Catalytic and asymmetric cyclopropanation of alkenes catalysed by rhenium(I) bipyridine and terpyridine tricarbonyl complexes†

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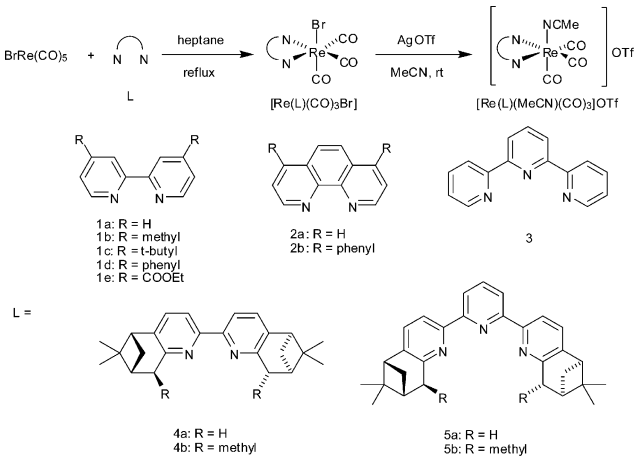
Re(I) tricarbonyl bipyridine and terpyridine complexes catalyse stereospecific cyclopropanation of alkenes; high selectivity of cyclopropane *vs* coupling and an ee of 73% and 62% for *cis*- and *trans*-cyclopropanes of styrene respectively were achieved with the $[Re(L)(CO)_3(MeCN)]OTf$ complex (L = chiral C_2-symmetric terpyridine ligand).

Introduction

Since the first isolation of a rhenium carbene complex in 1968,[1] their chemistry has been of great interest. Numerous examples, largely based on cyclopentadienyl (Cp),[2–5] imido,[6] phosphine,[7] and oxo[8] ligands, have been synthesised. A heterocyclic carbene complex with a bipyridine (bpy) ligand was also developed.[9] Although metal–carbenes are generally believed to be an active intermediate in catalytic cyclopropanation,[10] the study of rhenium carbene transfer has mainly focused on olefin metathesis[11] and aldehyde olefination,[12] and only rarely on olefin cyclopropanation.[13] One catalytic study with methyltrioxorhenium was reported but the active intermediate was not proposed to be a carbene.[14] We and others are interested in the development of metal–pyridyl catalysts for cyclopropanation.[15] Herein we report the use of rhenium(I) bpy, phenanthroline (phen) and terpyridine (tpy) complexes as catalysts for cyclopropanation. With chiral bpy and tpy, we have achieved asymmetric cyclopropanation with rhenium, previously unreported.

Results and discussion

The $[Re(L)(CO)_3Br]$ and $[Re(L)(MeCN)(CO)_3]OTf$ complexes used in this work were prepared by modified standard procedures.[16,17] Refluxing an equivalent amount of pyridyl ligand and $[BrRe(CO)_5]$ in degassed heptane for 3 h gave $[Re(L)(CO)_3Br]$ in high yield (Scheme 1). Reaction with AgOTf in acetonitrile gave $[Re(L)(MeCN)(CO)_3]OTf$ which should have a more labile coordination site. Both bromide and triflate complexes are air stable and were characterised by conventional spectroscopic methods. In the ^1H NMR spectrum, $[Re(\mathbf{5a})(CO)_3Br]$, $[Re(\mathbf{5a})(MeCN)(CO)_3]OTf$ and $[Re(\mathbf{5b})(MeCN)(CO)_3]OTf$ each appeared as two species in a 1 : 1 ratio. The pair of complexes were assigned to be stereoisomers coming from the 1,4-metallotropic shifts of the σ^2-terpyridine ligands.[18] For the structural characterisation, recrystallisation from CH_2Cl_2 gave crystals suitable for X-ray crystal analysis



Scheme 1

for $[Re(\mathbf{4a})(CO)_3Br]$ and $[Re(\mathbf{5b})(CO)_3Br]$, revealing them to be the first chiral rhenium bipyridine and terpyridine structures. As shown in Fig. 1 and 2, both show a distorted octahedral geometry around the central Re atom, with three facial carbonyl ligands and a bromide. Completing the sphere, the Re is coordinated to two nitrogen atoms of the chelating ligand to form a five-membered ring with small bite angles (75.16(37)° and 75.42(16)°, respectively). In $[Re(\mathbf{5b})(CO)_3Br]$, the –Re(1)–N(1)–C(12)–C(13)–N(2)– ring is not flat, being tilted from the plane by about 20°. Also, the *trans* angles at the site of Re(1) are within the range

