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TpRu complexes as recoverable Lewis acid catalysts for enantioselective solvent-free cycloaddition reactions (Tp = hydrotris(pyrazolyl)borate)

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Dedicated to Dr. José Antonio Abad (University of Murcia).

Abstract

The enantiomerically and diastereomerically pure dinitrogen-bridged complexes $[\{TpRu(L)\}_2(\mu\text{-}N_2)][PF_6]_2$ (L = *R*,*R*- or *S*,*S*-1,2-bis(diphenylphosphinoamino)cyclohexane (*R*,*R*- or *S*,*S*-dppach)) were prepared by reaction of the corresponding chloro-complexes [TpRuCl(L)] with $NaPF_6$ in dichloromethane under dinitrogen. The dinitrogen adducts react with neat methacrolein furnishing the labile complexes $[TpRu(methacrolein)(L)][PF_6]$ (L = *R*,*R*- or *S*,*S*-dppach). Both the dinitrogen and methacrolein derivatives are catalysts for the solvent-free regio- and enantioselective Diels–Alder reactions between methacrolein and cyclopentadiene or pentamethylcyclopentadiene, with moderate enantiomeric excesses ranging from 36 to *ca*. 70%. The metal complex can be easily recovered and re-utilised for further reactions. The dinitrogen complexes also catalyse the 1,3-dipolar cycloaddition reaction between methacrolein and benzylidenephenylamine N-oxide to yield 5-methyl-2-*N*-3-diphenyl-isoxazolidine-5-carbaldehyde with very high regioselectivity and 32% enantiomeric excess.

Keywords: Cycloaddition; Diels–Alder reaction; Ruthenium complexes; Phosphinoamine ligands; Asymmetric catalysis

1. Introduction

A major goal of green chemistry is to maximize the efficient use of raw materials minimizing the waste (the atom economy concept) [1–4]. This has to be adequately combined with the selectivity of the processes for an optimal synthetic efficiency. In this sense, very few chemical processes can compite with the Diels–Alder cycloaddition reaction in terms of chemical and stereochemical selectivity and atom economy [5]. Catalysts are most often required not only for accelerating this thermal reaction, but also for achieving the desired regio- and enantioselectivity in the final products. Arene [6–8] as well as half-sandwich [9–12] complexes of ruthenium containing a variety of chiral auxiliary co-ligands have been used successfully as Lewis acids catalysts for enantioselective Diels–Alder reactions. In particular, Kündig and co-workers [9–12] have achieved remarkable results in terms of activity, regio- and enantioselectivity by using cyclopentadienyl and indenyl ruthenium derivatives containing the C_2 chiral ligands *R*,*R*- or *S*,*S*-BIPHOP-F (BIPHOP-F = $(C_6F_5)_2POCHPhCHPhOP(C_6F_5)_2$).

Despite the fact of being an invaluable tool in the synthesis of complex organic molecules, few industrial processes make use of the Diels–Alder reaction. Therefore, the development of robust, air-stable Lewis acid catalysts for stereoselective Diels–Alder reactions which might be eventually used under industrial conditions is most desirable. Besides, and in order to minimize the impact in environment, its is convenient that the catalysts might be able to operate in solvent-free conditions, and easily recycled [13]. Some authors have been carrying out Diels–Alder reactions in supercritic CO_2, as one of the possible alternative ways to achieve the goal of developing atom efficient, environmentally friendly selective chemical processes [14].

We have recently reported the preparation of the diastereomerically and enantiomerically pure complex $[TpRu(N_2)(R,R\text{-dippach})][BAr'_4]$ (**1**, Ar′ = 3,5-$C_6H_3(CF_3)_2$; *R*,*R*-dippach = *R*,*R*-

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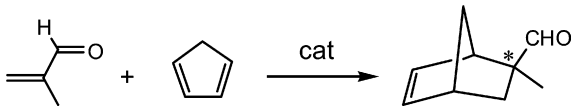
1,2-bis(diisopropylphosphinoamino)cyclohexane) [15]. We have found that this compound is a catalyst for the solvent-free Diels–Alder reaction of cyclopentadiene with methacrolein to give 2-methyl-bicyclo[2.2.1]hept-5-ene-2-carbaldehyde.



The reaction can be performed without the need of using inert atmosphere, the metallic complex being easily recovered at the end of the reaction without significant catalytic activity loss. Very good *exo*/*endo* selectivity is observed. As far as we are aware, the efficiency of chiral ruthenium compounds containing hydrotris(pyrazolyl)borate (Tp) as co-ligand had never been tested, despite the fact that the increased bulk of Tp compared to Cp or Cp* might anticipate a high selectivity in the products distribution. However, the overall catalytic activity of **1** is rather low. Most important of all, no enantiomeric excess was observed and a racemic mixture of enantiomers is the resulting product of the catalytic Diels–Alder reaction. The low activity of **1** as Lewis acid catalyst is attributable to the basic character of the *R*,*R*-dippach ligand favoured by the strong electron-releasing isopropyl substituents. This makes ruthenium a electron-rich metal centre, whereas for a Lewis acid catalyst an electron-poor metal centre is required. We have now switched from *R*,*R*-dippach to *R*,*R*- or *S*,*S*-dppach (*R*,*R*/*S*,*S*-dppach = *R*,*R*/*S*,*S*-1,2-bis(diphenylphosphinoamino)cyclohexane) [16]. The electron-withdrawing effect of the phenyl substituents provides a more suitable metal binding site for the activation of the dienophile, whereas the size of the phenyl groups expands the range of steric influence around the binding site. Thus, we have now synthesized the bridging dinitrogen complexes $[\{TpRu(L)\}_2(\mu\text{-}N_2)][PF_6]_2$ (L = *R*,*R*- or *S*,*S*-dppach). These materials are much more efficient Lewis acid catalyst precursors for Diels–Alder reactions, with enhanced regio- and enantioselectivity capabilities, and robust enough to operate in solvent-free reaction conditions under atmospheric oxygen and moisture. The catalyst is easily recoverable and can be re-utilised without significant activity loss. These systems have shown to be also effective catalysts for the enantioselective 1,3-dipolar cycloaddition reaction between methacrolein and benzylidenephenylamine N-oxide [17]. The results of these investigations are reported in the present work.

