Synthesis and Characterization of Triply-Bonded Titanium–Iron Complexes Supported by 2-(diphenylphosphino)pyrrolide Ligands

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ABSTRACT

The synthesis of several titanium–iron multiply bonded complexes supported by a 2-(diphenylphosphino)pyrrolide (NP) ligand is reported. Treatment of the homoleptic, 8-coordinate $\text{Ti}(\text{NP})_4$ monometallic precursors with FeCl_2 and KC_8 yielded the tetragonally-symmetric heterobimetallic complex $\text{Ti}(\mu_2\text{-NP})_4\text{Fe}$, **2**. X-ray crystallographic analysis reveals a short metal–metal distance (2.021(2) and 2.028(2) Å for two independent molecules in the asymmetric unit) consistent with a Fe–Ti triple bond. Theoretical calculations also indicate 3 bonding interactions. Further reduction of **2** by 2 electrons with KC_8 results in the isolation of the dianion, $[\text{K}_2][(\kappa^1\text{-NP})\text{Ti}(\mu_2\text{-NP})_3\text{Fe}]$, **3**, where one phosphine arm has decoordinated from Fe, and the Fe–Ti triple bond has shortened to 1.9474(7) Å. This shortening results from the local ligand field change about Fe from tetragonal to trigonal, which allows for significantly better orbital overlap with Ti.

GRAPHICAL ABSTRACT

INTRODUCTION

Metal-metal bonds between two first row transition metals have received significant recent attention owing to their potential utility as catalysts for multielectron transformations relevant to small molecule activation. Additionally, bonds between metals play important roles in both natural enzymatic systems[1–2] and heterogeneous processes[3–6], making the study of metal-metal bonding an important tool for understanding and improving these systems. Recent seminal work by Lu and Thomas has involved using bifunctional, hard-soft ligands to construct several heterobimetallic frameworks that can support diverse classes of trigonally-symmetric heterobimetallic transition metal cores[7–28]. A number of factors dictate the extent of metal-metal bonding in these complexes: for example, as the metal center periods become more disparate, orbital overlap decreases resulting in a loss of delta then pi bonding; while addition of more than 10 total electrons into the metal-metal manifold typically results in a population of metal-metal antibonding orbitals, decreasing the effective bond order[29–30]. In a trigonally symmetric system, the d_{yz} and d_{xz} orbital pair and $d_{x^2-y^2}$ and d_{xy} pair are each degenerate, allowing for formation of up to 5 bonds (two pi and two delta orbitals, in addition to d_{z^2} sigma bonding), making it an ideal symmetry to

observe periodic trends in bonding. We recently reported the synthesis of a series of pseudo-trigonal MNi ($M = Ti, Zr, Hf$) complexes supported by phosphinopyrrolides, where, due to symmetry constraints, only two bonding interactions can occur instead of three (from idealized trigonal geometry), illustrating how the extent of metal-metal bonding can be further manipulated by deviation from idealized metal geometries[31]. Additionally, Nagashima and Michaelis have carried out catalytic nucleophilic allylic amination reactions with low-symmetry ‘boat’ shaped heterobimetallic MTi ($M = Ni, Pd, Pt$) complexes[32–35]. Despite the prevalence of trigonally symmetric species, there are few examples of bimetallics displaying tetragonal symmetry that contain two different first row transition metals, akin to the tetragonal lantern complexes such as Cotton’s $[Re_2Cl_8]^{2-}$ complex[36–37]. A tetragonal environment, in contrast to a trigonal symmetry, significantly destabilizes $d_{x^2-y^2}$ due to metal-ligand antibonding interactions, and allows only for a maximum of 4 bonding interactions.

To further investigate cooperative Lewis acidic effects, impact of symmetry on heterobimetallic metal-metal bonding and to investigate the potential role of covalent $M-M$ bonding on fundamental organometallic reactivity, we are interested in synthesizing tetragonally-symmetric early-late transition metal complexes supported by phosphinopyrrolide group 4 metalloligands. Herein we report the synthesis and characterization of $Ti(\mu_2-NP)_4Fe$ ($NP = 2$ -diphenylphosphinopyrrolide) and the doubly reduced dianion $K_2Ti(\mu_2-NP)_4Fe$ and lend insight into metal-metal bonding in early-late bimetallic complexes.

