

On the Structural Analysis for the Coordination of Dinitrogen to Transition Metal Complexes

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Supplementary Material

- Table S1.** Experimental parameters retrieved from *Cambridge Structural Database* for mononuclear complexes having dinitrogen as ligand. All compounds having the structural motif **1a**.
- Table S2.** Experimental parameters retrieved from *Cambridge Structural Database* for binuclear complexes having dinitrogen as bridging ligand as **2a**.
- Table S3.** Experimental parameters retrieved from *Cambridge Structural Database* for heterobinuclear complexes having dinitrogen as bridging ligand as **2a**.
- Table S4.** Experimental parameters retrieved from *Cambridge Structural Database* for polynuclear complexes having dinitrogen as bridging ligand between two different metallic units.
- Table S5.** Experimental parameters retrieved from *Cambridge Structural Database* for binuclear complexes having dinitrogen as bridging ligand as **2b**.
- Table S6.** Experimental parameters retrieved from *Cambridge Structural Database* for binuclear complexes having dinitrogen as bridging ligand as **2c**.
- Table S7.** Experimental data for N-N distance of partially hydrogenated dinitrogen ligand in transition metal complexes retrieved from *Cambridge Structural Database*.
- Figure S1.** Variation of the N-N distance in mononuclear complexes as a function of: (a) coordination number of the metallic fragment, and (b) d electrons of the metal center.
- Figure S2.** Variation of the N-N distance in mononuclear complexes as a function of valence electrons for: (a) end-on mononuclear **1a**, (b) end-on binuclear **2a**, (c) side-on binuclear having bonded distances **2b**, and (d) side-on binuclear without bonded distances **2c**.
- Text S1.** Electron counting scheme to assign electronic configurations for the transition metal.

Table S1. Experimental parameters retrieved from *Cambridge Structural Database* for mononuclear complexes having dinitrogen as ligand. All compounds having the structural motif **1a**.

Refcode	L _n M	M	δ	CN	N-N	M-N	M-N-N
NEJZAE	Ti(η^5 -C ₅ Me ₄ (SiPhMe ₂) ₂)	Ti ^{II}	2	6	1.119	2.016	180.0
JALFOS	Ti(η^5 -C ₅ Me ₄ 'Pr) ₂ (N ₂)	Ti ^{II}	2	7	1.110	2.043	174.2
SIGJIC	Ti{(η^5 -C ₅ H ₃ 'Bu) ₂ SiMe ₂ }(μ -N≡N{Ti{(η^5 -C ₅ H ₃ 'Bu) ₂ SiMe ₂ }(N ₂)})	Ti ^{II}	2	7	1.101	2.068	176.0
SIGJJC	Ti{(η^5 -C ₅ H ₃ 'Bu) ₂ SiMe ₂ }(μ -N≡N{Ti{(η^5 -C ₅ H ₃ 'Bu) ₂ SiMe ₂ }(N ₂)})	Ti ^{II}	2	7	1.109	2.068	176.1
TULYOP	Ti(η^5 -C ₅ EtMe ₄) ₂ (μ -N≡N{Ti{(η^5 -C ₅ EtMe ₄) ₂ }(N ₂)})	Ti ^{II}	2	7	1.111	2.050	178.1
MCPNZR	Zr(η^5 -C ₅ Me ₅) ₂ (μ -N≡N{Zr(C ₅ Me ₅) ₂ (N ₂)})	Zr ^{II}	2	7	1.116	2.187	177.9
MCPNZR	Zr(η^5 -C ₅ Me ₅) ₂ (μ -N≡N{Zr(C ₅ Me ₅) ₂ (N ₂)})	Zr ^{II}	2	7	1.114	2.188	177.8
CAMVOB10	Cr(N ₂)(dmpe) ₂	Cr ⁰	6	5	1.122	1.874	178.2
UDEDUE	Cr(N ₂)({PhCH ₂ NCH ₂) ₂ {PhPCH ₂) ₂ } ₂	Cr ⁰	6	5	1.133	1.886	175.5
KOSNIP	V(N ₂)(dppe) ₂ ⁻	V ⁻¹	6	5	1.130	1.915	180.0
TUFPEP	Mo{Me ₃ SiNC ₂ H ₄ } ₃ N)	Mo ^{III}	3	4	1.086	1.990	179.1
TUFPEP	Mo{Me ₃ SiNC ₂ H ₄ } ₃ N)	Mo ^{III}	3	4	1.083	1.995	179.5
HUTQOC	Mo{Ar ₂ C ₆ H ₃ NC ₂ H ₄ } ₃ N)	Mo ^{III}	3	4	1.060	1.964	179.1
QAQRAB*	Mo(BuNC ₆ H ₃ Me ₂) ₃ ⁻	Mo ^{II}	4	3	1.170	1.840	178.8
HUTOES*	Mo{Ar ₂ C ₆ H ₃ NC ₂ H ₄ } ₃ N ⁻	Mo ^{II}	4	4	1.150	1.913	179.2
YUZNOX	Mo{(pyr ₂ C ₆ H ₃ NC ₂ H ₄ } ₃ N ⁻	Mo ^{II}	4	4	1.152	1.914	178.2
KILXIM	MoCl{(η^5 -C ₅ Me ₅)(PMes ₃) ₂	Mo ^{II}	4	6	0.744	2.159	174.1
AGISIT	Mo(N ₂)(depf) ₂	Mo ⁰	6	5	1.124	2.010	174.3
AGISIT	Mo(N ₂)(depf) ₂	Mo ⁰	6	5	1.122	2.021	173.8
AQUVOY	Mo(N ₂)({Ph ₂ PC ₂ H ₄ PPh} ₂ C ₃ H ₆)	Mo ⁰	6	5	1.118	2.037	175.9
AQUVOY	Mo(N ₂)({Ph ₂ PC ₂ H ₄ PPh} ₂ C ₃ H ₆)	Mo ⁰	6	5	1.106	2.050	177.2
ATUGAY	Mo(N ₂)(depf)(PMePh ₂) ₂	Mo ⁰	6	5	1.138	2.000	177.7

ATUGAY	Mo(N ₂)(depf)(PMePh ₂) ₂	5	1.140	1.988	179.1
BAPMUC	Mo(C≡NC ₆ H ₃ {C ₆ H ₃ ⁱ Pr ₂ H ₂ }) ₂ (⁶ -C ₆ H ₆)	6	5	1.041	2.075
BIWGAP10	Mo(PMe ₃) ₅	Mo ⁰	6	5	174.6
BUSZEU	Mo(N ₂)(PMe ₃) ₄	Mo ⁰	6	5	1.108
BUSZEU	Mo(N ₂)(PMe ₃) ₄	Mo ⁰	6	5	1.154
CILSEV	Mo(N ₂)(PPhPr ₂) ₃	Mo ⁰	6	5	1.142
CILSEV	Mo(N ₂)(PPhPr ₂) ₃	Mo ⁰	6	5	1.092
CIRLEU	Mo(N ₂)(Ph ₂ PC ₂ H ₄ SMe)(PMePh ₂) ₂	Mo ⁰	6	5	1.125
CIRLEU	Mo(N ₂)(Ph ₂ PC ₂ H ₄ SMe)(PMePh ₂) ₂	Mo ⁰	6	5	1.049
CUVVEH	Mo(N ₂)(dmpr)(PMePh ₂)	Mo ⁰	6	5	1.983
CUVVEH	Mo(N ₂)(dmpr)(PMePh ₂)	Mo ⁰	6	5	1.983
DAHTOV	Mo(N ₂)(PMePh ₂) ₄	Mo ⁰	6	5	1.134
DAHTOV	Mo(N ₂)(PMePh ₂) ₄	Mo ⁰	6	5	1.134
DAMSOA	Mo(N ₂){{EtC ₆ H ₄ } ₂ PC ₂ H ₄ P{C ₆ H ₄ Et}} ₂	Mo ⁰	6	5	1.154
DAMSOA	Mo(N ₂){{EtC ₆ H ₄ } ₂ PC ₂ H ₄ P{C ₆ H ₄ Et}} ₂	Mo ⁰	6	5	1.154
DOBHX*	Mo(N ₂)(PMe ₂ Ph)({Ph ₂ PC ₃ H ₆ } ₂ PPh)	Mo ⁰	6	5	1.117
DOBHX*	Mo(N ₂)(PMe ₂ Ph)({Ph ₂ PC ₃ H ₆ } ₂ PPh)	Mo ⁰	6	5	1.116
DOBHX*	Mo(N ₂)(PMe ₂ Ph)({Ph ₂ PC ₃ H ₆ } ₂ PPh)	Mo ⁰	6	5	1.198
DOBHX*	Mo(N ₂)(PMe ₂ Ph)({Ph ₂ PC ₃ H ₆ } ₂ PPh)	Mo ⁰	6	5	1.021
DOPENMO	Mo(CO)(dppe) ₂	Mo ⁰	6	5	1.216
DUKPEE	Mo(N ₂)(PMe ₃)({Ph ₂ PC ₃ H ₆ } ₂ PPh)	Mo ⁰	6	5	1.124
DUKPEE	Mo(N ₂)(PMe ₃)({Ph ₂ PC ₃ H ₆ } ₂ PPh)	Mo ⁰	6	5	1.119
GEPCEJ	Mo(N ₂)(16ane-S ₄)	Mo ⁰	6	5	1.109
GEPCEJ	Mo(N ₂)(16ane-S ₄)	Mo ⁰	6	5	1.105
HAJSOC	Mo({Ph ₂ CH ₂ } ₃ CMe)(clmpm)	Mo ⁰	6	5	1.069
KEDCUR	Mo(PMe ₃) ₂ {Ph ₂ PC ₃ H ₆ } ₂ PMe	Mo ⁰	6	5	1.132