2. Experimental

2.1. Material and methods

All synthetic operations for the preparation of metal complexes were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk techniques. Tetrahydrofuran, diethyl ether and petroleum ether (boiling point range 40–60 °C) were obtained oxygen- and water-free from an Innovative Technology, Inc. solvent purification apparatus. All solvents were deoxygenated immediately before use. The complex $[TpRuCl(PPh_3)_2]$ was obtained according to the literature [18]. The ligands *R*,*R*- and *S*,*S*-1,2-bis(diphenylphosphinoamino)cylohexane (*R*,*R*/*S*,*S*-dppach) were prepared following published procedures [16]. Benzylidenephenylamine N-oxide was prepared by condensation of benzaldehyde with *N*-phenylhydroxylamine in a minimum amount of EtOH [19]. IR spectra were recorded as Nujol mulls on a Perkin-Elmer SPECTRUM 1000 FT-IR spectrometer. Raman spectra were measured on a Jobin-Yvon LABRAM dispersive spectrometer equipped with a laser of $\lambda = 632.81$ nm as excitation source. NMR spectra were taken on a Varian Inova 400 MHz or a Varian Gemini 300 MHz equipment. Chemical shifts are given in ppm from $SiMe_4$ (^1H and $^{13}C\{^1H\}$), or 85% H_3PO_4 ($^{31}P\{^1H\}$). The enantiomeric excesses were determined by ^1H NMR spectroscopy by means of the chiral lanthanide shift reagent (+)-[Eu(hfc)$_3$] (hfc = 3-(heptafluoropropylhydroxymethylene)-(+)-camphorate). Optical rotations were measured on a Perkin-Elmer 341 polarimeter. Microanalysis was performed on a elemental analyser model LECO CHNS-932 at the Servicio Central de Ciencia y Tecnología, Universidad de Cádiz.

2.2. [TpRuCl(R,R-dppach)] (R,R-2) and [TpRuCl(S,S-dppach)] (S,S-2)

To a solution of $[TpRuCl(PPh_3)_2]$ (1.64 g, 1.87 mmol) in toluene (20 ml), either *R*,*R*-dppach or *S*,*S*-dppach (0.95 g, *ca.* 2.0 mmol) was added. The mixture was stirred for 12 h at 80 °C. Then the solvent was removed under vacuum and the residue washed three times with petroleum ether. The resulting microcrystalline pale yellow solid was filtered off and dried in vacuo. Yield: 0.98 g, 63%. Anal. Cald. for $C_{39}H_{42}N_8BClP_2Ru$: C, 56.3; H, 5.09; N, 13.5. Found: C, 56.0; H, 5.11; N, 13.2. IR (Nujol): ν(NH) 3262, ν(BH) 2453 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.55, 1.61, 1.64, 1.87 (m, 8H, $(CH_2)_4$), 2.49 (m, 2H, N*H*), 2.97, 3.58 (m, 1H each, C*H*C*H*), 5.58, 5.64, 5.92, 6.82, 7.36, 7.37, 7.39, 7.59 and 7.64 (m, 1H each, $HB(C_3H_3N_2)_3$), 6.41, 6.50, 6.84, 7.28, 7.32, 7.48, 7.49, 7.76, 8.43 (m, 20H, C_6H_5); $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 93.9 (d, $J_{pp} = 44.4$ Hz), 96.5 (d, $J_{pp} = 44.4$ Hz); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 22.9, 23.1, 37.8 and 38.5 (s, $(CH_2)_4$), 59.8 and 60.8 (s, *C*H*C*H), 104.3, 104.5, 105.2, 134.4, 135.0, 135.5, 143.1, 144.6 and 148.6 (s, $HB(C_3H_3N_2)_3$), 127.2, 127.4, 128.4, 129.5, 130.4, 131.4, 132.7, 133.6, 134.8, 134.9 (C_6H_5).

2.3. [{TpRu(R,R-dppach)}$_2$(μ-N$_2$)][PF$_6$]$_2$ (R,R-3) and [{TpRu(S,S-dppach)}$_2$(μ-N$_2$)][PF$_6$]$_2$ (S,S-3)

To a solution of either *R*,*R*-**2** or *S*,*S*-**2** (0.94 g, 1.12 mmol) in dichloromethane under dinitrogen, $AgPF_6$ (0.27 g, 1.07 mmol) was added. The mixture was stirred for 1 h at room temperature. Then it was filtered through celite in order to remove the precipitate of AgCl formed. The resulting yellow-orange solution was evaporated to almost dryness, and then petroleum ether was added. A yellow microcrystalline solid was obtained, which was filtered off, washed with two portions of petroleum ether and thoroughly dried *in vacuo*. If present, the remain-

ing traces of Ag^+ can be removed by dissolving the solids in CH_2Cl_2 under dinitrogen followed by exposure to direct sunlight for a brief period of time. After 24 h, the deposits of black metallic silver eventually formed are removed by filtration. Subsequent evaporation and precipitation with petroleum ether yielded the analytically pure product. Yield: 0.95 g, 93%. Anal. Cald. for $C_{78}H_{84}N_{18}B_2F_{12}P_6Ru_2$: C, 49.0; H, 4.43; N, 13.2. Found: C, 48.7; H, 4.54; N, 13.0. IR (Nujol): ν(NH) 3353, ν(BH) 2480 cm^{-1}. Raman: ν(N≡N) 2087 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.15, 1.30, 1.66, 1.82 (m, 8H, $(CH_2)_4$), 2.68 (m, 2H, N*H*), 3.00, 3.51 (m, 1H each, C*H*C*H*), 5.62, 5.98, 6.16, 6.87, 6.92, 7.49, 7.75, 8.00 and 8.18 (m, 1H each, $HB(C_3H_3N_2)_3$), 6.06, 6.50, 6.79, 6.99, 7.02, 7.31, 7.38, 7.44, 7.77, 8.02 (m, 20H, C_6H_5); $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 96.9 (d, J_{pp} = 45 Hz), 104.8 (d, J_{pp} = 45 Hz); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 24.3, 24.8, 34.9 and 35.0 (s, $(CH_2)_4$), 56.6 and 61.2 (s, *C*H*C*H), 105.9, 106.3, 106.4, 134.6, 136.1, 138.6, 142.2, 143.7 and 149.3 (s, $HB(C_3H_3N_2)_3$), 127.9, 128.5, 129.2, 129.7, 130.2, 131.1, 131.7, 132.9, 133.3 (C_6H_5).