MATERIALS AND METHODS

General Considerations and Instrumentation. All air- and moisture-sensitive compounds were manipulated in a glovebox under a nitrogen atmosphere. Solvents for air- and moisture-sensitive reactions were vacuum transferred from sodium benzophenone ketyl (THF, Et₂O, pentane, and *d*₆-benzene) or predried by passing through activated alumina columns of a SG Water solvent purification system. FeCl₂ was purchased from Aldrich and dried at 100 °C overnight under vacuum before use. KC₈ was prepared according to literature procedure[38]. ¹H, ¹³C and ³¹P spectra were recorded on Varian INOVA 500 MHz or Bruker Avance III 400 MHz spectrometers. Chemical shifts are reported with respect to residual protio-solvent impurity for ¹H (*s*, 7.16 ppm for C₆D₅H and *s*, 7.26 ppm for CHCl₃), solvent carbons for ¹³C (*t*, 128.39 ppm for C₆D₆, *t*, 77.36 ppm for CDCl₃), and H₃PO₄ for ³¹P (*s*, 0 ppm for C₆D₆ and CDCl₃).

X-ray Crystal Data: General Procedure. Crystals were removed quickly from a scintillation vial to a microscope slide coated with oil. Samples were selected and mounted on the tip of a 0.1 mm diameter glass capillary. Data collection was carried out on a Bruker APEX II CCD diffractometer with a 0.71073 Å Mo Kα-source or on a Bruker-AXS D8 Venture diffractometer with a 1.54178 Å Cu Kα-source. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. Details regarding refined data and cell parameters are available in Table 1.

Computational Details

DFT: All density functional theory (DFT) calculations were performed with the Gaussian 09 program package[39]. The structures were optimized with the M06-L functional and 6-311G+(d) basis sets for Ti, Fe, N, and P, 6-31G(d) for C, 6-31G

for H [40–44]. Frequency calculations were performed to confirm structures were local minima. Natural bond order (NBO) analysis was performed on the optimized structures to estimate the Mayer bond order[45].

Synthesis of $\text{Ti}(\text{2-PPh}_2)\text{C}_4\text{H}_3\text{N}_4\text{Fe}$, $\text{Ti}(\mu_2\text{-NP})_4\text{Fe}$ (2). Solid $\text{Ti}(\text{NP})_4$ (175 mg, 0.167 mmol, 1 equiv) and FeCl_2 (20.8 mg, 0.167 mmol, 1 equiv) were dissolved in 3 mL THF and cooled to $-35\text{ }^\circ\text{C}$. KC_8 (45 mg, 0.334 mmol, 2 equiv) was added and the solution allowed to stir for two hours while warming to room temperature. Solvent was removed *in vacuo* and the remaining solid redissolved in benzene, filtered through celite and pumped to dryness leaving 120 mg of crude 2 as a red/orange powder. 30 mg of crystals (16% yield) were obtained by slow diffusion of pentane into a concentrated benzene solution of crude 2. ^1H NMR (CDCl_3) δ , ppm: 4.86–4.96 (4H, br, pyrrole), 5.92–6.03 (4H, br, aryl), 6.08–6.16 (4H, t, pyrrole), 6.26–6.33 (4H, d, aryl), 6.43–6.49 (4H, br, aryl), 6.55–6.61 (4H, br, aryl), 6.62–6.69 (4H, t, aryl), 6.69–6.76 (4H, t, aryl), 6.76–6.85 (8H, m, pyrrole and aryl), 6.85–6.92 (4H, br, aryl), 7.08–7.16 (4H, br, aryl) 7.23–7.27 (4H, br, aryl). ^{13}C NMR (CDCl_3) δ , ppm: 111.7, 118.7, 126.5, 126.9, 126.9, 126.9, 128.6, 129.2, 130.0, 131.2, 132.4, 132.8, 135.1. ^{31}P NMR (CDCl_3) δ , ppm: 13.1 (4P, s). Anal calcd (%) for $\text{C}_{64}\text{H}_{52}\text{N}_4\text{P}_4\text{TiFe}$: C 69.33 H 4.74 N 5.05 Found: C 70.17 H 5.27 N 4.83.