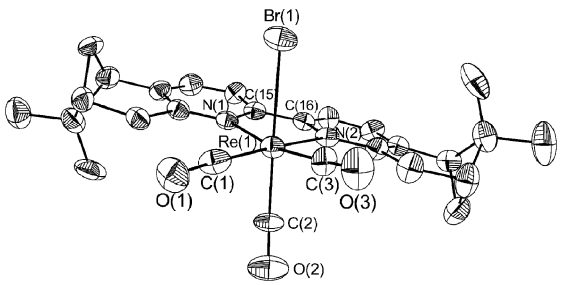


Fig. 1 An ORTEP drawing of $[Re(\mathbf{4a})(CO)_3Br]$. Selected bond lengths (Å) and angles (°): Re(1)–N(1) 2.264(1), Re(1)–N(2) 2.228(1), Re(1)–Br(1) 2.626(3), Re(1)–C(1) 1.869(1), Re(1)–C(2) 1.917(8), Re(1)–C(3) 1.940(8) Å, N(2)–Re(1)–C(1) 175.4(5), N(1)–Re(1)–C(3) 170.5(4), Br(1)–Re(1)–C(2) 178.0(3), N(1)–C(15)–C(16)–N(2) 6.8(2)°.

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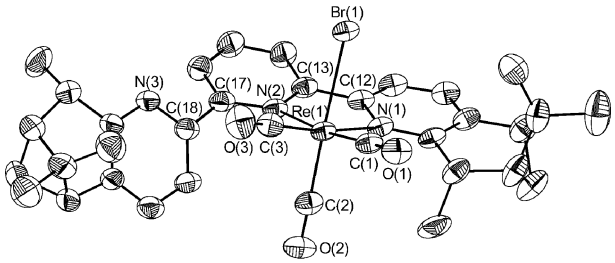


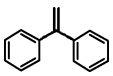
Fig. 2 An ORTEP drawing of [Re(**5b**)$(CO)_3$Br]. Selected bond lengths (Å) and angles (°): Re(1)–N(1) 2.234(4), Re(1)–N(2) 2.216(4), Re(1)–Br(1) 2.622(1), Re(1)–C(1) 1.893(6), Re(1)–C(2) 1.872(6), Re(1)–C(3) 1.920(6) Å, N(1)–Re(1)–C(3) 171.1(2), N(2)–Re(1)–C(1) 173.3(2), Br(1)–Re(1)–C(2) 176.5(2), N(1)–C(12)–C(13)–N(2) 7.56(8), N(2)–C(17)–C(18)–N(3) 137.96(6)°.

of 171.1–176.5°. Similar deviations from an ideal octahedral arrangement were also observed in [Re(**4a**)$(CO)_3$Br] (170.5–178.0°); all these can be attributed to the different electronic effect of the ligands.

Both rhenium bromide and triflate complexes used in this study are catalysts for cyclopropanation of alkenes with ethyl diazoacetate (EDA). By using [Re(**1a**)$(CO)_3$Br] as catalyst in CH_2Cl_2 (50 °C) and at a catalyst : EDA : styrene ratio of 1 : 50 : 250, the yield of cyclopropanes was low (28%). Yield was greatly improved (81%) when [Re(**1a**)(MeCN)$(CO)_3$]OTf was used as catalyst and benzene (50 °C) as solvent (Scheme 2). As they are generally more reactive, only the results of triflate complexes are discussed further. The catalytic activities of complexes with different pyridyl ligands are compared, as shown in Table 1. Overall, yields of cyclopropanes and coupling products were good. The chemoselectivities (cyclopropanes : coupling products) of the bidentate ligands **1a** and **2a** (entries 1 and 6) were better than the more bulky **3** (entry 8). The electronic effect of the substituent seems to be a very important factor; as can be observed with both bpy (entries 1–5) and phen (entries 6–7) ligands, the

Scheme 2

Table 1 Catalytic cyclopropanation of different alkenes with EDA using rhenium complexes as catalyst[a]

