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Supporting Information

Dinitrogen Fixation: Rationalizing Strategies Utilizing Molecular Complexes

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1. Summary of used complexes and reagents for N_2 to metal-nitride formation.

Table S1. Summary of used complexes and reagents for metal nitride formation.

Complex	*Reagent*	*Selectivity*[b]	*Ref.*
$Mo(N(^tBu)Ar)_3]_2$ (**1**)	N_2 *hν*	$[Mo(N)(N(^tBu)Ar)_3]$ (**2**)	[1] [2]
$[Mo(OSi(O^tBu)_3)_3]$ (**3**)	N_2	$[Mo(N)(OSi(O^tBu)_3)_3]$ (**4**)	[3]
$[Ti(Cp')(CH_2SiMe_3)_3]$ (**90**) Cp' = $C_5Me_4SiMe_3$	N_2/H_2	$\{[Ti(Cp')]_4(\mu_3\text{-}NH)_2(\mu_2\text{-}H)_4\}$	[4]
$\{[Ti(Cp')]_3(\mu_3\text{-}H)(\mu_2\text{-}H)_6\}$ (**5**) Cp' = $C_5Me_4SiMe_3$	N_2	$\{[(Cp')Ti]_3(\mu_2\text{-}NH)(\mu_3\text{-}N)(\mu_2\text{-}H)_2\}$ (**6**)	[4]
$\{[Ti(Cp')]_3(\mu_2\text{-}NH)(\mu_3\text{-}N)(\mu_2\text{-}H)_2\}$	^{15}N	$\{[(Cp')Ti]_3(\mu_3\text{-}^{15}N)(\mu_2\text{-}NH)_2(\mu_2\text{-}^{15}NH\}$	[4]
$[((anti\text{-}O_3)Nb)_2(\mu\text{-}H)_4][K(dme)]_2$ (**11**) *anti*-O_3 = $CH\{3,5\text{-}(^tBu)_2Ph\text{-}2\text{-}O)\}_3^{3-}$	N_2	$[((anti\text{-}O_3)Nb)_2(\mu\text{-}N)_2][K(thf)]_2$ (**12**)	[5]
$[(calix\text{-}O_4)_2Nb_2]$ (**13**)	N_2 N_2, TMEDA	$[(calix\text{-}O_4)Nb(N)]_2[Nb(calix\text{-}O_4)]$ (**14**) $[(calix\text{-}O_4)_2Nb_2(\mu\text{-}NNa(TMEDA)_2]$ (**15**)	[6, 7]
$[MoI_2(PCP)]$ (**18**) PCP = $1,3\text{-}[OP(^tBu)_2]_2C_6H_3^-$	Na(Hg)/N_2	$[MoI(N)(PCP)]^-$ (**19**)	[8]
$[Mo(PNP)I_3]$ (**20**) PNP = $1,3\text{-}[CH_2P(^tBu)_2]_2C_5H_3N$	$(CoCp^*_2)/N_2$ SmI_2/N_2	$[MoI(N)(PNP)]^-$ (**21**)	[9, 10]
$[Mo(PNP)Cl_3]$ (**24**) PNP = $N(CH_2CH_2P^tBu_2)_2^-$	i.) Na(Hg),/N_2 ii.) HOTf	$[Mo(HPNP)(N)Cl]^+$ (**23**)	[11]
$[W(PNP)Cl_3]$ PNP = $N(CH_2CH_2P^tBu_2)_2^-$	Na(Hg)/N_2	$[W(HPNP)(N)Cl]^+$	[12]
$[Mo(PPP)Cl_3]$ (**29**) PPP = $PhP(CH_2CH_2PCy_2)_2$	Na(Hg), NaI/N_2	$[Mo(N)I(PPP)]$ (**31**)	[13]
$[ReCl_2(PNP)]$ (**32**) PNP = $N(CH_2CH_2P^tBu_2)_2^-$	$CoCp^*_2/N_2$ Na(Hg)/N_2 E_{red} = -1.9 V *vs.* Fc/Fc^+	$[Re^VCl(N)(PNP)]$ (**33**)	[14]
$[ReCl_2(PNP)]$ (**35**) PNP = $N(CHCHP^tBu_2)_2$	$CoCp^*_2/N_2$ Na(Hg)/N_2 E_{red} = -1.67 V *vs.* Fc/Fc^+	$[Re^VCl(N)(PNP)]$ (**36**)	[15]
$[(NNN^{Si}V)_2(\mu\text{-}Cl)_2]$ (**37**) NNN^{Si} = $Me_3SiN(CH_2CH_2NSiMe_3)_2^{2-}$	KC_8/N_2	$[(NNN^{Si}V)_2(\mu\text{-}N)_2]$ (**38**) $[(NNN^{Si}V)_2(\mu\text{-}N)_2K]^-$ (**39**)	[16]
$[U(N^4)(DME)]^-$ (**40**)	$K\text{-}C_{10}H_8/N_2$	$[(UN^4)_2(\mu\text{-}NK)_2]^{2-}$ (**41**)	[17]