Synthesis of $[\text{K}_2][\text{Ti}(\text{2-PPh}_2)\text{C}_4\text{H}_3\text{N}_4\text{Fe}]$, $[\text{K}_2][(\kappa^1\text{-NP})\text{Ti}(\mu_2\text{-NP})_3\text{Fe}]$ (3). Solid $\text{Ti}(\text{NP})_4\text{Fe}$ (20 mg, 0.018 mmol, 1 equiv) is dissolved in benzene and solid KC_8 (5 mg, 0.036 mmol, 2 equiv) added. The reaction is allowed to stir for approximately ten minutes and then filtered giving a dark red solution. 5 mg (23%) of X-ray quality

crystals were obtained by slow diffusion of pentane into a concentrated benzene solution of **3**. ^1H NMR (C_6D_6) δ , ppm: 5.83–5.85 (1H, br), 5.98–5.96 (1H, br), 6.24–6.45(3H, br), 6.54–6.56(1H, br), 6.57–7.14 (36H, br), 7.29–7.43(5H, br), 7.84–8.0(3H, br), 8.19–8.29(2H, br). ^{31}P NMR (C_6D_6) δ , ppm: 27.9 (2P, t), 16.9 (1P, t) –30.4 (1P, s). Satisfactory elemental analysis was not obtained for this molecule because it decomposes over time during solvent removal *in vacuo*.

Table 1. Crystal and refinement data for complexes **2** and **3**.

	2	3
CCDC Number	1496978	1496979
Empirical Formula	$\text{C}_{64}\text{H}_{52}\text{FeN}_4\text{P}_4\text{Ti} \cdot 2(\text{C}_6\text{H}_6)$	$\text{C}_{64}\text{H}_{52}\text{FeN}_4\text{P}_4\text{TiK}_2 \cdot 2(\text{C}_6\text{H}_6)$
Formula weight	1108.75	1185.91
T (K)	123(2)	123(2)
<i>a</i> , Å	18.0499(4)	17.3366(6)
<i>b</i> , Å	18.0499(4)	12.4623(5)
<i>c</i> , Å	21.9628(6)	33.0415(13)
α, deg	90	90
β, deg	90	91.670(2)
γ, deg	90	90
Volume, Å ³	7155.5(3)	7135.7(5)
Z	4	4
Crystal System	Tetragonal	Monoclinic
Space Group	<i>P</i> _{4cc}	<i>P</i> _{21(n)}
<i>d</i> _{calc} , g/cm ³	1.316	1.247
θ Range, deg	4.03 to 72.18	2.67 to 72.110
μ, mm ⁻¹	1.316	4.809
Abs. Correction	Multi-scan	Multi-scan
GOF	1.048	1.071
<i>R</i> ₁ ^a	<i>R</i> ₁ = 0.0466	<i>R</i> ₁ = 0.0607
<i>wR</i> ₂ ^b [<i>I</i> > 2 · (<i>I</i>)]	<i>wR</i> ₂ = 0.0923	<i>wR</i> ₂ = 0.1502

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

RESULTS AND DISCUSSION

Figure 1. Synthesis of bimetallic TiFe complexes 2 and 3.

