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Conversion of Propargylic Alcohols to β-Oxo Esters Catalyzed by Novel Ruthenium-Phosphoramidite Complexes

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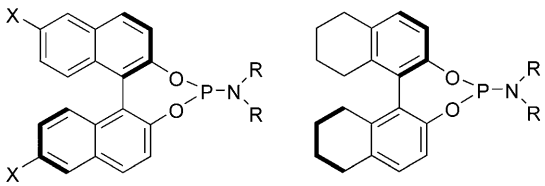
Abstract: A series of half-sandwich phosphoramidite complexes of ruthenium were synthesized and employed as catalysts in the atom-economical formation of β-oxo esters from carboxylic acids and propargylic alcohols. Reaction of the phosphoramidites (*R*)-BINOL-PNR_2 (R = Me, **1a**; *i*-Pr, **1b**; benzyl, **1c**) and (*rac*)-6,6′-dibromo-BINOL-$PNMe_2$ (**1d**) with the dimeric *p*-cymene-ruthenium dichloride complex, $[RuCl_2(p\text{-cymene})]_2$, gave the complexes $[RuCl_2(p\text{-cymene})(L)]$ (L = **1a**, **7a**; **1b**, **7b**; **1c**, **7c**; **1d**, **7d**) in 96–66% yield. Accordingly, reaction of (*R*)-BINOL(8H)-$PNMe_2$ (**2a**) and (*R*)-BINOL(8H)-PN(benzyl)$_2$ (**2b**) with $[RuCl_2(p\text{-cymene})]_2$ afforded the complexes $[RuCl_2(p\text{-cymene})(L)]$ (L = **2a**, **8a**; **2b**, **8b**) in 82% and 86% yield. In a similar reaction, treatment of (*R*)-BIPHEN-$PNMe_2$ (**9**) with $[RuCl_2(p\text{-cymene})]_2$ gave the complex $[RuCl_2(p\text{-cymene})(\mathbf{9})]$ (**11**) in 60% yield. Finally, phosphoramidite **1b** reacted with $[RuCl_2(C_6Me_6)]_2$ to give $[RuCl_2(C_6Me_6)(\mathbf{1b})]$ (**12**) in 78% yield. All novel complexes are catalytically active in the formation of β-oxo esters from propargylic alcohols and carboxylic acids. Standard conditions involve cyclohexane solvent, propargylic alcohol (1.0 equiv.), carboxylic acid (1.0 equiv.), ruthenium catalyst (1.5 mol%), and 90 °C for 5–18 h. Isolated yields of the β-oxo esters range from 87 to 16% and show broad substrate generality. The reaction proceeds without racemization if a chiral propargylic alcohol is employed. The method is practical as no additives are required and the exclusion of oxygen and moisture is not needed. Complex **7c** turned out to be the most effective catalyst (5 h reaction time), showing that the ligand structure has a profound impact on the catalytic performance. The crystal structure of **7a** was determined, confirming an octahedral coordination geometry about the ruthenium center.

Keywords: homogeneous catalysis; phosphoramidites; propargylic alcohols; ruthenium; X-ray structure determination

Introduction

Phosphoramidites (Figure 1) have recently attracted considerable interest as ligands in various transition metal-catalyzed organic reactions. Phosphoramidites are an attractive ligand class because they are relatively easy to synthesize and are air-stable.[1] They allow for steric and electronic fine tuning of their metal complexes because their "architecture" can be modified at several sites through choice of diol as well as substituents on the diol backbone and on the nitrogen.[2] Typically phosphoramidites are utilized *in situ* in combination with a metal complex precursor to yield efficient catalyst systems for such conversions as enantioselective conjugate enone addition reactions,[2a,g,3] hydrogenations,[4] allylic alkylations,[5] hydrosilylations,[6] vinylations,[7] cycloadditions,[8] Diels–



R = Me, X = H, **1a**
R = *i*-Pr, X = H, **1b**
R = CH_2Ph, X = H, **1c**
R = Me, X = Br, **1d**

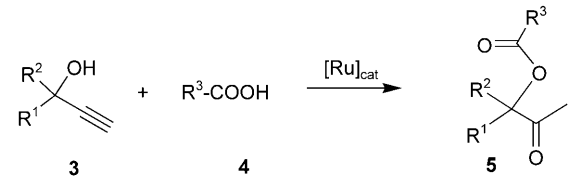
R = Me, **2a**
R = CH_2Ph, **2b**

Figure 1. Phosphoramidite ligands.

Alder[9] and Heck reactions.[10] The nature of the catalytically active species for these *in situ* catalyst systems is not always known.[11]

Phosphoramidites derived from BINOL (1,1′-binaphthyl-2,2′-diol) are the most prevalent, but others utilizing TADDOL, e.g., are known as well.[12] It has been shown that changes at the phosphoramidite skeleton have a profound impact on yields and enantioselectivities in catalytic applications of these ligands.[7]

β-Oxo esters are an important class of compounds.[13] Several synthetic methodologies to form these esters are known,[14] e.g., from propargylic alcohols by a two-step hydration/esterification procedure[14a,b] or by carboxylation of α-halo ketones.[14c,d] Addition of carboxylic acids (**4**) to propargylic alcohols (**3**) to form β-oxo esters (**5**) provides a quick, atom economical access to this class of compounds from simple starting materials in one step (Scheme 1). This



[Ru] = $[RuCl_2(p\text{-cymene})(PR_3)]$; R = Me, Ph (Dixneuf)
= $[Ru(\mu\text{-}O_2CH)(CO)_2(PPh_3)]_2$ (Dixneuf)
= bis(η^4-cyclooctadienyl)ruthenium/trialkylphosphine/maleic anhydride (Wanatabe)

Scheme 1. β-Oxo ester formation from propargylic alcohols.

reaction does not proceed without a catalyst. To date, only a few catalysts are known to promote this transformation. Watanabe described a mixture of bis(η^4-cyclooctadienyl)ruthenium, trialkylphosphine and maleic anhydride,[15] that functions as an active catalyst and Dixneuf showed that the half-sandwich complexes $[RuCl_2(p\text{-cymene})(PR_3)]$ (R = Ph, Me)[16a] and the dimeric complex $[Ru(\mu\text{-}O_2CH)(CO)_2(PPh_3)]_2$ also catalyze this reaction.[16b,c]