AGISAL	W(N ₂)(depf) ₂	W ⁰	6	5	1.121	1.994	174.3
AGISEP	W(N ₂)(depf) ₂	W ⁰	6	5	1.136	1.993	175.0
AGISEP	W(N ₂)(depf) ₂	W ⁰	6	5	1.139	1.999	174.0
BIYJEY*	W(N ₂)(PEt ₂ Ph) ₃ (μ-N≡N{W(N ₂)(PEt ₂ Ph) ₃ })	W ⁰	6	5	1.205	1.967	176.1
BIYJEY*	W(N ₂)(PEt ₂ Ph) ₃ (μ-N≡N{W(N ₂)(PEt ₂ Ph) ₃ })	W ⁰	6	5	1.200	1.979	173.8
BIYJEY*	W(N ₂)(PEt ₂ Ph) ₃ (μ-N≡N{W(N ₂)(PEt ₂ Ph) ₃ })	W ⁰	6	5	1.202	1.997	170.4
BIYJEY*	W(N ₂)(PEt ₂ Ph) ₃ (μ-N≡N{W(N ₂)(PEt ₂ Ph) ₃ })	W ⁰	6	5	1.203	1.995	175.3
BUYBUS	W(N ₂)(PM ₃) ₄	W ⁰	6	5	1.191	2.038	180.0
CUHVAD	W(N ₂)(PM ₃) ₄	W ⁰	6	5	1.160	1.967	179.0
CUHVAD	W(N ₂)(depr)(PMePh ₂)	W ⁰	6	5	1.139	1.972	179.8
CUHVIL	W(N ₂)(depr)(PMePh ₂)	W ⁰	6	5	1.134	1.955	179.3
CUHVIL	W(N ₂)(depf)(PMePh ₂)	W ⁰	6	5	1.125	1.943	178.9
DAMSUG	W(N ₂)(EtC ₆ H ₄) ₂ PC ₂ H ₄ P(C ₆ H ₄ Et) ₂	W ⁰	6	5	1.128	2.018	178.0
DAMSUG	W(N ₂)(EtC ₆ H ₄) ₂ PC ₂ H ₄ P(C ₆ H ₄ Et) ₂	W ⁰	6	5	1.134	2.005	177.9
DAYGEP	W(N ₂)(PMe ₂ Ph) ₄	W ⁰	6	5	1.126	1.983	177.7
DAYGEP	W(N ₂)(PMe ₂ Ph) ₄	W ⁰	6	5	1.119	2.016	178.0
DIDNAF	W(N ₂)(PEt ₂ Ph) ₄	W ⁰	6	5	1.146	1.986	179.2
DIDNAF	W(N ₂)(PEt ₂ Ph) ₄	W ⁰	6	5	1.139	1.995	179.4
DIDNEJ	W(PPr ₂ Ph) ₂ (η ⁶ C ₆ H ₅ Pr ₂)	W ⁰	6	5	1.126	1.980	175.4
DIXLEB	W(PM ₃) ₅	W ⁰	6	5	1.122	2.033	179.6
ROPYTE	W(N ₂)(dppe) ₂	W ⁰	6	5	1.123	2.012	179.7
ROPYOK	W(N ₂)(dppe) ₂	W ⁰	6	5	1.126	2.004	179.2
ROPYUQ	W(N ₂)(dppe) ₂	W ⁰	6	5	1.104	2.002	176.5
ROPZAX	W(N ₂)(dppe) ₂	W ⁰	6	5	1.119	2.004	177.6
UGUYEA	W(N≡CEi)(dppe) ₂	W ⁰	6	5	1.120	1.982	176.5
ZAVHAH	W(N ₂)(dppp) ₂	W ⁰	6	5	1.125	1.996	175.7
ZAVHEL	W(N ₂)(dppp)(Et ₂ PCH ₂) ₂ NMe	W ⁰	6	5	1.122	2.012	175.3

ZAVHEL	W(N ₂)(dppp)(Et ₂ PCH ₂) ₂ NMe)	W ⁰	6	5	1.129	2.010	176.3
ZAVHEL	W(N ₂)(dppp)(Et ₂ PCH ₂) ₂ NMe)	W ⁰	6	5	1.129	2.020	177.7
ZAVHUB	W(N ₂)(dppe)(Et ₂ PCH ₂) ₂ NMe)	W ⁰	6	5	1.120	2.033	175.7
ZAVHUB	W(N ₂)(dppe)(Et ₂ PCH ₂) ₂ NMe)	W ⁰	6	5	1.130	2.001	178.4
ZAVJAJ	W(N ₂)(PMePh ₂) ₄	W ⁰	6	5	1.132	2.001	179.4
ZAVJAJ	W(N ₂)(PMePh ₂) ₄	W ⁰	6	5	1.134	1.991	179.5
ZAVJEN	W(N ₂)(Ph ₂ PCH ₂) ₂ NMe) ₂	W ⁰	6	5	1.103	2.021	177.9
ZURKIG	W(N ₂)(dppe) ₂	W ⁰	6	5	1.126	1.997	178.9
ZURKIG	W(N ₂)(dppe) ₂	W ⁰	6	5	1.140	1.985	179.7
YAJTIM	MnH(dmpe) ₂	Mn ^I	6	5	1.127	1.817	178.6
BOJLIV	TcH(dppe) ₂	Tc ^I	6	5	0.976	2.050	177.7
KOWNAL	Re(SC ₆ H ₂ 'Pr ₃) ₃ (PPh ₃)	Re ^{III}	4	4	1.005	2.004	176.2
KOWNAL	Re(SC ₆ H ₂ 'Pr ₃) ₃ (PPh ₃)	Re ^{III}	4	4	1.108	1.994	178.3
XOLPUJ	Re({F ₅ C ₆ NC ₂ H ₄ } ₃ N)	Re ^{III}	4	4	1.087	1.943	177.6
SOMZEZ	ReCl(dpae) ₂ ⁺	Re ^{II}	5	5	1.585	1.716	168.6
BIBJAX	Re(NHPh)(PMe ₃) ₄	Re ^I	6	5	1.100	1.956	176.5
BURKMD	ReH(PEt ₂ Me) ₄	Re ^I	6	5	1.018	2.055	180.0
BUMLIE10	Re(PS ₂ Ph ₂)(PMe ₂ Ph) ₃ (CNMe)	Re ^I	6	5	1.128	1.828	173.9
CNMPRE	ReCl(PMe ₂ Ph) ₄	Re ^I	6	5	1.055	1.966	177.1
DAYSUR	ReCl(P{OMe}) ₃ (CNMe)	Re ^I	6	5	1.038	1.981	179.3
HEPVUU	ReCl(CO) ₂ (PPh ₃) ₂	Re ^I	6	5	1.080	1.981	177.7
HEPWAB	Re(pyCOO)(CO)(PPh ₃) ₂	Re ^I	6	5	1.145	1.911	177.6
NETMEF	Re(S ₂ CNEt ₂)(PMe ₂ Ph) ₃	Re ^I	6	5	1.140	1.928	178.6
NEVLEF	Re(tm)(PF ₃)(PPh ₃) ⁺	Re ^I	6	5	1.129	1.926	175.9
VOGNAG	ReH(PMe ₂ Ph) ₄	Re ^I	6	5	1.123	1.955	179.0
WIHXAM	Re'(Bu ₂ bipy)(pyCH ₂ NH ₂)(PPh ₃) ⁺	Re ^I	6	5	1.128	1.906	174.2

W1HSEQ	Re(N ₂)(P(OEt) ₂ Ph) ₄ ⁺	5	1.023	2.026	180.0
W1HSEQ	Re(N ₂)(P(OEt) ₂ Ph) ₄ ⁺	6	5	1.093	1.970
YATPOY	Re(NCS)(dppe) ₂	6	5	1.120	1.951
AWARAS	Fe({ ⁱ Pr ₂ PC ₆ H ₄ }) ₂ Si{C ₆ H ₄ SAd} ₂) ⁺	6	4	1.037	1.954
AWAROG	FeH({ ⁱ Pr ₂ PC ₆ H ₄ })Si{C ₆ H ₄ SAd} ₂)	6	4	1.116	1.828
WUVNAD	Fe({ ⁱ Pr ₂ PC ₆ H ₄ }) ₂ Si ⁺	6	4	1.091	1.913
GAMZAX	FeH({ ⁱ Pr ₂ PC ₆ H ₄ }) ₃ Si)	6	5	1.100	1.828
I1HWEU	Fe(SiH ₂ Mes) ₂ (ⁱ Pr ₂ C ₆ H ₃ im) ₂ Py)	6	5	1.148	1.826
I1XFAP	Fe({C ₆ H ₄ CH ₂ }) ₂ PPh)(PMMe ₃) ₂	6	5	1.113	1.804
NIYJEK	FeCl(depe) ₂ ⁺	6	5	1.099	1.730
NIYJEK	FeCl(depe) ₂ ⁺	6	5	1.085	1.783
OGIWUX	FeH(dnpppe) ₂ ⁺	6	5	1.112	1.834
PHSNFE	FeH(({Ph ₂ PC ₂ H ₄ PPh}) ₂ C ₂ H ₄) ⁺	6	5	1.074	1.866
RANKAT	FeH({ ⁱ Pr ₂ PC ₂ H ₄ }) ₃ N ⁺	6	5	1.114	1.803
SIGFOD	FeH ₂ (PEtPh ₂) ₃	6	5	1.135	1.786
TAGLAO10	FeH ₂ (dmppe) ₂ ⁺	6	5	1.112	1.825
WAMVUB	FeH(dnpppe) ₂ ⁺	6	5	1.178	1.801
YEQTIIY	FeH(depe) ₂ ⁺	6	5	1.071	1.823
YOGKEK	FeH({ ⁱ Pr ₂ PC ₂ H ₄ }) ₂ N ⁺	6	5	1.120	1.800
ZEGDIY	Fe(η^5 -C ₅ H ₅)(dippe) ⁺	6	5	1.132	1.756
COGBIK	Fe({ ⁱ Pr ₂ C ₆ H ₃ N=CMe}Py{C(=CH ₂)NC ₆ H ₃ 'Pr ₂ })	7	3	1.135	1.762
COGBOQ	Fe({ ⁱ Pr ₂ C ₆ H ₃ N=CMe}) ₂ Py ⁺	7	3	1.113	1.781
NIHPUQ	Fe({ ⁱ Pr ₂ PC ₆ H ₄ }) ₃ Si)	7	4	1.097	1.780
NIHQIF	Fe({Ph ₂ PC ₆ H ₄ }) ₃ Si)	7	4	1.106	1.819
WUVQOU	Fe({ ⁱ Pr ₂ PC ₆ H ₄ }) ₃ Si)	7	4	1.124	1.819
BARTIZ	Fe({ ⁱ Pr ₂ C ₆ H ₃ N=C ⁱ Pr}) ₂ Py)	8	3	1.112	1.817