2.4. [TpRu(methacrolein)(R,R-dppach)][PF_6] (R,R-**4**) and [TpRu(methacrolein)(S,S-dppach)][PF_6] (S,S-**4**)

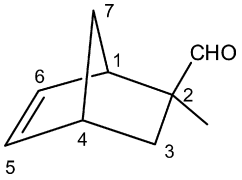
To a solution of either *R*,*R*-**2** or *S*,*S*-**2** (0.42 g, *ca*. 0.5 mmol), in dichloromethane, an excess of methacrolein (100 μL, 1.21 mmol) and $AgPF_6$ (0.12 g, 0.48 mmol) was added in this order. The mixture was stirred for 15 min at room temperature. Then it was filtered through celite in order to remove the precipitate of AgCl formed. The resulting dark orange solution was evaporated to almost dryness, and then petroleum ether was added. A dark orange microcrystalline solid was obtained, which was filtered off, washed with two portions of petroleum ether and dried *in vacuo*. Yield: 0.43 g, 88%. Anal. Cald. for $C_{43}H_{48}N_8BF_6OP_3Ru$: C, 51.1; H, 4.78; N, 11.1. Found: C, 51.3; H, 4.91, N, 10.9. IR (Nujol): ν(NH) 3350, ν(BH) 2473, ν(C=O) 1592 cm^{-1}. NMR spectra were recorded in $CDCl_3$ in the presence of a small amount of added methacrolein. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.49 (s, 3H, $H_2C{=}C(CH_3)CHO$), 1.63, 1.66, 1.84, 1.88 (m, 8H, $(CH_2)_4$), 2.68 (m, 2H, N*H*), 3.00 and 3.36 (m, 1H each, C*H*C*H*), 5.36, 6.10 (m, 1H each, $H_2C{=}C(CH_3)CHO$), 5.70, 6.09, 6.17, 6.39, 6.70, 7.60, 7.88, 8.01, 8.22 (1H each, $HB(C_3H_3N_2)_3$), 6.10, 6.42, 6.82, 7.05, 7.16, 7.30, 7.39, 7.72, 8.00 (m, 20H, C_6H_5), $H_2C{=}C(CH_3)CHO$ not observed; $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 96.7 (d, $^2J_{PP}$ = 44.5 Hz), 102.4 (d, $^2J_{PP}$ = 44.5 Hz); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 14.1 (s, $H_2C{=}C(CH_3)CHO$), 24.3, 24.7, 34.8, 34.9 (s, $(CH_2)_4$), 57.6 and 60.6 (s, C*H*C*H*), 142.4 (s, $H_2C{=}C(CH_3)CHO$), 106.5, 106.7, 107.1, 133.1, 133.3, 135.8, 137.3, 141.4 and 149.9 (s, $HB(C_3H_3N_2)_3$), 127.9, 128.4, 128.5, 128.7, 128.8, 130.1, 131.1, 131.5, 135.1 (C_6H_5), 208.0 (s, $H_2C{=}C(CH_3)CHO$).

This compound was also prepared by direct reaction of either *R*,*R*-**3** or *S*,*S*-**3** with an excess of neat methacrolein and subsequent precipitation with petroleum ether, in essentially quantitative yield.

2.5. Catalytic Diels–Alder reactions

Typical procedure: A test tube was loaded with 0.0125 mmol of *R*,*R*-**3** or *S*,*S*-**3** and methacrolein (0.20 mL, *ca*. 2.5 mmol). To this mixture, either freshly distilled cyclopentadiene or pentamethylcyclopentadiene (2.5 mmol) was added. The resulting orange–brown mixture was shaken for 1 h at 298 K in a thermostated bath. At the end of this time, petroleum ether (5 mL) was added. The resulting precipitate was filtered, washed with petroleum ether and dried *in vacuo* (92% average recovered yield based on Ru). The cycloadducts were isolated in essentially quantitative yield upon passing the solution through a short silica gel column and posterior removal of petroleum ether *in vacuo*, and identified by NMR by comparison with data in the literature [6–12].

exo-2-Methyl-bicyclo[2.2.1]hept-5-ene-2-carbaldehyde.



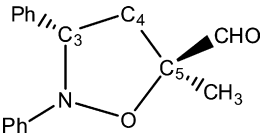
^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.75 (d br, J_{HH} = 11.4 Hz, C^3H^{endo}), 1.00 (s, 3H, CH_3), 1.39 (m br, 2H, C^7H_2), 2.24 (dd, 1H, J_{HH} = 12.2 Hz, $J_{HH'}$ = 3.7 Hz, C^3H^{exo}), 2.81 (s br, 1H, C^4H), 2.88 (s br, 1H, C^1H), 6.11, 6.29 (m, 1H each, $HC^4{=}C^6H$), 9.68 (s, 1H, C*H*O). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 10.9 (CH_3), 34.5 (C^3), 43.1 (C^4), 47.5 (C^1), 48.3 (C^7), 53.7 (C^2), 132.1 (C^6), 139.3 (C^5), 205.3 (*C*HO).

exo-1,2,4,5,6,7-Hexamethyl-bicyclo[2.2.1]hept-5-ene-2-carbaldehyde: ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.74 (d, 3H, J_{HH} = 6.4 Hz, $C^7(CH_3)$), 1.02 (s, 3H, $C^2(CH_3)$), 1.03 (d, J_{HH} = 12 Hz, 1H, C^3H^{endo}), 1.13 (s, 3H, $C^4(CH_3)$), 1.22 (s, 3H, $C^1(CH_3)$), 1.70 (s, 3H, $C^5(CH_3)$), 1.72 (s, 3H, $C^6(CH_3)$), 1.95 (m, 1H, C^7H), 2.07 (d, J_{HH} = 12 Hz, 1H, C^3H^{exo}), 9.89 (s, 1H, *C*HO). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 8.1 (s, $C^7(CH_3)$), 9.8 (s, $C^2(CH_3)$), 12.1 (s, $C^5(CH_3)$), 13.9 (s, $C^6(CH_3)$), 15.0 (s, $C^1(CH_3)$), 17.4 (s, $C^4(CH_3)$), 43.6 (s, C^3H_2)), 52.6 (s, C^4), 57.7 (s, C^2), 57.9 (s, C^7H), 60.7 (s, C^1), 134.1 (s, C^6), 137.2 (s, C^5), 207.7 (s, *C*HO).

2.6. Catalytic 1,3-dipolar cycloaddition reactions

To a test tube loaded with 0.0125 mmol of *R*,*R*-**3** or *S*,*S*-**3** and methacrolein (0.20 mL, *ca*. 2.5 mmol), benzylidenephenylamine N-oxide (0.53 g, 2.5 mmol) was added. A minimum amount of dichloromethane (150–200 μL) was added to the mixture in order to ensure the complete disolution of the reagents and catalyst. The mixture was left standing at 298 K for 18 h. After this time, petroleum ether was added. The resulting mixture was filtered through celite, and the volatiles removed in vacuo. NMR spectroscopy of the resulting oil confirmed the quantitative conversion to the *endo*-isomer of 5-methyl-2-*N*-3-diphenyl-isoxazolidine-5-carbaldehyde by comparison with

data in the literature [17].



