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Homogeneous Diels–Alder catalysis by organotungsten Lewis acid containing *tris*(2-pyridyl)phosphine ligand

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Abstract

The complex $[P(2\text{-py})_3W(CO)(NO)_2](BF_4)_2$ (**1**) is an excellent catalyst precursor for Diels–Alder reactions of 1,3-diene and α,β-unsaturated ketones and/or aldehydes with a catalyst loading as low as 0.3 mol%.

Keywords: Diels–Alder reaction; homogeneous catalysis; organotungsten Lewis acid; *tris*(2-pyridyl)phosphine complex.

The Diels–Alder (D–A) reaction is the most commonly used method for the synthesis of six-membered rings.[1] Lewis acid catalyzed D–A reactions generally provide better regio- and stereoselectivity than their corresponding thermal reactions.[2] However, most conventional Lewis acids are generally employed in large catalyst loading due to their extreme water-sensitivity and their potential in product binding. These Lewis acids are sometimes too active to prevent undesired side reactions. Thus, the study of low-valent transition metal complexes as Lewis acid catalysts for D–A reactions has become a subject of intense current interest.[3–6]

Recent reports[7] from this laboratory have demonstrated that the complex $[P(2\text{-py})_3W(CO)(NO)_2](BF_4)_2$ (**1**) possesses strong Lewis acidity upon loss of the CO ligand. The relative Lewis acid strength[8] of **1** is found to be comparable to that of BF_3.[7] With a view to studying the catalytic aspect of **1**, we report here the effective reactivity of **1** in catalyzing the D–A reactions of 1,3-dienes with α,β-unsaturated ketones and aldehydes (Scheme 1).

The catalyst precursor $[P(2\text{-py})_3W(CO)(NO)_2](BF_4)_2$ (**1**) can be easily synthesized in two steps in high yield from the commercially available $W(CO)_6$. In addition, the complex **1** can be stored as a crystalline solid in air for months without significant decomposition.

The isolated yields of D–A adducts from **1**-catalyzed D–A reactions were summarized in Table 1. The catalytic reactions[9] were usually conducted in CH_3NO_2 using a catalyst loading as low as 0.3 mol% (catalyst-to-dienophile mole ratio) and an initial diene-to-dienophile ratio of 1.2:1.0.

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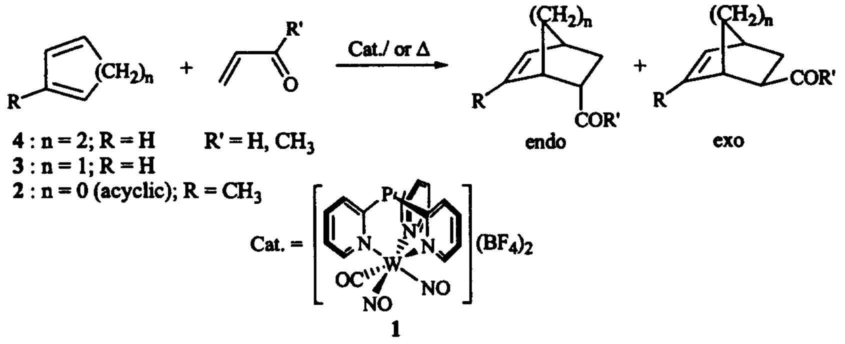

Scheme 1.

Table 1

Diels–Alder reactions catalyzed by complex **1** at various temperatures

entry[a]	diene	dienophile R'	cat. loading (mol %)[b]	solvent	temp. (°C)	time[c]	endo : exo[d]	product n	yield (%)[f]
1	3	CH_3	0.3	CH_2Cl_2	0	10 hr	93 : 7	1	91
2	3	CH_3	0.3	CH_3NO_2	0	1 hr	94 : 6	1	92
3	3	CH_3	0.3	CH_3NO_2	RT	30 min	94 : 6	1	87
4	3	CH_3	0.3	CD_3NO_2	70	< 3 min	93 : 7	1	93[g]
5	3	H	0.3	CH_2Cl_2	0	9 hr	93 : 7	1	90
6	4	CH_3	0.3	CH_2Cl_2	0	30 hr	99 : 1	2	85[h]
7	4	CH_3	0.3	CH_3NO_2	0	15 hr	99 : 1	2	81[h]
8	4	CH_3	0.3	CH_3NO_2	RT	12 hr	97 : 3	2	83
9	4	CH_3	0.3	CH_3NO_2	70	55 min	96 : 4	2	88
10	4	CH_3	2	CH_3NO_2	RT	2 hr	98 : 2	2	82
11	2	CH_3	0.3	CH_2Cl_2	0	35 hr	99 : 1	0	79
12	2	CH_3	0.3	CH_3NO_2	0	72 hr	—	Polymer[e]	91

[a]Initial diene-to-dienophile ratio of 1.2 : 1.0 for each entry. [b]Catalyst-to-dienophile mole ratio. [c]Time were for greater than 90% completion. [d]Determined by ^1H NMR. [e]Polymerization products were analyzed by ^1H and ^{13}C NMR in C_6D_6. [f]Isolated yield. [g]Analytical yield. [h]work from reference 4.