Entry	L	Alkene	Yield (%)[b]	Chemoselectivity[c]	*cis* : *trans*[d]
1	**1a**		89	9.6	33 : 67
2	**1b**		85	5.0	33 : 67
3	**1c**		84	4.9	36 : 64
4	**1d**		83	5.1	35 : 65
5	**1e**		81	3.1	33 : 67
6	**2a**		76	7.9	34 : 66
7	**2b**		82	3.9	33 : 67
8	**3**		78	4.1	34 : 66
9	**1b**		91	9.6	47 : 53
10			81	3.6	24 : 76
11			75	2.4	28 : 72
12			97	34	—
13			68	4.6	30 : 70
14			81	3.7	—

[a] Reaction conditions: catalyst : EDA : styrene = 1 : 50 : 250, benzene, 50 °C, 4 h addition of EDA and then stirring for additional 16 h (entries 1–8). Catalyst : EDA : alkene = 1 : 17 : 170, benzene, 70 °C, 10 h addition of EDA and then stirring for additional 14 h (entries 9–14). [b] Isolated yield of cyclopropanes and coupling products. [c] Cyclopropanes : coupling products. [d] Determined by GC-FID.

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chemoselectivities decreased with both electron-donating and -withdrawing substituents. In all cases, the *cis* : *trans* ratios were not dependent on the chelating effect or electronic properties of the ligands in the Re catalysts.

In order to optimise the yield of cyclopropanes, the reaction between cyclohexene, the poorest substrate, and EDA with the catalyst [Re(**1a**)(MeCN)$(CO)_3$]OTf was investigated. After increasing the temperature to 70 °C and adding the EDA over a longer time (6 h), no EDA remained and the chemoselectivity was improved (0.8). The cyclopropane : coupling ratio was further improved to 3.7 when a catalyst : EDA : alkene ratio of 1 : 17 : 170 was used and 10 h addition of EDA was employed. With this method, the catalytic results for other alkenes were obtained (entries 9–13). Complex [Re(**1a**)(MeCN)$(CO)_3$]OTf catalysed the cyclopropanation of *α*-substituted styrenes very efficiently. Very high cyclopropane selectivity was found for 1,1-diphenylethylene. *β*-Substituted styrenes and aliphatic alkenes were poorer substrates. For the straight chain alkenes (1-octene and *trans*-5-decene), no cyclopropane could be detected.

The catalytic asymmetric cyclopropanations catalysed by chiral Re catalysts were investigated in CH_2Cl_2, as higher enantioselectivities than benzene were usually obtained by this solvent. At a catalyst : EDA : styrene ratio of 1 : 50 : 250, different chiral catalysts and diazoacetate were screened and the results are shown in Table 2. The absolute configuration of the products from the reaction between styrene and EDA was determined by comparison with known compounds.[19]

With [Re(**5b**)(MeCN)$(CO)_3$]OTf as catalyst, the highest enantioselectivities of the *cis*- and *trans*-products, ee = 73 and 62%, respectively, were obtained; high chemoselectivities were also observed. When compared with **4b** (entry 1), the uncoordinated pyridine ring in tpy was found to be crucial in obtaining higher enantioselectivies and better cyclopropane selectivity. As in the case of **1a** and **3**, both the *cis* : *trans* ratios were found to be independent of the ligand used. For the sterically bulkier diazoacetates, no coupling product was observed and the yield of the cyclopropanes from *t*-butyl diazoacetate was very high.

The reactive intermediate of the cyclopropanation has also been studied. A linear relationship is observed in competition experiments of substituted styrenes *vs* styrene with [Re(**5b**)(MeCN)$(CO)_3$]OTf. The reaction rate was enhanced by electron-donating substituents (4-CH_3O and 4-CH_3) but retarded with electron-withdrawing groups (4-Cl and 3-NO_2) and this indicated that the intermediate is electrophilic in nature ($\rho^+ = -0.57$ correlated to σ^+). When monitored with ^{1}H NMR, the reactions of EDA with Re complexes of **1c** or **5b** gave new singlets at 11.68 and 12.03 ppm respectively. These intermediates can be tentatively assigned to carbene complexes.[20] Further evidence from ESI-MS analyses of the mixtures showed new species corresponding to [(Re=CHCOOEt)(**1c**)$(CO)_3]^+$ ($m/z = 625.2$) and [(Re=CHCOOEt)(**5b**)$(CO)_3]^+$ ($m/z = 806.8$), respectively.

