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Transition-metal mediated *exo* selective and enantioselective Diels–Alder reactions for the preparation of octalones with unusual stereochemistries. Reactions of 2-cobaloxime substituted 1,3-dienes with cyclohexenone in optically active Lewis acid catalyzed [4 + 2] cycloadditions

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Abstract

2-Cobaloxime-*E*-1,3-pentadienyl complexes (cobaloxime = pyridine(dimethyl or diphenylglyoxime)$_2$Cobalt (III)) react with cyclohexenone in enantioselective Lewis acid catalyzed [4 + 2] cycloaddition reactions. These cycloaddition reactions produce octalones with *cis* ring junctions through *exo* transition states. The octalones are removed from the cobalt via demetallation reactions which replace the cobalt with a hydrogen and provide pyr(dmg)$_2$CoMe which can be recycled into the synthesis of the starting dienyl complex. The enantiomeric purity of the demetallated octalones was determined by gas chromatographic analysis. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Dienyl complexes; Diels–Alder reactions; Cycloaddition reactions; Lewis acid catalysis

1. Introduction

Over the last several years, we have prepared cobalt substituted 1,3-dienes (**1**) and examined the rates, regioselectivities, and stereoselectivities of their reactions with dienophiles in Diels–Alder reactions [1]. Tada and co-workers have reported alternative preparations of some cobaloxime substituted dienes as well as results of their cycloaddition reactions [2]. The diastereoselectivities of the Diels–Alder reactions of these cobaloxime dienyl complexes (**1**) are unusual for acyclic dienes in that products arising from *exo* transition states are the major products. We have postulated that this *anti* (*exo*) selectivity is a result of metal ligand set-dienophile steric interactions which disfavor *endo* transition states. Other groups [3], in particular Wulff [4a] and Barluenga [4b], have also reported that the alternate strategy of transition-metal substitution in the dienophiles can be used to effect *exo* selective 4 + 2 cycloadditions.

Cyclohexenones (**2**) have traditionally been poor dienophiles in thermal and Lewis acid catalyzed Diels–Alder reactions [5]. Last year we reported that our very reactive cobaloxime substituted dienes (**1**) would react with these dienophiles under mild conditions to produce high yields of cycloadducts with excellent diastereoselectivity and without concomitant ring junction isomerization from *cis* to *trans* octalones [1h]. Here, we report our results for enantioselective Lewis acid catalyzed Diels–Alder reactions [6] of cobaloxime dienyl complexes (**1**) with cyclohexenone (**2**).

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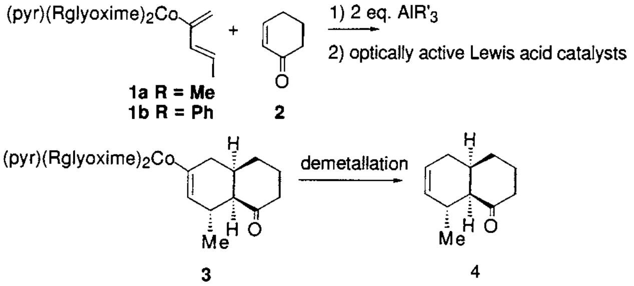
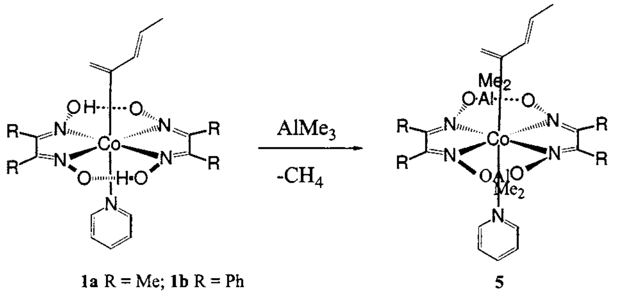
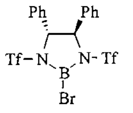


