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Simple routes to bulky silyl-substituted acetylide ligands and examples of V(III), Fe(II), and Mn(II) complexes†

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Synthesis of substituted phenylacetylide ligands 2,6-bis(trimethylsilyl)phenylacetylene (H1) and 2-(triphenylsilyl)-phenylacteylene (H2) is reported. Ligand 1 supports tetrahedral complexes of V(III), Fe(II), and Mn(II) (3–5). Complexes 3–5 are high-spin and redox active.

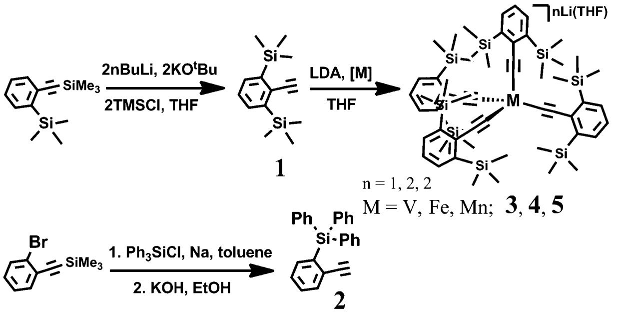
The acetylide ligand has enjoyed significant use in transition metal chemistry. A notable example of its utility includes the ability of the unsaturated π-system to mediate electronic communication between metal centers up to extended distances as in, for example, $[C_6F_5(PPh_3)_2Pt]_2(C{\equiv}C)_n$,[1] and $CpFe(C{\equiv}C)_2FeCp$.[2] Acetylide is a strongly donating ligand and it is well-known that strongly donating and tunable ligands such as phosphines and *N*-heterocyclic carbenes feature prominently in transition metal synthesis and catalysis. However, unlike phosphine and *N*-heterocyclic carbene ligands, facile routes to substituted acetylide ligands are not readily available. It has been established that the more strongly donating *N*-heterocyclic carbene ligand offers enhanced stability, and hence improved catalytic activity over analogous phosphine complexes in some instances.[3] We are exploring whether the more donating and anionic acetylide ligand can also serve as a tunable and highly donating ancillary ligand.

Herein we present routes to modify the electronic and steric properties of acetylenes by 2-or 2,6-substitution of the readily available phenylacetylene architecture by using silyl substituents. Transition metal complexes of moderately bulky acetylide ligands have previously been reported; use of *t*-butylsilox-substituted acetylide ligands enabled detailed electronic characterization of the octahedral and trigonally distorted, six-coordinate Ta, Zr, and Hf complexes.[4] Homoleptic complexes of $-C{\equiv}CH$ and $-C{\equiv}CSiMe_3$, for the first row transition metals from vanadium across to cobalt are also hexacoordinate.[5,6] In all of these examples the acetylide ligands are not bulky enough to prevent formation of octahedral complexes. The notable exceptions to this rule are complexes of Ni^{II}, Cu^{II}, and Zn^{II} which are four-coordinate due to an electronic preference at the metal center (rather than a steric preference).[7] We demonstrate that bulky acetylide ligand **1** prevents formation of six-coordinate complexes and supports coordinatively unsaturated, tetrahedral and high-spin complexes of V(III), Fe(II), and Mn(II).

The acetylide ligand **1** was obtained in two steps from readily available phenylacetylene (Scheme 1). In the first step, 2-trimethylsilylphenylacetylene was synthesized in 95% yield based on a reported procedure.[8] In the second step, incorporation of the second TMS substituent to yield TMS-protected **1** was achieved by subjecting 2-trimethylsilylphenylacetylene to a closely analogous procedure employed for its formation: two equivalents of *n*BuLi, followed by two equivalents of both KO^tBu and then TMSCl were added to 2-trimethylsilylphenylacetylene. Base hydrolysis of the unpurified reaction mixture yielded a mixture of the three deprotected isomers of **1** which were separated to give **1** in 49% yield (details are given in the ESI†).