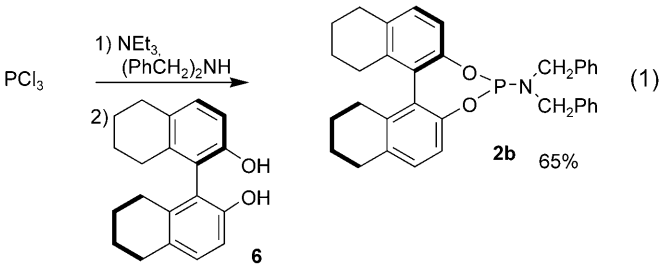
Steroids possessing a β-oxo ester motif in the C-17 position often show biological activity.[13a] β-Oxo esters are employed as intermediates in the formation of a chiral acyloin,[13b] a key structural feature of many natural products.[13c] It has been demonstrated that they are also efficient photolabile protecting groups for carboxylic acids.[13d]

It is known that a number of ruthenium complexes activate propargylic alcohols catalytically.[17] Herein, we explore ruthenium phosphoramidite complexes as catalysts for β-oxo ester formation as shown in Scheme 1. For this purpose, we synthesized several novel, electronically and sterically tuned phosphoramidite complexes of ruthenium, all of which are efficient catalysts for the conversion of propargylic alcohols and carboxylic acids to β-oxo esters. Herein we describe the influence of different phosphoramidite ligands on the reactivity of the metal complexes as well as experiments to better understand the mechanism of the reaction.

Results

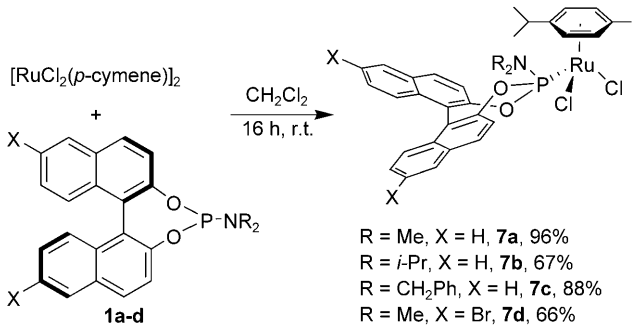
Synthesis of Novel Half-Sandwich Ruthenium-Phosphoramidite Complexes

First, a set of sterically and electronically tuned phosphoramidite ligands and their metal complexes were synthesized. The known chiral phosphoramidite ligands of the type **1a–d** and **2a** shown in Figure 1 were synthesized according to literature procedures.[1,7] Similarly, the new ligand **2b** was synthesized as outlined in Eq. (1). Phosphorus trichloride (PCl_3) was heated in toluene with dibenzylamine [$(PhCH_2)_2NH$] and triethylamine followed by the addition of commercial (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol (**6**) and the resulting slurry was stirred at room temperature for 24 h. After work-up, the chiral phosphoramidite **2b** was obtained as a white powder in 65% yield.



The dimeric ruthenium *p*-cymene chloro complex $[RuCl_2(p\text{-cymene})]_2$ is known to give half-sandwich complexes of the type $[RuCl_2(p\text{-cymene})(L)]$ when treated with monodentate phosphines[18a] or phosphoramidites.[18b,c] Accordingly, the ligands **1a–d** and **2a**, **b** were reacted with $[RuCl_2(p\text{-cymene})]_2$ under standard conditions (CH_2Cl_2, room temperature, 16 h). As exemplified in Scheme 2 for the ligand class **1**, chromatographic separation provided the novel chiral target complexes $[RuCl_2(p\text{-cymene})(L)]$ **7a–d** (Scheme 2) and **8a**, **b** (Figure 2) as red powders in 96–66% yields.

The complexes **7** and **8** differ in the substituents at the nitrogen of the phosphoramidite, but all are derived from BINOL (1,1′-binaphthyl-2,2′-diol) or 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol.
We were interested to determine if phosphoramidites derived from diols other than BINOL have an impact on the catalytic properties of their respective metal complexes. We also sought some steric tuning closer to the ruthenium metal center. Substituents in the



Scheme 2. Phosphoramidite complex synthesis.

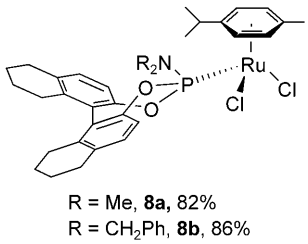
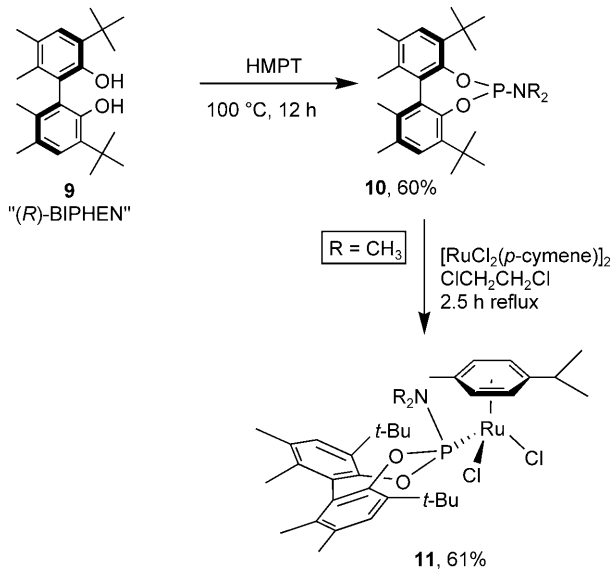


Figure 2. Phosphoramidite complexes.

3,3′-positions *ortho* to the oxygen substituents in BINOL seemed to hold the greatest promise. When coordinated to a metal, substituents in this position would point directly towards the metal center.