2. Results and discussion

We have previously surveyed a variety of achiral Lewis acid catalysts and developed a good, general protocol for Lewis acid catalyzed Diels–Alder reactions using the dienyl complexes (**1**) shown above [1d,h]. This protocol calls for the initial treatment of dienyl complexes (**1**) with two equivalents of $AlMe_3$, which results in CH_4 expulsion, and replacement of the bridging glyoxime OHs with $AlMe_2$ groups (**5**). This Lewis for Bronsted acid exchange in the metal's equatorial ligand set results in increased steric bulk of the ligands and enhanced *exo* diastereoselectivity of subsequent Diels–Alder reactions [1d,h]. After this equatorial ligand modification, the Lewis acid catalyst to be used in the Diels–Alder reaction and the dienophile were added. We adopted this procedure in the present study of optically active Lewis acid catalysts. The choice of possible optically active Lewis acids to screen was based on the reactivity of the achiral Lewis acids tested earlier [1d,h]. Highest yields, diastereoselectivities, and rates of reaction came from the use of the boron mono and dihalide containing Lewis acids as well as titanium dihalide Lewis acids so we picked four optically active Lewis acids of these types to screen for enantioselectivity [1d,h]. We chose cyclohexenone (**2**) as a test dienophile because of its extremely high *anti* (*exo*) diastereoselectivity in achiral Lewis acid catalyzed reactions of **1** [1d], the ease of demetallation of cycloadducts (**3**) to yield octalones (**4**), and the ease of enantiomer separation of octalones (**4**) using a commercially available Chiraldex G-TA GC column.



The Lewis acid catalysts screened (**6**–**9** shown below) are all readily available in high enantiomeric purity. The (−)-bis-trifluromethylsulfonamidebromoborane (**6**) reported by Corey [7] was prepared from the corresponding diamine [8]. Matteson [9] and Brown [10] have both reported the preparation of (+)-isopinocampheylchloroborane (**7**). Hawkins [11] has shown that (1*R*, 2*R*)-napthylcyclohexylborondichloride (**8b**) is an effective Diels–Alder catalyst. Nakai [12] and Reetz [13] reported the now heavily utilized (*R*)-1,1′-bi-2-naptholtitanium dichloride catalyst (**9**). Boron dichloride (**8b**) was prepared from the (1*R*, 2*R*) methoxy borinate ester (**8a**) and the structure of that compound was confirmed by single crystal X-ray crystallography [14].



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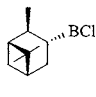

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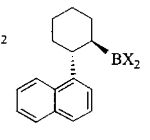
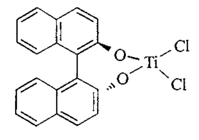


8a X = OMe
8b X = Cl



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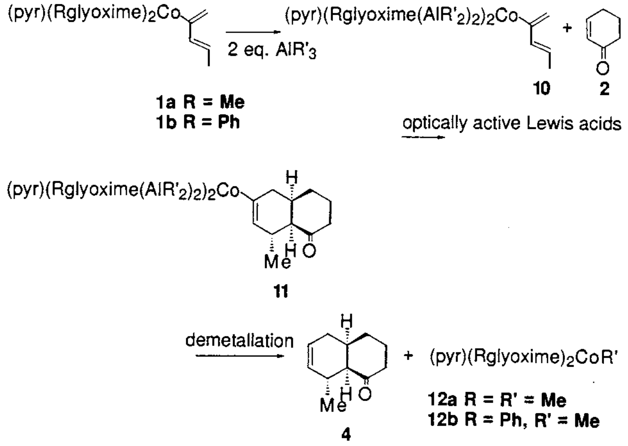