^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.19 (s, 3H, CH_3), 1.85 (ddd, J_{HH} = 12.6 Hz, $J_{HH'}$ = 7.6 Hz, $J_{HH''}$ = 1 Hz, 1H, C^4H), 2.95 (dd, J_{HH} = 12.6 Hz, $J_{HH'}$ = 7.8 Hz, 1H, C^4H), 4.50 (t, J_{HH} = 7.5 Hz, 1H, C^3H), 6.70–7.25 (m, 10H, Ph), 9.45 (d, J_{HH} = 1 Hz, C*H*O). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 18.7 (*C*H$_3$), 46.1 (*C*^{4}), 68.5 (*C*^{5}), 87.1 (*C*^{3}), 114.8, 121.6, 126.5, 127.5, 128.7, 141.0, 149.9 (*C*^{Ar}), 201.2 (*C*HO).

2.7. Reaction kinetics monitoring studies

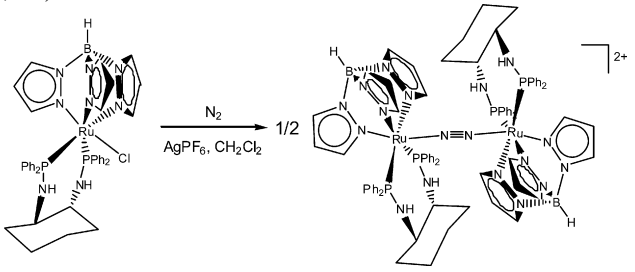
The solvent-free catalytic reactions were carried out as indicated above. Aliquots of 20 μL were taken at specified time intervals, dissolved in $CDCl_3$ and analyzed immediately by ^{1}H NMR spectroscopy. The conversion of the reaction was monitored by the disappearance of the peak corresponding to the aldehyde proton of methacrolein, and the increase of the peaks corresponding to the aldehyde protons of the *exo*- and *endo*-cycloadducts.

3. Results and discussion

3.1. Preparation and characterization of complexes 2–4

The complexes [TpRuCl(*R*,*R*-dppach)] (*R*,*R*-**2**) or [TpRuCl(*S*,*S*-dppach)] (*S*,*S*-**2**) were respectively obtained by thermal displacement of PPh_3 from [TpRuCl(PPh_3)$_2$] by either *R*,*R*-dppach or *S*,*S*-dppach in refluxing toluene. The NMR spectral properties of these derivatives are essentially consistent with those previously observed by us for the enantiomerically pure complex [TpRuCl(*R*,*R*-dippach)] [15]. Thus, the phosphorus atoms are inequivalent and hence a two-doublet pattern corresponding to an AM spin system is observed in the ^{31}P{^{1}H} NMR spectra, and all the protons of the pyrazol rings of the Tp ligand are inequivalent giving rise to nine separate resonances in the ^{1}H NMR spectra. These are characteristic spectral features of complexes containing the moieties {TpRu(*R*,*R*-/*S*,*S*-dppach)}, and hence displayed by all the metal complexes described in the present work.

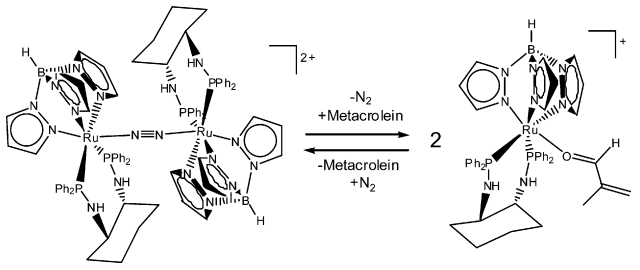
Chloride abstraction from *R*,*R*-**2** or *S*,*S*-**2** in dichloromethane under dinitrogen using $AgPF_6$ as halide scavenger leads to the bridging dinitrogen complexes [{TpRu(*R*,*R*-dppach)}$_2$(μ-N_2)][PF_6]$_2$ (*R*,*R*-**3**) or [{TpRu(*S*,*S*-dppach)}$_2$(μ-N_2)][PF_6]$_2$ (*S*,*S*-**3**).



The use of either $NaPF_6$ or NH_4PF_6 as halide scavenger failed to yield the dinitrogen complex: after 24 h stirring at room temperature the unreacted chloro-complex *R*,*R*-/*S*,*S*-**2** was recovered in essentially quantitative yield. Chloride abstraction from TpRu halide complexes is known to be an effective method for the preparation of cationic dinitrogen complexes, but so far only terminal dinitrogen complexes of the type [TpRu(N_2)(L_2)]$^+$ (L_2 = *R*,*R*-dippach, 1,2-diisopropylphosphinoaminoethane [15], 1,2-bis(diisopropylphosphino)ethane [20], (PEt_3)$_2$, (PMe^iPr_2)$_2$ [21], (PPh_3)$_2$ [22], $NMe_2CH_2CH_2PPh_2$ [23]) had been reported. However, the related systems containing the moieties {[CpRu(P)$_2$]$^+$} (P$_2$ = 1,2-bis(diisopropylphosphino)ethane, (PEt_3)$_2$, (PMe^iPr_2)$_2$) [24] are known to form either bridging or terminal dinitrogen derivatives by chloride abstraction from their respective chloro-complexes depending upon de reaction conditions. In some cases, i.e. [{CpRu(PEt_3)$_2$}$_2$(μ-N_2)]$^{2+}$, the formation of the bridging dinitrogen complex but not the terminal dinitrogen complex has been observed [24]. This seems to be the case also in our system, where no end-on dinitrogen complex has been isolated, at variance with the related *R*,*R*-dippach derivative **1**. No ν(N≡N) stretching bands are present in the IR spectrum of **3**. However, a medium intensity band at 2086 cm^{-1} is observed in the Raman spectrum, which is consistent with the presence of a bridging dinitrogen ligand in **3**, as it has been observed in the case of the complexes [{CpRu(P)$_2$}$_2$(μ-N_2)][BAr'_4]$_2$. The value of 2086 cm^{-1} observed for ν(N≡N) in the Raman spectrum compares well with those reported for [{CpRu(dippe)}$_2$(μ-N_2)][BAr'_4]$_2$ (2050 cm^{-1}) and for [{CpRu(PEt_3)$_2$}$_2$(μ-N_2)][BAr'_4]$_2$ (2064 cm^{-1}) [24], and it is well below the range of 2150–2190 cm^{-1} usually observed for the ν(N≡N) IR band in other CpRu and TpRu terminal dinitrogen complexes [15,20–23]. The NMR spectral features of **3** are similar to those observed for **2**. This observation suggests the equivalence of the two {[TpRu(dppach)]$^+$} fragments within the binuclear complex. Since the presence of a symmetry center is ruled out due to the presence of the enantiomerically pure phosphinoamine ligands, the equivalence should result most likely from a C_2 symmetry axis. In any case, we have previously reported that the NMR chemical shifts for bridging and terminal dinitrogen complexes of the type [{CpRu(P)$_2$}$_2$(μ-N_2)]$^{2+}$ and [CpRu(P)$_2$(N_2)]$^+$ respectively, are identical [24]. This comes from the fact that the chemical environment around each ruthenium atom remains the same, irrespectively of being a bridging or terminal dinitrogen complex. Hence, in the event of inequivalence of the {[TpRu(dppach)]$^+$} fragments in **3** differences in chemical shifts are not be expected to occur either. There is a recent example of a bridging dinitrogen complex in which the N_2 ligand bridges the two homochiral and C_1 symmetrical *S*-enantiomers of the [Ru(P^iPr_3)($N_2Me_2S_2$)] ($N_2Me_2S_2$ = {1,3-$SC_6H_4N(Me)CH_2$}$_2$) fragment in such a way that C_2 symmetry results for [{Ru(P^iPr_3)($N_2Me_2S_2$)}$_2$(μ-N_2)] [25]. A similar arrangement is likely to occur in our system. Unfortunately, all attempts to obtain single crystals suitable for X-ray structure analysis were unsuccessful, and hence all structural assignments must be taken with due caution.