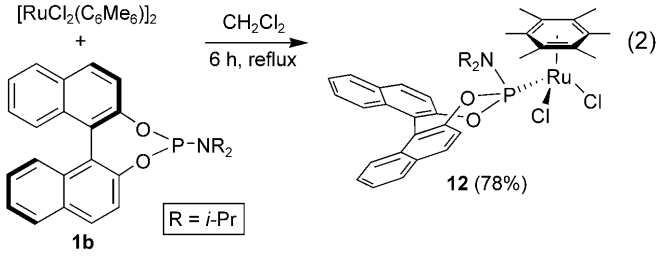
Thus, commercial (*R*)-5,5′,6,6′-tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diol ["(*R*)-BIPHEN", **9**] was heated to 100 °C for 12 h with hexamethylphosphorus triamide (HMPT) according to literature protocols (Scheme 3).[1a] After recrystallization, the new phosphoramidite **10** was obtained as a white powder



Scheme 3. Synthesis of ruthenium BIPHEN phosphoramidite complex **11**.

in 60% yield. Subsequently, ligand **10** was refluxed with $[RuCl_2(p\text{-cymene})]_2$ in $ClCH_2CH_2Cl$ and complex **11** was isolated by extraction with diethyl ether in 61% yield as a purple solid.[19]

In order to investigate the influence of the arene ligand at ruthenium, complex **12** was synthesized, which bears the hexamethylbenzene ligand, C_6Me_6, instead of the *p*-cymene ligand [Eq. (2)]. The



known[20] dimer $[RuCl_2(C_6Me_6)]_2$ was refluxed with phosphoramidite **1b** in CH_2Cl_2 for 6 h and the C_6Me_6 complex **12** was isolated as an orange powder in 78% yield, which showed *ca.* 95% spectroscopic purity.[19]

Complexes **7a–d**, **8a**, **b**, **11** and **12** were characterized by mass spectrometry, IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy and microanalysis. The ^{31}P NMR shifts ranged between 141 and 143 ppm for **7b–d** and **8a**. Deviations from this range were detected for complex **7a** (151.5 ppm), complex **8b** (136.8 ppm), for the (*R*)-BIPHEN complex **11** (125.6 ppm) and the C_6Me_6 complex **12** (158.3 ppm). The ^1H and ^{13}C NMR spectra are in accordance with the proposed structures. For example, the coordination geometry of **7** and **8** creates four inequivalent aromatic CH groups for the *p*-cymene ligand. Accordingly, these complexes exhibited six aromatic signals in the ^{13}C NMR and four aromatic signals in the ^1H NMR spectra for the *p*-cymene ligand. Similarly, the hydrogen atoms of the two NCH_2Ph groups in complex **7c** and **8b** are diastereotopic, and as a consequence, four individual signals were observed in the ^1H NMR.

To unequivocally establish the structures of the new phosphoramidite complexes, the crystal structure of complex **7a** was determined (Experimental Section and Table S1 in the Supporting Information).

The molecular structure is depicted in Figure 3 along with key structural data, confirming the half-sandwich configuration about ruthenium. Bond lengths and angles are as expected, and similar to those reported for closely related complexes.[18b] The bond angles around ruthenium range from 84.08(3)° for the P(1)–Ru(1)–Cl(1) angle to 94.30(11)° for the Cl(2)–Ru(1)–C(2) angle. Thus, the coordination geometry of the complex is best described as a slightly distorted octahedron. The bulky phosphoramidite

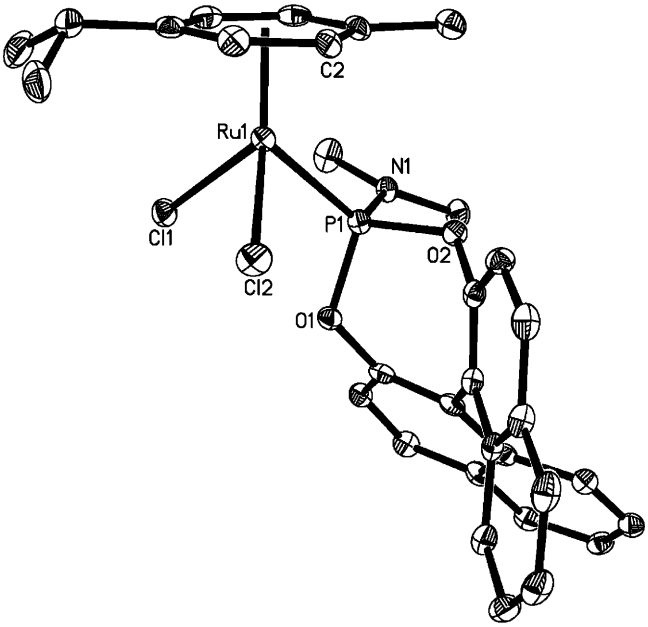


Figure 3. Molecular structure of complex **7a**. Key bond lengths (Å) and angles (°): Ru(1)–P(1) = 2.2778(10); P(1)–N(1) = 1.642(3); Ru(1)–Cl(1) = 2.4136(9);Ru(1)–Cl(2) = 2.3901(9); P(1)–Ru(1)–Cl(1) = 84.08(3); P(1)–Ru(1)–Cl(2) = 85.15(3); Cl(2)–Ru(1)–Cl(1) = 88.85(3); Cl(2)–Ru(1)–(C2) = 94.30(11); O(1)–P(1)–O(2) = 100.86(13); O(1)–P(1)–N(1) = 110.36(14); O(2)–P(1)–N(1) = 97.26(13).

ligand is directed opposite to the isopropyl substituent on *p*-cymene, presumably for steric reasons.

Application of the Ruthenium-Phosphoramidite Complexes in Catalysis

Since **7a** is the most easily accessible complex, it was employed for initial catalytic studies and optimizations. After screening different substrates and solvents, complex **7a** was found to be catalytically active for the addition of carboxylic acids to propargylic alcohols to give β-oxo esters (Scheme 1). The results of the catalytic experiments are summarized in Table 1 and Table 2 and characterization data (NMR, IR, MS) for the products are given in the Supporting Information. The best results were obtained when cyclohexane was used as solvent. Reactions conducted in THF or $ClCH_2CH_2Cl$ were incomplete or plagued by side products. Using 1.5 mol% of the catalyst and a 1:1 mol ratio of the reactants, moderate to good isolated yields were obtained after 18 h at 90 °C. The exclusion of moisture or air was not necessary.