BARTOF	Fe($\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CPH}\}_2\text{py}$)	Fe ⁰	8	3	1.116	1.790	176.5
COGBUW	Fe($\text{C}_5\text{H}_3\text{NAr}_2\right)_2\left(\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py}\right)$	Fe ⁰	8	4	1.130	1.808	178.6
EMEROE	Fe($\{^i\text{Pr}_2\text{PC}_6\text{H}_4\}_3\text{Si}\}^-$)	Fe ⁰	8	4	1.132	1.795	179.3
FIMTOL	Fe($\text{N}_2\right)_2\left(\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{im}\}_2\text{py}\right)$	Fe ⁰	8	4	1.114	1.847	175.0
FIMVAZ	Fe($\text{N}_2\right)_2\left(\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{im}\}_2\text{py}\right)$	Fe ⁰	8	4	1.113	1.820	179.2
FIMVED	Fe($\text{N}_2\right)_2\left(\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{im}\}_2\text{py}\right)(\eta^2\text{-C}_2\text{H}_4)$	Fe ⁰	8	4	1.121	1.820	175.3
FUTWIB	Fe($\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{im}\}_2\text{py}\)(\text{PMe}_3)$)	Fe ⁰	8	4	1.129	1.780	178.4
JAHKIN	Fe($\text{N}_2\right)_2\left(\{^i\text{Pr}_2\text{PC}_2\text{H}_4\}_3\text{P}\right)$	Fe ⁰	8	4	1.128	1.803	179.3
JAHKIN	Fe($\text{N}_2\right)_2\left(\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py}\right)$	Fe ⁰	8	4	1.089	1.834	178.4
JENDUC	Fe($\text{N}_2\right)_2\left(\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py}\right)$	Fe ⁰	8	4	1.104	1.880	171.8
JENDUC	Fe($\text{N}_2\right)_2\left(\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CPh}\}_2\text{py}\right)$	Fe ⁰	8	4	1.105	1.842	178.5
LAHHOR01	Fe($\text{N}_2\right)_2\left(\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CPh}\}_2\text{py}\right)$	Fe ⁰	8	4	1.106	1.865	170.3
LTHGOZ	Fe($\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py}\)(\eta^2\text{-C}_2\text{R}_4)$)	Fe ⁰	8	4	1.143	1.752	179.1
LIMQEE	Fe($\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py}\)(\text{tht})$)	Fe ⁰	8	4	1.105	1.854	172.0
LIMQEE	Fe($\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py}\)(\text{tht})$)	Fe ⁰	8	4	1.118	1.797	173.3
LIMQII	Fe($\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py}\)(\text{PEt}_3)$)	Fe ⁰	8	4	1.111	1.799	174.1
OMIHIC	Fe($\{^i\text{Pr}_2\text{PC}_6\text{H}_4\}_3\text{B}\}^-$)	Fe ⁰	8	4	1.085	1.798	178.2
OMIHOI	Fe($\{^i\text{Pr}_2\text{PC}_6\text{H}_4\}_3\text{B}\}^-$)	Fe ⁰	8	4	1.149	1.776	175.9
RUDBEY	Fe($\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{im}\}_2\text{Me}_2\text{C}_6\text{HN})(\text{N}_2)$)	Fe ⁰	8	4	1.148	1.773	179.8
RUDBEY	Fe($\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{im}\}_2\text{Me}_2\text{C}_6\text{HN})(\text{N}_2)$)	Fe ⁰	8	4	1.124	1.812	179.4
RUTZAI	Fe($\{\text{Et}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py}\)(\mu\text{-N}=\text{N}\{\text{Fe}(\{\text{Et}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py})(\text{N}_2)\})$)	Fe ⁰	8	4	1.121	1.849	176.1
RUTZAI	Fe($\{\text{Et}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py}\)(\mu\text{-N}=\text{N}\{\text{Fe}(\{\text{Et}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py})(\text{N}_2)\})$)	Fe ⁰	8	4	1.107	1.851	177.4
RUTZAI	Fe($\{\text{Et}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py}\)(\mu\text{-N}=\text{N}\{\text{Fe}(\{\text{Et}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py})(\text{N}_2)\})$)	Fe ⁰	8	4	1.098	1.836	174.9
RUTZAI	Fe($\{\text{Et}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py}\)(\mu\text{-N}=\text{N}\{\text{Fe}(\{\text{Et}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py})(\text{N}_2)\})$)	Fe ⁰	8	4	1.113	1.827	175.7
RUTZEM	Fe($\{\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{CPH}\}_2\text{py}\)(\mu\text{-N}=\text{N}\{\text{Fe}(\{\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{CPH}\}_2\text{py})(\text{N}_2)\})$)	Fe ⁰	8	4	1.102	1.854	179.2

ATALEM	Ru(CH=CHPh)Cl(P <i>i</i> Pr ₃) ₂	Ru ^{II}	6	4	1.089	1.868	179.2
BUCJEP	RuH(CO)(Mes ₂ im) ₂ ⁺	Ru ^{II}	6	4	0.997	2.011	180.0
LAXLUS	Ru({'Bu ₂ PC ₂ H ₂ } ₂ C ₆ H ₃)(CO) ⁺ ^a	Ru ^{II}	6	4	1.069	2.132	179.2
NEJXAC	Ru({MesN=CM ₂ }{ ₂ py})(Si{NR ₂ } ₂) ₂	Ru ^{II}	6	4	1.096	1.975	176.9
NEJXAC	Ru({MesN=CM ₂ }{ ₂ py})(Si{NR ₂ } ₂) ₂	Ru ^{II}	6	4	1.097	1.970	174.4
QACHIM	RuH({'Bu ₂ PC ₂ H ₄ } ₂ CH)	Ru ^{II}	6	4	1.117	1.964	178.7
TAMZUD	RuCl({'Bu ₂ PC ₂ H ₄ } ₂ O) ⁺	Ru ^{II}	6	4	1.054	1.946	175.2
TAZPEQ	Ru({'Bu ₂ PCH ₂ SiMe ₂ } ₂ NH) ⁺ ^a	Ru ^{II}	6	4	1.115	1.904	178.4
TUSFIW	Ru({'Bu ₂ PCH ₂ } ₂ C ₆ H ₃)(SiHCl ₂)	Ru ^{II}	6	4	1.099	2.014	178.3
TUVREI	Ru({'Pr ₂ PC ₆ H ₄ } ₃ Si) ⁺	Ru ^{II}	6	4	1.071	2.146	173.4
AVEYUW*	Ru({η ⁵ -C ₅ Me ₅ }(dcpe) ⁺	Ru ^{II}	6	5	1.085	1.998	166.9
ENAZPU10	Ru(N ₃)(en) ₂ ⁺	Ru ^{II}	6	5	1.107	1.893	179.4
ESAYED	RuCl({Me ₂ pz} ₂ CMeCO ₂)(PPh ₃)	Ru ^{II}	6	5	0.791	1.976	172.2
FELLTUM	Ru(C=C'Bu)(PPh ₃) ₂ (Me ₂ bipy) ⁺	Ru ^{II}	6	5	1.012	1.994	175.9
FUMBUL	RuF(Me ₄ -14ane-N ₄) ⁺	Ru ^{II}	6	5	1.144	1.847	176.3
FUTWUN	RuH({'Pr ₂ PC ₂ H ₄ } ₃ P) ⁺	Ru ^{II}	6	5	1.092	2.022	178.7
GEWPAZ	Ru(porphyrin)(thf)	Ru ^{II}	6	5	1.074	1.822	177.6
GUZTIE	Ru({η ⁵ -C ₅ Me ₅ }(dppe) ⁺	Ru ^{II}	6	5	1.083	1.975	175.6
ILEHEM	RuCl(Me ₂ dppe) ₂ ⁺	Ru ^{II}	6	5	1.015	1.964	178.8
LOQQJUW	Ru(HB{N ₂ C ₃ H ⁱ Pr ₂ } ₃)(dppe) ⁺	Ru ^{II}	6	5	1.105	1.921	175.6
OB1PEU	Ru({SC ₆ H ₄ NH}C ₂ H ₄) ₂ (P <i>i</i> Pr ₃)	Ru ^{II}	6	5	1.110	1.907	176.9
OBOHIX	RuHCl({'Bu ₂ PCH ₂ } ₂ py)	Ru ^{II}	6	5	1.107	1.925	179.1
OBOMIC	RuH({Cy ₂ PCH ₂ } ₂ C ₆ H ₃)(PPh ₃)	Ru ^{II}	6	5	1.112	2.014	178.4
PAPPEC	Ru(porphyrin){μ-C≡C{Ru(porphyrin)(N ₂) ²⁻ }}	Ru ^{II}	6	5	1.197	1.900	176.5
PAPPEC	Ru(porphyrin){μ-C≡C{Ru(porphyrin)(N ₂) ²⁻ }}	Ru ^{II}	6	5	1.124	1.923	176.9
PAPZUC	Ru(pz ₃ BH)({Pr ₂ P{NHC ₂ H ₄ NH}P <i>i</i> Pr ₂ }) ⁺	Ru ^{II}	6	5	0.999	1.933	170.2
PURJOC	RuH({py ₂ CH})(PPh ₃) ₂	Ru ^{II}	6	5	1.111	1.930	179.0