Conclusion

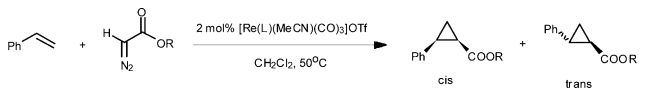
In summary, the present works show that chiral or achiral Re(I) carbene complexes can be generated and serve as good catalysts for asymmetric cyclopropanation. Further experiments are underway to characterise the intermediates and to develop more efficient and selective catalysts for asymmetric cyclopropanation.

Experimental

General experimental

Unless otherwise stated, all manipulations were carried out under nitrogen using standard Schlenk line technique. Benzene was distilled from sodium. Dichloromethane and MeCN were dried over CaH_2 and distilled prior to use. *tert*-Butyl diazoacetate (TDA), EDA, alkenes, [Re$(CO)_5$Br], AgOTf and all achiral ligands are commercially available and were used as received. (+)- and (−)-menthyl diazoacetate,[21a] **4a**,[21b] **4b**,[21b] **5a**[21c] and **5b**[15a] were prepared according to literature procedures. Complexes [Re(L)$(CO)_3$Br] (L = **1a**,[16a] **1b**,[16b] **1c**,[16c] **1d**,[16d] **1e**,[16e] **2a**,[16f] **2b**,[16g] **3**[16h]) and [Re(**L**)(MeCN)$(CO)_3$]OTf (**L** = **1a**,[17a] **1b**,[17b] **1c**,[17c] **1d**,[17d] **2a**,[17e] **2b**,[17f]) were synthesised using literature procedures. The cyclopropanation and competition reactions were monitored by gas chromatography using a 5% PH ME siloxane column. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 300 MHz Mercury NMR spectrometer. Positive ion mass spectra were taken on a PE SCIEX API 365 electrospray mass spectrometer. Elemental analyses were performed on a Vario EL III elemental analyser.

Table 2 Rhenium catalysed cyclopropanation of styrene and diazoacetate with different chiral ligands[a]



Entry	L	R	Yield (%)[b]	Chemoselectivity[c]	*cis* : *trans*[d]	Ee (%)[e] *cis* (1*R*,2*S*)	Ee (%)[e] *trans* (1*R*,2*R*)
1	**4b**	Ethyl	97	6.9	32 : 68	13	24
2	**5a**	Ethyl	96	7.8	22 : 78	29	38
3	**5b**	Ethyl	91	10.8	32 : 68	73	62
4	**5b**	*t*-Butyl	99	—	32 : 68	50	57
5	**5b**	(+)-Menthyl	73	—	24 : 76	1	45
6	**5b**	(−)-Menthyl	89	—	17 : 83	54	48

[a] Reaction conditions: catalyst : EDA : styrene = 1 : 50 : 250, CH_2Cl_2, 50 °C, 4 h addition of EDA and then stirring for 16 h. [b] Isolated yield of cyclopropanes based on expected product. [c] Cyclopropanes : coupling products. For entries 4–6, no coupling products were observed. [d] Determined by GC-FID. [e] Determined by chiral HPLC or chiral GC.

Procedure for preparation of [Re(L)(CO)$_3$Br]

Degassed heptane (3 mL) was added to a 25 mL pear-shaped flask containing [BrRe(CO)$_5$] (1 mmol) and polypyridine ligand (1 mmol) under nitrogen. The mixture was refluxed for 3 h, cooled to room temperature, and concentrated under vacuum. Hexane was then added and the solution was cooled in an ice bath. Yellow solid was precipated and filtered. It was then recrystallised in dichloromethane. The recrystallised solids were collected and dried under vacuum. The complexes obtained were characterised with ^{1}H NMR, IR, elemental analyses and ESI-MS.

[Re(4a)(CO)$_3$Br]. Yield: 0.66 g (95%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.72 (s, 3H), 0.75 (s, 3H), 1.32 (d, J = 9.4 Hz, 1H), 1.37 (d, J = 10.6 Hz, 1H), 1.44 (s, 3H), 1.45 (s, 3H), 2.50–2.60 (m, 2H), 2.69–2.77 (m, 2H), 2.90 (t, J = 5.9 Hz, 2H), 3.53 (dd, J = 17.0, 11.7 Hz, 2H), 3.79 (dd, J = 17.6, 5.9 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H); ν (KBr)/cm^{-1}: 2018 s (CO), 1896 br (CO); anal. calcd. for $C_{27}H_{28}BrN_2O_3Re$: C, 46.69; H, 4.03; N, 4.03, found: C, 45.57; H, 3.93; N, 3.94%; ESI-MS: m/z 616 [M − Br]$^+$.

