.o.)[S27] are summarized in Table S10. Cartesian coordinates of the optimized structures of **1c** and **2c** are listed in Tables S11 and S12.

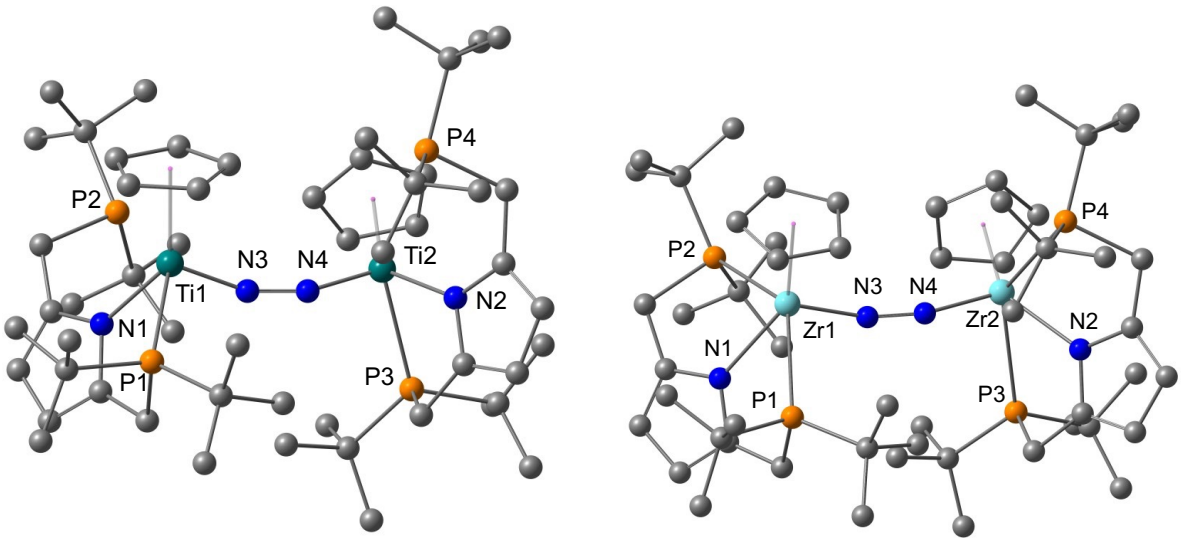


Figure S7. Optimized structures and selected geometric parameters of 1c and 2c in the closed-shell singlet state. Hydrogen atoms are omitted for clarity.

Table S10. Selected bond distances (Å), angles (deg), and the Mayer bond orders (b.o.) calculated for **1c** (M = Ti) and **2c** (M = Zr)

	1c	b.o.	**2c**	b.o.
M(1)-N(1)	2.110	0.49	2.335	0.37
M(1)-N(3)	1.757	1.50	1.923	1.42
M(1)-P(1)	2.621	0.67	2.866	0.43
M(1)-P(2)	3.713	0.12	2.992	0.38
N(3)-N(4)	1.261	1.40	1.281	1.21
M(1)-N(3)-N(4)	160.7		163.8	

Table S11. | Cartesian coordinate of 1c in the closed-shell singlet state. Units are presented in Å.

SCF energy (in THF) = -3815.87612136 hartree
Zero-point energy = 1.395020 hartree

Atom	Coordinates (Angstroms) X	Y	Z
Ti	-1.950120	-1.228264	0.256328
Ti	1.950186	1.228704	0.256266
P	-2.184937	-2.538485	-2.001557
P	-3.521090	1.644486	2.007367
P	2.185044	2.538144	-2.001789
P	3.520817	-1.644366	2.007550
N	-3.596246	-0.287598	-0.670017
N	3.596188	0.287574	-0.669897
N	-0.568983	-0.271858	-0.258569
N	0.569096	0.272234	-0.258428
C	-2.641621	-0.956809	-2.879382
H	-1.726797	-0.357779	-2.909702
H	-2.975017	-1.119512	-3.908601
C	-3.697992	-0.285619	-2.055880
C	-4.888524	0.302381	-2.448105
H	-5.239432	0.409268	-3.468131
C	-5.552220	0.703646	-1.251921
H	-6.500841	1.221563	-1.168437
C	-4.737470	0.334887	-0.188546
C	-4.937274	0.643148	1.263315
H	-4.974302	-0.277928	1.854064
H	-5.899176	1.150093	1.398277
C	-3.733451	-3.657584	-2.227394
C	-3.363520	-5.127887	-1.951171
H	-2.727249	-5.549538	-2.733385
H	-4.283206	-5.726161	-1.920286
H	-2.855014	-5.250284	-0.988261
C	-4.366265	-3.532503	-3.628338
H	-5.223899	-4.216072	-3.688918
H	-3.677591	-3.793025	-4.434206
H	-4.742838	-2.520157	-3.803611
C	-4.805552	-3.228157	-1.197399
H	-4.421016	-3.227895	-0.175396