The homoleptic titanium complex, $\text{Ti}(\text{NP})_4$ (1) ($\text{NP} = 2\text{-diphenylphosphinopyrrolide}$), has been previously synthesized and characterized[46]. Treatment of 1 with 1 equivalent of FeCl_2 and two equivalents of KC_8 leads to the formation of the diamagnetic 2 in low yield (Figure 1). The yield of this reaction is low due to unavoidable side reactions from which we have observed intractable mixtures of several low-valent, paramagnetic complexes that result from Ti-N cleavage and subsequent ligand decomposition[46]. The solid-state structure of 2 is presented in Figure 2 and selected bond lengths and angles can be found in Table 2. Complex 2 crystallizes in the P_{4CC} space group with two molecules in the asymmetric unit and where the ligands are symmetrically equivalent. All phosphinopyrrolide ligands are used to bridge the metal center giving it a *pseudo*- C_4 symmetry down the metal-metal axis. The Fe center is rigorously square pyramidal with Ti occupying the apical position of the square pyramid ($\angle \text{PFeP}$ ($^\circ$) = 89.991(1) 89.998(1) and $\angle \text{PFeTi}$ ($^\circ$) = 90.71(5) and 90.15(5)), and the Fe center is $\sim 0.03 \text{ \AA}$ out of the phosphine plane. The Ti center is *pseudo* square pyramidal, with the Ti sitting $\sim 0.42 \text{ \AA}$ above the N_4 plane. Ti-N distances in the two molecules of the asymmetric unit are 2.093(4) and 2.075(5)

Å, and the Fe–P bond lengths are 2.3655(12) and 2.3705(13) Å. At room temperature in a chloroform solution, **2** contains a single resonance by ^{31}P NMR consistent with the C_4 -symmetric solid-state structure.

Figure 2. Thermal ellipsoid drawing of **2** (top) and **3** (bottom). Solvent and Hydrogen atoms have been removed and the phosphine phenyl rings reduced to the *ipso* carbons for clarity. Selected bond distances and angles are provided in Table 2.

Table 2. Relevant bond lengths (Å) and angles (°) for **2** and **3**.

	2	3
	2.021(2)	1.9474(7)
Ti-Fe (Å)	2.028(2)	
FSR ^a	0.81	0.78
	2.3655(12)	2.2286(9)
P-Fe (Å)	2.3705(13)	2.1936(9)
		2.203(1)
	89.991(1)	106.87(3)
P-Fe-P (°)	89.998(1)	119.05(4)
		129.91(4)
	2.093(4)	2.206(3)
Ti-N (Å)	2.075(5)	2.146(3)
		2.187(3)
		2.195(3)
	26.21(13)	7.05(9)
Torsional Angle	27.45(14)	27.57(7)
(P-Fe-Ti-N) (°)		25.16(8)

$$^a\text{FSR} = M_D / \sum(M_C): M_D = \text{Metal-metal distance}, M_C = \text{Covalent Radii}$$

The independent molecules in the asymmetric unit of complex **2** feature remarkably short Fe-Ti distances of 2.028(2) and 2.021(2) Å (FSR = 0.81) indicative of a Ti-Fe triple bond. From DFT calculations using M06-L, the molecular orbitals (MOs) of **2** indicate three metal-metal bonding molecular orbitals: a σ bond between the Ti and Fe d_{z^2} orbitals and two degenerate π bonds formed from the d_{xz} and d_{yz} orbitals (Figure 3)[48]. NBO calculations predict a Mayer bond order of 1.48, slightly less than a double bond, resulting from significant polarization of the π symmetry orbitals to Fe.

Figure 3. Qualitative molecular orbital diagram and bonding molecular orbitals computed from M06-L calculations for complexes **2** and **3**.

Further reduction of **2** with 2 equivalents of KC_8 allowed for the isolation of doubly reduced complex **3**, K_2TiFe (Figure 1). Complex **3** is diamagnetic and contains three resonances that integrate 2:1:1 by ^{31}P NMR: a multiplet, triplet ($J_{pp} = 60$ Hz) and singlet. The solid-state structure of **3** is presented in Figure 2 and selected bond lengths and angles can be found in Table 2. Interestingly, only 3 phosphinopyrrolides bridge the two metal centers, rendering the geometry around iron *pseudo*-trigonal pyramidal. The fourth pyrrolide ligand remains bound to Ti through the nitrogen atom, while the phosphine is unbound and approximately 3.5 Å away from Ti. The multiplet corresponds to the two pseudo-trans phosphines, the triplet corresponds to the phosphine trans from the vacant coordination site and the singlet is the unbound phosphine arm, consistent with the pattern expected from the solid-state structure. Phosphine decoordination is due to the increased d-electron count at Fe: if one assumes that **2** is an 16-electron d^8 Fe center, addition of electrons into the d manifold would populate the $\text{d}_{x^2-y^2}$ orbital and cause ligand dissociation from the Fe square plane. The K^+ counteranions each remain tightly bound between two pyrrole aryl π systems further confirming a dianionic complex.