The results of the enantioselective Lewis acid catalyzed cycloadditions of dienyl complexes **1a** and **1b** with cyclohexenone are presented in Table 1. The mechanism of the Lewis acid mediated demetallation shown (**11**–**4**) and the control reactions to prove that the initially added achiral Lewis acid does not exchange with subsequently added Lewis acids have been reported previously [1h]. Corey's monohalogenated boron Lewis acid (**6**) [7] proved unreactive as a catalyst over the temperature range of −45 to 25°C and dienyl complex **1a** was recovered in a >85% yield at all temperatures (Table 1, entry 1). Since we had previously proven [1b,d,h] that diphenylglyoxime containing dienyl complex **1b** was less reactive than **1a**, it was not screened with Lewis acid **6**. Isopinocampheyldichloroborane (**7**) was an effective Lewis acid catalyst when used with dienyl complex (**1a**) providing **4** with >20:1 diastereoselectivity for the *anti* (*exo*) product (Table 1, entries 2–4). However, enantioselectivities were low at temperatures where the reaction proceeded with a reasonable rate. We have previously noted enhanced stereoselectivities in cycloadditions using dienyl complexes with larger equatorial ligands [1b,d,h], so diphenylglyoxime dienyl complex (**1b**) was also examined with Lewis acid (**7**) (Table 1, entry 6). Enantioselectivity improved (19% ee) but was still too low. We have noted that rates of our Diels–Alder cycloaddition slow substantially as the bulk of ligands and achiral catalysts increase [1b,d,h], but we decided to look at Hawkins bulky napthylcyclohexyl catalyst (**8b**) since it was also a boron dihalide and had proven an effective enantioselective Diels–Alder catalyst [11]. This catalyst (**8b**) proved unreactive when used with **1a** at −45°C (Table 1, entry 7) but would effect cycloadditions (10% ee) at −20°C (Table 1, entries 8 and 9). Switching to the diphenylglyoxime diene (**1b**) (Table 1, entry 11) required an increase in reaction temperature of up to 25°C to effect cycloaddition in 36 h. Enantioselectivity improved substantially to 31% ee. Further increases in reaction temperature were not possible due to the instability of dienyl complex (**1b**) toward Lewis acids at elevated temperatures [1b,d,h]. Instead, we tried using $AlEt_3$ instead of $AlMe_3$ in the initial Lewis acid for Bronsted acid exchange reaction (Table 1, entry 12). This change had increased equatorial ligand set bulk and enhanced diastereoselectivities in our earlier achiral Lewis acid studies [1d]. We did see a further large increase in enantioselectivity of up to 62% ee however, the isolated yield of this enantiomerically enriched octalone (**4**) was not as high as we had hoped for and this reaction was complicated by the isolation of the *trans* ring junction isomer in addition to **4**. Further increases in equatorial ligand size i.e the use of $AliBu_3$ instead of $AlEt_3$ shut the cycloaddition down (Table 1, entry 13) and use of the even bulkier binapthyl catalyst (**9**) also shut down the cycloaddition and we recovered **1b** in high mass balance (Table 1, entry 14). All the successful cycloadditions listed in Table 1 are also noteworthy in that the cobaloxime complex (**12a**, **b**) was recovered in a reusable form.

3. Conclusions

In conclusion, we have demonstrated for the first time that it is possible to effect Diels–Alder reactions of cobaloxime containing dienyl complexes (**1a** and **b**) with high *exo* (*anti*) diastereoselectivities and reasonable (up to 62% ee) enantioselectivities. We have reached the upper limit of steric bulk which can be tolerated in these cobaloxime dienyl complex cycloadditions so our future efforts on *exo* and enantioselective Diels–Alder reactions will focus on Cosalen dienyl complexes [1g].

Table 1
Cycloaddition reaction results

Entry	Diene	Catalyst	Time (h)	Temperature (°C)	Demetallation[a]	Yield **4**	%ee
1	**1a**	**6**	6–24	−45 to 25	N/A[b]	No rxn (%)	N/A[b]
2	**1a**	**7**	3.5	−45	Two steps	64	7
3	**1a**	**7**	3.5/2	−45/20[c]	In situ	72	7
4	**1a**	**7**	16	−20	Two steps	67	1
5	**1b**	**7**	10	−45	N/A[d]	No rxn	N/A[d]
6	**1b**	**7**	5	−20	Two steps	58	19
7	**1a**	**8**	24	−45	N/A	No rxn	N/A
8	**1a**	**8**	24	−20	Two steps	84	10
9	**1a**	**8**	36	−20/25	In situ	51	6
10	**1b**	**8**	24	0	N/A	No rxn	N/A
11	**1b**	**8**	36	25	In situ	65	31
12	**1b**	**8**	36	25	In situ	27[e]	62
13	**1b**	**8**	36	25	N/A[f]	No rxn	N/A[f]
14	**1b**	**9**	6–24	−45 to 25	N/A[g]	No rxn	N/A[g]

[a] Two steps means **3** was isolated then treated with excess $AlMe_3$ to demetallate to **4**. In situ means **3** was not isolated, instead the cycloaddition flask was allowed to warm to 25°C after the specified cycloaddition time to effect demetallation.