H	-5.639006	-3.941781	-1.249111
H	-5.198290	-2.232153	-1.408871
C	-0.678112	-3.217856	-2.960603
C	0.377849	-2.089963	-3.005559
H	0.602533	-1.687732	-2.015711
H	0.065095	-1.263002	-3.649975
H	1.307509	-2.497709	-3.422641
C	-0.055551	-4.412132	-2.208525
H	0.847918	-4.732869	-2.743203
H	-0.724237	-5.272471	-2.144182
H	0.246899	-4.130132	-1.198742
C	-1.010734	-3.634010	-4.405640
H	-1.500748	-2.828145	-4.962500
H	-1.648384	-4.521149	-4.445684
H	-0.075773	-3.878583	-4.927079
C	-4.150785	1.941452	3.797778
C	-4.538962	0.563078	4.380780
H	-5.455398	0.166203	3.932948
H	-4.719893	0.667685	5.458930
H	-3.741954	-0.177419	4.251223
C	-5.358123	2.883784	3.936729
H	-5.111000	3.911877	3.658400
H	-5.696485	2.899093	4.982692
H	-6.202889	2.555775	3.320646
C	-2.966259	2.474717	4.634353
H	-2.629250	3.461000	4.306805
H	-2.108199	1.793371	4.586025
H	-3.268434	2.560911	5.687342
C	-3.558797	3.288372	1.017047
C	-4.958216	3.803120	0.634794
H	-5.571329	4.036880	1.508425
H	-5.494282	3.077077	0.018228
H	-4.855767	4.724656	0.043875
C	-2.802191	4.382744	1.796479
H	-3.353050	4.724110	2.677837
H	-2.658305	5.254486	1.142979
H	-1.810984	4.044028	2.118655
C	-2.761360	3.002426	-0.276969
H	-1.756850	2.628854	-0.054946
H	-2.659309	3.933620	-0.850644
H	-3.254009	2.266502	-0.915382
C	-2.332476	-3.280116	1.516277

H	-2.956557	-4.066812	1.116781
C	-2.762802	-2.189456	2.306442
H	-3.780459	-1.988981	2.613885
C	-1.614293	-1.394762	2.607185
H	-1.607852	-0.468194	3.163816
C	-0.482392	-2.009516	2.019548
H	0.527641	-1.620581	2.023666
C	-0.925159	-3.160949	1.330552
H	-0.306113	-3.828661	0.750014
C	2.641740	0.956383	-2.879413
H	1.726924	0.357350	-2.909639
H	2.975148	1.118918	-3.908652
C	3.698086	0.285350	-2.055739
C	4.888750	-0.302530	-2.447723
H	5.239744	-0.409584	-3.467699
C	5.552362	-0.703504	-1.251387
H	6.501000	-1.221354	-1.167696
C	4.737447	-0.334663	-0.188168
C	4.937061	-0.642980	1.263721
H	4.974055	0.278049	1.854563
H	5.898947	-1.149945	1.398747
C	0.678221	3.217566	-2.960813
C	-0.377667	2.089612	-3.005781
H	-0.064908	1.262676	-3.650224
H	-1.307387	2.497305	-3.422787
H	-0.602241	1.687384	-2.015900
C	0.055643	4.411722	-2.208577
H	0.724191	5.272169	-2.144341
H	-0.246549	4.129627	-1.198747
H	-0.848000	4.732340	-2.743047
C	1.010833	3.633827	-4.405822
H	0.075854	3.878305	-4.927270
H	1.500942	2.828011	-4.962668
H	1.648386	4.521035	-4.445813
C	3.733590	3.657220	-2.227715
C	3.363627	5.127565	-1.951720
H	2.727392	5.549092	-2.734030
H	4.283296	5.725870	-1.920870
H	2.855088	5.250097	-0.988846
C	4.366415	3.531968	-3.628666
H	3.677700	3.792238	-4.434583
H	4.743151	2.519648	-3.803753