The reactions of *R*,*R*-**3** or *S*,*S*-**3** with an excess of methacrolein in dichloromethane yielded the corresponding O-bonded

methacrolein adducts [TpRu(methacrolein)(*R*,*R*-dppach)][PF_6] (*R*,*R*-**4**) or [TpRu(methacrolein)(*S*,*S*-dppach)][PF_6] (*S*,*S*-**4**).



The value of 1592 cm^{-1} for the ν(C=O) IR stretching band in these dark-orange compounds is consistent with the coordination of the methacrolein to ruthenium through the oxygen atom, rather than through the C=C bond in a η^2-fashion. These adducts can be also prepared by reaction of *R*,*R*-**2** or *S*,*S*-**2** with $AgPF_6$ in dichloromethane in the presence of methacrolein, or by direct reaction of *R*,*R*-**2** or *S*,*S*-**2** with neat methacrolein. The coordination of methacrolein to ruthenium is reversible. Thus, the complexes (*R*,*R*-/*S*,*S*-**4**) dissociate methacrolein in solution yielding equilibrium mixtures with the corresponding dinitrogen complexes *R*,*R*-**3** or *S*,*S*-**3**, according to the equation

$$2\,[\mathrm{TpRu(methacrolein)(dppach)}]^+ + \mathrm{N_2} \leftrightarrows [\{\mathrm{TpRu(dppach)}\}_2(\mu\text{-}\mathrm{N_2})]^{2+} + 2\,\mathrm{methacrolein}$$

Two doublets at 96.7 and 102.4 ppm ($^2J_{PP}$ = 45.5 Hz) attributable to *R*,*R*-/*S*,*S*-**4**, plus another two-doublet set corresponding to *R*,*R*-/*S*,*S*-**3** are observed in their $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$ at 298 K. From the relative intensities of the doublet signals for each of the species present it is possible to estimate the equilibrium constant K_{eq}:

$$K_{eq} = \frac{|[\{\mathrm{TpRu(dppach)}\}_2(\mu\text{-}\mathrm{N_2})]^{2+}||\mathrm{methacrolein}|^2}{|[\mathrm{TpRu(methacrolein)(dppach)}]^+|^2|\mathrm{N_2}|} \quad (1)$$

At 298 K, K_{eq} has a value of 8.68×10^{-2} (considering that the concentration of N_2 is included in the value of K_{eq}). The occurrence of this equilibrium requires that the characterisation in solution of *R*,*R*-/*S*,*S*-**4** by NMR spectroscopy has to be done in the presence of added methacrolein, in order to shift the equilibrium to the corresponding methacrolein adduct. Under these conditions, only the doublets attributable to the *R*,*R*-/*S*,*S*-**4** are observed in the $^{31}P\{^1H\}$ NMR spectra. The resonances for coordinated methacrolein as well as those for the Tp and the phosphinoamine ligands were assigned by means of 2D COSY and HSQC NMR experiments. Interestingly, the aldehyde proton of the coordinated methacrolein was not observed on the ^1H NMR spectrum. This might suggest rapid exchange with free methacrolein, or it maybe caused by a particular relaxation phenomenon, given the fact that the other protons and carbon atoms of the methacrolein ligand are clearly observed on the ^1H and $^{13}C\{^1H\}$ NMR spectra.

Both *R*,*R*-/*S*,*S*-**3** and *R*,*R*-/*S*,*S*-**4** are stable in the air as solids as well as in solution. This robust character as well as their solubility properties make these complexes excellent precursors for catalytic reactions which can be performed in the air in solvent-free conditions.

3.2. Enantioselective cycloaddition reactions

The enantiopure complexes *R*,*R*-/*S*,*S*-**3** or *R*,*R*-/*S*,*S*-**4**, have shown to be much more efficient catalysts for the solvent-free Diels–Alder reactions between methacrolein and cyclopentadiene or pentamethylcyclopentadiene than **1**. The reactions are performed without need of an inert atmosphere and in the absence of solvent, with catalyst loads of 0.5 mol%. In these conditions, the reactions proceed smoothly at room temperature, resulting in high conversions after 1 h (Fig. 1).

^1H NMR analysis of the cycloaddition products shows that these reactions are highly regioselective, with very major contents of the corresponding *exo*-derivatives. Enantioselectivity has been observed, at variance with the reactions catalysed by **1**. The enantiomeric excess of the catalysed reaction between methacrolein and cyclopentadiene is rather modest (36% ee in the *exo* adduct), but it raises significatively to near 70% in the case of the reaction of methacrolein with pentamethylcyclopentadiene (Table 1).