[b] This catalyst was used at four different temperatures: −45°C/16 h; −20°C/24 h; 0°C/24 h; 25°C/6 h and in each case dienyl complex **1a** was recovered unreacted in >85% mass balance.

[c] Reaction at −45°C for 3.5 h then warmed to 20°C for 2 h.

[d] A >95% recovery of the diene (**1b**).

[e] $AlEt_3$ was used as the initial Lewis acid instead of $AlMe_3$. These conditions also lead to the production of the *trans* ring junction diastereomer of **4** in a 44% yield.

[f] $AliBu_3$ was used as the initial Lewis acid instead of $AlMe_3$ leading to a >85% recovery of the diene (**1b**).

[g] This catalyst was used at four different temperatures: −45°C/16 h; −20°C/24 h; 0°C/24 h; 25°C/6 h and in each case dienyl complex **1b** was recovered unreacted in a >85% mass balance.

4. Experimental section

4.1. General methods

For a description of instrumentation and chromatographic adsorbents used see Ref. [1b]. Cobalt chloride hexahydrate used in the preparation of dienyl complexes was purchased from Strem Chemicals and used as received. Trimethylaluminum, triethylaluminum, triisobutylaluminum and 2-cyclohexen-1-one were purchased from Aldrich Chemicals and used as received. The compounds (3*E*)-1,3-pentadien-2-yl-(pyridine)bis-(dimethylglyoximato) cobalt(III) (**1a**) [1b,e], and (3*E*)-1,3-pentadien-2-yl-(pyridine)bis(diphenylglyoximato) cobalt(III) (**1b**) [1b,e], were prepared according to previously described methods. Enantioselectivities were determined using an HP 5890 Series II Gas Chromatograph with a Flame Ionization Detector. The GC column used was a Chiraldex G-TA 0.25 mm × 30 m trifluoroacetyl derivatized γ cyclodextrin column purchased from Advanced Separation Technologies, Incorporated (ASTEC). GC Method: injector temperature: 200°C; flow: 0.6 ml min^{-1}; split ratio: 75; oven program: initial temperature was 120°C for 2 min then ramp 7°C min^{-1} up to a final temp of 160°C. This method provided baseline resolution of the enantiomers of an authentic racemic sample of **4** [1h]; retention times of 10.018 and 10.355 min.

*4.2. Diels–Alder reaction of diene (**1a**) and 2-cyclohexen-1-one (**2**) catalyzed by isopinocampheyl boron dichloride Lewis acid (7) (two step demetallation preparation)*