N^4 = Et_8-calix[4]tetrapyrrole			
[(O-μ-OO)$_2$Nb$_2$] (**42**) OOO = {(3-Me,5-^{t}Bu)Ph-(2-O)CH$_2$Ph(2-O)(4-^{t}Bu)CH$_2$Ph-(2-O)(3-Me,5-^{t}Bu)}$^{3-}$	$LiBEt_3H/N_2$	[{(OO-μ-O)Nb}$_2$(μ-N)$_2$(Li-thf)$_2$] (**43**)	[18]
[(O-μ-NO)$_2$V$_2$] (**46**) ONO = {(3-Me,5-^{t}Bu)Ph-(2-O)CH$_2$Ph(2-NPhMe)(4-^{t}Bu)CH$_2$Ph-(2-O)(3-Me,5-^{t}Bu)}$^{3-}$	KH/N_2	[{(ONO)V}$_2$(μ-N)$_2$(K-dme)$_2$]$^{2-}$ (**47**)	[19]
[Ti(N_4^{Si})Cl] (**48**) N_4^{Si} = {N(CH$_2$CH$_2$NSiMe$_3$)$_3$}$^{3-}$	Mg/N_2	[{Mg(N_4^{Si})}(μ-NTi)$_2$(Mg(N_4^{Si})}] (**50**)	[20]
[{Fe(β-diketamin)}$_2$(μ-Cl)$_2$] (**52**) *β*-diketamin= (2,6-Me$_2$Ph)NC(Me)CHC(Me)N(2,6-Me$_2$Ph)	KC_8/N_2 Na/N_2	[{Fe(β-diketamin)}$_2$(μ-N){(μ-N)K$_2$Cl$_2$Fe(β-diketamin)] (**51**) [{Fe(β-diketamin)}$_2$(μ_2-N){K(thf)$_2$}(μ_3-N)Fe(β-diketamin)] (**53**)	[21] [22]
[Fe$_3$(cyclophane-*β*-diketamin)Br$_2$] (**54**) cyclophane-*β*-diketamin = (2,4,6-Et-Ph-1,3,5-CH$_2$-NC(Me)CHC(Me)N-)$_3$	KC_8/N_2	[Fe$_3$(μ-NH)$_{1-2}$(cyclophane-diketamin)] (**55**)	[23]
[Cp*Ta{N(^{i}Pr)C(R)N(^{i}Pr)}Cl$_3$] (**57**) Cp* = η^5-C$_5$Me$_5$, R = Me, NMe$_2$, Ph	KC_8/N_2	[{Cp*Ta[N(^{i}Pr)C(R)N(^{i}Pr)](μ-N)}$_2$] (**56**)	[24]
[Cp*Nb{N(^{i}Pr)C(R)N(^{i}Pr)}Cl$_3$] (**58**) R = Me, Ph	KC_8/N_2	[{Cp*Nb[N(^{i}Pr)C(R)N(^{i}Pr)](μ-N)}$_2$] (**59**)	[25]
[{Cp*MNEtC(R)NEt}$_2$(μ-N$_2$)] M = Mo (**60**), W (**61**); R = Ph	Na(Hg)/N_2	[{Cp*MNEtC(R)NEt}$_2$(μ-N)$_2$]	[26]
[MoCl$_4$·DME]	i.) MesMgBr/N_2 ii.) *hν*	[Mo(Mes)$_3$-N=Mo(Mes)$_3$] (**63**) Mes = 2,4,6-Me$_3$(C$_6$H$_2$)	[27]
{Re(P'NP')Cl$_3$] P'NP' = (2,6-OP^{i}Pr$_2$)C$_5$H$_3$N	i.) LiBHEt$_3$/N_2 ii.) *hν* (λ = 405)	[{Re(N)(P'NP')Cl] (**66**)	[28]
[{MoCp*(depf)}$_2$(N$_2$)] (**67**)	*hν* (λ > 400)	[{MoCp*(depf)}(N)] (**68**)	[29]
[{Cp*M{N(^{i}Pr)C(R)N(^{i}Pr)}}$_2$(μ-N$_2$)] M = Mo (**69**), W (**70**); R = Me	*hν*	[{Cp*M{N(^{i}Pr)C(R)N(^{i}Pr)}}$_2$(μ-N)$_2$] (M = Mo, **71**; M = W, **72)** [{Cp*M(N){N(^{i}Pr)C(R)N(^{i}Pr)}}$_2$] (**73**)	[30]
trans-[Mo(depe)$_2$(N$_2$)$_2$] (**74**) depe = Et$_2$PCH$_2$CH$_2$PEt$_2$	Oxidation, E_{red} = 0.5 V *vs.* Pt-wire	[Mo(depe)$_2$(N)] (**75**)	[31]

2. Summary of used complexes and reagents to functionalize nitride originating from N_2

Table S2. Summary of used complexes and reagents for nitride functionalization.

Nitride Complex	*Reagent*	*Selectivity*[b]	*Ref.*
$[Mo^{VI}(N^tBuAr)_3(N)]$ (**2**)	MeI	$[Mo^{VI}(N^tBuAr)_3(NR)]^+$	[32]
$[Nb^{V}(N^tBuAr')_3N][Na]$ (**77**)	RCOCl	RCN	[33]
$[Mo^{VI}(N^tBuAr)_3(^{15}N)]$ (**2-^{15}N**)	$(CF_3CO)_2O$	$CF_3CO^{15}NH_2$	[34]
$[Mo^{VI}(N^tBuAr)_3(N)]$ (**2**)	RC(O)Cl + R'_3SiOTf + Mg(anthracene) + MCl_2 (M = Sn, Zn)	RCN (R = Me, ^{t}Bu, Ph)	[35]
$[(ONO)V^V(\mu\text{-}N)]_2[K(dme)]_2$ (**47**)	CO or isocyanide	potassium isocyanate **81** or carbodiimide complex **82**.	[19]
$[((anti\text{-}O_3)Nb^V)_2(\mu\text{-}N)_2][K(thf)]_2$ (**12**)	MeI, CO_2	Imide, ureate complex **79**.	[5, 36]
$[(Cp^*Mo[N(^iPr)C(Me)N(^iPr)])_2(\mu\text{-}N_2)]$ (**69**)	R_3ECl (R_3E = Me_3Si, Ph_3Si, Me_3Ge or Me_3C) + CO or CO_2	RNCO	[37]
$[Re^V(PNP)Cl(N)]$ (**33**) (*PNP* = $((^tBu)_2P(CH_2CH_2)N)$	MeOTf	Imide complex **83**.	[38]
$[Re^V(PNP)Cl(N)]$ (**33**) (*PNP* = $((^tBu)_2P(CH_2CH_2)N)$	EtOTf, $(KN(SiMe_3)_2)$, NCS	MeCN	[39]
$[Re^V(PNP)Cl(N)]$ (**33**) (*PNP* = $((^tBu)_2P(CH_2CH_2)N)$	i.) BnBr, AgOTf, DTBMP, ii.) $(KN(SiMe_3)_2)$ iii.) NCS	PhCN	[40]
$[Re^V(PNP)Cl(N)]$ (**33**) (*PNP* = $((^iPr)_2P(CH_2CH_2)N)$	i.) $h\nu$ (390 nm) ii.) PhC(O)Cl iii.) E = -1.67 V, N_2	PhCN + $PhC(O)NH_2$	[41]
$[(Cp'Ti)_4(\mu^3\text{-}NH)_2(\mu^3\text{-}N)_2]$ (**89**) (Cp' $=C_5Me_4SiMe_3$)	RC(O)Cl (R = aryl, Bn, Me, ^{t}Bu)	RCN	[42]
$[Mo^{IV}(PPP^{Cy})(N)(I)]$ (**31**)	1,2-bisdimethylsilyethane	Bis(silyl)amine	[13]
$[\{Ta^V(NN)Cp^*(\mu\text{-}N)\}_2]$ (**56**)	$PhSiH_3$	Silylimido complex **92**.	[24]
$[(Mo^{II}(NN)Cp^*)_2(\mu\text{-}N_2)]$ (**60**) [a]	Me_3SiCl + ^{i}PrOH	$HN(SiMe_3)_2$	[43]