[Re(4b)(CO)$_3$Br]. Yield: 0.54 g (75%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.80 (s, 3H), 0.94 (s, 3H), 1.35 (d, J = 10.0 Hz, 1H), 1.47 (s, 3H), 1.50 (s, 3H), 1.51 (d, J = 10.6 Hz, 1H), 1.62 (d, J = 6.7 Hz, 3H), 1.71 (d, J = 6.7 Hz, 3H), 2.28–2.37 (m, 2H), 2.53–2.66 (m, 2H), 2.91 (t, J = 5.9 Hz, 2H), 3.96–4.03 (m, 2H), 7.49 (d, J = 8.2 Hz, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.56 (d, J = 8.2 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H); ν (KBr)/cm^{-1}: 2020 s (CO), 1888 br (CO); anal. calcd. for $C_{29}H_{32}BrN_2O_3Re$: C, 48.20; H, 4.43; N, 3.88, found: C, 48.32; H, 4.43; N, 3.95%; ESI-MS: m/z 643 [M − Br]$^+$.

[Re(5a)(CO)$_3$Br]. Yield: 0.69 g (89%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.66 (s, 3H), 0.72 (s, 3H), 0.77 (s, 3H), 0.84 (s, 3H), 1.30 (d, J = 9.7 Hz, 2H), 1.41 (d, J = 9.7 Hz, 2H), 1.42–1.79 (m, 12H), 2.39–2.44 (m, 2H), 2.53–2.58 (m, 2H), 2.71–2.77 (m, 4H), 2.87–2.96 (m, 4H), 3.09–3.19 (m, 2H), 3.33–3.40 (m, 2H), 3.44–3.52 (m, 2H), 3.73 (dd, J = 17.9, 2.6 Hz, 2H), 7.42 (dd, J = 7.6, 5.3 Hz, 2H), 7.53 (dd, J = 7.9, 1.8 Hz, 2H), 7.58 (dd, J = 7.6, 1.8 Hz, 2H), 7.66–7.73 (m, 2H), 7.92 (t, J = 7.0 Hz, 2H), 8.04 (td, J = 7.9, 2.1 Hz, 2H), 8.13 (dd, J = 8.2, 1.2 Hz, 2H); ν (KBr)/cm^{-1}: 2019 s (CO), 1915 s (CO), 1885 s (CO); anal. calcd. for $C_{32}H_{31}BrN_3O_3Re\cdot(CH_3CN)_{0.5}\cdot(Et_2O)$: C, 51.30; H, 4.94; N, 5.66, found: C, 52.98; H, 4.89; N, 5.51%; ESI-MS: m/z 692 [M − Br]$^+$.

[Re(5b)(CO)$_3$Br]. Yield: 0.74 g (92%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.74 (s, 3H), 0.84 (s, 3H), 1.40 (d, J = 8.8 Hz, 2H), 1.45 (s, 3H), 1.46 (s, 3H), 1.50 (d, J = 7.0 Hz, 3H), 1.64 (d, J = 7.0 Hz, 3H), 2.20 (td, J = 6.2, 3.2 Hz, 1H), 2.31 (td, J = 9.4, 3.2 Hz, 1H), 2.62 (q, J = 5.9 Hz, 2H), 2.88 (t, J = 5.6 Hz, 1H), 2.93 (t, J = 6.2 Hz, 1H), 3.30–3.32 (m, 1H), 3.94–3.97 (m, 1H), 7.36–7.39 (m, 2H), 7.54 (d, J = 7.9 Hz, 1H), 7.62–7.65 (m, 1H), 7.95 (d, J = 7.9 Hz, 1H), 8.03 (t, J = 7.9 Hz, 1H), 8.11 (d, J = 7.9 Hz, 1H); ν (KBr)/cm^{-1}: 2020 s (CO), 1916 s (CO), 1891 s (CO); anal. calcd. for $C_{34}H_{35}BrN_3O_3Re\cdot(CH_3CN)_{0.5}\cdot(CH_2Cl_2)_{0.5}$: C, 49.42; H, 4.38; N, 5.68, found: C, 50.07; H, 4.36; N, 5.70%; ESI-MS: m/z = 800 [M + H]$^+$, 720 [M − Br]$^+$.