QINXUG	RuH ₂ (P ⁱ Pr ₃) ₂ (μ-N≡N{RuH ₂ (P ⁱ Pr ₃) ₂ (N ₂)})	Ru ^{II}	6	5	1.107	2.008	176.3
QINXUG	RuH ₂ (P ⁱ Pr ₃) ₂ (μ-N≡N{RuH ₂ (P ⁱ Pr ₃) ₂ (N ₂)})	Ru ^{II}	6	5	1.133	1.919	178.3
QQJLIL	Ru(pyCH=N-NC{Ph})O(PPh ₃) ⁺	Ru ^{II}	6	5	1.171	2.177	176.0
RAFKAK	RuH(^t Bu ₂ PCH ₂) ₂ C ₆ H ₃)(μ-N≡N{RuH(^t Bu ₂ PCH ₂) ₂ C ₆ H ₃ }(N ₂)})	Ru ^{II}	6	5	1.121	1.890	177.0
RAXVUJ	RuH({py ₂ CCO ₂ H})(PPh ₃) ₂	Ru ^{II}	6	5	1.006	1.922	172.9
RAZKEI	RuCl(Me ₄ -16ane-N ₄) ⁺	Ru ^{II}	6	5	1.098	1.942	174.5
RIPHED	Ru(HB{N ₂ C ₃ H ₃ }) ₃ (Ph ₂ PC ₂ H ₄ NMe ₂) ⁺	Ru ^{II}	6	5	1.090	2.046	178.5
ROMMOV	Ru(H ₁₂ C ₆ PC ₆ H ₄ PC ₆ H ₁₂) ⁺	Ru ^{II}	6	5	1.096	1.992	172.1
RUVVOU	Ru(η ⁵ -C ₅ Me ₅) ^t Pr ₂ PCH ₂ quin) ⁺	Ru ^{II}	6	5	1.108	1.904	176.1
SAFQOG	Ru({SC ₆ H ₄ NMe})C ₂ H ₄)(PCy ₃)	Ru ^{II}	6	5	1.101	1.893	179.3
TANBEQ	RuCl ₂ (^t Pr ₂ PC ₂ H ₄) ₂ O	Ru ^{II}	6	5	1.073	1.912	173.5
TIMCAU	Ru(η ⁵ -C ₅ H ₅) ^t Pr ₂ P{HNC ₆ H ₄ NH}P ^t Pr ₂) ⁺	Ru ^{II}	6	5	1.094	1.959	175.2
TIMCAU	Ru(η ⁵ -C ₅ H ₅) ^t Pr ₂ P{HNC ₆ H ₄ NH}P ^t Pr ₂) ⁺	Ru ^{II}	6	5	1.100	2.053	179.4
TUVQOR	RuH(^t Pr ₂ PC ₆ H ₄) ₂ Si)	Ru ^{II}	6	5	1.008	1.899	166.0
VEBZUX	Ru(pz ₃ BH)(PEt ₃) ₂ ⁺	Ru ^{II}	6	5	1.093	2.005	175.4
VIRMAK	RuH ₂ (^t Cy ₂ PC ₃ H ₆) ₂ PPh)	Ru ^{II}	6	5	1.087	1.961	175.7
XOQYAD	Ru(η ⁵ -C ₅ H ₅)(dippe) ⁺	Ru ^{II}	6	5	1.128	1.884	177.0
XUWHON	Ru(OH)(Me ₄ -14ane-N ₄) ⁺	Ru ^{II}	7	4	1.097	2.050	178.5
TUVQAD	Ru(^t Pr ₂ PC ₆ H ₄) ₃ Si)	Ru ⁰	8	4	1.109	1.997	180.0
FUTWOH	Ru(^t Pr ₂ PC ₂ H ₄) ₃ P)	Ru ⁰	8	4	1.130	1.973	177.9
TUVRIM	Ru(^t Pr ₂ PC ₆ H ₄) ₃ Si) ⁻	Os ^{II}	6	4	1.120	1.896	179.1
MIJTIJ	OsH(^t Bu ₂ PCH ₂ SiMe ₂) ₂ NH) ⁺	Os ^{II}	6	5	1.112	1.909	176.1
CAJCEV	OsCl(SC ₆ F ₅)(PMe ₂ Ph) ₃	Os ^{II}	6	5	1.078	1.956	174.8
DONLUO	Os(PPh ₃) ₂ (napyl) ₂ N ⁺	Os ^I	7	4	1.100	2.014	179.6
TUYQEHEH	Os(^t Pr ₂ PC ₆ H ₄) ₃ Si)	Os ⁰	8	4	1.136	1.965	178.2
TUVROS	Os(^t Pr ₂ PC ₆ H ₄) ₃ Si) ⁻	Co ^I	8	3	1.112	1.841	175.5
ICIDON	Co({ ^t Pr ₂ C ₆ H ₃ N≡CMe} ₂ py) ⁺						

RANLEY	$\text{Co}(\{\text{iPr}_2\text{C}_6\text{H}_3\text{N=CR}\}\text{py}\{\text{C}(=\text{CH}_2)\text{NC}_6\text{H}_3\text{iPr}_2\})$	8	3	1.094	1.808	178.9
RANLEY	$\text{Co}(\{\text{iPr}_2\text{C}_6\text{H}_3\text{N=CR}\}\text{py}\{\text{C}(=\text{CH}_2)\text{NC}_6\text{H}_3\text{iPr}_2\})$	Co ^I	8	3	1.098	1.815
JOCGUD	$\text{Co}(\{\text{Ph}_2\text{PC}_2\text{H}_4\}_3\text{P})^+$	Co ^I	8	4	1.084	1.853
PPHCHN10	$\text{CoH}(\text{PPh}_3)_3$	Co ^I	8	4	1.103	1.783
POTLAM	$\text{CoH}(\text{PPh}_3)_3$	Co ^I	8	4	1.121	1.832
LUWTUT	$\text{Co}(\{\text{iPr}_2\text{PC}_6\text{H}_4\}_3\text{Si})$	Co ^I	8	4	1.123	1.814
XAJQOQ	$\text{Co}(\{\text{iPr}_2\text{C}_6\text{H}_3\text{N=CMe}\}_2\text{PY})$	Co ⁰	9	3	1.104	1.788
XAJQOQ	$\text{Co}(\{\text{iPr}_2\text{C}_6\text{H}_3\text{N=CMe}\}_2\text{PY})$	Co ⁰	9	3	1.011	1.817
BOYNOT	$\text{Co}(\{\text{iPr}_2\text{C}_6\text{H}_3\text{N=CMe}\}_2\text{PY})$	Co ⁰	9	3	1.035	1.803
DIVWIP	$\text{RhCl}(\{\text{iPr}_2\text{C}_6\text{H}_3\text{im}\})_2$	Rh ^I	8	3	1.093	1.889
HNBP RH10	$\text{Rh}(\{\text{Bu}_2\text{PCH}_2\text{SiMe}_2\}_2\text{N})$	Rh ^I	8	3	1.160	1.846
TYATUY	$\text{RhH}(\text{PBu}_2\text{Ph})_2$	Rh ^I	8	3	1.073	1.970
REVLEJ	$\text{RhCl}(\{\text{iPr}_2\text{C}_6\text{H}_3\text{in}\})_2$	Rh ^I	8	3	1.109	1.889
XARDAW	$\text{Rh}(\{\text{Bu}_2\text{PC}_2\text{H}_4\}_2\text{CMe})$	Rh ^I	8	3	0.964	2.032
XOBJUU	$\text{Rh}(\{\text{iPr}_2\text{C}_6\text{N}_2\text{C}_3\text{HMe}_2\})(\eta^2\text{-C}_8\text{H}_{14})$	Rh ^I	8	3	1.090	1.943
ILIBIP	$\text{Rh}(\{\text{iPr}_2\text{C}_6\text{H}_3\text{N=CMe}\}_2\text{PY})$	Rh ^I	8	3	1.116	1.898
PUWYAH	$\text{IrPh}(\text{HB}\{\text{N}_2\text{C}_3\text{HMe}_2\}_3)(\text{PMe}_3)^+$	Ir ^{III}	6	5	1.095	1.949
QEKSOO	$\text{IrMe}(\text{HB}\{\text{N}_2\text{C}_3\text{HMe}_2\}_3)(\text{PMe}_3)^+$	Ir ^{III}	6	5	1.126	1.863
UYICOV	$\text{IrH}_2(\{\text{Cy}_2\text{PC}_6\text{H}_4\}_2\text{SiMe})$	Ir ^{III}	6	5	1.183	1.910
UYICOV	$\text{IrH}_2(\{\text{Cy}_2\text{PC}_6\text{H}_4\}_2\text{SiMe})$	Ir ^{III}	6	5	1.121	1.910
UYICUB	$\text{IrH}_2(\{\text{Cy}_2\text{PC}_6\text{H}_4\}_2\text{SiMe})$	Ir ^{III}	6	5	1.148	1.937
ANAZEV	$\text{IrH}(\text{P}^+\text{iPr}_2\text{Ad})_2$	Ir ^I	8	3	1.108	1.933
ANIKOY	$\text{Ir}(\text{N}_2)(\text{Mes}_2\text{im})_2^+$	Ir ^I	8	3	0.982	2.055
ANIKOY	$\text{Ir}(\text{N}_2)(\text{Mes}_2\text{im})_2^+$	Ir ^I	8	3	1.078	1.926
ANIKUE	$\text{Ir}(\text{Mes}_2\text{im})_2(\text{thf})^+$	Ir ^I	8	3	1.109	1.840
EXULUE	$\text{Ir}(\{\text{iPr}_2\text{C}_6\text{H}_3\text{N}\}_2\text{C}_3\text{HMe}_2)(\eta^2\text{-C}_8\text{H}_{14})$	Ir ^I	8	3	1.107	1.903

KEVJEB	$\text{Ir}^{\text{l}}\{\text{'Bu}_2\text{PCH}_2\}_2\text{C}_6\text{H}_3)$	8	3	1.107	1.949	176.0
KEVJEB	$\text{Ir}^{\text{l}}\{\text{'Bu}_2\text{PCH}_2\}_2\text{C}_6\text{H}_3)$	8	3	1.107	1.944	179.2
KEVJEB	$\text{Ir}^{\text{l}}\{\text{'Bu}_2\text{PCH}_2\}_2\text{C}_6\text{H}_3)$	8	3	1.107	1.947	179.6
KEVJEB	$\text{Ir}^{\text{l}}\{\text{'Bu}_2\text{PCH}_2\}_2\text{C}_6\text{H}_3)$	8	3	1.109	1.948	178.8
QOSOHO	$\text{Ir}^{\text{l}}\{\text{'Pr}_2\text{PC}_6\text{H}_3\text{Me}\}_2\text{N}$	8	3	1.128	1.859	176.2
WUHPIZ	$\text{Ir}^{\text{l}}\{\text{'Bu}_2\text{PCH}_2\}_2\text{C}_6\text{H}_9)$	8	3	1.064	1.875	174.6
WUQSEH	$\text{Ir}^{\text{l}}\{\{\text{CF}_3\}_3\text{C}_6\text{H}_{12}\}_2\text{PO}\}_2\text{C}_6\text{H}_3)$	8	3	1.107	1.977	176.5
WUQUTUY*	$\text{Ir}^{\text{l}}\{\{\text{CF}_3\}_3\text{C}_6\text{H}_{12}\}_2\text{PO}\}_2\text{C}_6\text{H}_3)$	8	3	1.087	1.987	172.5
YUDXUR	$\text{Ir}^{\text{l}}\{\text{'Pr}_2\text{PC}_6\text{H}_3\text{Me}\}_2\text{N}$	8	3	1.132	1.884	179.3
OLOVOB*	$\text{IrCl}(\text{Mes}_2\text{im})_2(\eta^2\text{-C}_8\text{H}_{14})$	8	4	1.147	1.814	166.5
OLOVOB*	$\text{IrCl}(\text{Mes}_2\text{im})_2(\eta^2\text{-C}_8\text{H}_{14})$	8	4	1.159	1.850	166.5
POTLEQ	$\text{Ir}^{\text{l}}\{\text{'Pr}_2\text{PC}_6\text{H}_4\}_3\text{Si}$	8	4	1.094	2.032	177.4
UY1DEM	$\text{Ir}^{\text{l}}\{\text{Cy}_2\text{PC}_6\text{H}_4\}_2\text{SiMe})(\text{PMe}_3)$	8	4	1.150	1.907	179.1
LARGAO	$\text{Ni}^{\text{II}}\{\text{'Pr}_2\text{PC}_6\text{H}_4\}_3\text{Si}\}^+$	8	4	1.087	1.905	179.8
LARGUI	$\text{Ni}^{\text{II}}\{\text{Ph}_2\text{PC}_6\text{H}_4\}_3\text{Si}\}^+$	8	4	1.083	1.891	175.2
IBUNOK	$\text{Ni}^0\{\text{'Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}\}_2\text{py}$	10	3	0.921	1.908	178.3
RANLUO	$\text{Ni}^0(\text{PPh}_3)(\text{dbpe})$	10	3	1.112	1.830	177.5

^b Agostic interaction of type C-H···M are presented, and it not included (see text).