Tertiary aliphatic and aromatic propargylic alcohols could be converted to the corresponding esters (entries 9–15, Table 1) as well as secondary aliphatic and aromatic alcohols (entries 3–8) and the primary propargylic alcohol prop-2-yn-1-ol (**3a**, entries 1 and 2). Both acetic and benzoic acid can be used. As outlined in Table 2, cyclic tertiary propargylic alcohols were converted to the corresponding cyclic β-oxo esters and 2-bromobenzoic acid could be employed as well (Table 1, entries 2, 5, 8, 13 and 15 and Table 2, entries 2 and 5).

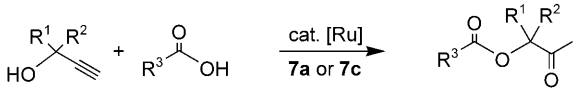
The yields showed only moderate substrate dependence but did not exceed 57% for complex **7a** under the reaction conditions reported here. Conversions with **7a** reached 100%, but side products formed during the reaction (*vide infra*). Next, electronically or sterically modified ruthenium complexes were tested to determine whether the catalytic activity could be improved.

Screening of the metal complexes **7b**, **7c**, **8a**, **8b**, **11** and **12** revealed that all complexes are catalytically active in the title reaction. Further investigations revealed that the *N*-benzyl complex **7c** catalyzed the transformation at higher reaction rates than the *N*-methyl complex **7a**, as it took only 5 h at 90 °C for complete conversion. Complex **7a** required 18 h to completely convert the starting materials. The isolated yields from **7c** were higher in all cases than those from **7a**, as seen in Table 1 and Table 2. For complex **7a**, the yields range from 16 to 57%, whereas they range from 24 to 87% for complex **7c**. GC analyses showed, in general, fewer side products than the corresponding reactions with catalyst **7a**. Thus, exchange of a methyl group on nitrogen in the phosphoramidite ligand in **7a** for a benzyl group in **7c** resulted in a complex with much better catalytic performance.

In order to assess the relative activity of the complexes **7**, **8**, **11** and **12**, the complexes were utilized under strictly comparable conditions for β-oxo ester formation from benzoic acid **4a** and 2-phenyl-3-butyn-2-ol **3e** (entry 12 in Table 1). Conversion and relative yields were determined by GC/MS after two and four hours reaction time and the results are summarized in Table 3. For comparison, the known complex $[RuCl_2(p\text{-cymene})(PPh_3)]$,[18a] which was previously shown to be catalytically active in the reaction,[16a] was tested as well.

It turns out that among the complexes **7**, **8**, **11** and **12**, the *N*-benzyl complex **7c** exhibited the highest activity. Complete conversion after 4 h was observed for this specific test reaction, and the product was detected in 97% GC yield. Isolated yields were somewhat lower, presumably due to the presence of light or oligomeric by-products. The octahydro *N*-benzylphosphoramidite complex **8b** showed comparable activity. Lower conversions and yields were observed with the *N*-isopropyl complex **7b** and the *N*-methyl complex **7a**. When the *p*-cymene ligand was exchanged by C_6Me_6 (complex **12**), the activity dropped as well. Also, electron-withdrawing bromo substituents in the BINOL backbone (complex **7d**) lowered the catalytic activity. Obviously the *N*-benzyl substituent makes a

Table 1. β-Oxo ester formation.

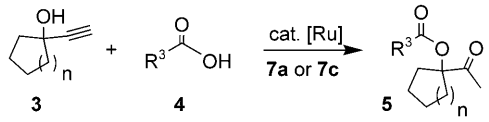


3 4 5

Entry	Propargylic alcohol **3**	Carboxylic acid **4**	Product **5**	Yield[a] Catalyst **7a**[b]	Yield[a] Catalyst **7c**[c]
1	$R^1 = R^2 = H$ (**3a**)	R^3 = Ph (**4a**)	**5a**	41%	67%
2	$R^1 = R^2 = H$ (**3a**)	R^3 = 2-bromophenyl (**4b**)	**5b**	38%	77%
3	R^1 = Ph, R^2 = H (**3b**)	$R^3 = CH_3$ (**4c**)	**5c**	31%	47%
4	R^1 = Ph, R^2 = H (**3b**)	R^3 = Ph (**4a**)	**5d**	53%	74%
5	R^1 = Ph, R^2 = H (**3b**)	R^3 = 2-bromophenyl (**4b**)	**5e**	50%	78%
6	R^1 = *n*-pentyl, R^2 = H (**3c**)	$R^3 = CH_3$ (**4c**)	**5f**	21%	24%
7	R^1 = *n*-pentyl, R^2 = H (**3c**)	R^3 = Ph (**4a**)	**5g**	40%	56%
8	R^1 = *n*-pentyl, R^2 = H (**3c**)	R^3 = 2-bromophenyl (**4b**)	**5h**	46%	61%
9	$R^1 = R^2$ = Ph (**3d**)	$R^3 = CH_3$ (**4c**)	**5i**	41%	55%
10	$R^1 = R^2$ = Ph (**3d**)	R^3 = Ph (**4a**)	**5k**	39%	68%
11	R^1 = Ph, $R^2 = CH_3$ (**3e**)	$R^3 = CH_3$ (**4c**)	**5l**	57%	71%
12	R^1 = Ph, $R^2 = CH_3$ (**3e**)	R^3 = Ph (**4a**)	**5m**	44%	79%
13	R^1 = Ph, $R^2 = CH_3$ (**3e**)	R^3 = 2-bromophenyl (**4b**)	**5n**	52%	82%
14	R^1 = *i*-Bu, $R^2 = CH_3$ (**3f**)	R^3 = Ph (**4a**)	**5o**	36%	71%
15	R^1 = *i*-Bu, $R^2 = CH_3$ (**3f**)	R^3 = 2-bromophenyl (**4b**)	**5p**	47%	86%

[a] Isolated yields after column chromatography. GC/MS of the crude product showed complete consumption of the propargylic alcohol and one major peak for the product.
[b] *Conditions:* propargylic alcohol (0.7 mmol), carboxylic acid (0.7 mmol), catalyst **7a** (0.012 mmol) 18 h in cyclohexane (3 mL) at 90 °C.
[c] *Conditions:* propargylic alcohol (0.7 mmol), carboxylic acid (0.7 mmol) and the catalyst **7c** (0.006–0.012 mmol), 5 h in cyclohexane (3 mL) at 90 °C.

