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Communication

Tris(pyrrolyl-α-methyl)amines that Sterically Protect a Trigonal Metal Site

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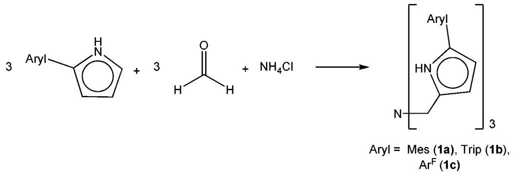
Three substituted tris(pyrrolyl-α-methyl)amines ($H_3[Aryl_3TPA]$) (Aryl $=$ 2,4,6-$C_6H_2Me_3$, 2,4,6-C_6H_2(*i*-Pr)$_3$ (Trip), or 3,5-$C_6H_3(CF_3)_2$) have been prepared. An X-ray study of [$Trip_3$TPA]MoCl shows it to be a distorted trigonal bipyramidal species in which the 2,4,6-triisopropylphenyl substituents surround and protect the apical chloride. Attempts to prepare other Mo, Zr, and Hf complexes yielded species in which one pyrrole-containing arm remained free (Mo) or dimethylamine remained in the coordination sphere of $[Aryl_3TPA]^{3-}$ complexes (Zr, Hf).

We have been exploring complexes of the earlier metals that contain a substituted triamidoamine ligand ($[(RNCH_2CH_2)_3N]^{3-}$),[1] especially versions in which R is an aryl group,[2] and in particular molybdenum complexes in which R is 3,5-(2,4,6-i-$Pr_3C_6H_2)_2C_6H_3$ or HIPT (HexaIsoPropylTerphenyl).[3–5] The main focus is reduction of dinitrogen, i.e., complexes such as $[HIPTN_3N]Mo(N_2)$ ($[HIPTN_3N]^{3-} = [(HIPTNCH_2CH_2)_3N]^{3-}$) will catalyze the reduction of dinitrogen with protons and electrons at room temperature and pressure.[4] A trianionic ligand that sterically protects a trigonal coordination site is a key feature of these catalysts. An interest in other trianionic four-coordinate ligands that might enforce a trigonal sterically protected binding site drew us to substituted variations of tris(pyrrolyl-α-methyl)amine (H_3TPA) introduced by Odom.[6]

The desired substituted pyrroles can be prepared through Pd-catalyzed cross-coupling between pyrrolylzinc chloride and aryl halides reported by Sadighi.[7] The $H_3[Aryl_3TPA]$ species where Aryl $=$ 2,4,6-$C_6H_2Me_3$ (Mes, **1a**),[8] 2,4,6-C_6H_2-(*i*-Pr)$_3$ (Trip, **1b**), or 3,5-$C_6H_3(CF_3)_2$ (Ar^F, **1c**) can then be prepared through a triple Mannich reaction in either ethanol/water or isopropanol/water at 55 °C (eq 1).[6] As one would expect, Mannich reactions that produce **1a**, **1b**, and **1c** require both higher temperatures and longer reaction times than reactions involving pyrrole itself.



(1)

Attempted syntheses of [$Aryl_3$TPA]MoCl species followed the protocol established for synthesizing [$HIPTN_3N$]MoCl.[3] Addition of either **1a** or **1c** to $MoCl_4(THF)_2$ in THF followed by 3 equiv of LiN(TMS)$_2$ led to intractable mixtures. However, the analogous reaction with **1b** gave [$Trip_3$TPA]-MoCl (**2**) in low isolated yield (14%) after crystallization from pentane at −30 °C. (Compound **2** is highly soluble, and crystallization requires weeks.) The ^{1}H NMR spectrum of **2** at 23 °C (benzene-d_6) is broad and featureless, consistent with a five-coordinate Mo(IV) complex of this general type in which $S = 1$.[3] The measured μ_{eff} (Evans' method[9]) of 2.34 μ_B is consistent with this proposal.