Table S2. Experimental parameters retrieved from Cambridge Structural Database for binuclear complexes having dinitrogen as bridging ligand as 2a.

Refcode	L _n M	M	d̄	CN	N-N	M-N ^a	N-M-M ^a	M-N-N-M
NTOCTI	Ti(C ₆ H ₄ Me)(η ⁵ -C ₅ H ₅) ₂	Tr ^{II}	1	7	1.162	1.962	176.5	180.0
DAVXII	Ti{PhPC ₂ H ₄ } ₂ {NSi ₂ Me ₄ } ₂)}	Tr ^{II}	2	4	1.255	1.783	177.7	119.4
DAVXII	Ti{PhPC ₂ H ₄ } ₂ {NSi ₂ Me ₄ } ₂)}	Tr ^{II}	2	4	1.245	1.795	179.0	141.8
MIQPIM	Ti(CH ₂ SiMe ₃){'Pr ₂ PC ₂ H ₄ } ₂ NSiMe ₂ N'Bu)	Tr ^{II}	2	4	1.287	1.783	173.1	146.0
JOGZUA	TiCl{Me ₃ Si} ₂ N)(Me ₄ en)	Tr ^{II}	2	4	1.290	1.762	168.5	16.9
JOLJUJ	TiCl{Me ₃ Si} ₂ N)(py) ₂	Tr ^{II}	2	4	1.263	1.760	175.4	180.0
XOLCOQ	Ti{'PrN}CNMe ₂) ₂	Tr ^{II}	2	4	1.282	1.733	180.0	90.0
ZOPMAS	Ti{Me ₃ SiN}CPH) ₂	Tr ^{II}	2	4	1.273	1.764	177.6	132.8
QEJFOB	Ti(η ⁵ -C ₅ H ₅){'Pr ₂ C ₆ H ₃ N} ₂ C ₃ HMe ₂)	Tr ^{II}	2	5	1.273	1.804	164.2	105.1
SEQZAP	Ti{Me ₂ SiN}CPH) ₂ (py)	Tr ^{II}	2	5	1.262	1.795	173.8	73.3
WIQGUY	Ti{'PrNC ₆ H ₄ } ₂ O)(PM ₃ H ₂)	Tr ^{II}	2	5	1.265	1.812	177.8	166.4
UPOGAI	Ti(η ⁵ -C ₅ Me ₅){'PrN}CMe)	Tr ^{II}	2	5	1.270	1.775	166.8	170.9
TULYUV	Ti(η ⁵ -C ₅ Me ₄ {C ₆ H ₃ Me ₂ }) ₂	Tr ^{II}	2	6	1.157	2.030	177.3	40.5
NACKAE	Ti(η ⁵ -C ₅ H ₃ {SiMe ₃ }) ₂	Tr ^{II}	2	6	1.163	1.994	176.5	159.5
NACKAE	Ti(η ⁵ -C ₅ H ₃ {SiMe ₃ }) ₂	Tr ^{II}	2	6	1.165	1.994	177.2	180.0
NPMCTI	Ti(η ⁵ -C ₅ Me ₅) ₂	Tr ^{II}	2	6	1.166	2.010	177.4	25.2
NPMCTI	Ti(η ⁵ -C ₅ Me ₅) ₂	Tr ^{II}	2	6	1.155	2.023	177.4	29.1
RARMAY	Ti(η ⁵ -C ₅ HMe ₄) ₂	Tr ^{II}	2	6	1.170	1.987	178.5	180.0
SIGJAU	Ti(η ⁵ -C ₅ H ₂ Me{'Pr}) ₂	Tr ^{II}	2	6	1.168	1.971	177.1	180.0
SIGJEW	Ti{η ⁵ -C ₅ H ₂ 'Bu(SiMe ₂) ₂ SiMe ₂)}	Tr ^{II}	2	6	1.174	2.010	178.8	13.1
SIGJIC	Ti{η ⁵ -C ₅ H ₃ 'Bu ₂ SiMe ₂)}	Tr ^{II}	2	6	1.165	1.991	172.1	73.4
TULYOP	Ti(η ⁵ -C ₅ EtMe ₄) ₂ (N ₂)	Tr ^{II}	2	7	1.150	2.051	177.2	8.2
GEFFUS	Ti(η ⁵ -C ₅ H ₅) ₂ (PM ₃)	Tr ^{II}	2	7	1.204	1.919	170.0	87.7
SIGJIC	Ti{η ⁵ -C ₅ H ₃ 'Bu ₂ SiMe ₂)(N ₂)}	Tr ^{II}	2	7	1.153	1.996	177.1	30.2

PAKDAH	Ti(η^5 -C ₅ Me ₅) $(\eta^6$ -C ₅ H ₄ =CR ₂)	Ti ^I	3	6	1.159	2.008	169.8	26.4
PAKDEL	Ti(η^5 -C ₅ Me ₅) $(\eta^6$ -C ₅ H ₄ =CR ₂)	Ti ^I	3	6	1.163	2.001	170.8	28.7
PAKDEL	Zr(η^5 -C ₅ H ₅) $(^i\text{Pr}_2\text{PCH}_2\text{SiMe}_2)_2$ N	Zr ^{II}	2	6	1.301	1.921	170.4	26.4
PEFYII	Zr(η^5 -C ₅ Me ₅) (N_2)	Zr ^{II}	2	7	1.182	2.081	177.0	107.6
MCPNZR	Zr(η^5 -C ₅ Me ₅) $(\eta^2$ - $\{^i\text{Pr}, \text{Me}\}$ {Indenyl})	Zr ^{II}	2	7	1.198	2.061	144.1	36.5
IFECAY	Hf(η^5 -C ₅ HM ₄) ₂ (CF ₃ SO ₃)	Hf ^{III}	1	7	1.190	2.059	175.0	180.0
CUHLOH	Hf(η^5 -C ₅ HM ₄) ₂ (CH ₃)	Hf ^{III}	1	7	1.180	2.052	172.8	180.0
CUJJEX	V(OC'Bu ₂ Me) ₃	V ^{III}	2	3	1.225	1.773	178.2	180.0
ABIHOK	V(OC'Bu ₂ Me) ₃	V ^{III}	2	3	1.233	1.771	178.6	180.0
LIBLIR	V(^iPr ₂ N) ₃	V ^{III}	2	3	1.276	1.743	177.4	26.8
REZYOK	V($\{^i\text{PrNCH}_2\}_3$ CM e)	V ^{III}	2	3	1.257	1.707	180.0	90.0
WARPUA	V(CH ₂ 'Bu) ₃	V ^{III}	2	3	1.250	1.725	180.0	90.0
BOQJEX	V($=\text{NC}'\text{BuCH}'\text{Bu}$) $(^i\text{Pr}_2\text{PC}_6\text{H}_3\text{Me})_2$ N	V ^{III}	2	4	1.222	1.845	178.0	111.4
PIZQOF	V($=\text{CH}'\text{Bu}$) $(^i\text{Pr}_2\text{PC}_6\text{H}_3\text{Me})_2$ N	V ^{III}	2	4	1.247	1.757	176.4	166.0
NOREQQ	V(Mes ₂ N) ₃ ^{(0.5)-}	V ^{III,II}	2.5	3	1.223	1.756	172.0	99.7
NOQRIU	V(Mes ₂ N) ₃ ⁻	V ^{II}	3	3	1.230	1.740	178.3	180.0
NOQROA	V(Mes ₂ N) ₃ ⁻	V ^{II}	3	3	1.225	1.763	175.7	21.6
LAWDIX	V($\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{NC}(=\text{CH}_2)\}_2\text{Py}$)(thf)	V ^{II}	3	4	1.242	1.777	167.2	12.4
LEZZUL	V($\{\text{Me}_3\text{SiN}\}_2\text{CPh}_2$) ₂	V ^{II}	3	4	1.235	1.757	176.5	99.3
QIVNIT	V(η^5 -C ₄ H ₂ NMe{CPh ₂ C ₄ H ₃ N} ₂)	V ^{II}	3	5	1.249	1.752	177.1	149.0
SEBXOM	V(Me ₂ NCH ₂ C ₆ H ₄) ₂ (py)	V ^{II}	3	5	1.228	1.832	171.4	41.6
TAHXIL	V(η^5 -C ₅ H ₄ CH ₂ NMe ₂) $(\eta^2$ -C ₂ Ph ₂)(PMe ₃)	V ^I	4	5	1.212	1.767	175.0	157.4
LAQQOK	V($\{^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}_2\}_2\text{Py}$)(thf)	V ⁰	5	4	1.259	1.777	162.4	44.5
ZADZAF	Nb(Cy ₂ N) ₃	Nb ^{III}	2	3	1.345	1.812	180.0	90.0
MIQDEV	NbCl($\{\text{PhNSiMe}_2\text{CH}_2\}_2\text{PPh}_2$)	Nb ^{III}	2	4	1.237	1.843	176.4	180.0
POFYIS	Nb(OAr) ₄ ⁻	Nb ^{III}	2	4	1.390	1.748	180.0	90.0