Procedure for preparation of [Re(L)(MeCN)(CO)$_3$]OTf

In a 25 mL pear-shaped flask charged with [Re(L)(CO)$_3$Br] (0.5 mmol) and MeCN (5 mL), AgOTf (0.6 mmol) was added under nitrogen. The mixture was stirred in the dark for 3 h. It was then filtered through Celite® and reduced to dryness. The crude product, dissolved in minimal amount of MeCN, was agitated gently and the dark solid formed was removed by filtration. Hexane or Et$_2$O was then added dropwise to the solution until a precipite formed. The solid was then collected and dried under vacuum. The complexes were characterised with ^{1}H NMR, IR, elemental analyses and ESI-MS.

[Re(1e)(MeCN)(CO)$_3$]OTf. Yield: 0.35 g (91%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.50 (t, J = 7.0 Hz, 6H), 2.28 (s, 3H), 4.56 (q, J = 7.0 Hz, 4H), 8.21 (dd, J = 5.6, 1.5 Hz, 2H), 9.02–9.20 (m, 2H), 9.12 (dd, J = 5.6, 0.6 Hz, 2H); ν (KBr)/cm^{-1}: 2309 w (CN), 2041 s (CO), 1945 s (CO), 1938 s (CO), 1158 m (SO$_3$), 1029 m (SO$_3$); anal. calcd. for $C_{22}H_{19}F_3N_3O_{10}ReS\cdot(Et_2O)_{0.6}$: C, 36.41; H, 3.11; N, 5.22, found: C, 37.82; H, 3.09; N, 5.18%; ESI-MS: m/z = 612.2 [M − CF$_3$SO$_3$]$^+$.

[Re(3)(MeCN)(CO)$_3$]OTf. Yield: 0.30 g (86%). ^{1}H NMR (300 MHz, CD$_3$CN): δ 1.97 (s, 3H), 7.62 (t, J = 6.5 Hz, 1H), 7.72–7.78 (m, 2H), 7.88 (d, J = 7.6 Hz, 1H), 8.04 (t, J = 7.6 Hz, 1H), 8.33 (t, J = 8.2 Hz, 1H), 8.40 (t, J = 7.9 Hz, 1H), 8.61 (t, J = 8.8 Hz, 2H), 8.79 (d, J = 4.4 Hz, 1H), 9.07 (d, J = 5.3 Hz, 1H); ν (KBr)/cm^{-1}: 2289 w (CN), 2035 s (CO), 1919 br (CO), 1166 m (SO$_3$), 1032 m (SO$_3$); anal. calcd. for $C_{21}H_{14}F_3N_4O_6ReS\cdot(CH_2Cl_2)_{1.25}$: C, 33.41; H, 2.06; N, 7.01, found: C, 33.24; H, 2.07; N, 6.95%; ESI-MS: m/z = 545.4 [M − CF$_3$SO$_3$]$^+$.

[Re(4a)(MeCN)(CO)$_3$]OTf. Yield: 0.36 g (89%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.65 (s, 3H), 0.75 (s, 3H), 1.26 (d, J = 9.9 Hz, 1H), 1.46 (s, 3H), 1.48 (s, 3H), 1.49 (d, J = 3.8 Hz, 1H), 2.33 (s, 3H), 2.55–2.58 (m, 2H), 2.74–2.82 (m, 2H), 2.96–3.01 (m, 2H), 3.40 (dd, J = 17.6, 2.9 Hz, 2H), 3.60 (ddd, J = 17.6, 7.6, 2.9 Hz, 2H), 7.72 (d, J = 3.6 Hz, 1H), 7.75 (d, J = 3.2 Hz, 1H), 8.27 (d, J = 7.9 Hz, 1H), 8.32 (d, J = 7.9 Hz, 1H); ν (KBr)/cm^{-1}: 2294 w (CN), 2034 s (CO), 1919 br (CO), 1159 m (SO$_3$), 1030 m (SO$_3$); anal. calcd. for $C_{30}H_{31}F_3N_3O_6ReS\cdot CH_2Cl_2$: C, 41.84; H, 3.71; N, 4.72, found: C, 41.17; H, 3.64; N, 4.79%; ESI-MS: m/z = 656.6 [M − CF$_3$SO$_3$]$^+$.