Table 2. Cyclic β-oxo ester formation.



3 4 5

Entry	Propargylic alcohol **3**	Carboxylic acid **4**	Product **5**	Yield[a] Catalyst **7a**[b]	Yield[a] Catalyst **7c**[c]
1	n = 1 (**3g**)	R^3 = Ph (**4a**)	**5q**	40%	77%
2	n = 1 (**3g**)	R^3 = 2-bromophenyl (**4b**)	**5r**	52%	86%
3	n = 2 (**3h**)	$R^3 = CH_3$ (**4c**)	**5s**	16%	43%
4	n = 2 (**3h**)	R^3 = Ph (**4a**)	**5t**	42%	61%
5	n = 2 (**3h**)	R^3 = 2-bromophenyl (**4b**)	**5u**	49%	87%

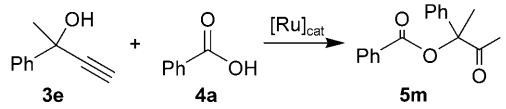
[a] Isolated yields after column chromatography.
[b] Conditions identical to those in Table 1.
[c] Conditions identical to those in Table 1.

big difference, because the two phosphoramidite complexes **7c** and **8b** bearing this substituent showed the highest activity among the phosphoramidite complexes under investigation. The complex [$RuCl_2$(*p*-cymene)(PPh_3)] showed performance comparable to *N*-benzyl complex **7c**.

Reactivity Studies

Analysis of the crude reaction mixtures of the catalytic experiments by GC/MS (and in some cases by NMR) revealed that an unsaturated hydrocarbon constituted the major side product for catalyst **7a**. A

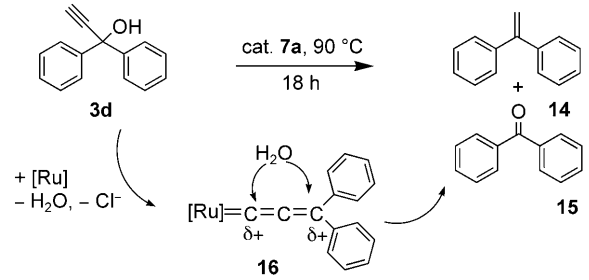
Table 3. Comparison of different catalysts.



Catalyst[a]	Conversion[b] [%]		Yield[c] [%]	
	2 h	4 h	2 h	4 h
7a	25	61	20	49
	16[d]	35[d]	8[d]	15[d]
	22[e]	54[e]	21[e]	38[e]
7c	77	100	75	97
	66[d]	92[d]	64[d]	90[d]
7b	68	90	56	86
12	20	73	15	63
8a	26	59	20	37
8b	75	98	73	95
7d	12	52	12	45
$[RuCl_2(p\text{-cymene})(PPh_3)]$	66	100	61	84

[a] *Conditions:* 0.7 mmol propargylic alcohohl **3e**, 0.7 mmol benzoic acid **4a**, 0.012 mmol catalyst in cyclohexane (3 mL) at 90 °C.
[b] Determined by the peak intensity of the starting material *vs.* the total peak area in the GC/MS.
[c] Determined by the peak intensity of the product *vs.* the total peak area in the GC/MS.
[d] In toluene.
[e] In a 6:1 cyclohexane/*p*-cymene mixture.

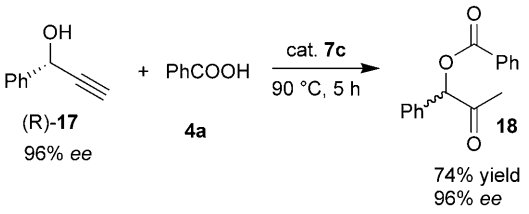
ketone was also detected in some cases. Other side products typically were detected only in trace quantities. As exemplified by propargylic alcohol **3d** in Scheme 4, the major side product arises from the



Scheme 4. Side product formation.

cleavage of the triple bond, which presumably occurs *via* an allenylidene intermediate **16** (Scheme 4). This reaction pattern has previously been observed.[21] Accordingly, when propargylic alcohol **3d** was heated with a catalytic amount of **7a** in cyclohexane in the absence of a carboxylic acid, at about 75% conversion the cleavage products **14** and **15** were detected by GC/MS in approximately a 1:1 ratio (Scheme 4).

For the catalytic experiments in Table 1 and Table 2, racemic (or achiral) propargylic alcohols were employed. As assessed by ^{1}H NMR experiments with a chiral shift reagent for some of the reactions in Table 1, virtually no enantiomeric excesses were obtained with the chiral complex **7a** as catalyst. In order to obtain additional information concerning the stereochemistry of the reaction, the commercial chiral propargylic alcohol (*R*)-**17** (96% *ee*) was subjected to β-oxo ester formation with catalyst **7c**, as shown in Eq. (3). The reaction proceeded without racemization. The enantiomeric excess for the product **18** was 96% as determined by chiral GC and the traces of the experiments are displayed in the Supporting Information.



(3)

To gain further insight into relative reactivities and the course of the reaction, product formation for the reaction in entry 12 in Table 1 was followed over time by GC for the most active phosphoramidite complex **7c**. An induction period of about 30 min was observed, as seen in Figure 4. The same experiment was performed with $[RuCl_2(p\text{-cymene})(PPh_3)]$. This complex gave an almost identical trace (see Figure 4), demonstrating that its activity is close to that of the *N*-benzyl complex **7c**. The C_6Me_6 complex **12** exhibited a longer induction period and a slower reaction rate for the same reaction under identical conditions. The longest induction period (about 80 min) and slowest reaction rate was observed with the complex **7a**.

To determine if arene loss from the metal complex is one of the steps in the mechanism of the reaction, toluene and a 6:1 mixture of cyclohexane/*p*-cymene were employed as solvent in the test reaction summarized in Table 3. The reaction is only slightly slower when coordinating aromatic compounds are present, suggesting that arene loss is not a part of the reaction.