MIQPOS	Fe(<i>i</i> Pr ₂ PC ₂ H ₄) ₂ NSiMe ₂ N <i>t</i> Bu)	Fe ^I	7	3	1.166	1.851	173.8	180.0
PECMAM	Fe(<i>i</i> Pr ₂ C ₆ H ₃ N) ₂ C ₃ HMe ₂) <i>t</i> Bu-py)	Fe ^I	7	3	1.151	1.815	171.4	28.5
PECMEQ	Fe(<i>i</i> Pr ₂ C ₆ H ₃ N) ₂ C ₃ H <i>t</i> Bu ₂) <i>t</i> Bu-py)	Fe ^I	7	3	1.167	1.795	170.8	100.8
MOGMAX	Fe(η^6 : η^1 - <i>i</i> Pr ₂ C ₆ H ₃ N) ₂ C <i>t</i> Bu)	Fe ^I	7	4	1.124	1.833	176.8	180.0
TAGFUE	FeH _{0.5} (Me ₂ PC ₃ H ₆) ₃ P) ^{(0.5)+c}	Fe ^I	7	4.5	1.127	1.852	177.1	130.5
OLAXEE	Fe(<i>i</i> Pr ₂ PCH ₂) ₃ BPh) ^{(0.5)-}	Fe ^{I,0}	7.5	3	1.171	1.813	178.0	180.0
NAWKIH	Fe(<i>i</i> Pr ₂ PCH ₂ NC ₆ H ₄) ₃ NAl)	Fe ⁰	8	3	1.146	1.843	180.0	153.7
BALWUG	Fe(CO) ₂ (P{OMe}) ₃ ₂	Fe ⁰	8	4	1.129	1.877	175.9	180.0
RUTZAI	Fe(<i>i</i> Et ₂ C ₆ H ₃ N=CMel) ₂ py)(N ₂)	Fe ⁰	8	4	1.137	1.876	175.4	74.4
ABATIG	Fe(<i>i</i> Et ₂ C ₆ H ₃ N=CMel) ₂ py)(N ₂)	Fe ⁰	8	4	1.124	1.889	175.1	136.0
RUTZEM	Fe(Me ₂ C ₆ H ₃ N=CPh) ₂ py)(N ₂)	Fe ⁰	8	4	1.124	1.880	175.0	92.1
RAFKAK	RuH(H ₂ B{N ₂ C ₃ H(CF ₃) ₂ } ₂) <i>t</i> Pr ₂ NH) ^b	Ru ^{II}	6	4	1.138	1.915	179.5	30.7
ABATIG	RuH(H ₂ B{N ₂ C ₃ H(CF ₃) ₂ } ₂) <i>t</i> Pr ₂ NH) ^b	Ru ^{II}	6	4	1.122	1.923	175.6	136.8
AVEYOQ	RuH(<i>i</i> Bu ₂ PCH ₂) ₂ C ₆ H ₃) ₂ O ₅ ^c	Ru ^{II}	6	4.5	1.134	2.038	178.2	141.1
AYEHAN	Ru(dcpb)($\{\mu$ -Cl $\}_3$ Rh $\{\eta^4$ -C ₅ Ph ₄ O $\}$)	Ru ^{II}	6	5	1.123	2.007	171.4	180.0
DOMQUR	RuH(SiMe ₃)(PM ₂ e ₃) ₃	Ru ^{II}	6	5	1.119	1.974	164.4	43.7
EHIJOU	Ru(<i>i</i> SC ₆ H ₄ NMe) ₂ C ₂ H ₄)(P <i>i</i> Pr ₃)	Ru ^{II}	6	5	1.103	2.073	172.4	22.7
EHIJUA	Ru(<i>i</i> SC ₆ H ₄ NMe) ₂ C ₂ H ₄)(P <i>i</i> Pr ₃)	Ru ^{II}	6	5	1.119	1.960	173.2	55.0
FIRBOY	Ru(MeCO) ₂ CH ₂ (P <i>i</i> Pr ₃)	Ru ^{II}	6	5	1.125	1.957	173.5	47.9
FIXVOY	RuCl(PMe ₃) $\{\mu$ -Cl $\}_3$ Ru $\{\eta^6$ -C ₆ H ₃ <i>t</i> Pr ₃ $\}$	Ru ^{II}	6	5	1.120	1.910	174.9	180.0
HAFCUO	Ru(<i>i</i> OP(OEt) ₂) ₃ CoCp)(bipy) ⁺	Ru ^{II}	6	5	1.132	1.903	170.2	29.9
JENDOW	Ru(η^5 -C ₅ H ₄)SiMe ₂ {B ₁₀ H ₁₀ C ₂ }(PPh ₃)	Ru ^{II}	6	5	1.099	2.014	167.2	19.1
JINXIO	RuCl(<i>p</i> z ₃ BH)(PCy ₃)	Ru ^{II}	6	5	1.117	1.956	163.3	73.7
JINXIO	RuCl(<i>p</i> z ₃ BH)(PCy ₃)	Ru ^{II}	6	5	1.116	1.952	164.5	48.4
NOMGOL	RuCl ₂ (Me ₂ NCH ₂) ₂ py)	Ru ^{II}	6	5	1.110	1.955	173.4	5.5
OBOHET	RuCl ₂ (<i>i</i> Bu ₂ PCH ₂) ₂ py)	Ru ^{II}	6	5	1.119	1.965	176.9	177.7

PETGUR	RuCl ₂ (<i>t</i> 'Bu ₂ PCH ₂)py(CH ₂ NEt ₂) ⁺	Ru ^{II}	6	5	1.121	1.960	173.7	14.6
QINXUG	RuH ₂ (N ₂)(P <i>t</i> Pr ₃) ₂	Ru ^{II}	6	5	1.113	2.051	177.4	87.6
QISPOY	Ru(η ⁵ -C ₅ Me ₅)(<i>i</i> Pr ₂ PC ₂ R ₂ O)	Ru ^{II}	6	5	1.132	1.995	164.5	82.0
XOQQXOQ	Ru(η ⁵ -C ₅ H ₅)(dippe) ⁺	Ru ^{II}	6	5	1.118	1.980	170.7	180.0
XOQQXUW	Ru(η ⁵ -C ₅ H ₅)(PEt ₃) ₂ ⁺	Ru ^{II}	6	5	1.114	1.977	172.3	180.0
LURROG	RuH(<i>t</i> Me ₂ C ₆ H ₃ N=CMe ₂) ₂ py)	Ru ^I	7	4	1.132	1.953	177.3	148.4
QABJOU	Ru(<i>t</i> MesN=CMe) ₂ py)	Ru ⁰	8	3	1.161	1.916	173.4	179.7
MAHDOQ	Os({OC ₆ H ₄ CH=N}) ₂ C ₆ H ₁₀)(<i>t</i> Bu-py) ⁺	Os ^{III}	5	5	1.146	1.866	175.2	180.0
MAHDUW	Os({OC ₆ H ₄ CH=N}) ₂ C ₆ H ₁₀)(thiazole) ⁺	Os ^{III}	5	5	1.145	1.870	172.2	180.0
JAYTAE	Os(NCMe)(NH ₃) ₄ ^{(2.5)+}	Os ^{III,II}	5.5	5	1.138	1.883	179.2	180.0
MAHDAC	Os({OC ₆ H ₄ CH=N}) ₂ C ₆ H ₁₀)(Me-py) ^{(0.5)+}	Os ^{III,II}	5.5	5	1.137	1.892	176.8	130.6
MAHDEG	Os({OC ₆ H ₄ CH=N}) ₂ C ₆ H ₁₀)(thiazole) ^{(0.5)+}	Os ^{III,II}	5.5	5	1.164	1.881	178.2	158.6
NUWKUL	OsCl ₂ (terpy) ^{(0.5)+}	Os ^{III,II}	5.5	5	1.132	1.939	171.8	36.6
AVEQIB	Os(η ⁵ -C ₅ Me ₅)(PMe ₃) ₂ ⁺	Os ^{II}	6	5	1.136	1.969	171.8	61.1
XUWBEX	Co({SC ₆ H ₄ } ₂ PPh)(bipy)	Co ^{II}	7	5	1.166	1.910	175.9	180.0
VUGQAQ	Co({ <i>i</i> Pr ₂ C ₆ H ₃ N}) ₂ C ₃ H'Bu ₂)	Co ^I	8	2	1.139	1.840	177.4	180.0
YEGJEA	Co({ <i>i</i> Pr ₂ PC ₆ H ₃ Me ₂ N})	Co ^I	8	3	1.144	1.766	178.7	102.2
ZOXXEP*	Co(HB{N ₂ C ₃ H ₂ (CH ₂)'Bu}) ₃)	Co ^I	8	3	1.141	1.811	173.7	88.6
VIJDUN	CoH(PMe ₃) ₃	Co ^I	8	4	1.129	1.814	179.8	180.0
OLAXII	Co({ <i>i</i> Pr ₂ PCH ₂ } ₃ BPh) ^{(0.5)-}	Co ^{I,0}	8.5	3	1.147	1.806	174.6	180.0
CUZTEW	Co({Ph ₂ PCH ₂ } ₃ CMe)	Co ⁰	9	3	1.178	1.761	170.6	180.0
HIMFOY	Rh({'Bu ₂ PCH ₂ } ₂ C ₆ H ₂ MeO)	Rh ^I	8	3	1.127	1.913	175.2	14.4
HNIPRH	RhH(P <i>t</i> Pr ₃) ₂	Rh ^I	8	3	1.140	1.978	172.9	172.5
JELRAU	Rh({ <i>i</i> Pr ₂ PO}) ₂ C ₆ H ₃)	Rh ^I	8	3	1.122	1.978	174.8	148.7
JELRAU	Rh({ <i>i</i> Pr ₂ PO}) ₂ C ₆ H ₃)	Rh ^I	8	3	1.105	1.971	175.7	142.7
NISFUR	Rh({ <i>i</i> Pr ₂ PC ₆ H ₃ Me}) ₂ N)	Rh ^I	8	3	1.119	1.905	177.7	16.7
QIVHIM	Rh(CH ₂)'Bu)({'Bu ₂ PCH ₂ }P'Bu ₂)	Rh ^I	8	3	1.106	1.973	169.6	3.8

		3	4	5	6	7	8	9	10	Total
TACREV	Rh(<i>{Et₂NCH₂}₂C₆HMe₂</i>)	Rh ^I	8	3	1.130	2.021	174.2	86.5		
	Rh(<i>{iPr₂PCH₂}₂C₆H₃</i>)	Rh ^I	8	3	1.108	1.969	177.3	147.5		
	Rh(<i>{Me₂C₆H₃N=CMe₂}₂Py</i>)	Rh ⁰	9	3	1.130	1.936	176.9	137.1		
	IrPh ₂ (HB ₂ N ₂ C ₃ HMe ₂) ₃	Ir ^{III}	6	5	1.125	1.937	173.7	31.9		
	Ir(<i>{'Bu₂PO}</i>) ₂ C ₆ H ₂ C ₆ H ₃ {CF ₃ } ₂)	Ir ^I	8	3	1.119	1.982	172.9	125.3		
	Ir(<i>{'Bu₂PCH₂}₂C₆H₃</i>)	Ir ^I	8	3	1.134	2.012	179.3	74.4		
DABKEX	Ir(<i>{'Bu₂PO}</i>) ₂ C ₆ H ₂ C ₆ H ₃ {CF ₃ } ₂)	Ir ^I	8	3	1.177	1.997	178.3	141.2		
KEVJTF	Ir(<i>{'Bu₂PCH₂}₂C₆H₃</i>)	Ni ^I	9	2	1.121	1.833	173.3	15.4		
PULRAP	Ni(<i>{iPr₂C₆H₃N}</i>) ₂ C ₃ H ^b Bu ₂)	Ni ⁰	10	2	1.128	1.785	178.3	135.1		
ROZQED	Ni(PCy ₃) ₂									
CHPNIN	Ni(PCy ₃) ₂									

^a Mean values for between two parameters. ^b Agostic interaction of type C-H···M are presented, and it not included (see text). ^c Asymmetric complex having different coordination for each metal atom.