[a] *in-situ* generation of the metal nitride

3. Summary of used complexes and reagents for stoichiometric N_2 protonation and N_2-hydrogenation

Table S3. Summary of used complexes and reagents for stoichiometric N-H bond formation.

Complex	*Reagent*	*Selectivity*[b]	*Ref.*
trans-[W(N_2)$_2$(dppe)$_2$](**94**) dppe = $Ph_2PCH_2CH_2PPh_2$	HX (X= Cl, Br)	*trans*-[W(NH-NH)(dppe)$_2$X]$^+$ (**97**)	[44]
trans-[*Mo*(N_2)$_2$(depe)$_2$] (**95**) dppe = $Et_2PCH_2CH_2PEt_2$	HX (X = Cl, Br)	*trans*-[Mo(NH-NH)(dppe)$_2$X]$^+$ (**98**)	[45]
trans-[W(N_2)$_2$(depf)$_2$] (**103**) depf = Et_2PFcPEt_2	HOTf	*trans*-[W(N-NH_2)(depf)$_2$OTf]$^+$ (**101**)	[46]
trans-[W(N_2)$_2$(depr)$_2$] (**104**) depr = Et_2PRuCp_2PEt_2	HOTf	*trans*-[W(N-NH_2)(depr)$_2$OTf]$^+$	[47]
trans-[W(N_2)$_2$(depc)$_2$] (**105**)	HOTf	*trans*-[W(N-NH_2)(depc)$_2$OTf]$^{++}$	[48]
trans-[*Mo*(N_2)$_2$(depf)$_2$] (**106**)	HOTf	*trans*-[Mo(N-NH_2)(depf)$_2$OTf]$^+$ (**102**)	[46]
trans-[*Mo*(N_2)$_2$(depc)$_2$] (**107**)	HOTf	*trans*-[Mo(N-NH_2)(depc)$_2$OTf]$^+$	[48]
trans-[W(N_2)$_2$(depf)(PPh_2Me)$_2$] (**108**)	H_2SO_4	NH_4^+	[46]
trans-[Mo(N_2)$_2$(depf)(PPh_2Me)$_2$] (**110**)	H_2SO_4	NH_4^+	[46]
trans-[W(N_2)$_2$(depc)(PPh_2Me)$_2$] (**109**)	H_2SO_4	NH_4^+	[48]
trans-[W(N_2)$_2$(PPh_2Me)$_4$] (**121**)	HCl	*trans*-[W(NH=NH)(Me_2PPh)$_4$Cl]$^+$ (**122**)	[45]
trans-[W(N_2)$_2$($MePPh_2$)$_4$] (**121**)	H_2SO_4	NH_3	[49]
cis-[W(N_2)$_2$(Me_2PPh)$_4$] (**123**)	H_2SO_4	NH_3	[49]
cis-[Mo(N_2)$_2$(Me_2PPh)$_4$] (**124**)	H_2SO_4	NH_3, NH_2-NH_2	[50]
cis-[Mo(N_2)$_2$(PPP)PPh_3] (**125**) PPP = *bis*-(2-diphenylphosphinoethylene)phenylphosphine	HBr	NH_3	[51]
cis-[Mo(N_2)$_2$(PPP)(depf)] (**127**)	HBr	NH_3	[52]
trans-[Cr(N_2)$_2$(dmpe)$_2$] dmpe = $Me_2PCH_2CH_2PMe_2$	HOTf	[Cr(N-NH_2)(dmpe)$_2$(OTf)]$^+$	[53]
[Cr(N_2)$_2$($P^{Ph}{}_4N^{Bn}{}_4$)] (**130**) $P^{Ph}{}_4N^{Bn}{}_4$ = 1,5,9,13-benzylaza-3,7,11,15-phenylphosphocyclohexadecane	HOTf HOTf, $CoCp_2$	[Cr(N_2H)($P^{Ph}{}_4N^{Bn}{}_4$)]$^+$ (**131**) (DFT) $N_2H_5^+$, NH_4^+	[54]
[Cr(N_2)$_2$($P^{Ph}{}_4N^{Bn}{}_4$)] (**130**)	TEMPOH	NH_3	[55]
[Fe(N_2)(DMeOPrPE)$_2$] (**113**)	HOTf	[Fe(N-NH_2)(DMeOPrPE)$_2$]$^+$	[56]