Diene complex (**1a**) (100 mg, 0.23 mmol) was dissolved in CH_2Cl_2 (3.2 ml) and cooled to −45°C. The compound $AlMe_3$ (230 µl of a 2.0 M solution in hexane, 0.46 mmol), which had been cooled to 0°C, was added and gas evolution as well as a color change from light to dark orange was noted. A standard stock solution of 2-cyclohexen-1-one (1.0 ml of a 0.254 M solution in CH_2Cl_2, 0.254 mmol) which had been cooled to 0°C, was then added quickly. Isopinocampheyl boron dichloride (**7**) (115 µl of a 1.0 M solution in CH_2Cl_2; 0.115 mmol) was then added and allowed to stir under N_2 for 6 h. Water (1.5 ml) was then added and the mixture was allowed to warm to 25°C, and CH_2Cl_2 (10 ml) was added. The solution was dried with $MgSO_4$, vacuum filtered, and the salts were washed with CH_2Cl_2 (25 ml). The cycloadduct product was purified on silica gel (ethyl acetate). The solvent was removed by rotary evaporation and the resultant orange powder was vacuum dried to give **3** (R = Me) (107 mg, 0.213 mmol, 93%) identical by ^{1}H-NMR comparison to previously reported material [1h]. Complex (**3**) (R = Me) was then dissolved in dry THF (5 ml) and cooled to 0°C, and $AlMe_3$ (120 µl of a 2.0 M solution in hexane, 0.240 mmol) was added via syringe. After 0.5 h, the solution was warmed to 25°C and allowed to stir for 2.0 h. Water (2.0 ml) was added and the solution was stirred for 10 min, CH_2Cl_2 (25 ml) was added. The solution was then dried over $MgSO_4$. The Mg salts were removed by vacuum filtration and washed with CH_2Cl_2 (10 ml). The solvent was removed by rotary evaporation and the resulting orange oil was chromatographed on silica using 1:1 Et_2O/hexane to give **4** as a pale yellow oil after solvent removal (19.9 mg, 0.136 mmol, 64%). This yellow oil was identical by spectroscopic comparison to **4** reported previously [1h]. Resolution of the enantiomers of **4** was carried out using the method described in the general methods section above. Further silica elution with EtOAc, followed by removal of solvent with rotary evaporation and high vacuum gave an orange solid, **12a**, (64.5 mg, 0.168 mmol, 73%) identical by spectroscopic comparison to pyr$(DMG)_2$CoMe reported and characterized previously [1b,d,h, 15].

*4.3. Diels–Alder reaction of diene (**1a**) and 2-cyclohexen-1-one (**2**) catalyzed by isopinocampheyl boron dichloride Lewis acid (7) (in situ cleavage)*

The diene complex (**1a**) (100 mg, 0.23 mmol) was dissolved in CH_2Cl_2 (3.2 ml) and cooled to −45°C, and $AlMe_3$ (230 µl of a 2.0 M solution in hexane, 0.46 mmol), which had been cooled to 0°C, was added and gas evolution as well as a color change from light to dark orange was noted. A standard stock solution of 2-cyclohexen-1-one (1.0 ml of a 0.254 M solution in CH_2Cl_2, 0.254 mmol) which had been cooled to 0°C, was then added quickly. Isopinocampheyl boron dichloride (**7**) (115 µl of a 1.0 M solution in CH_2Cl_2, 0.115 mmol) was added and allowed to stir under N_2 for 3.5 h at −45°C. The reaction was then warmed to 20°C and allowed to stir for another 2 h. Water (1.5 ml) was then added followed by CH_2Cl_2 (10 ml). The solution was dried with $MgSO_4$, vacuum filtered and the salts were washed with CH_2Cl_2 (25 ml). The solvent was removed by rotary evaporation and the resulting orange oil was chromatographed on silica using 1:1 Et_2O/hexane to give **4** as a pale yellow oil after solvent removal (27.3 mg, 0.167 mmol, 72%). This yellow oil was identical by spectroscopic comparison to **4** reported above. The mixture of enantiomers of **4** was resolved using the method described above. Further elution with EtOAc, followed by removal of solvent with rotary evaporation and high vacuum gave an orange solid, **12a**, (43.9 mg, 0.114 mmol, 49%) identical by spectroscopic comparison to pyr$(DMG)_2$CoMe reported and characterized previously [1b,d,h, 15].

4.4. Diels–Alder reaction of diene (**1b**) and 2-cyclohexen-1-one (**2**) catalyzed by isopinocampheyl boron dichloride Lewis acid (**7**)