Table S4. Experimental parameters retrieved from *Cambridge Structural Database* for polynuclear complexes having dinitrogen as bridging ligand between two different metallic units.

Refcode	A:B	(L _n M) _A	(L _n M) _B	M _A M _B	d ^f	CN	N-N	M-N ^a	N-M-M ^a	M-N-N-M
JUVVEB	1:2	ZrCl ₂	Mo(<i>{Me₃SiNC₂H_{4}}</i> ₃ N})	Zr ^{II} Mo ^{III}	2, 3	3, 4	1.249	1.978, 1.796	176.0, 176.9	108.7
JUVVEB	1:2	ZrCl ₂	Mo(<i>{Me₃SiNC₂H_{4}}</i> ₃ N})	Zr ^{II} Mo ^{III}	2, 3	3, 4	1.245	1.974, 1.796	170.6, 177.9	53.7
JUVVAX	1:2	VCl(thf)	Mo(<i>{Me₃SiNC₂H_{4}}</i> ₃ N})	V ^I Mo ^{III}	4, 3	3, 4	1.217	1.864, 1.836	169.3, 178.1	15.3
JUVVAX	1:2	VCl(thf)	Mo(<i>{Me₃SiNC₂H_{4}}</i> ₃ N})	V ^I Mo ^{III}	4, 3	3, 4	1.220	1.861, 1.827	172.1, 178.3	28.1
MONPRE10	1:2	MoCl ₄	ReCl(PMe ₂ Ph) ₄	Mo ^{IV} Re ^I	2, 6	5, 5	1.158	1.979, 1.878	178.7, 177.2	12.1
IBIBEA	1:2	WCIMes ₃	WMes ₃ ⁻	W ^{IV} W ^{IV}	2, 2	4, 4	1.272	1.788, 1.881	177.2, 178.8	98.8
IBIBEA	1:2	WCIMes ₃	WMes ₃ ⁻	W ^{IV} W ^{IV}	2, 2	4, 4	1.272	1.802, 1.861	179.2, 177.0	27.3
IBEZUK	2:2	WMes ₃ ⁻	WMes ₃ ⁻	W ^{IV} W ^{IV}	2, 2	4, 4	1.264	1.856, 1.856	177.4, 177.4	39.3
IBEZUK	2:2	WCIMes ₃	WMes ₃ ⁻	W ^{IV} W ^{IV}	2, 2	4, 4	1.211	1.932, 1.825	177.9, 178.8	1.8
TUFPAL*	1:3	Fe	Mo(<i>{Me₃SiNC₂H_{4}}</i> ₃ N})	Fe ⁰ Mo ^{III}	8, 3	2, 4	1.196	1.857, 1.860	155.6, 173.8	16.8
TUFPAL*	1:3	Fe	Mo(<i>{Me₃SiNC₂H_{4}}</i> ₃ N})	Fe ⁰ Mo ^{III}	8, 3	2, 4	1.251	1.844, 1.809	174.5, 175.4	120.9
TUFPAL*	1:3	Fe	Mo(<i>{Me₃SiNC₂H_{4}}</i> ₃ N})	Fe ⁰ Mo ^{III}	8, 3	2, 4	1.273	1.818, 1.823	175.5, 178.5	168.5

^a Individual parameter for each metal atom, M_A and M_B.

IJIHUE	Zr(η^5 -C ₅ H ₃ {SiMe ₃ } ₂) ₂	Zr ^{II}	2	6	1.466	2.114	40.6	139.4	180.0
QAWBEW	Zr(η^5 -C ₅ H ₂ Me ₂ Ph) ₂	Zr ^{II}	2	6	1.379	2.095	38.4	141.5	176.9
QIDYOR	Zr{ $\{\eta^5$ -C ₅ H ₂ 'Bu(SiMe ₃) ₂ }SiMe ₂)	Zr ^{II}	2	6	1.241	2.281	31.5	148.5	180.0
WEZVED	Zr{ $\{\eta^5$ -C ₅ H ₃ 'Bu} ₂ SiMe ₂)	Zr ^{II}	2	6	1.407	2.089	39.3	138.7	167.2
VISHUB	Hf(η^5 -C ₅ HMe ₄){ $\{^i$ PtN} ₂ CNMe ₂)	Hf ^{II}	2	5	1.599	2.027	46.4	128.2	156.3
VISHUB	Hf(η^5 -C ₅ HMe ₄){ $\{^i$ PtN} ₂ CNMe ₂)	Hf ^{II}	2	5	1.593	2.026	46.3	129.8	160.0
VISJAJ	Hf(η^5 -C ₅ Me ₅){ $\{^i$ PtN} ₂ CMe)	Hf ^{II}	2	5	1.611	2.020	47.0	128.2	157.6
VISJEN	Hf(η^5 -C ₅ HMe ₄){ $\{^i$ PtN} ₂ CMe)	Hf ^{II}	2	5	1.630	2.023	47.5	122.5	146.7
VISJIR	Hf(η^5 -C ₅ Me ₅){EtN} ₂ CMe)	Hf ^{II}	2	5	1.634	2.020	47.7	123.4	148.6
VISKAK	Hf(η^5 -C ₅ Me ₅){ $\{^i$ PtN} ₂ CNMe ₂)	Hf ^{II}	2	5	1.581	2.027	45.9	132.9	169.1
VISKIS	HfBr(η^5 -C ₅ HMe ₄){ $\{^i$ PtN} ₂ CMe)	Hf ^{II}	2	6	1.253	2.197	33.1	143.8	165.2
REBREW	Hf(η^5 -C ₅ HMe ₄) ₂	Hf ^{II}	2	6	1.423	2.081	40.0	140.0	180.0
QAGLIV	Hf{ $\{\eta^5$ -C ₅ H ₃ 'Bu} ₂ SiMe ₂)	Hf ^{II}	2	6	1.457	2.055	41.5	136.8	167.9
UXOSIK	Hf(η^5 -C ₅ H ₂ Me ₃) ₂	Hf ^{II}	2	6	1.457	2.059	41.4	138.6	180.0
ADOPOZ	Cr{ $\{^i$ Pr ₂ C ₆ H ₃ N} ₂ C ₃ HMe ₂)	Cr ^I	5	2	1.249	2.021	36.0	144.0	180.0
DNPNTS	NiPh ₂ ²⁻	Ni ⁰	10	2	1.359	1.909	41.7	91.9	100.6
DNPNTS	NiPh ₂ ²⁻	Ni ⁰	10	2	1.358	1.913	41.6	92.1	100.7

^a Mean values for two or four parameters. ^b Angle θ defined in the text. ^c Asymmetric complex having different coordination number for each metal atom.

	3	4	5	6	7	8	9	10	Total
3d	Sc: 3 (3) 1.24–1.28	Ti: 1 (1) 1.22	V <i>n.a.</i>	Cr: 1 (1) 1.25	Mn <i>n.a.</i>	Fe <i>n.a.</i>	Co <i>n.a.</i>	Ni: 2 (1) 1.36	7 (6) 1.22–1.36
4d	Y: 8 (7) 1.01–1.40	Zr: 15 (15) 1.24–1.58	Nb <i>n.a.</i>	Mo <i>n.a.</i>	Tc <i>n.a.</i>	Ru <i>n.a.</i>	Rh <i>n.a.</i>	Pd <i>n.a.</i>	23 (22) 1.01–1.58
5d	La: 2 (2) 1.23–1.24	Hf: 10 (9) 1.25–1.63	Ta <i>n.a.</i>	W <i>n.a.</i>	Re <i>n.a.</i>	Os <i>n.a.</i>	Ir <i>n.a.</i>	Pt <i>n.a.</i>	12 (11) 1.23–1.63
<i>Total</i>		13 (12) 1.01–1.40	26 (25) 1.22–1.63	— <i>n.a.</i>	1 (1) 1.25	— <i>n.a.</i>	— <i>n.a.</i>	2 (1) 1.36	42 (39) 1.01–1.63

Table S6. Experimental parameters retrieved from *Cambridge Structural Database* for dinuclear complexes having dinitrogen as bridging ligand as **2c**.

Refcode	L _n M	M	d̄	CN	N-N	M-N ^a	N-M-N ^a	M-N-M ^a	θ ^b
LUNPEQ	Ti({pyrCPh ₂ } ₂ C ₄ H ₂ NMe) ⁻	Ti ^I	3	2	2.477	1.811	86.3	93.7	180.0
VEMXEQ	V({Me ₃ SiNC ₂ H ₄ } ₂ NSSiMe ₃)	V ^{II}	3	3	2.501	1.815	87.1	92.9	180.0
VEMXEQ	V({Me ₃ SiNC ₂ H ₄ } ₂ NSSiMe ₃)	V ^{II}	3	3	2.467	1.811	85.6	94.4	180.0
WAWRUH	VCl(η ⁵ -C ₅ Me ₅)	V ^{II}	3	4	2.446	1.771	87.4	92.6	180.0
YALYAM	V(η ⁵ -C ₅ Me ₅)(N ₃)	V ^{II}	3	4	2.449	1.773	87.4	92.6	180.0
YUBSAP	V(N{SiMe ₃ } ₂) ₂ ^{(0.5)-}	V ^{I,II}	3.5	2	2.421	1.770	86.3	93.7	179.8
QOTSIB	Nb(OAr) ₄ ²⁻	Nb ^{II}	3	4	2.609	1.907	86.3	93.7	180.0
L1KVAD	Ta(η ⁵ -C ₅ Me ₅)(iPr ₂ N ₂ CM ₆)	Ta ^{II}	3	5	2.574	1.907	84.9	95.0	173.6
L1KVAD	Ta(η ⁵ -C ₅ Me ₅)(iPr ₂ N ₂ CM ₆)	Ta ^{II}	3	5	2.586	1.910	85.2	94.6	173.4
LIQDOF	Ta(η ⁵ -C ₅ Me ₅)(iPr ₂ N ₂ CM ₆)	Ta ^{II}	3	5	2.563	1.903	84.6	95.4	180.0
ZUJQUQ	Cr(N <i>i</i> Pr ₂) ₂	Cr ^{II}	4	2	2.383	1.736	86.7	93.3	179.4
LIYHEH	W(CH ₂ ⁱ Bu)(OC ₆ H ₃ ⁱ Pr ₂) ₂	W ^{III}	3	3	2.542	1.882	84.9	95.1	180.0
TIQYIB	W(OC ₆ H ₃ ⁱ Pr ₂) ₃	W ^{III}	3	3	2.557	1.895	84.6	95.4	180.0
TIQYIB	W(OC ₆ H ₃ ⁱ Pr ₂) ₃	W ^{III}	3	3	2.559	1.896	84.6	95.4	180.0

^a Mean values for two or four parameters. ^b Angle θ defined in the text.

