HFEP Studies of Organovanadium(III) Complexes with Relevance to Catalytic Processes

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Introduction
Early transition metal complexes such as those of Ti and V have applications as polymerization catalysts. However, the use of Electron Paramagnetic Resonance (EPR) towards the study of paramagnetic catalytically relevant organometallic complexes has been minimal and the application of High-Frequency and High-Field EPR (HFEPR) towards systems that are "EPR-silent" due to large zero-field splitting (zfs) has been essentially nonexistent. HFEPR can yield data on the electronic structure of these catalysts that is not available by other techniques. Our initial foray into this area is to study organometallic complexes of V(III) (3d^2, S=1 as obtained at 300 K by solution state magnetic measurements).

The specific complexes in our initial study comprise sterically highly protected β-diketiminate (NacNac= [ArNC(CH3)2]2CH; NacNac* = ArNC7H5) ligands combined with amido or halo ligands to give pseudo four-coordinate V(III) with the general formula: (NacNac)VCl(L), L = Cl, N[tol]Mes (tol = C6H4-p-CH3, Mes = 2,4,6-Me3C6H2), and (NacNac*)VCl2 [1]. These complexes are interesting from a reactivity standpoint since they can undergo two-electron chemistry with substrates such as azides to afford the first examples of neutral, four coordinate V(V) nitrides, such as (NacNac)V(N)(Ntol)2 [2]. The nitrides can behave as electrophiles in reacting with π-acids such as CO and CN(2,6-Me2C6H3) to reduce the complex back to V(III) with extrusion of N2. HFEPR can be used to observe both the azide precursor and the nitride reduction product. Additionally, an organometallic V(III) complex with a "pincer" type ligand, (PNP)V(CH2tBu)2 (PNP = N[2-P(CHMe2)2-4-methylphenyl]2) was investigated, which is a precursor to a transient, highly reactive, four-coordinate alkylidene (PNP)V=CHtBu that can undergo a variety of useful transformations.

Experimental
The NHMFL EMR Facility with the superconducting 15/17 T magnet was used to study polycrystalline samples of the above complexes prepared under inert atmosphere.

Results and Discussion
All the V(III) complexes investigated gave HFEPR spectra. In two cases, ((PNP)V(CH2tBu)2 and (NacNac*)VCl2), well-defined spectra characteristic for S = 1 were found. A representative spectrum and simulations are shown for (PNP)V(CH2tBu)2 in Figure 1. In the case of (NacNac)VCl2 and (NacNac*)VCl(N[tol]Mes), however, the signals surprisingly were characteristic of very small magnitude zfs. Hence, these complexes merit investigation by conventional (X-band) EPR, which might demonstrate that V(III) in these two complexes is not the "EPR-silent" state as is commonly assumed.

Conclusions
This preliminary study shows promising results and represents the first application of HFEPR at the NHMFL to bona fide organometallic complexes, with pronounced reactivity but, moreover, with catalytic relevance. The correlation between electronic properties as revealed by HFEPR and function will be a challenge.

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References