A single-crystal X-ray diffraction study of **2** revealed it to be a pseudotrigonal bipyramidal molecule in which the three pyrrolyl nitrogens occupy approximately equatorial positions and chloride and N(4) occupy axial positions (Figure 1). The Mo(1)−Cl(1) and Mo(1)−N(4) bond lengths are similar to the analogous distances in crystallographically

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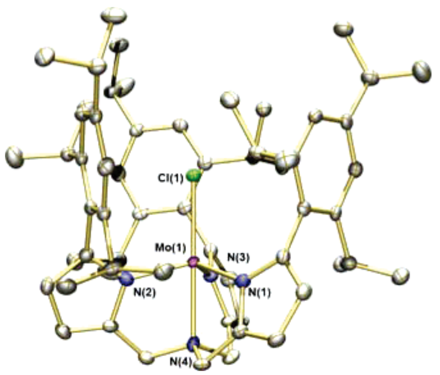
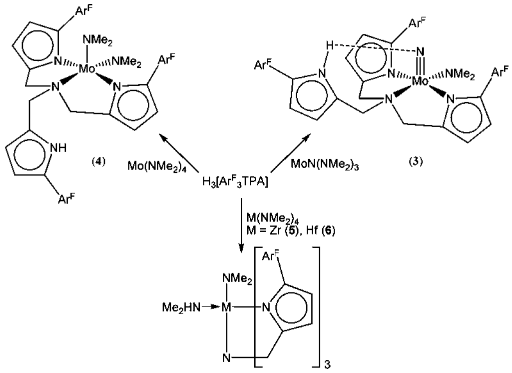


Figure 1. POV-Ray rendering of **2** with thermal ellipsoids at 50% probability. Hydrogen atoms and co-crystallization pentane omitted; (Å) Mo−N(1) = 2.004(3), Mo−N(2) = 2.009(3), Mo−N(3) = 2.009(3), Mo−N(4) = 2.213(3), Mo−Cl(1) = 2.3095(13).

Scheme 1



characterized substituted TREN analogues[5a,10] and the average Mo(1)−$N_{Pyrrolyl}$ bond length (2.007 Å) is similar to what has been observed in recently prepared Mo(η^1-Pyrrolyl) complexes.[11] The Trip substituents interdigitate to form a cavity 6.2 Å deep, which is ~0.9 Å shallower than that found in $[(3,5\text{-}(2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2C_6H_3NCH_2CH_2)_3N]MoCl$.[5a] Compound **2** appears to be thermally unstable at 22 °C under dinitrogen over a period of days.

Dimethylamido complexes were also employed as precursors (Scheme 1). Reactions of either **1a** or **1b** with $Mo(N)(NMe_2)_4$ or $M(NMe_2)_4$ (M = Mo, Zr, or Hf) were incomplete in the temperature range studied (23−100 °C; 12−48 h). In contrast, a reaction between **1c** and $Mo(N)(NMe_2)_3$ in dichloromethane at 22 °C (Scheme 1) yielded the highly crystalline complex, $Mo(N)(NMe_2)(H[Ar^F{}_3TPA])$ (**3**). Solution ^1H and ^{19}F NMR at 23 °C (CD_2Cl_2) confirmed that **3** is a C_s symmetric species containing one unreacted (protonated) “arm”.

The proposed structure of **3** was confirmed through a single-crystal X-ray diffraction study (Figure 2). Complex **3** has a distorted square-pyramidal geometry in which the nitride occupies the axial position. Two pyrrolyls, the donor nitrogen, and a dimethylamide comprise the basal coordination set. Close inspection of the structure reveals what appears to be a hydrogen bond between the proton of the remaining pyrrole and the nitride, judging from the fact that the distance between N(1) and N(5) (2.893(3) Å) is shorter than the sum of their Van der Waals radii (3.10 Å). Attempts to form a trispyrrolyl complex through addition of bases ($LiN(TMS)_2$, NEt_3, *n*-BuLi, etc.) or acids (2,6-lutidinium chloride or *N*,*N*-dimethylanilinium chloride), as well as attempts at substituting the dimethylamido ligand with a halogen using TMSCl or TMSI, have led either to no reaction or to decomposition.