The diene complex (**1b**) (200 mg, 0.30 mmol) was dissolved in CH_2Cl_2 (5 ml) and cooled to −20°C, and $AlMe_3$ (300 μl of a 2.0 M solution in hexane, 0.60 mmol), which had been cooled to 0°C, was added and gas evolution as well as a color change from light to dark orange was noted. A standard stock solution of 2-cyclohexen-1-one (1.30 ml of a 0.254 M solution in CH_2Cl_2, 0.33 mmol) which had been cooled to 0°C, was added quickly. Isopinocampheyl boron dichloride Lewis acid (**7**) (150 μl of a 1.0 M solution in CH_2Cl_2, 0.150 mmol) was added and the solution was allowed to stir under N_2 for 5 h. Isopropanol/water (1:1, 1.5 ml) was then added and the mixture was allowed to warm to 25°C at which point CH_2Cl_2 (10 ml) was added. The solution was dried with $MgSO_4$ and then vacuum filtered and the salts were washed with CH_2Cl_2 (25 ml). The cycloadduct product was purified on silica gel (CH_2Cl_2). The solvent was removed by rotary evaporation and the resultant orange powder was vacuum dried to give **3** (R = Ph) (184 mg, 0.241 mmol, 80%) identical by ^{1}H-NMR comparison to material reported previously [1h]. The cycloadduct was dissolved in dry THF (5 ml) and cooled to 0°C and $AlMe_3$ (180 μl of a 2.0 M solution in hexane, 0.36 mmol) was added via syringe. After 0.5 h, the solution was warmed to 25°C and allowed to stir for 2.0 h. Water (2.0 ml) was added and stirred for 10 min, CH_2Cl_2 (25 ml) was added and the solution was dried over $MgSO_4$. The Mg salts were removed by vacuum filtration and washed with CH_2Cl_2 (10 ml). The solvent was removed by rotary evaporation and the resulting orange oil was chromatographed on silica using 1:1 Et_2O/hexane to give **4** as a pale yellow oil after solvent removal (23.0 mg, 0.140 mmol, 58%) This yellow oil was identical by spectroscopic comparison to **4** reported above. Resolution of the enantiomers of **4** was carried out using the method described above. Further elution with EtOAc, followed by removal of the solvent with rotary evaporation and high vacuum gave an orange solid (**12b**), (99.6 mg, 0.162 mmol, 67%) identical by spectroscopic comparison to pyr(DPG)$_2$CoMe reported and characterized previously [1b,d,h].

4.5. Diels–Alder reaction of diene (**1a**) and 2-cyclohexen-1-one (2) catalyzed by Lewis acid (**8b**) (two step cleavage)

The diene complex (**1a**) (100 mg, 0.23 mmol) was dissolved in CH_2Cl_2 (3.2 ml) and cooled to −20°C, and $AlMe_3$ (230 μl of a 2.0 M solution in hexane, 0.46 mmol), which had been cooled to 0°, was added and gas evolution as well as a color change from light to dark orange was noted. A standard stock solution of 2-cyclohexen-1-one (1.0 ml of a 0.254 M solution in CH_2Cl_2, 0.254 mmol) which had been cooled to 0°C, was then added quickly. The Lewis acid (**8b)** (230 μl of a 0.5 M solution in CH_2Cl_2, 0.115 mmol) was added and allowed to stir under N_2 for 24 h. Water (1.5 ml) was subsequently added and the mixture was allowed to warm to 25°C before CH_2Cl_2 (10 ml) was added. The solution was dried with $MgSO_4$, vacuum filtered and the salts were washed with CH_2Cl_2 (25 ml). The cycloadduct product was purified on silica gel (ethyl acetate). The solvent was removed by rotary evaporation and the resultant orange solid was vacuum dried to give **3** (R = Me) (156.6 mg, 0.205 mmol, 89%) identical by ^{1}H-NMR comparison to material reported previously [1h]. Complex (**3**) (R = Me) was then demetallated using the same second step procedure described above for Lewis acid (**7**) and **1a**. The resulting orange oil was chromatographed on silica using 1:1 Et_2O/hexane to give **4** as a pale yellow oil after solvent removal (28.3 mg, 0.173 mmol, 84%). This yellow oil was identical by spectroscopic comparison to **4** reported above. Resolution of the enantiomers of **4** was carried out using the method described above. Further elution with EtOAc, followed by removal of solvent with rotary evaporation and high vacuum gave an orange solid, **12a**, (64.5 mg, 0.167 mmol, 55%) identical by spectroscopic comparison to pyr(DMG)$_2$CoMe reported and characterized previously [1b,d,h, 15].

