# Transition metal dinitrogen complexes supported by a versatile monoanionic [$N_2P_2$] ligand†

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**By adjusting to the steric and electronic requirements of differing metal centers, the new multidentate monoanionic ligand [$N_2P_2$] has demonstrated a unique ability to stabilize a range of transition metal–dinitrogen complexes in a variety of oxidation states and coordination geometries.**

Ligands that play supporting roles in transition metal chemistry are typically chosen on a metal-by-metal basis, with due attention being paid to the steric and electronic requirements of the particular metal in question. The hapticity or denticity of these ligands can be tailored to provide the requisite number of donors with appropriate electronic properties (*e.g.* hardness or softness) for the particular metal, and organic substituents are incorporated to provide steric control at the metal center. These fundamental concepts have led to the discovery of a wide range of interesting compounds, many of which demonstrate unusual reactivity patterns. In the course of our work on new tetradentate monoanionic ligands,[1,2] we have discovered a versatile ligand capable of supporting a range of metal–dinitrogen complexes from early-to-late in the transition series. This unusual finding results from the hemilabile nature of the ligand which allows it to change its coordinating properties to meet the metal's steric and electronic demands.

Our recent work on the tetradentate monoanionic ligand $^tBuN(H)SiMe_2N(CH_2CH_2P^iPr_2)_2$, H[$N_2P_2$], has demonstrated its ability to stabilize a range of first-row transition metal complexes in a variety of coordination geometries.[3] To probe the utility of the [$N_2P_2$] ligand, our preliminary focus is on reduced metal complexes. Here we describe our initial results and demonstrate the ability of [$N_2P_2$] to stabilize bridging $N_2$ complexes of early and late first-row transition metals. In addition, a zirconium complex containing a side-on bound $N_2$ moiety exhibiting an extremely long N–N bond distance is reported.

Metathesis reactions between $MX_n(THF)_y$ (M = Ti, Mn, Fe, Zr) and Li[$N_2P_2$] in toluene or DME led cleanly to ligated metal-halide starting materials [$N_2P_2$]$TiCl_2$ (**3**), [$N_2P_2$]MnCl (**4**), [$N_2P_2$]FeCl (**5**), and [$N_2P_2$]$ZrCl_3$ (**6**). Reduction of **3** with $KC_8$ in diethyl ether under $N_2$, followed by crystallization from the same solvent, yielded fluffy crystalline material of ([$N_2P_2$]TiCl)$_2$(μ-$N_2$) (**7**) in 57% yield. X-Ray quality crystals of **7** were not forthcoming due to its inherently poor crystallinity; however, Raman spectroscopic measurements showed a high degree of activation of the N–N bond with an observed $\nu_{N–N}$ at 1300 $cm^{-1}$.

Reaction of **7** with two equivalents of $LiCH_2SiMe_3$ in pentane, followed by filtration and crystallization from pentane, yielded orange-brown crystals of the diamagnetic compound ([$N_2P_2$]Ti-($CH_2SiMe_3$))$_2$(μ-$N_2$) (**8**) in 34% yield. The X-ray structure of **8** reveals a five-coordinate titanium in a square-based pyramidal geometry with an end-on bridging $N_2$ (Fig. 1).‡ The [$N_2P_2$] ligand is bound $\kappa^3$ to the metal center through the anionic nitrogen, the basal nitrogen, and one phosphine. Due to steric constraints, the second phosphine is unable to coordinate to the titanium center. This result attests to the strength and stability of the Ti–N bonds in **8** and is, to the best of our knowledge, the first report of an alkylation of such a complex.[4] The short Ti-(μ-$N_2$) bond distances (1.783(4) and 1.782(3) Å) and the elongated N–N bond length (1.286(4) Å) are similar to related non-cyclopentadienyl supported diamagnetic titanium dinitrogen compounds such as {[PhC($NSiMe_3$)$_2$]$_2$Ti}$_2$(μ-$N_2$)[5] (1.771(5) and 1.759(5) Å (Ti-(μ-$N_2$)) and 1.275(6) Å (N–N), {[($Me_3Si$)$_2$N]TiCl($C_6H_5N$)$_2$}$_2$(μ-$N_2$)[6] (1.759(3) Å (Ti-(μ-$N_2$)) and 1.263(7) Å (N–N)), and {[PhP($CH_2SiMe_2NSiMe_2CH_2$)$_2$PPh]Ti}(μ-$N_2$)[7] (1.783(4) Å (Ti-(μ-$N_2$)) and 1.255(7) Å (N–N)). In addition, the $\nu_{N–N}$ at 1270 $cm^{-1}$ also indicates a high degree of activation of the $N_2$ moiety and agrees well with the value observed in the spectrum of **7** as well as the previously reported literature value of 1284 $cm^{-1}$ for [($Me_3Si$)$_2$NTiCl(TMEDA)]$_2$(μ-$N_2$)].[8]