The increase of the enantiomeric excess when pentamethylcyclopentadiene is used remarks the importance of the steric effects in the enantioselectivity of these reactions, as already pointed out by Kündig and co-workers [9–12]. The use of TpRu catalysts containing either *S*,*S*-dppach or *R*,*R*-dppach as co-ligands keeps essentially the same values for *exo*/*endo* regioselectivity and enantioselectivity for the cycloaddition products, although the absolute configurations at C2 of the resulting major enantiomers in the mixture are inverted as inferred from comparison of their respective ^1H NMR spectra with added (+)-[Eu(hfc)$_3$] (hfc = 3-(heptafluoropropylhydroxymethylene)-

Table 1
Experimental results for the solvent-free Diels–Alder reactions between methacrolein and the specified diene and catalyst at 298 K

Entry	Catalyst	Catalyst load (mol%)	Diene	Conversion after 1 h[a] (%)	Exo:endo ratio[a]	Enantiomeric excess (ee)[b] (%)
1	**1**	5	C_5H_6	15	95:5	0
2	*S*,*S*-**3**	0.5	C_5H_6	56	98:2	36[c]
3	*S*,*S*-**3**	0.5	C_5Me_5H	100	95:5	68
4	–	–	C_5H_6	<1	78:22	0
5	–	–	C_5Me_5H	30	65:35	0

[a] Determined by ^1H NMR spectroscopy.
[b] Determined by ^1H NMR spectroscopy for the *exo* isomer by means of the chiral shift reagent (+)-[Eu(hfc)$_3$].
[c] 2*R* absolute configuration of the major enantiomer in the mixture, determined by polarimeter measurement, by comparison with the reference values reported in the literature for the 2*R*-*exo*-enantiomer [26].

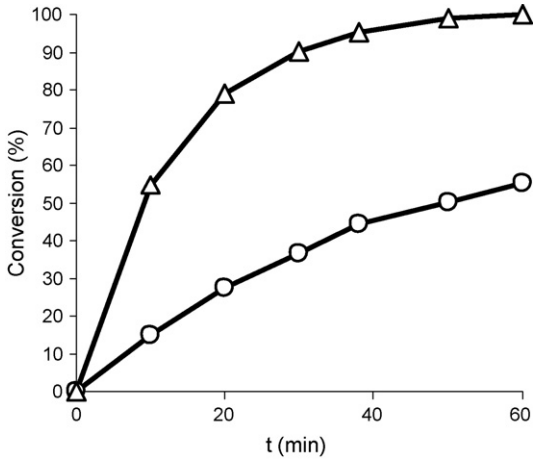
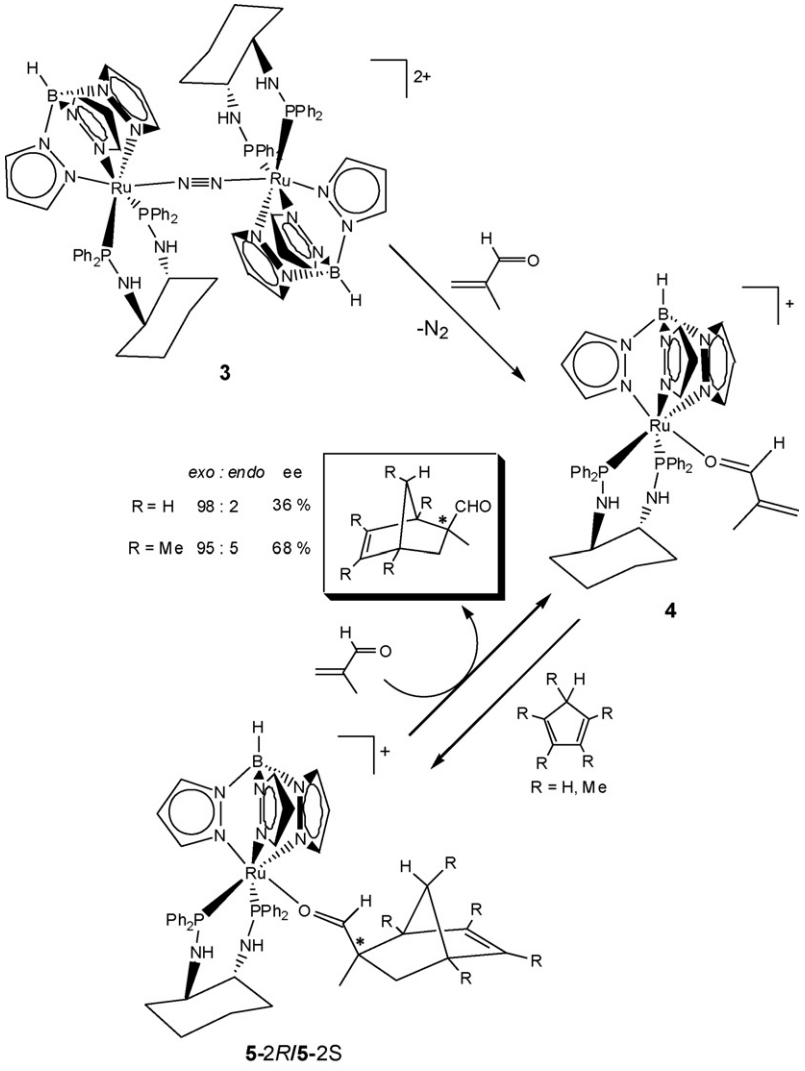


Fig. 1. Plot of conversion as a function of time for the reaction of methacrolein and cyclopentadiene (◯) or pentamethylcyclopentadiene (△) catalyzed by 3 at 293 K. The reactions were done with a mixture 1:1 methacrolein:diene at 0.5% catalyst load. Aliquots of 20 μL were taken at the specified time intervals, dissolved in $CDCl_3$ and analyzed by ^1H NMR spectroscopy.

(+)-camphorate). Thus, *S*,*S*-**3** leads to a major content of the 2*R*-*exo*-enantiomer of 2-methyl-bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (determined by polarimeter measurement, by comparison with the reference values reported in the literature for this enantiomer [26]), whereas if *R*,*R*-**3** is used as catalyst, the resulting major enantiomer has the absolute configuration *S* at C2. It is important to mention that the enantiomeric excesses in these reactions are strongly dependent on the purity of the catalyst. Small impurities of other Lewis acids eventually present in the reaction mixture might also catalyze the Diels–Alder reaction through a non-enantioselective pathway decreasing the enantiomeric excess. Hence, care must be taken in ensuring the purity of the catalyst precursors prior to use in enantioselective processes. Since Ag^+ is a Lewis acid impurity likely to be present, we monitored the reaction between methacrolein and cyclopentadiene in the presence of 0.5% $AgPF_6$, in order to check the possible effects on the cycloaddition reaction. We did not detect by ^1H NMR spectroscopy any noticeable conversion into cycloadduct occurs after 1 h of reaction, either under solvent-free conditions or in $CDCl_3$ solution. These observations