H	5.223926	4.215674	-3.689382
C	4.805885	3.228131	-1.197767
H	5.639590	3.941395	-1.250461
H	5.198149	2.231807	-1.408576
H	4.421943	3.229009	-0.175538
C	3.558809	-3.288337	1.017404
C	2.761377	-3.002648	-0.276671
H	2.659386	-3.933919	-0.850232
H	3.254070	-2.266818	-0.915171
H	1.756829	-2.629066	-0.054834
C	2.802395	-4.382710	1.796985
H	2.658487	-5.254517	1.143572
H	1.811213	-4.044067	2.119295
H	3.353386	-4.724000	2.678298
C	4.958269	-3.802968	0.635138
H	5.571451	-4.036663	1.508735
H	5.494229	-3.076909	0.018497
H	4.855852	-4.724530	0.044251
C	4.150366	-1.941266	3.798057
C	4.539446	-0.563016	4.380719
H	3.743088	0.178102	4.250685
H	5.456329	-0.167038	3.933003
H	4.719976	-0.667358	5.458964
C	2.965441	-2.473575	4.634669
H	2.627644	-3.459589	4.307117
H	2.107929	-1.791539	4.586359
H	3.267557	-2.560014	5.687657
C	5.357088	-2.884363	3.937225
H	5.109291	-3.912386	3.659218
H	5.695487	-2.899560	4.983174
H	6.202028	-2.557097	3.320990
C	2.332313	3.280544	1.516612
H	2.956285	4.067285	1.116983
C	2.762857	2.189827	2.306556
H	3.780579	1.989390	2.613830
C	1.614520	1.394850	2.607190
H	1.608216	0.468304	3.163819
C	0.482452	2.009496	2.019706
H	-0.527516	1.620390	2.023834
C	0.924986	3.161142	1.330883
H	0.305743	3.828839	0.750523

Table S12. | Cartesian coordinate of 2c in the closed-shell singlet state. Units are presented in Å.

SCF energy (in THF) = -3793.38257058 hartree
Zero-point energy = 1.392516 hartree

Atom	Coordinates (Angstroms) X	Y	Z
Zr	2.406713	-0.744357	-0.512232
P	2.639173	-2.098245	2.003085
P	3.647373	1.676111	-1.758161
N	0.636161	-0.094453	-0.134616
N	3.878709	0.359661	0.925412
C	2.784638	-0.514373	2.978846
H	1.797109	-0.047371	2.930531
H	3.024229	-0.686411	4.032137
C	3.815675	0.337067	2.306565
C	4.826182	1.120044	2.846983
H	5.020656	1.271084	3.902996
C	5.549740	1.666001	1.743442
H	6.403380	2.333631	1.779229
C	4.947401	1.171234	0.594663
C	5.260617	1.428357	-0.844967
H	5.741925	0.558420	-1.308740
H	5.938889	2.278313	-0.964938
C	1.175714	-3.005611	2.830431
C	-0.022932	-2.031867	2.783585
H	0.098215	-1.214084	3.499583
H	-0.936823	-2.574228	3.057531
H	-0.173108	-1.598163	1.792111
C	1.430063	-3.390294	4.299862
H	0.502464	-3.794321	4.727570
H	1.721301	-2.523209	4.902477
H	2.201213	-4.157572	4.406117
C	0.798882	-4.260804	2.017541
H	0.587369	-4.009716	0.976120
H	-0.112974	-4.700464	2.442552
H	1.574341	-5.028687	2.036170
C	4.298580	-3.014659	2.377499
C	5.354090	-2.529929	1.356121
H	5.038128	-2.722598	0.325476

H	6.290042	-3.078677	1.529008
H	5.561713	-1.462578	1.455772
C	4.832799	-2.714231	3.791835
H	5.751582	-3.293405	3.956467
H	4.123441	-2.986222	4.577452
H	5.086209	-1.655729	3.901333
C	4.147813	-4.538844	2.204466
H	3.738071	-4.808514	1.225716
H	3.516605	-4.988262	2.974730
H	5.139876	-5.002492	2.284332
C	3.006595	3.364163	-1.084768
C	2.045985	4.011287	-2.101174
H	1.543620	4.861942	-1.621883
H	1.269327	3.314088	-2.427864
H	2.560811	4.395264	-2.985071
C	4.138071	4.348643	-0.730493
H	4.759079	3.958505	0.081657
H	3.689308	5.288219	-0.380753
H	4.782291	4.586232	-1.579820
C	2.200381	3.082623	0.200122
H	1.792099	4.030428	0.573729
H	2.814563	2.641794	0.987664
H	1.369169	2.400270	0.010987
C	4.227002	1.887242	-3.576513
C	3.004379	1.843362	-4.519622
H	2.377121	0.964633	-4.344422
H	3.350684	1.808249	-5.561013
H	2.371113	2.726182	-4.413826
C	5.029352	3.176238	-3.843336
H	5.403056	3.153321	-4.876210
H	5.898008	3.259129	-3.181469
H	4.425736	4.079739	-3.735376
C	5.164985	0.700141	-3.907382
H	6.147022	0.823141	-3.440582
H	5.320716	0.661062	-4.993088
H	4.763389	-0.264585	-3.592829
C	1.268395	-1.935802	-2.538607
H	0.339618	-1.496415	-2.880889
C	2.568409	-1.604129	-2.993393
H	2.792931	-0.904319	-3.782397
C	3.516754	-2.381906	-2.267504
H	4.593761	-2.357128	-2.385712