	3	4	5	6	7	8	9	10	Total
3d	Sc <i>n.a.</i>	Ti: 1 (1) 2.48	V: 5 (4) 2.42–2.50	Cr: 1 (1) 2.38	Mn <i>n.a.</i>	Fe <i>n.a.</i>	Co <i>n.a.</i>	Ni <i>n.a.</i>	7 (6) 2.38–2.50
4d	Y <i>n.a.</i>	Zr <i>n.a.</i>	Nb: 1 (1) 2.61	Mo <i>n.a.</i>	Tc <i>n.a.</i>	Ru <i>n.a.</i>	Rh <i>n.a.</i>	Pd <i>n.a.</i>	1 (1) 2.61
5d	La <i>n.a.</i>	Hf <i>n.a.</i>	Ta: 3 (2) 2.56–2.95	W: 3 (2) 2.54–2.56	Re <i>n.a.</i>	Os <i>n.a.</i>	Ir <i>n.a.</i>	Pt <i>n.a.</i>	6 (4) 2.54–2.95
Total	— <i>n.a.</i>	1 (1) 2.48	9 (7) 2.42–2.95	4 (3) 2.38–2.56	— <i>n.a.</i>	— <i>n.a.</i>	— <i>n.a.</i>	— <i>n.a.</i>	14 (11) 2.38–2.95

Table S7. Experimental data for N-N distance of partially hydrogenated dinitrogen ligand in transition metal complexes retrieved from *Cambridge Structural Database*.

Motif	Refcodes	Data	Range	Mean(st.dev.)
<i>end-on</i>				
Tr(η^1 -N ₂ H ₂)	1	1	1.17	1.17(-)
Tr(η^1 -N ₂ H ₃)	1	1	1.38	1.38(-)
Tr(η^1 -N ₂ H ₄)	30	46	1.38-1.48	1.45(2)
Tr(η^1 -N ₂ H ₅)	5	5	1.42-1.46	1.44(1)
Tr ₂ (η^1 : η^1 -N ₂ H ₂)	23	25	1.23-1.42	1.32(6)
series A	15	17	1.23-1.32	1.28(2)
series B	8	8	1.34-1.42	1.39(3)
Tr ₂ (η^1 : η^1 -N ₂ H ₄)	20	23	1.42-1.49	1.45(2)
<i>side-on</i>				
Tr(η^2 -N ₂ H ₂)	3	4	1.40-1.43	1.42(1)
Tr(η^2 -N ₂ H ₃)	2	2	1.39-1.41	1.40(1)
Tr(η^2 -N ₂ H ₄)	5	5	1.43-1.46	1.44(1)
Tr ₂ (η^2 : η^2 -N ₂ H ₂)	10	10	1.39-1.47	1.44(2)

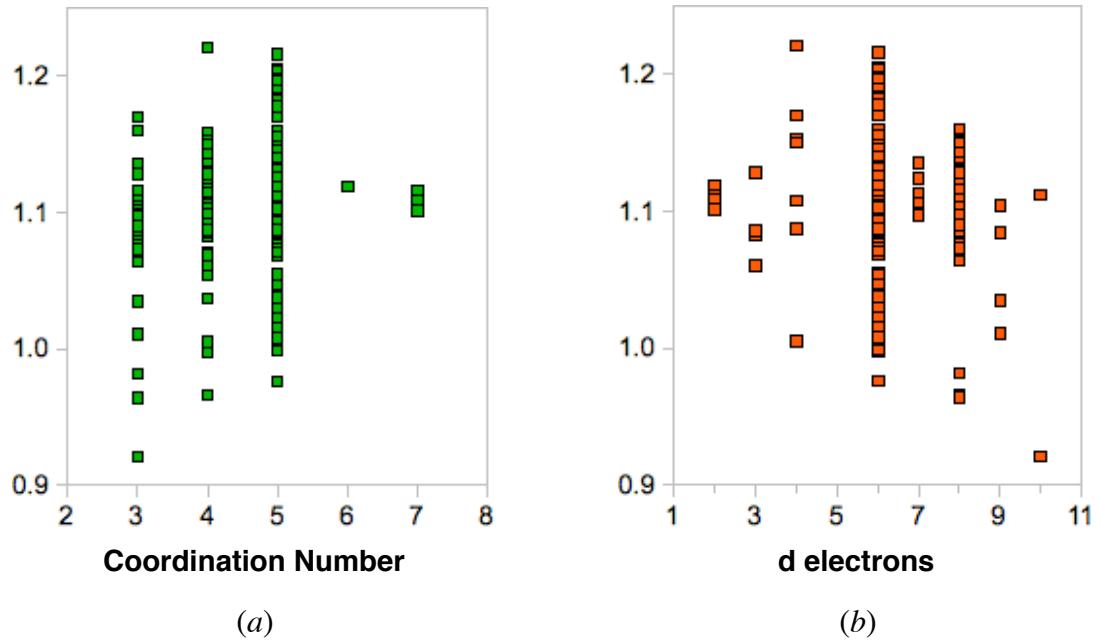


Figure S1. Variation of the N-N distance in mononuclear complexes as a function of: (a) coordination number of the metallic fragment, and (b) d electrons of the metal center.

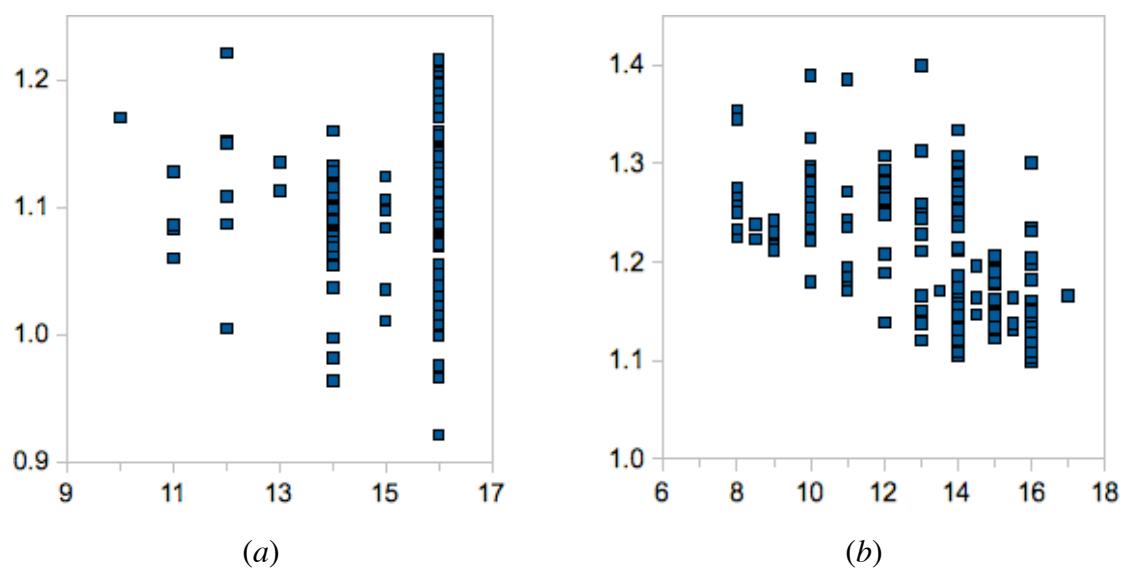


Figure S2. Variation of the N-N distance in mononuclear complexes as a function of valence electrons for:
 (a) end-on mononuclear **1a**, (b) end-on binuclear **2a**, (c) side-on binuclear having bonded distances **2b**, and (d) side-on binuclear without bonded distances **2c**.

Text S1. Electron counting scheme to assign electronic configurations for the transition metal.

- (a) Nitrogen ligand (N_2) is neutral, and it is considered only one position in the coordination sphere of the transition metal. Similar count effects are applied to carbonyl (CO), lineal nitriles (NCR) and also isonitriles (CNR).
- (b) Amines (NH_3 , $NH_{3-x}R_x$, en, ...) and imines ($R'N=CR_2$), including aromatic ones (py, bipy, terpy) are neutral. However, their deprotonated ligands as amides (NR_2^-) or imides (NR^2^-) are anionic.
- (c) Oxygen ligands as ethers (OR_2 , thf, ...), and sulfur analogs (SR_2 , tht) are also neutral. Its deprotonated ligands such as alkoxo or thiolato (RO^- , RS^- , ...) are anionic.
- (d) Phosphines (PR_3), diphosphines ($R_2P^{\wedge}PR_2$), and polyphosphines are neutral. Equally, it is applied to arsines (AsR_3), phosphites ($P\{OR\}_3$), and phosphorous trifluoride (PF_3).
- (e) Monoatomic ligands such as halides (Cl^- , Br^- , ...) and hydride (H^-) are monoanionic. Single monoanion ligands included azide (N_3^-) and thiocyanate (SCN^-). Other single polyanionic ligands as oxo(2-), sulfido(2-) and nitrido(3-) are presented.
- (f) Carboxilates (RCO_2^-) and its derivatives such as amidinates ($RC\{NR'\}_2^-$) or dithioxanthates ($R_2NCS_2^-$) are monoanionic, and donor of four electrons in two fold positions when they act as bidentate mode. Similar count is applied to dithiophosphinates ($R_2PS_2^-$).
- (g) Organyls as alkyls (CH_3^- , CH_2R^- , ...) and aryls ($C_6H_{5-x}R_x^-$) are monoanionic ligands. Analog count is applied to alkynyls (RCC^-) and silyls ($SiH_{3-x}R_x^-$). Alkenyls (CHR^{2-} and CR_2^{2-}) are generally considered as dianionic ones. The only exception is taken for electron-rich *N*-heterocyclic carbenes such as 2-imidazolyl or 2-imidazolidinyl, which is assigned as neutral ligands.
- (h) Olefins (C_2R_4) are neutral ligands and two-electrons donors in a single position. Similarly, bisalkenes such as 1,5-cyclooctadiene (cod) or 1,3-butadiene are four-electrons donors in two positions. Other π -ligands having an even number of atoms such as benzene derivatives ($\eta^6-C_6H_{6-x}R_x$) are also neutral ligands and six-electrons donors in a three fold positions. However, odd-arenes are related with even aromatic ones, and cyclopentadienyl type ligands ($\eta^5-C_5H_{5-x}R_x^-$) are considered anionic and analogous to benzene derivatives.
- (i) Macroyclic ligands are counted as the sum of each donor ligands (*e.g.*, a porphyrin is dianionic having four donating interactions with two electrons per bond).