The **1**-catalyzed reaction of cyclopentadiene (**3**) and methyl vinyl ketone (MVK) at ambient temperature was complete in 30 minutes, however the corresponding thermal reaction was 83% complete in 20 hours (entries 3, Tables 1 and 2). Under the same conditions, the **1**-catalyzed reaction of cyclohexadiene (**4**) and MVK was complete in 12 hours (entry 8, Table 1). In contrast, the thermal reaction was only 5% complete in 24 hours (entry 7, Table 2). Higher reaction rates can be obtained by increasing the catalyst loading. The reaction of **4** and MVK was complete in 2 hours using a catalyst loading of 2 mol% (entry 10, Table 1). The rates of both **1**-catalyzed and uncatalyzed systems can also be enhanced by increasing reaction temperature. At 70°C and 0.3 mol% **1**, the reactions of **3** with MVK and **4** with MVK were complete in <3 and 55 minutes, respectively (entries 4 and 9, Table 1). The corresponding uncatalyzed reactions were complete in 90 minutes and 7% complete in 6 hours, respectively (entries 4 and 8, Table 2). The observed rates of **3** and MVK are higher than those of **4** and MVK in both catalyzed and uncatalyzed systems. From ab initio calculations,[10] the estimated intrinsic barrier for the gas phase uncatalyzed D–A reaction of **3** and MVK is 5 kcal/mol lower than that of uncatalyzed **4** and MVK system (this translates to a ratio of approximate 4000 in rate constants at room temperature). This result is, at least qualitatively, consistent with the experimental rate differences between **3**/MVK and **4**/MVK systems.

In order to minimize the thermal interference, the catalytic reactions were also carried out at milder

Table 2
Uncatalyzed Diels–Alder reactions at various temperatures

entry[a]	diene	dienophile R'	solvent	temp. (°C)	time (hours)	endo : exo[b]	product n	conversion[c] (%)
1	3	CH_3	CH_2Cl_2	0	24	85 : 15	1	86
2	3	CH_3	CH_3NO_2	0	22	86 : 14	1	82
3	3	CH_3	CH_3NO_2	RT	20	88 : 12	1	83
4	3	CH_3	CH_3NO_2	70	1.5	81 : 19	1	91
5	3	H	CH_2Cl_2	0	24	81 : 19	1	83
6	4	CH_3	CH_2Cl_2	0	24			<5
7	4	CH_3	CH_2Cl_2	RT	24			5
8	4	CH_3	CH_3NO_2	70	6			7
9	2	CH_3	CH_2Cl_2	0	24			<5

[a] Initial diene-to-dienophile ratio of 1.2 : 1.0 for each entry. [b] Determined by ^{1}H NMR and GC. [c] The percentage conversion is determined by ^{1}H NMR.

conditions. At 0°C, the catalytic reaction of **3** and MVK was complete in an hour, while the thermal reactions were 82% complete in 22 hours (entries 2, Tables 1 and 2). Under the same conditions, the catalytic reaction of **4** and MVK was complete in 15 hours, however, the thermal reactions were <5% complete in 24 hours in CH_2Cl_2 (entry 7, Table 1; entry 6, Table 2). Furthermore, the **1**-catalyzed reaction of **3** and acrolein in CH_2Cl_2 was complete in 9 hours, while the uncatalyzed reaction took 24 hours to complete (entry 5, Table 1).

It is noteworthy that complex **1** provides not only efficiencies but also excellent *endo*-selectivity even at very mild conditions. In addition, **1** can be washed away from the reaction mixture[11] after the reaction to allow an easier process of product isolation.

The rates of most D–A catalyses are generally unaffected by solvents.[12] However, we have noticed in our study that the rates are, to a certain degree, influenced by the media.[13] The **1**-catalyzed reaction of **3** and MVK was complete in 10 hours in CH_2Cl_2, while the same reaction was completed within 1 hour in CH_3NO_2 (entries 1 and 2, Table 1). Also, the reactions of **4** and MVK were complete in 30 hours in CH_2Cl_2, and 15 hours in CH_3NO_2 (entries 6 and 7, Table 1). These results might imply that either a certain degree of change in charge separation of substrates takes place ongoing from the initial state to the transition structure or the solvent effect induces the change of Lewis acidity of the catalyst.

The diene polymerization reaction is often observed as a side reaction during the course of Lewis acid catalyzed D–A reaction. We have demonstrated in our system[14] that the degree of polymerization can be excluded by reducing the solvent polarity. When the catalytic reaction of isoprene (**2**) and MVK was carried out in CH_2Cl_2 (μ=1.60), the product was dominated by the D–A adduct (entry 11, Table 1). In contrast, polyisoprene became the only detectable product when the catalysis was conducted in CH_3NO_2 (μ=3.73) (entry 12, Table 1).

In conclusion, the stable complex $[P(2\text{-py})_3W(CO)(NO)_2](BF_4)_2$ (**1**) is an effective Lewis acid catalyst precursor for the D–A reactions of 1,3-diene and α,β-unsaturated ketones and aldehydes. Both the rates and the branching ratio of diene polymerization versus D–A reaction are found to be strongly solvent dependent. However, the actual mechanisms based on reactivity and selectivity are still speculative. The study of reaction mechanisms and reaction kinetics as well as a theoretical modeling of the catalytic system is currently in progress.

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