

complementary methods, TDXD and simultaneous TG-MS coupling techniques.

[1] Vaidhyanathan R., Natarajan S., Rao C.N.R., *J. Solid State Chem.*, 2004, **177**, 1444.

Keywords: hydrothermal, mixed carboxylates, thermal analysis

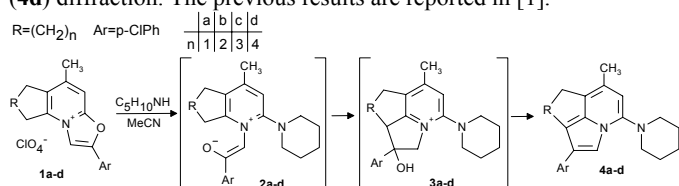
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Diffraction Study of Recyclization of Oxazolopyridinium Salts to Indolizines

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In the course of our systematic study of structure/reactivity relationships for heterocycles, the reaction of recyclization of oxazolo[3,2-*a*]pyridinium salts with annelated cycloalkane fragments of different size revealed some unexpected peculiarities. All obtained compounds were studied by single crystal (**1a-d**, **3c**, **4b,c**) or powder (**4d**) diffraction. The previous results are reported in [1].



As discovered earlier, compounds **1b,d** easily gave corresponding indolizines **4b,d**. In the case of compound **1c** the reaction suddenly stopped at the non-predicted intermediate **3c** (with ClO_4^- anion). It can be explained by the less distortion of 7-membered ring connected to a non-planar bicycle than in **4c**. Dehydration of **3c** led to **4c**. Compound **1a** was also attacked by piperidine, but only resin was formed. In this case, the unstable intermediate **2a** is unable to react further because compounds **3a** and **4a** have high angle distortions as the AM1 molecular model shows.

[1] *Acta Cryst.*, 2004, E60, o1096-o1097, o1301-o1302, o2313-o2314.

Keywords: structure/reactivity relationship, organic chemistry, powder diffraction

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Structure and Properties of Safe and Powerful Noble-Metals Oxidation Reagents

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Molecular CT-complexes obtained by reacting acceptors such as diiodine with S-donor molecules, have been extensively studied mainly due to their intrinsic structural, spectroscopic, chemical and physical properties and, recently, to their applicability as conducting materials or as oxidation reagents towards transition metals. With the view to synthesize complexing-oxidizing agents capable to dissolve noble-metals (NMs) in mild conditions, we have chosen exa- and epta-atomic cyclic dithioamides as bidentate S,S-donors. By reacting the $\text{N,N}'$ -dialkyl-perhydrodiazepine-2,3-dithione (R_2dazdt , $\text{R}=\text{Me}$ (**a**), Et (**b**)) class of ligands with I_2 the expected 1:2 CT-complexes, $\text{R}_2\text{dazdt}\cdot 2\text{I}_2$ (**1**), have been obtained as proved by structural and spectroscopic characterization.^[1] Instead, by using the $\text{N,N}'$ -dialkyl-piperazine-2,3-dithione (R_2pipdt , $\text{R}=\text{Me}$, Et , Pr^i (**c**)) class, which shows an exa-atomic ring in spite of the hepta-atomic one in R_2dazdt , the unexpected triiodide salt of the protonated donors, $[\text{R}_2\text{pipdtH}]\text{I}_3$ (**2**), have been isolated. The different nature and structure of the two class of reagents is reflected on a different reactivity towards NMs: while class **1** adducts are capable to oxidize Pd and Au metal but are inactive towards Pt, class **2** reagents are capable to dissolve Pt metal too. Further studies are in progress in order to clarify the different

behaviour of the two class of ligands and the source of H^+ in the reaction.

[1] Serpe A., et al., *Chem. Commun.*, 2005, 1040, and refs therein.

Keywords: charge-transfer complexes, halogens, noble-metals

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Nickel(II) Carbosilane Dendrimers: Structure and Polymerization Catalysis

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Nickel(II) compounds containing sterically demanding α -diimine ligands, and related chelates, have been found to be attractive catalysts for the production of polyolefins.^[1] Dendrimers can be used as well-defined supports for active centers in homogeneous phase, which catalytic applications are being widely studied,^[2] including those in polymerization processes.^[3] In this work, a series of carbosilane dendritic compounds $\text{G}_n\text{-ONNMe}_m\text{NiBr}_2$ ($n = 0, 1, 2, 3$; $m = 0, 2, 3$), from monometallic to metallo-dendritic structures containing up to sixteen ($n = 3$) terminal pyridylimine nickel complexes, have been synthesized, and the crystal structure of some model compounds have been determined. The nickel complexes, in combination with methylaluminoxane (MAO), convert ethylene into mixtures of toluene-insoluble polyethylene and oily oligomers. The variation of the pyridylimine ligand framework by m methyl substituents has a decisive influence on the activities of the nickel compounds. Also, the generation of the dendritic precursor (n) acutely affects the catalyst performance and the microstructure of the insertion products as well. Thus, higher generation catalysts show superior oligomerization activities and produce less branched polyethylene.

[1] Ittel S.D., Johnson L.K., Brookhart M., *Chem. Rev.*, 2000, **100**, 1169. [2] Astruc D., Chardac F., *Chem. Rev.*, 2001, 101, 2991. [3] Müller C., Ackerman L.J., Reek J.N.H., Kamer P.C.J., van Leeuwen P.W.N.M., *J. Am. Chem. Soc.*, 2004, **126**, 14960.

Keywords: nickel, dendrimers, polymerization

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Solid-state Formation of a Coordination Polymer Starting from a Monomeric Thiodiacetate Manganese Complex

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Compounds $[\text{Mn}(\text{tda})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$ (**1**) and $[\text{Mn}(\text{tda})(\text{H}_2\text{O})]_n$ (**2**) ($\text{tda} = \text{thiodiacetate}$, $\text{S}(\text{CH}_2\text{COO})_2^{2-}$) were obtained by the reaction of aqueous solutions of manganese dichloride and a 1:1 mixture of Na_2CO_3 and thiodiacetic acid with the appropriate work-up. The X-ray study of **1** shows that the complex is a monomer containing the typical tridentate thiodiacetate ligand with a facial configuration. For compound **2**, as previously reported by us [1], we propose a structure similar to that published for the homologous cadmium derivative [2], namely a 2D-polymer with $\{\text{Mn}(\text{tda})(\text{H}_2\text{O})\}$ subunits bridged by the carboxylate groups of tda.

In this communication we will report the unprecedented solid-state polymerization of compound $[\text{Mn}(\text{tda})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$ (**1**) to afford $[\text{Mn}(\text{tda})(\text{H}_2\text{O})]_n$ (**2**). The formation of a coordination polymer from the corresponding monomer occurred in the solid state and the process can be monitored straightforwardly by IR spectroscopy.

Additionally, we will describe some preliminary results concerning the use of these derivatives and the related oxydiacetate compounds as catalyst precursors in the oxidation reaction of alcohols to aldehydes with dioxygen, a "clean reagent".

[1] Grirrane A., Pastor A., Galindo A., Ienco A., Mealli C., *Chem. Commun.*, 2003, 512. [2] Whitlow S.H., *Acta Cryst.*, 1975, **B31**, 2531.

Keywords: thiodiacetate, crystal structures, oxydiacetate