The Fe-P bond lengths in **3** have contracted by greater than 0.15 Å to ~2.208 Å, while the Ti-N distances have lengthened by ~0.1 Å to ~2.18 Å. The shortening of the Fe-P bond distances is likely due to increased Fe-P backbonding by the reduced Fe species, since the complex is now formally dianionic and only 3 phosphines now compete for backdonation[49]. The large increase in the Ti-N bond distances indicates that at least one of the two reductive events is Ti-based[31]. The Ti-Fe distance has shortened by 0.08 Å to 1.9469(8) Å (FSR = 0.78), while the Fe has been pulled below the P_3 plane by ~

0.26 Å. This distortion from planarity is most likely caused by the increased Ti–Fe bond strength, as well as the relaxed geometric constraints imposed by 3 bridging ligands instead of 4.

Similarly to 2, the MOs from DFT calculations on 3 also show three Ti–Fe bonding molecular orbitals. In contrast to 2, the trigonal geometry at Fe breaks the degeneracy of the two π bonding orbitals, although they remain close in energy (Table S2). Similarly, the nonbonding Fe $d_{x^2-y^2}$ orbital has been significantly lowered in energy on account of the ligand field change from tetragonal to trigonal. NBO calculations indicate a Mayer bond order of 1.83, significantly higher than 2 and is in agreement with the shorter FSR observed in the solid-state structure. It is interesting that nominal population of a nonbonding orbital (Fe $d_{x^2-y^2}$) results in an increase in the Ti–Fe bond strength in 3. This can be rationalized from a simple increase in the Lewis basicity of the reduced Fe center, which should result in decreased polarization of the π bonding Ti–Fe orbitals. The Mulliken charges for 3 increase by about 0.5 electrons for Fe and decrease by about 1 electron for Ti compared to 2 (Table S3). This qualitative behavior correlates with the shorter Fe–Ti distance and suggests better Fe to Ti electron donation.

The d^{10} complex 3 presents an interesting contrast to the previously-reported d^{10} complex, $(\kappa^2\text{-NP})\text{Ti}(\mu_2\text{-NP})_3\text{Ni}$. This Ti/Ni complex contains a Ti–Ni double bond that is strongly polarized toward Ni, while the filled Ni d_{yz} orbital remains disengaged from π bonding. Thus, the bonding is significantly *stronger* in the TiFe analogue compared to TiNi. This periodic trend is expected based on previous results observed by Thomas and Lu[29–30] which showed that M–M bonding and orbital overlap among first row transition metals increases as the

difference in group number between the two metals decreases. Another difference between **3** and the TiNi complex is that the 4th phosphine arm remains decoordinated in **3**, while it binds to Ti in TiNi. This observation is also consistent with Fe being a more effective donor than Ni: the more electron-rich Ti center in TiFe **3** is less prone to phosphine coordination than TiNi. For further comparison, Lu recently reported a d⁹ N₄Ti^{IV}P₃Fe^{I-} complex supported by a heptadentate *tris*(amide)amine scaffold[28]. In Lu's complex, the Ti-Fe bond is 2.0636(7) Å, longer than that found in d⁸ **2** and d¹⁰ **3**, indicating that the electron-poor Ti pyrrolide with no *trans* ligand may form stronger bonds than the π-donating amide framework that has an apical amine donor.

CONCLUSIONS

An early-late, titanium-iron, tetragonally symmetric bimetallic complex supported by a phosphinopyrrolide ligand has been synthesized and characterized. X-ray crystallographic and computational analysis shows a metal-metal triple bond consisting of a sigma and two pi interactions. Further reduction by two electrons results in the isolation of the dianion, K₂TiFe, where one ligand arm has decoordinated from iron and the metal-metal bond has shortened to 1.9474(7) Å. In this instance, additional electrons into the metal-metal bonding manifold cause ligand dissociation rather than weakening of the metal-metal bond. In fact, the change from tetragonal to pseudo-trigonal symmetry serves to increase the bond order.

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