Moving further to the right in the periodic table, the reduction of **4** with Na[naphthalide] in THF under $N_2$ was examined. Following crystallization from pentane, ([$N_2P_2$]Mn)$_2$(μ-$N_2$) (**9**) was isolated in 24% yield as a dark red crystalline solid. The X-ray structure of **9** reveals a four-coordinate manganese in a tetrahedral environment with an end-on bridging $N_2$ (Fig. 2).§The [$N_2P_2$] ligand is bound $\kappa^3$ once again; however, in the case of manganese, the anionic nitrogen and both phosphines are coordinated while there is no interaction with the basal nitrogen in the solid-state.

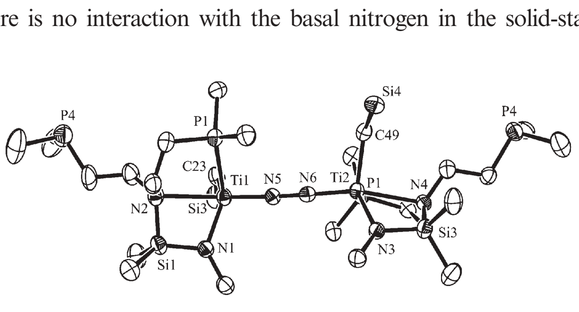

**Fig. 1** Thermal ellipsoid plot (50%) of **8**. Hydrogen atoms, iso-propyl methyl, *tert*-butyl methyl groups, and solvent molecules have been omitted for clarity.

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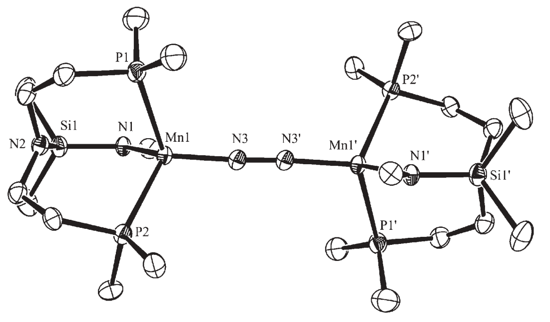

**Fig. 2** Thermal ellipsoid plot (50%) of **9**. Hydrogen atoms, iso-propyl methyl and *tert*-butyl methyl groups have been omitted for clarity. The prime character (′) in the atom labels indicates that these atoms are at equivalent positions ($-x$, $-y$, $1 - z$).

Manganese dinitrogen complexes appear to be quite rare, and compound **9** is only the second crystallographically characterized dimeric $N_2$ manganese species.

The N–N bond length (1.208(6) Å) is significantly longer than the distance reported previously for $\{\eta^5\text{-}C_5H_4CH_3Mn(CO)_2\}_2(\mu\text{-}N_2)$[9] (1.118(7) Å) likely due to increased π back-bonding into the π* orbital of the $N_2$ moiety as a result of the low coordination number of **9** and the omission of other π accepting ligands. The increased activation of the N–N bond seen in the X-ray structure of **9** is also reflected in the Raman spectrum where the $\nu_{N\text{–}N}$ is observed at 1685 $cm^{-1}$ compared to 1975 $cm^{-1}$ previously reported for $\{\eta^5\text{-}C_5H_4CH_3Mn(CO)_2\}_2(\mu\text{-}N_2)$.[9] The solution magnetic moment (8.7 $\mu_B$) is very close to the spin-only value of 8.9 $\mu_B$ for eight unpaired electrons.