Discussion

The preceding data show for the first time that ruthenium phosphoramidite complexes are efficient catalysts for β-oxo ester formation from propargylic alcohols and carboxylic acids. The ruthenium complexes **7**, **8**, **11** and **12** described herein are easily accessed in

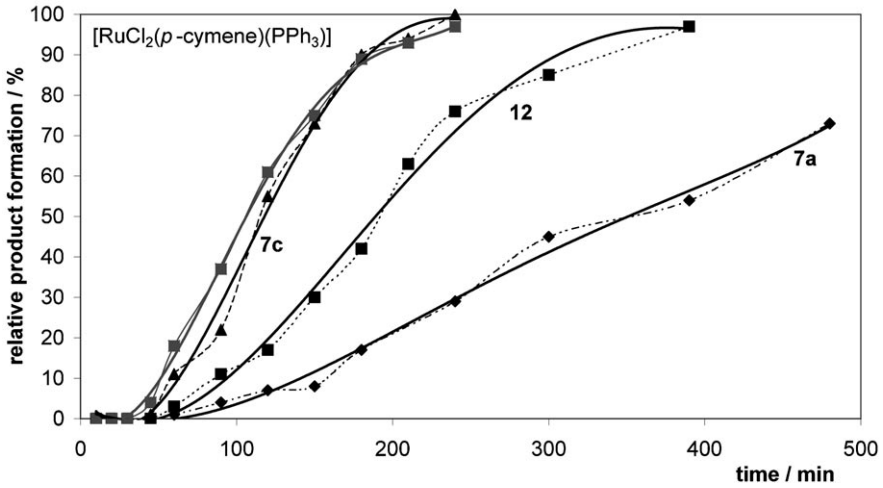


Figure 4. Product formation of the reaction in entry 12 in Table 1 followed over time by GC for different catalysts.

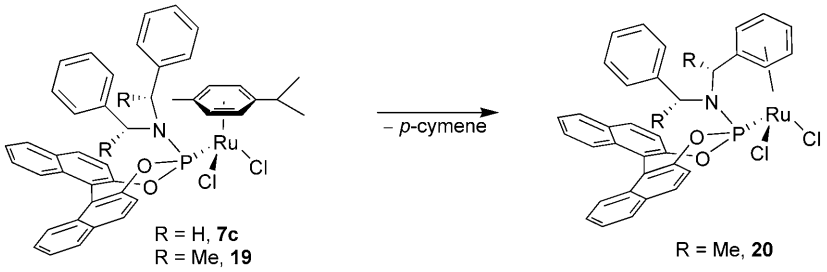
good yields from phosphoramidite ligands, which are in turn synthesized in one or two steps from commercially available starting materials according to literature procedures. The ligand has a profound impact on the catalytic activity. The *N*-benzyl complex **7c** showed the highest activity, with isolated yields of β-oxo esters ranging from 24 to 87%. The catalytic performance of **7a** was lower, with isolated yields ranging from 16 to 57%. The lowest yields were obtained with aliphatic propargylic alcohols and acetic acid (24–21%, Table 1, entry 6). This might be in part due to the fact that those substrates and products are UV inactive, making isolation by column chromatography more difficult. But in general catalysts **7a** and **7c** showed a remarkable substrate generality, as primary, secondary and tertiary propargylic alcohols could be converted to the corresponding β-oxo esters. Both aromatic and aliphatic propargylic alcohols and carboxylic acids can be employed in all possible combinations.

The complex **7c** exhibits activity comparable to the other catalysts known to promote this reaction. Watanabe's catalyst system was catalytically active in the conversion of 3-methyl-1-butyn-3-ol and 1-ethynylcyclohexanol to the corresponding β-oxo acetic acid esters in 54 and 61% yields.[15] The complex [$RuCl_2$(*p*-cymene)(PPh_3)] catalyzed the transformation of prop-2-yn-1-ol and various carboxylic acids to the corresponding β-oxo esters in 92–30% yields,[16a] but exhibited much lower activity with sterically more demanding propargylic alcohols.[16b] As demonstrated in Table 3 and Figure 4, GC yields for **7c** and [$RuCl_2$(*p*-cymene)(PPh_3)] for this specific test reaction are comparable.

Dixneuf demonstrated that the dimeric complex [$Ru(\mu\text{-}O_2CH)(CO)_2(PPh_3)]_2$ exhibited higher activity to give the corresponding β-oxo esters from prop-2-yn-1-ol and various α-hydroxy carboxylic acids in 69–60% yields (80 °C, 10–24 h).[16b] The same dimeric ruthenium complex was applied in the conversion of sterically hindered tertiary propargylic alcohols of steroids and bulky carboxylic acids to obtain the corresponding β-oxo esters in 94–56% yields.[16c] In these cases, three equivalents of acetic acid or formic acid were required, and reaction times were 15–16 h at 90 °C. Pivalic acid could be employed in equimolar amounts but required 42–100 h reaction times. Thus the conditions (5 h at 90 °C, equimolar amounts of carboxylic acid and propargylic alcohol) described herein for complex **7c** compare well with previously described catalyst systems.

It has been described in the literature that some half-sandwich complexes of ruthenium form their catalytically active species in solution by loss of the *p*-cymene ligand.[17a] Mezzetti reported that complexes closely related to those described herein lose their *p*-cymene ligand in solution at elevated temperatures.[18b] The data in Figure 4 clearly show an induction period for the title reaction, suggesting that the initial step is the formation of the catalytically active species. However, from the data in Table 3 it cannot clearly be concluded that the formation of this species involved arene loss. For both catalysts **7a** and **7c**, the reaction is only slightly slower when toluene is utilized as solvent or when a large excess of *p*-cymene is present in the reaction mixture.