[Re(4b)(MeCN)(CO)$_3$]OTf. Yield: 0.35 g (85%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.77 (s, 3H), 0.78 (s, 3H), 1.40 (d, J = 10.3 Hz, 2H), 1.50 (d, J = 6.7 Hz, 3H), 1.51 (s, 6H), 1.56 (d, J = 7.0 Hz, 3H), 2.25 (s, 3H), 2.32–2.37 (m, 2H), 2.58–2.67 (m, 2H), 2.96–3.04 (m, 2H), 3.83–3.90 (m, 2H), 7.68 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 3.5 Hz, 1H), 7.81 (d, J = 3.5 Hz, 1H), 8.05 (d, J = 7.9 Hz, 1H); ν (KBr)/cm^{-1}: 2289 w (CN), 2035 s (CO), 1922 s (CO), 1157 w (SO$_3$), 1031 w (SO$_3$); anal. calcd. for $C_{32}H_{35}F_3N_3O_6ReS\cdot(CH_3CN)_{0.5}\cdot(CHCl_3)_{0.8}$: C, 42.78; H, 3.93; N, 5.17, found: C, 43.68; H, 3.83; N, 5.06%; ESI-MS: m/z = 683.8 [M − CF$_3$SO$_3$]$^+$.

[Re(5a)(MeCN)(CO)$_3$]OTf. Yield: 0.39 g (89%). ^{1}H NMR (300 MHz, CD$_3$CN): δ 0.68 (s, 3H), 0.72 (s, 3H), 0.73 (s, 3H), 0.78 (s, 3H), 1.22 (d, J = 9.7 Hz, 1H), 1.28 (d, J = 9.7 Hz, 1H), 1.34 (d, J = 10.0 Hz, 1H), 1.42 (d, J = 10.0 Hz, 1H), 1.450 (s, 3H), 1.454 (s, 3H), 1.46 (s, 3H), 1.47 (s, 3H), 1.96 (s, 3H), 1.97 (s, 3H), 2.40–2.43 (m, 2H), 2.52–2.58 (m, 2H), 2.80 (q, J = 5.3 Hz, 4H), 2.95

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(t, $J = 5.6$ Hz, 2H), 3.05–3.14 (m, 4H), 3.26 (dt, $J = 18.2$, 3.2 Hz, 2H), 3.45 (td, $J = 18.0$, 2.9 Hz, 2H), 3.57 (td, $J = 17.6$, 2.8 Hz, 2H), 7.53–7.54 (m, 4H), 7.84 (dd, $J = 7.0$, 0.9 Hz, 2H), 7.87 (ddd, $J = 7.6$, 3.5, 1.2 Hz, 2H), 8.27 (dd, $J = 8.2$, 4.1 Hz, 2H), 8.33 (t, $J = 7.6$ Hz, 2H), 8.48 (dt, $J = 8.2$, 1.2 Hz, 2H); ν (KBr)/cm^{-1}: 2301 w (CN), 2031 s (CO), 1921 br (CO), 1165 m (SO_3), 1031 m (SO_3); anal. calcd. for $C_{35}H_{34}F_3N_4O_6ReS{\cdot}(H_2O){\cdot}(CH_2Cl_2)_{2.5}$: C, 40.50; H, 3.69; N, 5.03, found: C, 41.63; H, 3.73; N, 4.97%; ESI-MS: $m/z = 733.6$ [M − CF_3SO_3]$^+$.