Moving on further to iron, reduction of **5** with $KC_8$ in THF under $N_2$, followed by crystallization from pentane, yielded $([N_2P_2]Fe)_2(\mu\text{-}N_2)$ (**10**) in 65% yield. The X-ray structure of **10** is comparable with that of **9** with the $[N_2P_2]$ ligand coordinated in the same manner (Fig. 3).¶The N–N bond length in **10** (1.166(3) Å) is shorter than in **9**; however, the N–N distance is significantly longer than the value observed in free $N_2$ (1.098 Å) and is similar to the related complexes $\{[PhB(CH_2P^iPr_2)_3]Fe\}_2(\mu\text{-}N_2)$[10] (1.138(6) Å) and $\{([ArNC(^tBu)]_2CH)Fe\}_2(\mu\text{-}N_2)$[11] (1.182(5) Å), where Ar = 2,6-diisopropylaniline. The $\nu_{N\text{–}N}$ occurs at 1760 $cm^{-1}$ and agrees well with the value of 1778 $cm^{-1}$ reported for $\{([ArNC(^tBu)]_2CH)Fe\}_2(\mu\text{-}N_2)$.[11] The solution magnetic moment was found to be 7.0 $\mu_B$, which is slightly higher than the spin-only value of 6.9 $\mu_B$ for six unpaired electrons; however, the magnetic moment observed for **10** is lower than the values seen in the related compounds $\{[PhB(CH_2P^iPr_2)_3]Fe\}_2(\mu\text{-}N_2)$[12] (8.2 $\mu_B$) and $\{([ArNC(^tBu)]_2CH)Fe\}_2(\mu\text{-}N_2)$[13] (8.4 $\mu_B$). One particularly interesting feature of **10** is the apparent reversible binding of $N_2$. Thus when a dark red solution of **10** is held under reduced pressure, the color changes to dark lime green. This green solution remains unchanged at room temperature if the solution is held under vacuum or if an argon atmosphere is established. Once exposed to $N_2$, however, the solution returns to dark red, reforming the bridging $N_2$ complex as confirmed by its successful re-isolation. Thus far, we have been unable to identity the nature of the green species due to a high degree of twinning in our isolated samples; however, efforts to obtain crystals suitable for an X-ray diffraction study are still under way.

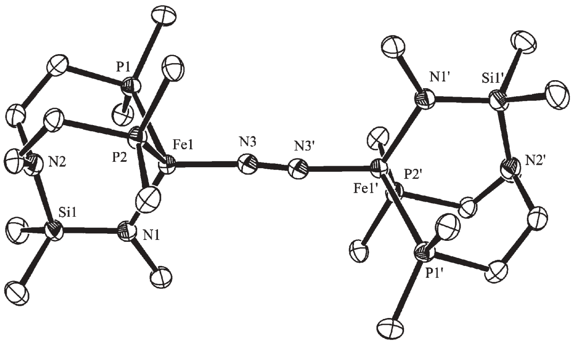

**Fig. 3** Thermal ellipsoid plot (50%) of **10**. Hydrogen atoms, iso-propyl methyl and *tert*-butyl methyl groups have been omitted for clarity. The prime character (′) in the atom labels indicates that these atoms are at equivalent positions ($2 - x$, $-y$, $2 - z$).

We were also interested in the suitability of $[N_2P_2]$ for larger second row metals. Reduction of **6** with two equivalents of $KC_8$ in THF under $N_2$, followed by crystallization from pentane, yielded $([N_2P_2]ZrCl)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**11**) in 17% yield.[14] Though only a limited number of side-on bound $N_2$ complexes of zirconium have been isolated,[15] two of these compounds have shown remarkable reactivity in which functionalization of the $N_2$ moiety has been achieved with $H_2$, silanes, and alkynes.[14–16] The X-ray structure of **11** (Fig. 4) reveals a six-coordinate zirconium complex with the $[N_2P_2]$ ligand bound in the same manner as was observed in **8** and a side-on bound bridging $N_2$.|| The most striking feature of this complex is the extremely long N–N bond distance of 1.576(9) Å. The long N–N bond distance is comparable to the N–N bond lengths observed in the related compounds $\{[N(SiMe_2CH_2P^iPr_2)_2]Zr\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$[16] (1.548(7) Å), $\{PhP(CH_2SiMe_2NPh)_2Zr(THF)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$[7] (1.503(3) Å) and $\{[PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh]Zr\}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$[17] (1.43(1) Å). To the best of our knowledge, **11** contains the longest N–N bond distance of any structurally characterized transition metal $N_2$ compound to date.[15] Further studies on the reactivity of **11** with small molecules are under way.