Synthesis of 2-(triphenylsilyl)phenylacetylene (**2**) was achieved by heating a mixture of 2-bromo(phenylacetylene), sodium metal and triphenylsilylchloride at reflux in toluene for 16 h.[9] Upon workup, TMS-protected **2** was obtained in 50% yield. Compound **2** could be obtained after removal of the TMS protecting group by reaction with KOH in ethanol solution (90% yield).

Transition metal complexes of **1** were prepared by salt metathesis reactions between the appropriate metal halide salt; $VCl_3{\cdot}3THF$ suspended in benzene, or $FeCl_2$, or MnI_2 suspended in THF and the lithium salt of **1**. Following reaction for 24 h, workup afforded $[Li{\cdot}4THF][(2,6\text{-}(Me_3Si)_2PhC{\equiv}C)_4V(\text{III})]$ (**3**) as



Scheme 1

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dark blue needle-shaped crystals in 42% yield, $[Li{\cdot}THF]_2[(2,6\text{-}(Me_3Si)_2PhC{\equiv}C)_4Fe(\textsc{ii})]$ (**4**) as yellow block-shaped crystals in 34% yield, or $[Li{\cdot}THF]_2[(2,6\text{-}(Me_3Si)_2PhC{\equiv}C)_4Mn(\textsc{ii})]$ (**5**) as colorless block-shaped crystals in 45% yield, respectively. A single crystal X-ray crystallography experiment revealed in each case, that the bulky acetylide ligand had successfully constrained the coordination number of the first row transition metal ion to four (Fig. 1 and 2, S1, S2†). As mentioned previously, the more commonly observed $[M(C{\equiv}CR)_n]^{m-}$ formulation has $n = 6$.[5,6] We have thus far been unsuccessful in our attempts to prepare transition metal complexes of **2** and we speculate that the great steric bulk of **2** may hinder formation of metal–ligand bonds. New approaches are under way to overcome the current obstacles.

Solid state structures of **3–5** confirmed formation of tetrahedral complexes. Complex **3** has the most regular tetrahedral geometry and the C–M–C bond angles are each defined by the symmetry of the space group as 109.4°. In **4** and **5** the lithium ions are coordinated between pairs of the C≡C π-bonds and two of the C–M–C angles are pinched whereas two are wider than 109.4° at 101.3 Å. In all three of the complexes, the C≡C bond lengths are very close to an ideal C≡C triple bond; 1.220(3), 1.208(8), and 1.225(2) Å, which indicates that there is no M≡C–C–R (carbene) or M=C=C–R (cummulene) character to the M–C–C–R moiety. The C≡C bond length in free acetylene is 1.2022(2) Å.[10]

Electrochemical measurements were performed using the cyclic voltammetry method on all compounds in 0.1 M Bu_4NPF_6 THF solution (Fig. 3, S3–S5). For each of the complexes an irreversible oxidation wave is observed; at +0.17 and +1.11 V *vs.* SCE for **3**, at −0.23 V for **4** and at +0.35 V for **5**. No reversible oxidation events were observed. Somewhat surprisingly, the complexes each display reduction chemistry including reversible electrochemical behavior in some cases. Compound **3** can be reduced at −2.24 V and this process is followed by another irreversible process at −2.74 V *vs.* SCE (Fig. 3). In contrast, **4** and **5** both display just one pseudo-reversible reduction event at −2.12 V (ΔE_p = 100 mV) and −2.11 V (ΔE_p = 90 mV), respectively. A cyclic voltammogram for the ligand, **1**, was collected under same conditions and revealed no electrochemical events (Fig. S3†). However, it is still possible that the reduction events observed for complexes **3–5** arise from reduction of the ligands and that these events become more favorable after the ligand is coordinated to the positively charged metal center. At present, we have no conclusive evidence to rule out this possibility. The presence of multiple reduction events in **3** suggests that at least one of them is metal-based.