$[Fe(N_2)(dppe)_2]$ (**112**)	HCl	NH_3, NH_2-NH_2	[57]
$[Fe(dmpe)_2(N_2)]$ (**111**)	$H(OEt_2)_2OTf$/THF $H(OEt_2)_2OTf$/Pentane	NH_3 NH_2-NH_2	[58]
$[(Cp^*)_2Zr(N_2)$-(μ^2-N_2)-$Zr(N_2)(Cp^*)_2]$ (**133**)	HCl/Toluene	NH_2-NH_2	[59]
$[(NEt_2CS_2)_3Nb]_2(\mu$-$N_2)$ (**134**) $[(NEt_2CS_2)_3Ta]_2(\mu$-$N_2)$ (**135**)	HCl HCl	NH_2-NH_2, NH_3 NH_2-NH_2, NH_3	[60, 61]
$\{[(Me_3Si)_2N]_2(thf)Y\}_2(\mu$-$\eta^2$:$\eta^2$-$N_2[K(thf)_6]$ (**138**)	$[Et_3NH][BPh_4]$	$\{[(Me_3Si)_2N]_2(thf)Y\}_2(\mu$-$N_2H_2)$ (**139**)	[63]
{[bis-(2-^{t}Bu-4-Me-phenolate)methylene]Th(dme)Cl} (**140**)	N_2/K-naphthalinide	{[bis-(2-^{t}Bu-4-Me-phenolate)methylene]Th(dme)NH_2} (**141**)	[63]
$M_2(mTP)_2$ (M = U, **142** and M = Th, **143**) mTP = $[\{2$-$(OC_6H_2$-^{t}Bu-2,4$)_2CH\}$-C_6H_4-1,3$]^{4-}$	KC_8/N_2	$K_4[M_2(\mu$-$N_2H_2)(mTP)_2]$ (M = U, **144**; Th, **145**)	[64]
$[K_3\{[U(OR)_3]_2(\mu$-N) (μ-η^2:η^2-$N_2)\}]$ (R = Si(O^{t}Bu)) (**147**)	HCl, H_2	NH_3	[65]
cis-$[W(N_2)_2(PPh_2Me)_4]$ (**123**)	ZrHCpCl (**148**) $CoH(CO)_4$ (**151**) $HFeCo(CO)_{12}$ (**149**) $(H)_2Fe(CO)_4$ (**150**)	NH_3, NH_2-NH_2	[66]
trans-$[W(N_2)_2(dppe)_2]$ (**93**)	$Ru(H)_2Cp(dtfpe)Cl$ (**152**)	NH_3	[67]
trans-$[W(N_2)_2(dppe)_2]$ (**93**)	$[Ru(H_2)(dppe)_2Cl]^+$ (**153**)	NH_3	[68]
cis-$[W(N_2)_2(PPh_2Me)_4]$ (**123**)	$[(Cp^*M)_2(\mu$-$SH)_3]$ {M = Ir, Rh} (**154, 155**) $[(PPP$-$Fe)_2(\mu$-$SH)_3]$ (**156**) {PPP = $MeC(CH_2PPh_2)_3$}	NH_3	[69]
[Cr(diaminopyridine)Cl] (**157**)	NaH	[Cr(N-H)(diaminopyridine)Na(thf) (**158**)	[70]
$[(P_2N_2)Zr$-(μ-N_2)-$Zr(P_2N_2)]$ (**159**) $[P_2N_2$ = $\{(Ph$-$PCH_2SiMe_2)_2N\}_2]$	H_2	$[(P_2N_2)Zr$-(μ-N-NH)-$Zr(P_2N_2)]$ (**160**)	[71]
$[(CpMe_4H)_2Zr$-(μ-N_2)-$Zr(CpMe_4H)_2]$ (**161**)	H_2	NH_3	[72]
[(PNP)Ti-(μ-H)$_4$-Ti(PNP) (**163**)	-	[(PNP)HTi-(μ-N)(μ-NH)-Ti(PNP)] (**165**)	[73]
$[Ta(H)_4(SiO)_n]$ (**167**)	-	$[(\equiv OSi)_2Ta(=NH)(NH_2)]$ (**169**)	[74]

4. Summary of used complexes and reagents for stoichiometric N_2 silylation.

Table S4. Summary of used complexes and reagents for stoichiometric silylation of metal-dinitrogen complexes.

Complex	*Reagent*	*Selectivity*	*Ref.*
[Mo(N_2) Cp*(depf)] (**170**)	Me_3SiCl	[Mo(N=N-$SiMe_3$) Cp*(depf)] (**171**)	[75]
Mg(thf)$_4$[Co(PhBP$^{iPr}{}_3$)(N_2)]$_2$ (**172**) [$P_3{}^B$ = Tris-[2-(diisopropylphosphino)-phenyl]borane]	Me_3SiCl	[(PhBP$^{iPr}{}_3$)CoN=N-TMS] (**174**)	[76]
[Co(EP$^{Ph}{}_3$)Cl] (E=N, **175**; E=CMe, **176**) EP$^{Ph}{}_3$ = E($CH_2CH_2PPh_2$)$_3$		[Co(XP$^{Ph}{}_3$)(N=NTMS)] (E=N, **177**; E=CMe, **178**)	[77]
[Fe($P_3{}^B$)Cl] (**179**) ($P_3{}^B$ = [tris-(2-diisopropylphosphino)-borane)	N_2/Na(Hg) $ClMe_2SiCH_2CH_2SiMe_2Cl$	[($P_3{}^B$)Fe=N-N($Me_2SiCH_2CH_2SiMe_2$)] (**181**)	[78]
[Fe_2($P_2{}^B$)$_2$(N_2)] (**183**) ($P_2{}^B$ = [bis-(2-diisopropylphosphino)-phenylborane)	Na/$ClMe_2SiCH_2CH_2SiMe_2Cl$	[($P_2{}^B$)Fe=N-N($Me_2SiCH_2CH_2SiMe_2$)] (**184**)	[79]
[Fe(N_2)AltraPhos]$^-$ (**188**) AltraPhos = Al[N(*o*-$C_6H_4NCH_2$P*i*Pr_2)$_3$	KC_8/$ClMe_2SiCH_2CH_2SiMe_2Cl$	[Fe{N_2($SiMe_2CH_2$)$_2$}AltraPhos] (**189**)	[80]
[(*μ*-η^1:η^2-N_2){Ta(NPN)H}$_2$] (**190**) [NPN = ($PhNSiMe_2CH2$)$_2$PPh)]	$RSiH_3$ {R = ^{n}Bu, Ph}	[{Ta(NPN)}$_2$(*μ*-$NSiH_2R$)$_2$] (**194, 195**) (R = Ph, ^{n}Bu)	[81]
[{(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf}$_2$(μ_2,η^2,η^2-N_2)] (**196**)	$CySiH_3$	[{(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf}(*μ*-H){*μ*,η^1,η^2-N(SiH_2Cy)N}] (**197**)	[82]

5. Summary of used complexes and reagents for stoichiometric N-C bond formation.

Table S5. Summary of used complexes and reagents for stoichiometric N_2-functionalization for N-C bond formation.