4.6. Diels–Alder reaction of diene (**1a**) and 2-cyclohexen-1-one (**2**) catalyzed by Lewis acid (**8b**) (in situ cleavage)

The diene complex (**1a**) (100 mg, 0.23 mmol) was dissolved in CH_2Cl_2 (3.2 ml) and cooled to −20°C, $AlMe_3$ (230 μl of a 2.0 M solution in hexane, 0.46 mmol), which had been cooled to 0°C, was added and gas evolution as well as a color change from light to dark orange was noted. A standard stock solution of 2-cyclohexen-1-one (1.0 ml of a 0.254 M solution in CH_2Cl_2, 0.254 mmol) which had been cooled to 0°C, was then added quickly. The Lewis acid (**8b**) (230 μl of a 0.5 M solution in CH_2Cl_2, 0.115 mmol) was then added and allowed to stir under N_2 for 36 h at −20°C. The reaction was then warmed to 20°C and allowed to stir for another 2 h. Water (1.5 ml) was added followed by CH_2Cl_2 (10 ml). The solution was dried with $MgSO_4$, vacuum filtered and the salts were washed with CH_2Cl_2 (25 ml). The solvent was removed by rotary evaporation and the resulting orange oil was chromatographed on silica using 1:1 Et_2O/hexane to give **4** as a pale yellow oil after solvent removal (19.2 mg, 0.117 mmol, 51%) This yellow oil was identical by spectroscopic comparison to **4** reported above. The mixture of enantiomers of **4** was resolved using the method described above. Further elution with EtOAc, followed by removal of the solvent with rotary evaporation and high vacuum gave an orange solid, **12a**, (49.4 mg, 0.129 mmol, 56%) identical by spectroscopic comparison to pyr(DMG)$_2$CoMe reported and characterized previously [1b,d,h, 15].

*4.7. Diels–Alder reaction of diene (**1b**) and 2-cyclohexen-1-one (**2**) catalyzed by Lewis acid (**8b**) (in situ cleavage)*

The diene complex (**1b**) (150 mg, 0.225 mmol) was dissolved in CH$_2$Cl$_2$ (4 ml) and cooled to -20°C, AlMe$_3$ (225 µl of a 2.0 M solution in hexane, 0.450 mmol), which had been cooled to 0°C, was added and gas evolution as well as a color change from light to dark orange was noted. A standard stock solution of 2-cyclohexen-1-one (1.0 ml of a 0.254 M solution in CH$_2$Cl$_2$, 0.254 mmol) which had been cooled to 0°C, was then added quickly. The Lewis acid **(8b)** (230 µl of a 0.5 M solution in CH$_2$Cl$_2$, 0.115 mmol) was added and the solution was warmed to 25°C and allowed to stir under N$_2$ for 36 h. Water (1.5 ml) was added followed by CH$_2$Cl$_2$ (10 ml). The solution was dried with Na$_2$SO$_4$, vacuum filtered and the salts were washed with CH$_2$Cl$_2$ (25 ml). The solvent was removed by rotary evaporation and the resulting orange oil was chromatographed on silica using 1:1 Et$_2$O/hexane to give **4** as a pale yellow oil with other byproducts. This product was then chromatographed on a silica prep plate using 1:4 Et$_2$O:pentane ($R_f = 0.58$) to give a pale yellow oil (21.3 mg, 0.130 mmol, 58%). This yellow oil was identical by spectroscopic comparison to **4** reported above. The mixture of enantiomers of **4** was resolved using the method described above. The organometallic product from the cleavage reaction is eluted from the original silica column with 1:1 Et$_2$O:pentane. The solvent was removed by rotary evaporation and the orange powder was vacuum dried to give **12b**, (115 mg, 0.182 mmol, 81%) identical by spectroscopic comparison to pyr(DPG)$_2$CoMe reported and characterized previously [1b,d,h].

5. Supplementary material

Details of the crystallographic characterization of **8a** are available from C.S. Day at the following e-mail address (daycs@wfu.edu).

Acknowledgements

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