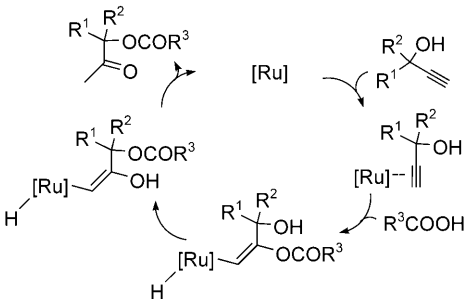
To date we do not have a satisfactory explanation for why the phosphoramidite complex **7c** with *N*-benzyl substituents exhibits better catalytic performance than the corresponding phosphoramidite complexes with *N*-alkyl substituents. It is known that in several cases bulky ligands prevent inactivating degradation and dimerization reactions of the catalytically active metal complexes. However, steric congestion cannot be the only cause for the increased reactivity of **7c** compared to **7a**, as the isopropyl groups in **7b**



Scheme 5. Stabilizing effect of benzyl groups in phosphoramidite complexes.

and the *tert*-butyl groups in **11** should have a similar stabilizing effect. On the other hand, Mezzetti reported that complex **19** with an architecture similar to **7c** forms a π-complex **20** upon loss of *p*-cymene as shown in Scheme 5.[18b,22] He also showed that phosphoramidites can act as two-, four-, six-, or eight-electron donors.[22] Arene loss opens free coordination sites, which might initiate catalyst decomposition for the catalytic systems described herein. For complex **7c**, the open coordination site could temporarily be occupied by the phenyl group of the *N*-benzyl substituent as in **20** (Scheme 5). Such an arrangement could increase the life time of the catalytically active species from **7c** in solution, resulting in higher conversion rates and yields. The methyl groups on the phosphoramidite ligand in **7a** provide less protection than the *N*-benzyl groups in **7c**. This might result in faster catalyst decomposition for **7a**, lowering its performance.

Watanabe[15] and Dixneuf[16c] have suggested a mechanism for the reaction that involves an Ru(η^2-alkyne) intermediate (Scheme 6). The carboxylic acid adds to the triple bond and the resulting enol ester complex undergoes an intramolecular transesterification to provide the final product. This mechanism is consistent with the stereochemistry of our reactions. The lack of enantioselectivity might have different causes, one of which could be a high reaction temperature of 90 °C. However, assuming the mechanism depicted in Scheme 6, the C–O bond at the stereocenter would not be cleaved, resulting in racemic products from racemic starting materials as well as little racemization of enantiopure starting material. Accordingly, Dixneuf reported retention of configuration in his studies.[16c]



Scheme 6. Proposed mechanism for β-oxo ester formation.[15,16c]

Conclusions

In conclusion, this work shows for the first time that half-sandwich phosphoramidite complexes of ruthenium are catalytically active in the formation of β-oxo esters from aromatic and aliphatic primary, secondary and tertiary propargylic alcohols and aromatic and aliphatic carboxylic acids. The atom-economical process is catalyzed with good substrate generality, and both sterically congested substrates and carboxylic acids in equimolar amounts can be employed in the reaction. Exclusion of moisture or air is not necessary. The ligand structure has a profound impact on the catalytic activity of the phosphoramidite complexes. The transformation proceeds without racemization of a chiral propargylic alcohol, which is in accordance with the previously suggested mechanism for the reaction. Further investigations to better understand the reactivity and mechanism of the reaction are underway.

Experimental Section

General remarks and characterization data of the products can be found in the Supporting Information.

[(*R*)-BINOL(8H)-*N*,*N*-dibenzyl-phosphoramidite] (2b)

To a Schlenk flask containing triethylamine (0.25 mL, 1.9 mmol) and dibenzylamine (0.36 mL, 1.9 mmol), toluene (10 mL) was added followed by phosphorus trichloride (0.15 mL, 1.7 mmol), which upon addition, yielded a white smoke. The white slurry was heated to 70 °C for 12 h during which the color changed to yellow. After cooling to room temperature, triethylamine was added (0.5 mL, 3.58 mmol) followed by (*R*)-5,5′,6,6′,7,7′,8,8′-octahydro-bi-2-naphthol (**6**, 0.500 g, 1.70 mmol). Additional 4 mL toluene were added and the slurry stirred at room temperature for 24 h. Diethyl

ether (5 mL) was added and the slurry was filtered over silica on a 15M frit and the filtrate was dried under oil-pump vacuum, yielding a white solid. The solid was purified by flash filtration (1×4 in, silica) using CH_2Cl_2/hexanes 1:3 to pack/elute. The solvent was removed and the residue dried in high vacuum affording **2b** as a white foam; yield: 0.570 g (1.10 mmol, 65%).

"{$RuCl_2$(*p*-cymene)[(*R*)-BINOL-*N,N*-dimethyl-phosphoramidite]}" (7a)

To a Schlenk flask containing phosphoramidite **1a** (1.123 g, 3.125 mmol), CH_2Cl_2 (20 mL) was added followed by [$RuCl_2$(*p*-cymene)]$_2$ (0.990 g, 1.62 mmol) to obtain a dark red solution. The solution was allowed to stir under a nitrogen atmosphere at room temperature for 2.5 h, and then the solvent was removed under oil-pump vacuum, yielding a red solid. Isopropyl alcohol (5 mL) was added and the solid was collected by filtration over a medium frit (10–15M). It was then washed with isopropyl alcohol (2×1 mL) and dried under vacuum affording **7a** as a red solid; yield: 1.988 g (2.987 mmol, 96%).

"{$RuCl_2$(*p*-cymene)[(*R*)-BINOL-*N,N*-diisopropyl-phosphoramidite]}" (7b)

To a Schlenk flask containing **1b** (0.212 g, 0.510 mmol), CH_2Cl_2 (8 mL) was added followed by [$RuCl_2$(*p*-cymene)]$_2$ (0149 g, 0.243 mmol) and the solution turned dark red. The solution was allowed to stir under nitrogen for 18 h. Solvent was removed under oil-pump vacuum, yielding a red solid. The crude product was flash chromatographed (1×4.5 in, silica, CH_2Cl_2/diethyl ether, 49:1 v/v). Upon drying under oil-pump vacuum, **7b** was obtained as a red solid; yield: 0.232 g (0.326 mmol, 67%).

"{$RuCl_2$(*p*-cymene)[(*R*)-BINOL-*N,N*-dibenzyl-phosphoramidite]}" (7c)

To a Schlenk flask containing **1c** (0.250 g, 0.489 mmol), CH_2Cl_2 (5 mL) was added followed by [$RuCl_2$(*p*-cymene)]$_2$ (0.150 g, 0.245 mmol) and the solution turned dark red. The solution was allowed to stir under nitrogen for 18 h. Solvent was removed under oil-pump vacuum, yielding a red solid. The crude product was purified by flash filtration over 1×5 in, silica, using CH_2Cl_2/Et_2O 9:1 to pack/elute; the red band was collected. Upon drying under oil-pump vacuum, **7c** was obtained as a red solid; yield: 0.351 g (0.429 mmol, 88%).