[Re(5b)(MeCN)(CO)$_3$]OTf. Yield: 0.39 g (86%). ^{1}H NMR (300 MHz, CD_3CN): δ 0.69 (s, 3H), 0.72–0.78 (m, 9H), 1.30 (d, $J = 10.0$ Hz, 4H), 1.42 (d, $J = 7.0$ Hz, 3H), 1.44–1.55 (m, 18H), 1.58 (d, $J = 6.7$ Hz, 3H), 1.96 (s, 3H), 1.97 (s, 3H), 2.18–2.28 (m, 2H), 2.32–2.37 (m, 2H), 2.64–2.69 (m, 4H), 2.94–2.96 (m, 2H), 3.04–3.09 (m, 2H), 3.24–3.30 (m, 2H), 3.79–3.84 (m, 2H), 7.35 (d, $J = 7.3$ Hz, 1H), 7.48 (d, $J = 7.6$ Hz, 2H), 7.74–7.87 (m, 4H), 8.11 (d, $J = 7.3$ Hz, 2H), 8.26–8.34 (m, 4H), 8.44 (d, $J = 8.2$ Hz, 1H); ν (KBr)/cm^{-1}: 2291 w (CN), 2036 s (CO), 1937 s (CO), 1921 s (CO), 1162 m (SO_3), 1031 m (SO_3); anal. calcd. for $C_{37}H_{38}F_3N_4O_6ReS{\cdot}(CH_2Cl_2)$: C, 45.88; H, 4.02; N, 5.63, found: C, 45.14; H, 3.96; N, 5.72%; ESI-MS: $m/z = 762$ [M − CF_3SO_3]$^+$.

General procedure for catalytic cyclopropanation and competition

To a two-neck round bottom flask was charged rhenium(I) triflate complex (0.02 mmol), solvent (2 mL) and alkene (5 mmol) under nitrogen. The mixture was heated to 50 °C. A solution of diazoacetate (1 mmol) in solvent (0.5 ml) was slowly added to it over a period of 4 h with a syringe pump and was stirred for 16 h. The solvent was then removed and the crude product was purified by column chromatography. The cyclopropanes obtained are known compounds and were characterised by ^{1}H NMR, and GC-MS. The enantiomeric excesses of the cyclopropanes were determined as followed: for cyclopropanes using EDA, they were determined by HPLC with a Daicel OJ chiral stationary phase in hexane–i-PrOH (97 : 3). For cyclopropanes using TDA, they were determined by GC with a Chiraldex β-PH column (30 m × 0.25 mm). For cyclopropanes using (+)-menthyl and (−)-menthyl diazoacetate, they were determined by GC with a 5% PH ME siloxane column (25 m × 0.2 mm × 0.33 μm film thickness). For the competition experiment, a similar procedure was employed but the EDA solution (1.65 M) was added in one portion. The relative amounts of the desired cyclopropanes were determined by GC.

X-Ray structure analysis of [Re(4a)(CO)$_3$Br] and [Re(5b)(CO)$_3$Br]

Selected crystal data for [Re(**4a**)(CO)$_3$Br]: $C_{27}H_{28}BrN_2O_3Re$, $M = 694.64$, triclinic, primitive, space group $P1$, $a = 9.593(1)$, $b = 10.549(1)$, $c = 13.618(2)$ Å, $\alpha = 76.415(2)$, $\beta = 85.266(2)$, $\gamma = 81.798(2)°$, $V = 1324.2(3)$ Å^3, $Z = 2$, $D_c = 1.742$ g cm^{-3}, λ (Mo-Kα) = 0.71069 Å, $F_{000} = 676$, μ (Mo-Kα) = 61.33 cm^{-1}. Crystal dimensions 0.15 × 0.20 × 0.38 mm, 11107 reflections measured, 9270 unique ($R_{int} = 0.018$), $R = 0.028$ [$I > 2.00\sigma(I)$] and w$R2 = 0.031$ [$I > 2.00\sigma(I)$]. Flack parameter = 0.076(10). CCDC 651262.† Selected crystal data for [Re(**5b**)(CO)$_3$Br]: $C_{34}H_{35}N_3O_3ReBr$, $M = 799.78$, orthorhombic, primitive, space group $P2_12_12_1$, $a = 7.893(2)$, $b = 14.212(3)$, $c = 28.551(6)$ Å, $V = 3202.7(1)$ Å^3, $Z = 4$, $D_c = 1.659$ g cm^{-3}, λ (Mo-Kα) = 0.71069 Å, $F_{000} = 1576$, μ (Mo-Kα) = 50.85 cm^{-1}. Crystal dimensions 0.45 × 0.25 × 0.12 mm, 75842 reflections measured, 7435 unique ($R_{int} = 0.035$), $R = 0.029$ [$I > 2.00\sigma(I)$] and w$R2 = 0.029$ [$I > 2.00\sigma(I)$]. Flack parameter = −0.019(8). CCDC 651263.†

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