C	2.793044	-3.182755	-1.349866
H	3.214871	-3.896493	-0.656592
C	1.404250	-2.906015	-1.515117
H	0.593213	-3.355554	-0.962809
N	-0.631580	0.092475	-0.133083
Zr	-2.402335	0.748416	-0.497223
P	-2.644165	2.058220	2.035917
P	-3.642750	-1.644842	-1.791127
N	-3.875205	-0.382268	0.919900
C	-2.788705	0.461393	2.989759
H	-1.800083	-0.002718	2.938087
H	-3.032236	0.617484	4.044637
C	-3.815702	-0.381887	2.301398
C	-4.826219	-1.175018	2.826764
H	-5.023016	-1.343233	3.879755
C	-5.546492	-1.703882	1.712807
H	-6.399760	-2.372558	1.735810
C	-4.942080	-1.189777	0.573672
C	-5.255053	-1.419959	-0.870530
H	-5.739231	-0.542282	-1.316299
H	-5.931208	-2.269177	-1.006468
C	-1.185811	2.959397	2.879637
C	0.017206	1.991796	2.819060
H	-0.103032	1.159560	3.518333
H	0.927593	2.532657	3.107276
H	0.173125	1.578378	1.819863
C	-1.444659	3.319440	4.354533
H	-0.520171	3.722088	4.790203
H	-1.731861	2.441193	4.942659
H	-2.220572	4.080342	4.471889
C	-0.812882	4.229176	2.087669
H	-0.603830	3.996991	1.041473
H	0.099526	4.662665	2.517882
H	-1.589155	4.995644	2.121740
C	-4.307230	2.966102	2.415789
C	-5.355924	2.499018	1.379214
H	-5.034921	2.712796	0.354273
H	-6.294356	3.041727	1.557757
H	-5.561089	1.429302	1.456436
C	-4.847945	2.638400	3.821565
H	-5.767311	3.214464	3.993740
H	-4.141405	2.894767	4.614989

H	-5.101764	1.578015	3.909295
C	-4.159217	4.493705	2.272563
H	-3.746020	4.782909	1.301034
H	-3.532809	4.930227	3.054028
H	-5.152847	4.953186	2.356671
C	-3.001214	-3.347546	-1.155564
C	-2.042761	-3.975983	-2.185860
H	-1.545164	-4.839497	-1.724899
H	-1.262076	-3.275472	-2.495386
H	-2.557771	-4.337960	-3.078950
C	-4.132447	-4.338653	-0.818215
H	-4.752343	-3.964895	0.002523
H	-3.682708	-5.284570	-0.487338
H	-4.778108	-4.560353	-1.670777
C	-2.191460	-3.092957	0.132725
H	-1.787579	-4.049522	0.488339
H	-2.801244	-2.663061	0.929679
H	-1.357015	-2.412002	-0.046604
C	-4.226576	-1.813827	-3.610928
C	-3.005672	-1.743221	-4.554494
H	-2.383277	-0.864635	-4.361955
H	-3.353460	-1.688857	-5.594587
H	-2.367110	-2.624486	-4.467453
C	-5.025338	-3.098518	-3.907221
H	-5.402162	-3.051566	-4.938127
H	-5.891578	-3.199936	-3.244875
H	-4.418591	-4.002450	-3.822935
C	-5.169520	-0.621492	-3.908590
H	-6.155713	-0.770195	-3.458199
H	-5.313256	-0.541777	-4.993651
H	-4.780354	0.333851	-3.551658
C	-1.273046	1.976432	-2.503743
H	-0.354184	1.533914	-2.868178
C	-2.582774	1.676499	-2.954315
H	-2.824961	1.001709	-3.759770
C	-3.512265	2.449355	-2.200526
H	-4.590602	2.443592	-2.308538
C	-2.767166	3.214486	-1.269087
H	-3.171490	3.916005	-0.553475
C	-1.384560	2.922108	-1.454807
H	-0.562507	3.343700	-0.897184

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