



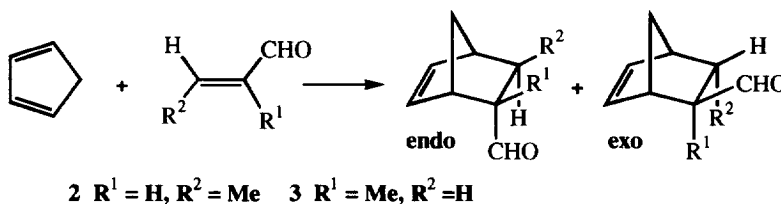
## Investigations into the Use of Niobium and Tantalum Complexes as Lewis Acids

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**Abstract:** The Lewis acidity of niobium and tantalum compounds has been studied with respect to simple Diels-Alder reactions. The results show that these compounds have excellent Lewis acidity.  
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No work has previously been carried out concerning the Lewis acidity of niobium and tantalum compounds and their mediation in Diels-Alder reactions. We have investigated the Lewis acidity of both  $\text{NbCl}_5$  and  $\text{TaCl}_5$  with respect to the Diels-Alder reactions of cyclopentadiene **1** with methacrolein **2** or crotonaldehyde **3** as shown in Scheme 1. The use of these reactions allows comparisons to be made with other work in the Lewis acid area.<sup>1</sup> The metal pentachloride (0.15eq.) was stirred for 1h with the diene **1** (5.00eq.) and the dienophile **2** or **3** (1.00eq.) in dry diethylether, under dry argon at  $-78^\circ\text{C}$ . Under these conditions it was observed that the reaction of **1** with **2** was catalysed by  $\text{NbCl}_5$  to give the Diels-Alder product with an endo:exo ratio of 10:90 and in a yield of 62%. When **2** was replaced by **3** under the same conditions, a very low yield (13%) of the major isomer was achieved with and the endo:exo ratio was 94:6. The reaction did not proceed when  $\text{TaCl}_5$  was used instead of  $\text{NbCl}_5$  under the above conditions. The reaction yielded an intractable gum. Reaction between cyclopentadiene and the dienophiles **2** and **3** does not occur under the above conditions without the presence of a catalyst.<sup>1</sup> Given that  $\text{NbCl}_5$  showed Lewis acid properties, we felt that it might be possible to substitute the chloride ligands for chiral moieties and still retain the Lewis acidity leading to new chiral catalysts. Indeed, reduction in the reactivity of  $\text{TaCl}_5$  by substitution of chloride for nitrogen or oxygen might give useful catalytic Lewis acidity. Tables 1 and 2 show the results for the reaction of **1** with **2** or **3** when  $\text{NbCl}_5$  or  $\text{TaCl}_5$  was complexed to two bidentate chiral ligands. Lewis acid catalysis *and* enantioselectivity (entries 7 and 8 in Table 1, entry 1 in Table 2) are only seen when exactly two equivalents of bidentate ligand are used. Proton NMR of the active catalyst indicates that there is chelation by two bidentate ligands about the niobium.



Scheme 1

The enantiomeric excesses of the major isomers from the reaction of **1** with **2** and **3** were determined by proton NMR after conversion of the crude product to the acetal using (2*R*,4*R*)-pentanediol.<sup>2</sup>

**Table 1.** Results for the Diels-Alder Reaction Between Cyclopentadiene and Crotonaldehyde or Methacrolein in the Presence of Niobium Complexes of Some Bidentate Ligands.<sup>3</sup>

Bidentate ligand	Dienophile	
	Crotonaldehyde	Methacrolein
1) L-Phenylalanine	18%; 85:15	42%; 25:75
2) L-Alanine	27%; 95:5	44%; 7:93
3) L-Leucine	10%; 93:7	27%; 13:87
4) L-Isoleucine	20%; 94:6	40%; 8:92
5) L-Tryptophan	10%; 84:16	57%; 22:78
6) L-Valine	5%; 95:5	13%; 13:87
7) Diethyl-L-tartrate	9%; 93:7	61%; 6:94; 25%
8) Diisopropyl-L-tartrate	16%; 94:6	52%; 3:97; 40%

**Table 2.** Results for the Diels-Alder Reaction Between Cyclopentadiene and Crotonaldehyde or Methacrolein in the Presence of Tantalum Complexes of Some Bidentate Ligands.<sup>3</sup>

Bidentate ligand	Dienophile	
	Crotonaldehyde	Methacrolein
1) Diethyl-L-tartrate	42%; 90:10	78%; 6:94; 7%
2) Diisopropyl-L-tartrate	24%; 95:5	55%; 6:94
3) (+)-2,3- <i>O</i> -Isopropylidene-L-threitol	14%; 99:1	49%; 16:84
4) (-)-2,3- <i>O</i> -Isopropylidene- 1,1,4,4-tetraphenyl-L-threitol	72%; 86:14	50%; 9:91
5) (-)-2,3- <i>O</i> -Isopropylidene- 1,1,4,4-tetra(2-naphthyl)-L-threitol	42%; 99:1	75%; 10:90

The excellent endo:exo ratios obtained in the above results show that complexes of niobium or tantalum have great potential as Lewis acids. With the diethyl- and diisopropyl-L-tartrates as ligands there is also a degree of enantioselectivity. Our investigations into the use of niobium and tantalum complexes in Lewis acid mediated catalytic asymmetric synthesis are being directed at improving the enantioselectivities and developing asymmetric Lewis acids capable of mediating in a range of reaction types.

## REFERENCES AND NOTES

1. Narasaka, K. *Synthesis*, **1991**, 1-11.
2. Furuta, K.; Shimizu, S.; Miwa, Y. and Yamamoto, H. *J. Org. Chem.*, **1989**, *54*, 1481-1483.
3. The entries in Tables 1 and 2 are; yield; endo: exo; enantiomeric excess of major isomer if over 5%.