Complex	*Reagent*	*Selectivity*	*Ref.*
trans-[W(N_2)$_2$(dppe)$_2$)] (**94**)	RCOBr {R = Me, Et, Ph, *p*-OMePh}	*trans*-[W(N-NHC(O)R)(dppe)$_2$Br$_2$] (**201-204**) (R = Et, Ph, *p*-OMePh)	[83]
trans-[Mo(N_2)$_2$(dppe)$_2$)] (**95**)	RCOCl {R = Me, Et}	*trans*-[Mo(N-NHC(O)R)(dppe)$_2$Br$_2$] (**205-206**)	[83]
trans-[W(N_2)$_2$(dppe)$_2$)] (**94**)	R-X (R = Me, Et, ^{n}Pr, ^{i}Pr, ^{t}Bu,, X = Cl, Br	[(dppe)$_2$W(-N=NR)] {R = Me, Et, ^{n}Pr, ^{i}Pr, ^{t}Bu} (**207-211**) [(dppe)$_2$W(=N-NR$_2$)] {R = Me} (**214**)	[84]
trans-[Mo(N_2)$_2$(dppe)$_2$)] (**95**)	R-X {R = Me, Et}	[(dppe)$_2$Mo(-N=NR)] {R = Me, Et} (**212-213**)	[85]
trans-[W(N_2)$_2$(dppe)$_2$)] (**94**)	ClCH$_2$CH$_2$CH$_2$CH$_2$Cl	[(dppe)$_2$W(=N-N(CH$_2$)$_4$)] (**215**)	[86]
[(PhMe$_2$P)$_3$Re(N_2)Cl$_2$]	RCOCl (R = Me, Ph)	[(PhMe$_2$P)$_3$Re(N_2COR)Cl$_2$]	[84]
[M(PhB(CH$_2$P^{iPr})$_3$)Cl]{M = Fe, Co} (**216**, **173**)	N_2/Mg/MeOTs	M(PhB(CH$_2$P^{iPr})$_3$)(N=NMe), M = Fe (**218**), Co (**217**)	[76]
[Fe(P$_3$^{X})L] (L = Cl, Br) (**219-220**) (X = B, Si)	N_2/Na(Hg)/MeOTf N_2/KC$_8$/MeOTf	Fe(P$_3$^{x})(N-NMe$_2$) (**221-222**)	[87]
[Zr((*η*^{5}-C$_5$Me$_4$R)$_2$SiMe$_2$)]$_2$(*μ*-*η*^{2},*η*^{2}-N_2) (**223**)	CO_2	[Zr((*η*^{5}-C$_5$Me$_4$R)$_2$SiMe$_2$)]$_2$(*μ*-*η*^{2},*η*^{2}-OCON-NOCO)] (**224**)	[88]
[{(η^5-C$_5$Me$_4$H)$_2$Hf}$_2$-(*μ*$_2$-*η*^{2},*η*^{2}-N_2)] (**225**)	CO_2	[{(η^5-C$_5$Me$_4$H)$_2$Hf}$_2${NN(CO_2)$_2$}] (**226**)	[89]
[{(η^5-C$_5$Me$_4$H)$_2$Hf}$_2$-(*μ*$_2$-*η*^{2},*η*^{2}-N_2)] (**225**)	PhNCO	[{(η^5-C$_5$Me$_4$H)$_2$Hf}$_2$(N$_5$C$_3$O$_3$Ph$_3$)]	[89]
[{(η^5-C$_5$Me$_4$H)Sc{(NEt)$_2$CNEt$_2$}$_2$(*μ*$_2$-*η*^{2},*η*^{2}-N_2)] (**227**)	EtBr	[{(η^5-C$_5$Me$_4$H)Sc{(NEt)$_2$CNEt$_2$}$_2$-(*μ*$_2$-*η*^{2},*η*^{2}-N_2Me)]	[24]
[{(η^5-C$_5$Me$_4$H)Sc{(N^i*Pr*)$_2$C^{t}Bu}$_2$(*μ*$_2$-*η*^{2},*η*^{2}-N_2)]$^-$ (**228**)	Xs MeOTf	[{(η^5-C$_5$Me$_4$H)Sc{(N^i*Pr*)$_2$C^{t}Bu}$_2${*μ*$_2$-*η*^{2},*η*^{2}-(MeN-NMe)}] (**229**)	[90]
[(*μ*-*η*^{1}:*η*^{2}-N_2)Ta$_2$(NPN)$_2$(*μ*-H)$_2$] (**190**)	PhCH$_2$Br	[(NPN)Ta-(*η*^{1}-NCH$_2$Ph:*μ*^{2}-N)(*μ*-H)$_2$TaBr(NPN)] (**231**)	[91]
[(*μ*-*η*^{1}:*η*^{2}-N_2)Ta$_2$(NPN)$_2$(*μ*-H)$_2$] (**190**)	Ph-N=C=N-Ph X=N=C=S	[(NPN)Ta-(*μ*-*η*^{1}:*η*^{2}-{κ^2-N(Ph)C(N-Ph)N-N}(*μ*-H)$_2$TaBr(NPN)] [(NPN)(X=N=C=N)Ta-(*μ*-N)(*μ*-S)-Ta(NPN)]	[92]
[(P$_2$N$_2$)Zr-(*μ*-N_2)-Zr(P$_2$N$_2$)] (**159**)	H-C≡C-Ar Ar = Ph, *p*-MePh, *p*-^{t}BuPh	[(P$_2$N$_2$)Zr-{*μ*-η^2:η^2-N-N(CH=CHAr)}(*μ*-C≡CPh)-Zr(P$_2$N$_2$)] (**233-235**)	[93]
[(O$_3$C)$_2$Ti$_2$(*μ*-N_2)K$_3$(thf)$_3$][K(thf)$_6$] (**236**) O$_3$C = (*o*-OPh)$_3$C^{4-}	CO_2 ^{t}BuNCO	[(O$_3$C)$_2$Ti$_2${*μ*-(*κ*^{2}:*κ*^{2}-(OCO)$_2$N-N(COO-)} (**237**) [(O$_3$C)$_2$Ti$_2${*μ*-(*κ*^{2}:*κ*^{2}-(N^{t}BuCON)$_2$} (**238**)	[94]

