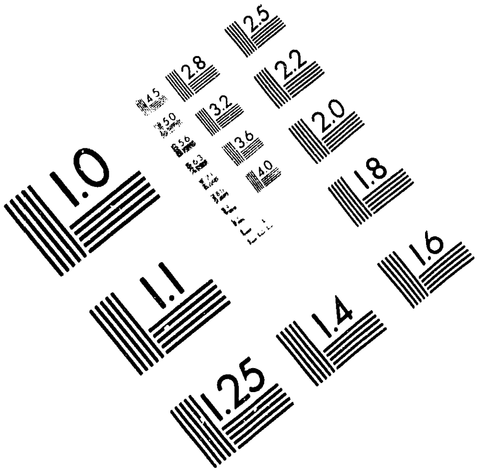

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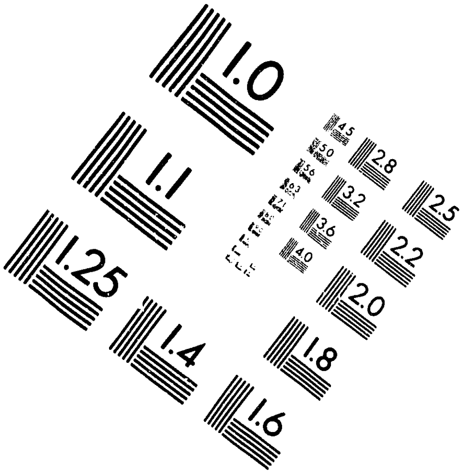

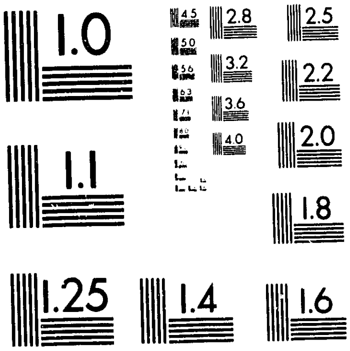

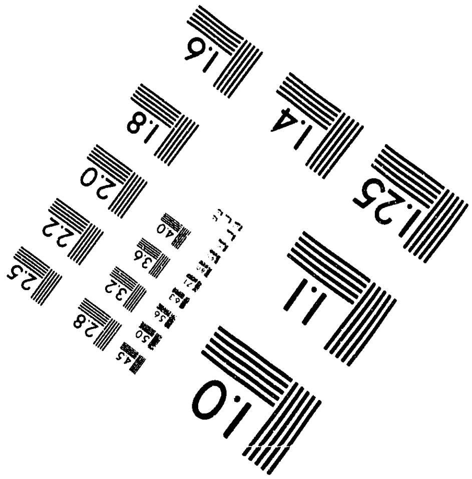

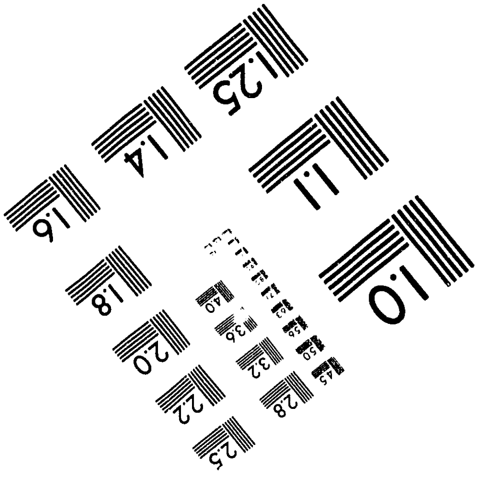

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Progress Report - ER14273

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During the past 8 months we have made significant progress in elucidating the mechanism of the O_2 activation by tris(pyrazolyl)borate cobalt complexes, which provided the starting point for this project. Specifically, we have prepared a series of Tp^iCo-complexes (Tp^i = hydridotris(3-*i*-propyl-5-methylpyrazolyl)borate), which have allowed us to probe the origin of the hydrogen atom required for the formation of hydroxide in eq.1 (Tp' = hydridotris(3-*t*-butyl-5-methylpyrazolyl)borate).[1]