To summarize, the implementation of a flexible, hemilabile design allows the $[N_2P_2]$ ligand to stabilize a range of interesting

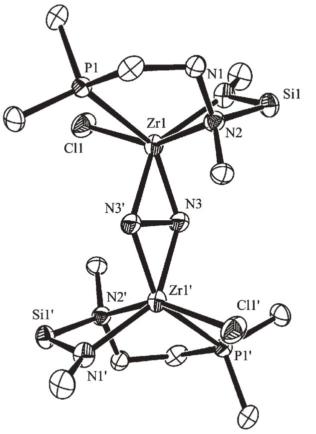

**Fig. 4** Thermal ellipsoid plot (50%) of **11**. Hydrogen atoms, iso-propyl methyl and *tert*-butyl methyl groups have been omitted for clarity. The prime character (′) in the atom labels indicates that these atoms are at equivalent positions ($-x$, $2 - y$, $1 - z$).

transition metal complexes in a variety of coordination geometries. The [$N_2P_2$] ligand adapts its coordination geometry in accord with the steric and electronic demands of the range of metals explored: with early transition metals, it prefers to use both (harder) nitrogen donors and only one phosphine, while with late metals, it employs both phosphines and the amido nitrogen. A broad range of dinitrogen compounds with titanium, manganese, iron, and zirconium has thereby been isolated. The demonstrated variable denticity of the [$N_2P_2$] ligand opens up the possibility that transient lower-coordinate early metal derivatives can be generated which might then be stabilized by fully-bound ($\kappa^4$) [$N_2P_2$]. The reaction chemistry of these and related [$N_2P_2$] metal complexes will be the focus of future publications.

## Notes and references

‡ Crystal data for **8**: $C_{59.50}H_{142}N_6P_4Si_4Ti_2$, $M_r$ = 1273.83, $T$ = 148(2), monoclinic, space group $P2(1)/c$, $a$ = 19.224(4), $b$ = 18.899(4), $c$ = 23.297(5) Å, $\beta$ = 109.599(2)°, $V$ = 7974(3) Å$^3$, $\mu$(MoK$\alpha$) = 0.376 mm$^{-1}$, $Z$ = 4, 13 477 reflections measured, 6508 unique ($R_{int}$ = 0.0856), final $R$ indices [$I > 2\sigma(I)$] $R1$ = 0.0578, w$R2$ = 0.1176. CCDC 652414. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709763h

§ Crystal data for **9**: $C_{22}H_{51}MnN_3P_2Si$, $M_r$ = 502.63, $T$ = 151(2), orthorhombic, space group $Pbca$, $a$ = 18.381(2), $b$ = 15.4611(17), $c$ = 19.772(2) Å, $V$ = 5619.0(11) Å$^3$, $\mu$ = 0.640 mm$^{-1}$, $Z$ = 8, 4787 reflections measured, 3249 unique ($R_{int}$ = 0.1055), final $R$ indices [$I > 2\sigma(I)$] $R1$ = 0.0534, w$R2$ = 0.1263. CCDC 652417. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709763h

¶ Crystal data for **10**: $C_{22}H_{51}FeN_3P_2Si$, $M_r$ = 503.54, $T$ = 154(2), monoclinic, space group $P2(1)/c$, $a$ = 11.6476(11), $b$ = 18.0559(18), $c$ = 13.3821(13) Å, $\beta$ = 102.0550(10)°, $V$ = 2752.3(5) Å$^3$, $\mu$ = 0.721 mm$^{-1}$, $Z$ = 4, 5248 reflections measured, 4422 unique ($R_{int}$ = 0.0162), final $R$ indices [$I > 2\sigma(I)$] $R1$ = 0.0331, w$R2$ = 0.0909. CCDC 652415. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709763h

‖ Crystal data for **11**: $C_{22}H_{51}ClN_3P_2SiZr$, $M_r$ = 574.36, $T$ = 151(2), triclinic, space group $P\bar{1}$, $a$ = 11.956(2), $b$ = 12.070(3), $c$ = 12.438(2) Å, $\alpha$ = 111.752(4), $\beta$ = 110.138(3), $\gamma$ = 100.111(3)°, $V$ = 1467.6(5) Å$^3$, $\mu$ = 0.630 mm$^{-1}$, $Z$ = 2, 5812 reflections measured, 3736 unique ($R_{int}$ = 0.0556), final $R$ indices [$I > 2\sigma(I)$] $R1$ = 0.0651, w$R2$ = 0.1336. CCDC 652416. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709763h

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