	$PhC{=}C{=}CH_2$	$[(O_3C)_2Ti_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}NN(C(CH_3)CHPh)\}]$ (**239**)or, $[(O_3C)_2Ti_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}NN(C(CH_2)CH_2Ph)\}]$ (**240**)	
$[K_3\{[U(OR)_3]_2(\mu\text{-}N)\ (\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)\}]$ (R = Si(O^{t}Bu)) (**147**)	CO	KCN + $[K_2([U(OR)_3]_2(\mu\text{-}O)(\mu\text{-}NCO)_2)]$ (**241**)	[65]
$[K_2([U(OR)_3]_2(\mu\text{-}O)\ (\mu\text{-}\eta^2{:}\eta^2\text{-}N_2))]$ (**243**) (R = Si(O^{t}Bu))	CO	$[K_2\{[U(OR)_3]_2(\mu\text{-}O)_2(\mu\text{-}NCN)\}]$ (**244**) +'NCNCO' (*not identified*)	[95]

6. Summary of complexes and reagents for catalytic N_2 protonation.

Table S6. Molecular catalysts for N_2 protonation, conditions for highest TON reported

Catalyst	Reductant (equiv.)[a]	Proton source (equiv.)	Solvent	Reaction conditions	TON[a]	Ref.
[{(Tren^{TMS})Ti}$_2$(μ-η^1:η^1:η^2:η^{2}N$_2$K$_2$)] (**49**)	KC_8 (600)	[Cy$_3$PH]I (600)	Et_2O	1 atm of N_2, - 78 °C	9	[96]
[V(OXyl)(PNP')(N$_2$)] (**262**)	KC_8 (200)	[HOEt$_2$][BAr$^F{}_4$] (184)	Et_2O	1 atm of N_2, - 78 °C	6	[97]
Mg[Mg$_2$Mo$_8$O$_{22}$(OMe)$_6$(MeOH)$_4$] (**245**)	Na/Hg	solvent	Methanol	1 atm of N_2, 20 °C	1000[b]	[98]
[Mo(N$_2$)(HIPTN$_3$N)] (**246**)	CrCp$^*{}_2$ (36)	[LutH]{BAr$^F{}_4$]	Hexane	1 atm of N_2, 25 °C	3.78	[99]
[Mo(N$_2$)$_2$(PNP)]$_2$(*μ*-N$_2$) (**22**)	CoCp$_2$ (72)	[LutH][OTf] (96)	Toluene	1 atm of N_2, 25 °C	11.5	[100]
[Mo(N)(PNP)Cl][OTf] (**253**)	CoCp$_2$ (36)	[LutH][OTf] (48)	Toluene	1 atm of N_2, 25 °C	3	[101]
[Mo(N$_2$)$_2$(*p*-OMe-PNP)]$_2$(*μ*-N$_2$) (**254**)	CoCp$_2$ (216)	[LutH][OTf] (288)	Toluene	1 atm of N_2, 25 °C	17	[102]
[Mo(Cl$_3$)(*p*-OFc-PNP)](**255**)	CoCp$^*{}_2$ (360)	[LutH][OTf] (480)	Toluene	1 atm of N_2, 25 °C	41.5	[103]
[Mo(N$_2$)$_2$(*p*-Fc-PNP)]$_2$(*μ*-N$_2$) (**256**)	CoCp$_2$ (216)	[LutH][OTf] (288)	Toluene	1 atm of N_2, 25 °C	18.5	[104]
[Mo(Cl$_3$)(*p*-OFc(PNP)$_2$)](**257**)	CoCp$^*{}_2$ (360)	[LutH][OTf] (480)	Toluene	1 atm of N_2, 25 °C	22	[103]
[Mo(N)(PPP)Cl] (**26**)	CoCp$^*{}_2$ (36)	[ColH][OTf] (48)	Toluene	1 atm of N_2, 25 °C	5.5	[105]
[Mo(N$_2$)$_2$(PCP)]$_2$(*μ*-N$_2$) (**263**)	CrCp$^*{}_2$ (72)	[LutH][OTf] (96)	Toluene	1 atm of N_2, 25 °C	58	[106]
[MoI$_3$(PNP)] (**20**)	CoCp$^*{}_2$ (180)	[ColH][OTf] (180)	Toluene	1 atm of N_2, 25 °C	26	[9]
[Mo(N)I(PNP)]$^-$ (**21**)	CoCp$^*{}_2$ (180)	[ColH][OTf] (180)	Toluene	1 atm of N_2, 25 °C	6.1	[9]
[MoI$_3$(PNP)] (**20**)	SmI_2 (360)	HOCH$_2$CH$_2$OH (360)	THF	1 atm of N_2, 25 °C	21.4	[10]
[MoI$_2$(PNP')] (**258**)	SmI$_2$(thf)$_2$ (180)	HOCH$_2$CH$_2$OH (180)	THF	1 atm of N_2, 25 °C	6.1	[107]
[Mo(N$_2$)$_2$(PCP)]$_2$(*μ*-N$_2$) (**263**)	SmI_2 (360)	HOCH$_2$CH$_2$OH (360)	THF	1 atm of N_2, 25 °C	18	[10]
[Mo(N$_2$)$_2$(PCP)]$_2$(*μ*-N$_2$) (**263**)	SmI_2 (14400)	H_2O (14400)	THF	1 atm of N_2, 25 °C	2175	[10]
[Fe(PNP')(N$_2$)] (**260**)	KC_8 (40)	[HOEt$_2$][BAr$^F{}_4$] (38)	Et_2O	1 atm of N_2, - 78 °C	3.5	[108]
[Na(12-crown-4)$_2$][Fe(P$_3{}^B$)(N$_2$)] (**264**)	KC_8 (50)	[HOEt$_2$][BAr$^F{}_4$] (46)	Et_2O	1 atm of N_2, - 78 °C	3.5	[109]
[Na(12-crown-4)$_2$][Fe(P$_3{}^B$)(N$_2$)] (**264**)	CoCp$^*{}_2$ (486)	[H$_2$NPh$_2$][OTf] (966)	Et_2O	1 atm of N_2, - 78 °C	6.4	[110]
[K(Et$_2$O)$_{0.5}$][Fe(P$_3{}^C$)(N$_2$)] (**265**)	KC_8 (40)	[HOEt$_2$][BAr$^F{}_4$] (38)	Et_2O	1 atm of N_2, - 78 °C	2.3	[111]