(1) $$Tp'Co(O_2) + Tp'Co(N_2) \rightarrow 2\,Tp'CoOH$$

We have prepared both $Tp^iCo(CO)$ (**1**) and a dinitrogen complex, which we currently formulate as $Tp^iCo(\mu_2\text{-}N_2)CoTp^i$ (**2**); the latter assignment is supported by its similarity to the structurally characterized $Tp^{np}Co(\mu_2\text{-}N_2)CoTp^{np}$ (**3**, Tp^{np} = hydridotris(3-neopentyl-pyrazolyl)borate), recently prepared in our laboratory. Reaction of **2** with O_2 <u>in solution</u> directly yielded $Tp^iCo(\mu_2\text{-}OH)_2CoTp^i$ (**4**), which has been structurally characterized. Note, that in the related Tp'-system both the carbonyl (Tp'Co(CO)) and the dinitrogen complex ($Tp'Co(N_2)$) produced $Tp'Co(O_2)$ when exposed to O_2; the lesser steric hindrance of the isopropyl groups of the Tp^i-ligand apparently increases the rate of the bimolecular reaction (analogous to eq.1) dramatically and thus precludes the preparation of $Tp^iCo(O_2)$ in this way. In a similar vein, <u>dissolved</u> **1** reacts with O_2 to yield $Tp^iCo(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}CO_3)CoTp^i$ (**5**), which has also been structurally characterized. However, hydrolysis of the products of the reaction of **2** with O_2, followed by analysis with GC-Ms and ^1H NMR, showed the presence of ca 10 % of 3-isopropenyl-5-methyl-pyrazole, i.e. a dehydrogenation product of the ligand. The formation of this compound is consistent with our hypothesis that a reactive cobalt-oxo fragment (here $Tp^iCo\text{-}O^\cdot$) is formed as an intermediate and abstracts hydrogen from the ligand (the formation of isopropyl radical is presumably followed by disproportionation to yield 1/2 equivalent of the dehydrogenated isopropenyl moieties).

In a bid to prepare the elusive dioxygen complex by other routes we have found that exposure of solid **1** to O_2 for several hours yields $Tp^iCo(O_2)$ (**6**). In the crystal lattice the bimolecular reaction of **6** with **1**, which thwarted success in solution, cannot proceed, thus enabling isolation of **6**. Interestingly, **6** is much less stable than the analogous Tp'Co(O2), which is an amazingly robust material. The mechanism of the thermal decomposition of dissolved **6** at room temperature is currently under investigation. NMR experiments indicate the formation of $Tp^iCo(\mu_2\text{-}O_2)CoTp^i$ (**7**) as an intermediate. This interesting molecule, the analog of which completely eluded us in Tp'-chemistry (presumably due to greater steric hindrance), can be prepared independently by reaction of **2** with O_2 at low temperature (-78°C). Upon warming it decomposes with simple first order kinetics, yielding the expected hydroxide **4**.

We find that the use of the Tp^i-ligand has shed considerable light on the reaction mechanism of the O_2-activation (eq.1), as delineated in the original proposal. Our basic mechanistic hypothesis seems to be borne out. We are currently tying up the loose ends of this part of the project and anticipate its completion and preparation of a manuscript describing these results by this summer.

In a spin-off of the work described above we are following up on some unusual observations concerning several carbonyl complexes prepared during the course of our project. Following the discovery of the unusual side-on coordination mode of the superoxide ligand in $Tp'Co(O_2)$,[1] we have wondered whether other small ligands (e.g. N_2, NO, CO) might show unusual bonding modes to the TpCo-fragment. Indeed, the crystal structure of $Tp^nCo(CO)$ (Tp^n = hydridotris(3-*t*-butyl-pyrazolyl)borate) shows a most tantalizing disorder problem, which is most successfully modeled by assuming crystallographic averaging over two molecules with bent Co-C-O linkages. There are ca 10,000 crystal structures of metal carbonyls, and terminal CO always binds in a linear end-on fashion. A bent CO-ligand (for electronic rather than steric reasons) would be of considerable novelty. We are thus preparing other derivatives - using various pyrazoles - in the hopes of preparing and structurally characterizing a molecule which unambiguously shows the Co-C-O geometry without disorder. The preparative work involved is also useful for our oxidation work; for example, the dinitrogen complex **3**, which first alerted us to the possibility of bridging N_2, was originally prepared in pursuit of the CO-problem.

Looking ahead, during the next year we plan to emphasize the assembly of a catalytic system by means of the approaches outlined in the original proposal (i.e. hardening of the ligand against hydrogen atom abstraction, shifting of the O2 binding equilibrium etc.). A first step in this direction will be the introduction of fluorinated ligands to overcome the self-destruction problem of the metal complexes.

References:

1) J. W. Egan Jr., B. S. Haggerty, A. L. Rheingold, S. C. Sendlinger, K. H. Theopold, *J. Am. Chem. Soc.* **1990**, *112*, 2445.

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