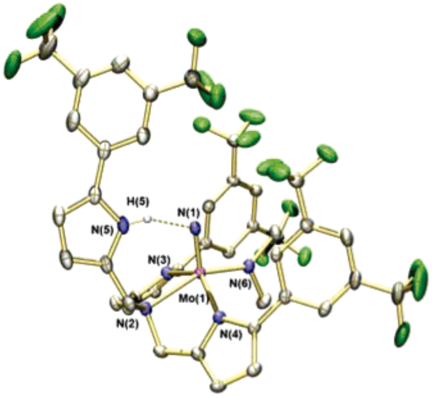


Figure 2. POV-Ray rendering of **3** with thermal ellipsoids at 50% probability. Hydrogen atoms, co-crystallized dichloromethane, and minor component of disorder are omitted; (Å) Mo−N(1) = 1.657(2), Mo−N(2) = 2.330(2), Mo−N(3) = 2.108(2), Mo−N(4) = 2.096(2), Mo−N(6) = 1.926(2).

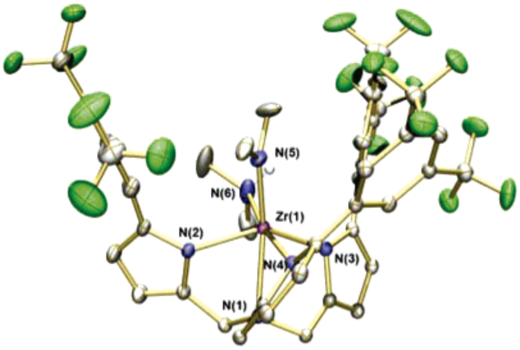


Figure 3. POV-Ray rendering of one of the two independent molecules in the asymmetric unit of **5** with thermal ellipsoids at 50% probability. Hydrogen atoms and co-crystallized dichloromethane omitted; (Å) Zr−N(1) = 2.346(2), Zr−N(2) = 2.199(2), Zr−N(3) = 2.220(2), Zr−N(4) = 2.221(2), Zr−N(5) = 2.040(3), Zr−N(6) = 2.441(3).

Reaction of **1c** with $Mo(NMe_2)_4$ in pentane at −30 °C (Scheme 1) readily yields the highly crystalline five-coordinate complex $Mo(NMe_2)_2(H[Ar^F{}_3TPA])$ (**4**) in which again only two pyrrolyls are attached to the metal. Resonances in the ^1H and ^{19}F NMR spectra of **4** at 23 °C (in CD_2Cl_2) were slightly paramagnetically shifted. A single-crystal X-ray study revealed that **4** is a square-based pyramidal geometry similar to **3** with a dimethylamide occupying the axial position rather that a nitride. (see Supporting Information.) The “free arm” of the ligand in **4** is pointed “down” instead of “up”, as it is in **3**.

In contrast to the results obtained with molybdenum, reactions between **1c** and either $Zr(NMe_2)_4$ or $Hf(NMe_2)_4$ in

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dichloromethane yielded Zr(NMe$_2$)(NHMe$_2$)[Ar^F$_3$TPA] (**5**) or Hf(NMe$_2$)(NHMe$_2$)[Ar^F$_3$TPA] (**6**) in good yield (87% and 85%, respectively). ^{1}H and ^{19}F NMR spectra at 23 °C (CD$_2$Cl$_2$) show that **5** and **6** have C_3 symmetry on the NMR time scale. At this stage, we believe that C_3 symmetry results from dissociation of dimethylamine. A single-crystal X-ray study of **5** shows that it adopts a highly distorted octahedral geometry in the solid state (Figure 3) in which N(6) is the remaining dimethylamine nitrogen.

In conclusion, three new H$_3$[Aryl$_3$TPA] species have been prepared that serve as precursors to Mo, Zr, and Hf complexes, several of which contain [Aryl$_3$TPA]$^{3-}$ ligands. Issues remain in terms of obtaining the desired five-coordinate trispyrrolyl complexes, perhaps in part because of the poor π-bonding ability of the pyrrolyl groups compared to the amido groups in aryl-substituted triamidoamine complexes. Whether [Ar$_3$TPA]Mo complexes have the subtle balance of properties required for catalytic dinitrogen reduction remains to be determined. However, complexes that contain protective [Aryl$_3$TPA]$^{3-}$ ligands could prove useful for other purposes.[8]

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Supporting Information Available: Experimental details for the synthesis of all compounds and the X-ray structural studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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