[Na(12-crown-4)$_2$][Fe(P_3^{Si})(N_2)] (**266**)	KC_8 (1800)	[$HOEt_2$][BAr^F_4] (1500)	Et_2O	1 atm of N_2, - 78 °C	1.9	[112]
[K(thf)$_2$][Ru(P_3^{Si})(N_2)]	KC_8 (50)	[$HOEt_2$][BAr^F_4] (46)	Et_2O	1 atm of N_2, - 78 °C	2.2	[113]
[K(thf)$_2$][Os(P_3^{Si})(N_2)]	$CoCp^*_2$ (1800)	[H_2NPh_2][OTf] (1500)	Et_2O	1 atm of N_2, - 78 °C	60	[113]
[FeH(PPP)]$_2$(N_2)] (**268**)	KC_8 (3600)	[$HOEt_2$][BAr^F_4] (3000)	Et_2O	1 atm of N_2, - 78 °C, Hg lamp	33.4	[114]
[Fe(N_2)($P^{Ph}P_2^{Cy}$)(H)$_2$] (**268**)	KC_8 (200)	[$HOEt_2$][BAr^F_4] (200)	Et_2O	1 atm of N_2, - 80 °C	1.4	[115]
[Fe(CAAC)$_2$][BAr^F_4]] (**269**)	KC_8 (50)	[$HOEt_2$][BAr^F_4] (50)	Et_2O	1 atm of N_2, - 95 °C	1.7	[116]
[Fe(depe)$_2$$N_2$] (**270**)	$CoCp^*_2$ (270)	[H_2NPh_2][OTf] (360)	Et_2O	1 atm of N_2, - 78 °C	12.3[c]	[117]
[Co(PNP')(N_2)] (**261**)	KC_8 (40)	[$HOEt_2$][BAr^F_4] (38)	Et_2O	1 atm of N_2, - 78 °C	2.2	[118]

[a] equivalents per catalyst. [b] based on the equivalents of reductant. [c] in N_2H_4

7. Summary of complexes and reagents for catalytic N_2 silylation

Table S7. Molecular catalysts for N_2 silylation, conditions for highest TON reported.

Catalyst	Reductant (equiv.)[a]	Silyl source (equiv.)	Solvent	Reaction conditions	TON[a]	Ref.
$K_2[\{(Xy\text{-}N_3N)Ti\}_2(\mu_2\text{-}N_2)]$ (**306**)	K (1500)	Me_3SiCl (1500)	THF	1 atm of N_2, 50 °C	6.3	[119]
$[V\{(Me_3SiNCH_2CH_2)_2NSiMe_3\}(\mu\text{-}N)]_2$ (**38**)	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	11.5	[120]
$K[V\{(Me_3SiNCH_2CH_2)_2NSiMe_3\}(\mu\text{-}N)]_2$ (**39**)	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	12	[120]
$[V\{(Me_3SiNCH_2CH_2)_2NSiMe_3\}(\mu\text{-}Cl)]_2$	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	5.5	[120]
$[VCl\{N(SiMe_3)_2\}_2(thf)]$	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	5.5	[120]
$[VCl_2(tmeda)_2]$ (**307**)	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	6	[120]
$[Na(thf)][V(N_2)_2(dppe)_2]$ (**308**)	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	10.5	[120]
$[CrCl_3]$	Li (50)	Me_3SiCl (50)	THF	1 atm of N_2, 25 °C	2.7	[121]
$[Cr(N_2)_2(P^{Ph}{}_4N^{Bn}{}_4)]$ (**130**)	Na (10^5)	Me_3SiCl (10^5)	THF	1 atm of N_2, 25 °C	17	[55]
$[Cr(Cy_2PC_6H_4\text{-}(\eta^5\text{-}C_5H_4Et_4)(N_2)_2]$ (**275**)	K (2000)	Me_3SiCl (2000)	Et_2O	1 atm of N_2, 25 °C	13	[122]
trans-$[W(N_2)_2(dppe)_2]$ (**94**)	Na (100)	Me_3SiCl (100)	THF	1 atm of N_2, 30 °C	1.7	[123]
trans-$[Mo(N_2)_2(dppe)_2]$ (**95**)	Na (100)	Me_3SiCl (100)	THF	1 atm of N_2, 30 °C	4.9	[123]
$[Mo(N_2)_2(PMe_2Ph)_4]$ (**124**)	Na (200)	Me_3SiCl (200)	THF	1 atm of N_2, 30 °C	18.3	[123]
$[Mo(N_2)_2(depf)_2]$ (**106**)	Na (8000)	Me_3SiCl (8000)	THF	1 atm of N_2, 25 °C	226	[124]
$[Mo(PP^{Cy}{}_3)Cl][BPh_4]$ (**276**)	K (200)	Me_3SiCl (200)	THF	1 atm of N_2, 50 °C	5.9	[125]
$[Mo(PP^{Cy}{}_3)(=N\text{-}N(SiMe_3)_2]$ (**278**)	K (200)	Me_3SiCl (200)	THF	1 atm of N_2, 50 °C	7.5	[125]
$[Mo(PP^{Cy}{}_3)(=N(SiMe_3)]$ (**279**)	K (200)	Me_3SiCl (200)	THF	1 atm of N_2, 50 °C	5.9	[125]
$[Mo(PPP)Cl_3]$ (**28**)	K (400)	Me_3SiCl (400)	THF	1 atm of N_2, 25 °C	19.2	[126]
$[\{Mo(PMe_3)Cp^*\}_2(\mu_2\text{-}H)_8\{FeN(SiMe_3)_2\}]$ (**295**)	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	34.5	[127]
$[\{Mo(PMe_3)Cp^*\}_2(\mu_2\text{-}H)_8\{MnN(SiMe_3)_2\}]$ (**296**)	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	6	[127]
$[\{Mo(PMe_3)Cp^*\}_2(\mu_2\text{-}H)_8\{FeS(2,4,6\text{-}^iPr_3C_6H_2)\}]$ (**297**)	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	32.5	[127]
$[\{Mo(PMe_3)Cp^*\}_2(\mu_2\text{-}H)_8\{FeS(2,6\text{-}(SiMe_3)_2C_6H_3)\}]$ (**298**)	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	34.5	[127]