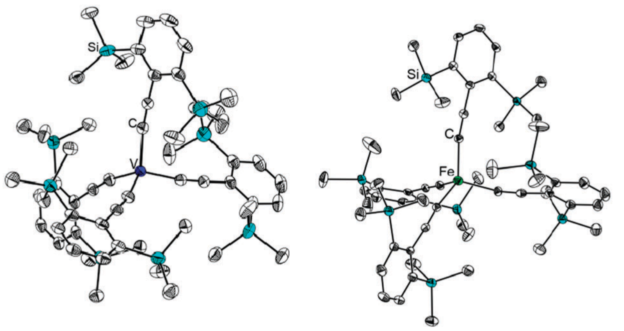

Fig. 1 Solid state structure of complexes **3** and **4**. Blue, green, white, light blue atoms represent vanadium, iron, carbon and silicon atoms, respectively. Thermal ellipsoids shown at 40% probability and H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg) for **3**, [**4**]: M–C, 2.023(2) [2.043(3)]; C≡C, 1.218(3) [1.219(5)]; C-Ar, 1.437(3) [1.445(5)]; C–M–C, 105.5(1), 106.8(1), 116.4(1) [103.4(2), 122.7(1)]; M–C≡C, 169.8(2) [165.3(3)]; C≡C-Ar, 177.3(2) [177.0(4)].

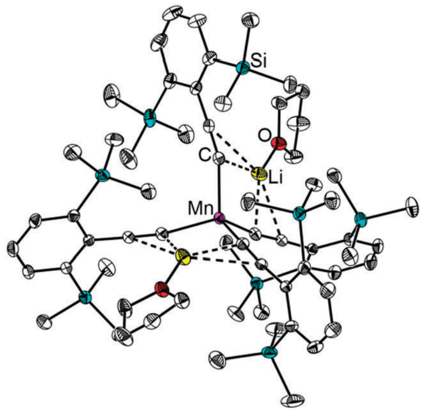

Fig. 2 Solid state structure of complex **5** showing the coordination of Li^+ ions to the alkyne ligands. Complex **4** displays an identical Li^+ coordination pattern. Purple, white, light blue atoms represent manganese, carbon and silicon atoms, respectively. Thermal ellipsoids shown at 40% probability and H atoms omitted for clarity.

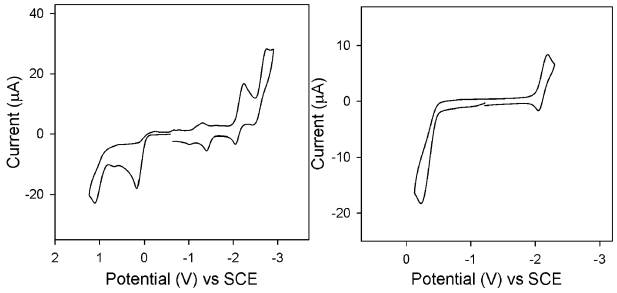

Fig. 3 Electrochemical measurements for complexes **3** and **4** recorded in 0.1 M Bu_4NPF_6 THF solution with a glassy carbon working electrode. Scan rate 100 mVs^{-1}.

Magnetic susceptibility measurements performed on complexes **3–5** confirm the expected high spin states generally associated with tetrahedral geometries. Each of the complexes displays temperature independent behavior from 5–300 K and the magnetic susceptibilities of the complexes at room temperature are 2.78, 5.08, and 6.01 μ_B for V(III), Fe(II), and Mn(II), respectively. These magnetic moments imply electronic configurations for each of the ions which are d^2, high-spin d^4 and high-spin d^5, respectively. The high-spin state for Fe(II) acetylide complexes is unknown. Previously reported alkynyl complexes of Fe(II) are all low-spin because the smaller –C≡CH and $–C{\equiv}CSiMe_3$ ligands permitted an octahedral coordination geometry.[5,6]

We have demonstrated that the bulky acetylide ligand **1** can be employed to reduce the coordination number of the acetylide complexes of V(III), Fe(II), and Mn(II) down to four and alter the electronic structure of the transition metal ions compared with the –C≡CH ligand. The resulting complexes have a tetrahedral coordination geometry in each case. Future work will focus on exploration of higher oxidation states of these complexes and on exploiting the unsaturated metal centers toward the activation of small molecules.

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