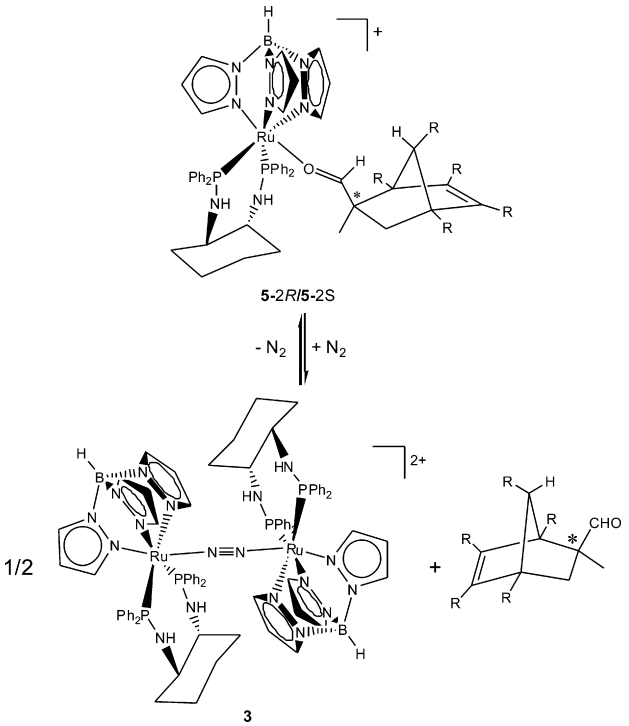


Scheme 1. Proposed reaction sequence for the enantioselective Diels–Alder reactions catalysed by **3**. For the sake of clarity, only the major *exo*-cycloadduct is shown. The chiral centre at C2 is marked with *.

seem to rule out in principle a pronounced side effect of the Ag^+ ion on the cycloaddition reactions catalysed by TpRu complexes under the study conditions. In any case, for better reproducibility of the results the presence of Ag^+ and other Lewis acid impurities is to be avoided.

The catalytic activity of these TpRu complexes can be rationalised in terms of activation of methacrolein by coordination to ruthenium through the oxygen atom, followed by the subsequent [4+2] cycloaddition reaction of cyclopentadiene or pentamethylcyclopentadiene to the C=C bond of the coordinated methacrolein. The resulting cycloadduct is released upon reaction with more methacrolein, until complete consumption of the dienophile (Scheme 1).

The red-brown materials isolated at the end of the reaction upon addition of petroleum ether and subsequent filtration in essentially quantitative yields based on ruthenium, consist of a mixture of two diastereomeric complexes resulting from the respective coordination of each of the 2*R* and 2*S* enantiomeric cycloaddition products to the {[TpRu(dppach)]$^+$} fragment, namely **5**-2*R* and **5**-2*S*, as shown in Scheme 1. As it occurs with the methacrolein adduct **4**, these complexes are labile and dissociate the cycloaddition product furnishing equilibrium mixtures with **3**. Hence, **5**-2*R* and **5**-2*S* are also catalytic precursors, and can be used in further Diels–Alder reactions.



The occurrence of this equilibrium makes the NMR spectra extremely complicated, due to the simultaneous presence in different proportions of the two diastereisomers **5**-2*R* and **5**-2*S*, the dinitrogen complex **3** and free cycloaddition product. If the spectra are recorded in the presence of an excess of free cycloadduct, the dinitrogen complex is not observed, but in these cases the spectra are obscured by the increased intensity of the signals for the free cycloadduct. Only the $^{31}P\{^1H\}$ NMR spectra remain clear enough to show the presence of each of the species present in the mixture. Thus, we have gathered NMR spectral evidence in support of the catalytic cycle shown in Scheme 1, monitoring by $^{31}P\{^1H\}$ NMR spectroscopy the Diels–Alder reaction of methacrolein with cyclopentadiene in $CDCl_3$ or CD_2Cl_2 catalysed by *S*,*S*-**3** (Fig. 2).

After addition of a slight excess of cyclopentadiene, the ^1H NMR spectra indicate the beginning of the catalytic formation of the corresponding cycloadduct. The $^{31}P\{^1H\}$ NMR signals corresponding to the methacrolein adduct disappear being replaced by two sets of two doublet signals in the intensity ratio *ca*. 2:1 These two sets of signals are attributed respectively to the two diastereomers resulting from the coordination of each of the enantiomers 2*R* or 2*S* of the cycloadduct to the {[TpRu(*S*,*S*-dppach)]$^+$} fragment (*S*,*S*-**5**-2*R* and *S*,*S*-**5**-2*S*, respectively). In fact, from the intensity ratio of the resonances in the $^{31}P\{^1H\}$ NMR spectrum the approximate value of the enantiomeric excess can be estimated (33%), resulting very close to the value more accurately determined by ^1H NMR using (+)-[Eu(hfc)$_3$] (36%). The addition at this stage of more methacrolein to the reaction mixture causes the restoration of the $^{31}P\{^1H\}$ NMR spectrum of *S*,*S*-**4**, so the cycle can start over again.

We have observed that addition of solvent (i.e. dichloromethane or chloroform) to the neat reaction mixtures has a strong deactivating effect on the rate of the cycloaddition reaction. Addition of 2 mL of solvent results in the practical quenching of the catalysed reaction. If we assume that the controlling step in the catalytic cycle proposed above is the cycloaddition reaction between the diene and the metal-bound methacrolein in complex **4**, then we can consider that the reaction rate *r* is given by

$$r = k_{cat}|\text{diene}||\mathbf{4}| \quad (2)$$

At higher concentrations of diene and of **4**, the reaction would take place faster. Given the fact that this is a solvent-free process, higher concentrations of **4** can be achieved by increasing the catalyst load, but also by keeping the volume of liquids at a minimum. On the other hand, an excess of diene would increase the reaction rate, but at the same time it would decrease the reaction rate due to the dilution effect over the concentration of **4**. In fact, we have noticed that the reactions carried out with excess of cyclopentadiene over methacrolein are slower than those carried out using equimolar amounts of the reagents. If we rewrite Eq. (1) as a function of the number of mmol of diene and **4**, and the total volume (equivalent to the sum of volume of diene plus volume of methacrolein), the following equation is obtained in the case of cyclopentadiene (CpH):

$$\frac{r}{k_{cat}} = \frac{(\text{mmol of CpH})(\text{mmol of catalyst})}{[0.082(\text{mmol of CpH} + \text{mmol of methacrolein})]^2} \quad (3)$$

A plot of r/k_{cat} against mmol of CpH is shown in Fig. 3, assuming the initial amounts of 0.01 mmol of catalyst **4** and 1 mmol of methacrolein.