$[Fe(CO)_5]$	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25°C	12.5	[128]
$[Fe(SiMe_3)_2(CO)_4]$	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25°C	14.5	[128]
$[FeCp(CO)_2]_2$	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	8.5	[128]
$[FeCp_2]$	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	6.5	[128]
$[Fe(\eta^5\text{-}C_5H_4SiMe_3)_2]$	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	11.5	[128]
$[Fe(\eta^5\text{-}C_5H_2(SiMe_3)_3\}_2]$	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	17	[128]
$[Fe(PSiP)H(PMe_3)N_2]$ (**285**)	Na (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	13	[129]
$[Fe[SiCHSi](H)(N_2)(PMe_3)]$ (**287**)	KC_8 (1800)	Me_3SiCl (1800)	Dioxane	1 atm of N_2, 25 °C	37.2	[130]
$[Fe(CAAC)_2][BAr^F{}_4]]$ (**269**)	KC_8 (600)	Me_3SiCl (600)	Et_2O	1 atm of N_2, 25 °C	12.2	[116]
$[Fe(depe)_2N_2]$ (**270**)	KC_8 (1500)	Me_3SiCl (1500)	Et_2O	1 atm of N_2, 25 °C	60.5	[131]
$[Fe(P_4N_2)N_2]$ (**289**)	KC_8 (500)	Me_3SiCl (500)	Toluene	1 atm of N_2, 25 °C	5.5	[132]
$[Fe(N_2)(P^{Ph}P_2{}^{Cy})(H)_2]$	K (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25°C	14.5	[115]
$[Fe(N_2)_2(P^{Ph}P_2{}^{Cy})$ (**290**)	K (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	16	[115]
$[Fe(N_2)_2(P^{tBu}P_2{}^{Cy})$ (**291**)	K (600)	Me_3SiCl (600)	THF	1 atm of N_2, 25 °C	7.3	[115]
$[Fe_3$(cyclophane-*β*-diketamin)$Br_2]$ (**54**)	KC_8 (500)	Me_3SiCl (500)	Et_2O	1 atm of N_2, - 34 °C	41.5	[133]
$[Fe_4(\mu\text{-}H)_4(\mu_3\text{-}H)_2\{N(SiMe_3)_2\}_2(PMe_3)_4]$ (**292**)	Na (600)	Me_3SiCl (600)	DME	1 atm of N_2, 25 °C	80	[134]
$[Fe_6(\mu\text{-}H)_{10}(\mu_3\text{-}H)_2(PMe_3)_{10}]$ (**293**)	Na (600)	Me_3SiCl (600)	DME	1 atm of N_2, 25 °C	91.5	[134]
$[Fe_4(\eta^6\text{-}C_7H_8)(\mu\text{-}H)_2\{\mu\text{-}N(SiMe_3)_2\}_2\{N(SiMe_3)_2\}_2]$ (**294**)	Na (600)	Me_3SiCl (600)	DME	1 atm of N_2, 25 °C	74	[134]
$[Fe_4(\mu\text{-}H)_4(\mu_3\text{-}H)_2(SDmp)_2(PMe_3)_4]$	Na (600)	Me_3SiCl (600)	DME	1 atm of N_2, 25 °C	52	[134]
$[Co_2(CO)_8]$	Na (600)	Me_3SiCl (600)	DME	1 atm of N_2, 25 °C	18	[135]
$[Co_2(CO)_8]$	Na (600)	Me_3SiCl (600)	DME	1 atm of N_2, 25 °C + 2 equiv. bipy.	20	[135]
$[Co(SiMe_3)(CO)_4]$	Na (600)	Me_3SiCl (600)	DME	1 atm of N_2, 25 °C	18	[135]
$[CoCp_2]$	Na (600)	Me_3SiCl (600)	DME	1 atm of N_2, 25 °C	4	[135]
$[Co_2(P_3N_3)]$ (**299**)	KC_8 (2000)	Me_3SiCl (2000)	THF	1 atm of N_2, 25 °C	195	[135]
$[Co(ICy)_2(N_2)]$ (**300**)	KC_8 (2000)	Me_3SiCl (2000)	Et_2O	1 atm of N_2, 25 °C	125	[136]
[Co(NpNP)] (**302**)	KC_8 (1500)	Me_3SiCl (2000)	THF	1 atm of N_2, - 40 °C	100	[137]
[Co(QuiNacNacP)Cl] (**303**)	KC_8 (1000)	Me_3SiCl (1500)	THF	1 atm of N_2, 25 °C	38	[138]

[Co(PSiP)(PMePh$_2$)N$_2$] (**304**)	Na (600)	Me$_3$SiCl (600)	THF	1 atm of N$_2$, 25 °C	20.5	[129]
[Rh(PNP')N$_2$] (**305**)	KC$_8$ (600)	Me$_3$SiCl (600)	THF	1 atm of N$_2$, - 40 °C	11.5	[139]
[U$_2$(*m*TP)$_2$] (**309**) *m*TP = [{2-(OC$_6$H$_2$-^{t}Bu-2,Me-4)$_2$CH}-C$_6$H$_4$-1,3]$^{4-}$	K (85)	Me$_3$SiCl (60) [HNEt$_3$][BPh$_4$]	C$_6$H$_6$	1 atm of N$_2$, 25 °C	3.2[c]	[64]

[a] equivalents per catalyst. [b] based on the equivalents of reductant. [c] in HMDS

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