We can consider this plot as a measure of the expected variation of the initial reaction rate as a function of the amount of cyclopentadiene. After a steep increase in the rate a maximum is reached, but soon afterwards, the reaction rate falls rapidly as a consequence of the dilution effect over the catalyst. Therefore,

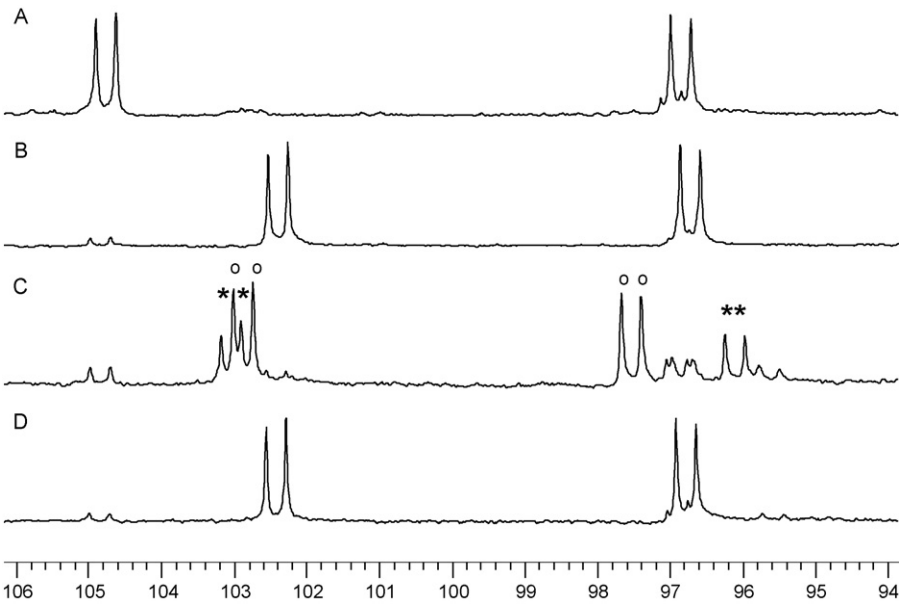
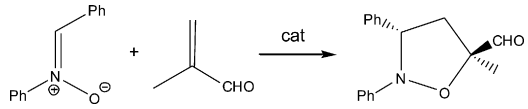


Fig. 2. $^{31}P\{^{1}H\}$ NMR spectra in $CDCl_3$ at 298 K of: (A) compound *S*,*S*-**3**. (B) Upon addition of an excess of methacrolein, showing the formation of *S*,*S*-**4**. (C) At the end of the reaction with cyclopentadiene. The peaks marked with (*) and (◯) correspond respectively to the diastereomeric adducts *S*,*S*-**5**-2 *R* and *S*,*S*-**5**-2*S*. (D) Upon addition of an excess methacrolein, showing the regeneration of *S*,*S*-**4**.

the optimal conditions for which these solvent-free catalysed reactions reach the highest rates involve the use of equimolar amounts of diene and methacrolein. Achieving faster rates under these conditions would necessarily imply the use if increasingly higher catalyst loads.

Kündig and co-workers recently demonstrated that the complex [CpRu(Me_2CO)(*R*,*R*-BIPHOP-F)][SbF_6] can reversibly bind both nitrones and enals, and hence can be used as effective catalysts for enantioselective 1,3-dipolar cycloaddition reactions [17]. These reactions lead to isoxazolidines in moderate to high enantio- and regioselectivities and complete *endo*/*exo* selectivity. In a similar fashion, the complexes *R*,*R*-**3** and *S*,*S*-**3** have shown to be also active catalytic precursors for the enantioselective 1,3-dipolar cycloaddition reaction between methacrolein and benzylidenephenylamine N-oxide to yield 5-methyl-2-*N*-3-diphenyl-isoxazolidine-5-carbaldehyde.



Since the benzylidenephenylamine N-oxide is a solid, in this particular case a minimum amount of dichloromethane (usually 150–200 μL) has to be added in order to ensure the solubilization of reagents and catalyst. The reaction mixture is allow to stand at room temperature for a period of 18 h. After this time, NMR showed the quantitative conversion to the *endo* isomer of 5-methyl-2-*N*-3-diphenyl-isoxazolidine-5-carbaldehyde, with only traces of the regioisomer *endo*-4-methyl-2-*N*-3-diphenyl-isoxazolidine-4-carbaldehyde being present. The enantiomeric excess for this reaction is moderate (32%), but it indicates clearly the capability of **3** for acting as Lewis acid catalyst for enantioselective 1,3-dipolar cycloaddition reactions. It is logical to assume for the 1,3-dipolar reactions a pathway similar to that shown in Scheme 1, in which the diene has been replaced by the nitrone, and in which the preference of aldehyde over nitrone coordination is essential for the occurrence of the entire catalytic cycle [17]. Further studies are underway in order to exploit this novel feature of these TpRu complexes and its application to the synthesis of complex heterocyclic molecules.

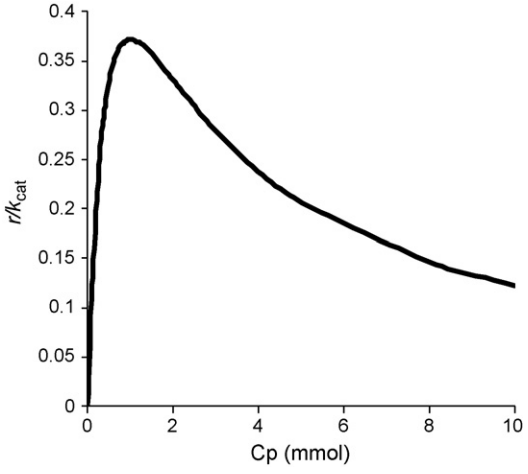


Fig. 3. Plot of r/k_{cat} against the amount of CpH according to Eq. (3) (considering the initial values of 0.01 mmol for the load of catalyst **4**, and 1 mmol of methacrolein).

4. Conclusion

The present work demonstrates that TpRu complexes with chiral phosphinoamine ligands can be effectively used as Lewis acids catalysts for enantioselective solvent-free Diels–Alder reactions in a very convenient fashion, which does not require the use of inert atmosphere, the resulting metal complex

being easily recoverable and re-usable as catalyst for further reactions. These systems also catalyse the 1,3-dipolar cycloaddition reaction between methacrolein and benzylidenephenylamine N-oxide to yield 5-methyl-2-*N*-3-diphenylisoxazolidine-5-carbaldehyde with very high regioselectivity and moderate enantiomeric excess. Our investigations at present focus in the introduction of modifications in the substituent groups of the phosphinoamine ligands in order to improve the enantiomeric excess, as well as in the isolation and possible structural characterisation of all of the intermediate species involved in the catalytic cycle. These results will be reported in due course.

Acknowledgments

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