"{$RuCl_2$(*p*-cymene)[(*rac*)-6,6′-dibromo-BINOL-*N,N*-dimethyl-phosphoramidite]}" (7d)

To a Schlenk flask containing **1d** (0.206 g, 0.398 mmol), CH_2Cl_2 (3 mL) was added followed by [$RuCl_2$(*p*-cymene)]$_2$ (0.111 g, 0.181 mmol) to obtain a dark red solution. The solution was allowed to stir under nitrogen atmosphere at room temperature for 2.5 h, and then the solvent was removed under oil-pump vacuum, yielding a red solid. Diethyl ether (2×2.5 mL) was added and the resulting slurry was stirred and the solvent decanted. The solid was then dried under vacuum affording **7d** as a red solid; yield: 0.198 g (2.99 mmol, 66%).

"{$RuCl_2$(*p*-cymene)[(*R*)-BINOL(8H)-*N,N*-dibenzyl-phosphoramidite]}" (8b)

To a Schlenk flask containing [$RuCl_2$(*p*-cymene)]$_2$ (0.144 g, 0.235 mmol), a solution of **2b** (0.245 g, 0.471 mmol) in CH_2Cl_2 (6 mL) was added. The resulting red solution was stirred at room temperature for 16 h after which the solvent was removed under high vacuum. Hexanes (5 mL) were added and the slurry filtered over Celite® (~1 cm). The solid was washed with hexanes (30 mL) and the eluent discarded. The product was then washed down using CH_2Cl_2/Et_2O 9:1 (25 mL) until the Celite® was no longer red. The solution was dried under high vacuum, affording **8b** as a red solid; yield: 0.333 g (0.403 mmol, 86%).

"(*R*)-BIPHEN-*N,N*-dimethyl-phosphoramidite" (10)

To a Schlenk flask containing (*R*)-5,5′,6,6′-tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diol ["(*R*)-BIPHEN″, **9**] (0.217 g, 0.613 mmol), toluene (6 mL) was added followed by hexamethylphosphorus triamide (0.14 mL, 0.77 mmol) and NH_4Cl (0.010 g). The clear solution was heated at 100 °C for 12 h under nitrogen atmosphere. Upon cooling the solvent was removed and the solid was dried under oil-pump vacuum. Diethyl ether (2 mL) was added to the white residue and the resulting suspension was cooled to −18 °C for 1 h and then filtered over a medium frit (10–15M). The solid was washed with cold diethyl ether (2×1 mL). The filtrate was concentrated under vacuum to 1 mL and stored at −18 °C for 1 h. The suspension was filtered over a medium frit again and both crops were dried under oil-pump vacuum to give **10** as a white solid; yield: 0.160 g (0.374 mmol, 61%).

"{$RuCl_2$(*p*-cymene)[(*R*)-BIPHEN-*N,N*-dimethyl-phosphoramidite]}" (11)

To a Schlenk flask containing **10** (0.145 g, 0.339 mmol), $ClCH_2CH_2Cl$ (5 mL) was added and the solid dissolved. [$RuCl_2$(*p*-cymene)]$_2$ (0.099 g, 0.162 mmol) was then added and the resulting red solution was refluxed under a nitrogen atmosphere for 2.5 h. The solvent was removed and the dark red solid was dried under oil-pump vacuum and then extracted with diethyl ether (3×2 mL). The solvent was removed from the extracts and the product was dried under oil-pump vacuum to give **11** as a purple solid; yield: 0.143 g (0.195 mmol, 60%).[19]

"{$RuCl_2(C_6Me_6)$[(*R*)-BINOL-*N,N*-diisopropyl-phosphoramidite]}" (12)

To a Schlenk flask containing **1b** (0.100 g, 0.241 mmol), CH_2Cl_2 (5 mL) was added followed by [$RuCl_2(C_6Me_6)$]$_2$ (0.080 g, 0.120 mmol) and the solution turned dark red-brown. The solution was refluxed under nitrogen for 6 h. Solvent was removed under oil-pump vacuum, yielding an orange solid. The crude product was washed with 2×4 mL dry Et_2O and the solvent decanted. Upon drying under oil-pump vacuum, **12** was obtained as an orange solid; yield: 0.140 g (0.187 mmol, 78%) in 95% spectroscopic purity.[19]

Typical Procedure for Catalytic Experiments

In a screw-capped vial, 2-phenyl-3-butyn-2-ol (**3e**, 0.100 g, 0.684 mmol) and benzoic acid (**4a**, 0.084 g, 0.688 mmol) were dissolved in cyclohexane (3 mL). The catalyst (**7c**) (5 mg, 0.007 mmol) was added and the sealed vial immersed in a heating mantle preheated to 90 °C. After 5 h all volatiles were removed from the sample and the residue was purified by flash chromatography (silica, CH_2Cl_2/cyclohexane, 2:1 v/v) to obtain the product **5m** as a yellow oil; yield: 0.146 g (0.544 mmol, 79%).

X-Ray Structure Determination for 7a

Preliminary examination and X-ray data collection were performed using a Bruker Kappa Apex II single crystal X-ray diffractometer equipped with an Oxford Cryostream LT device. Intensity data were collected by a combinations of ω and ø scans. Apex II, SAINT and SADABS software packages were used for data collection, integration and correction of systematic errors, respectively.[23a]

Crystal data and intensity data collection parameters are listed in Table S1 (Supporting Information). Structure solution and refinement were carried out using the SHELXTL-PLUS software package.[23b] The structure was solved by direct methods and refined successfully in the space group, $P2_12_12_1$. The non-hydrogen atoms were refined anisotropically to convergence. All hydrogen atoms were treated using appropriate riding model (AFIX m3). Tables of calculated and observed structure factors are available in electronic format.

CCDC 689545 contains the supplementary crystallographic data for compound **7a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information

Table S1 containing crystal data and structure refinement for complex **7a**, general remarks and characterization data for the ligands and metal complexes described in the Experimental Section, ^{1}H and ^{13}C NMR spectra and IR spectroscopic and mass spectrometry data of all compounds in Table 1 and Table 2, and GC traces for the experiment shown in Eq. (3) are available as Supporting Information.

Acknowledgements

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[19] Complex **11** contained small amounts ($<5\%$, ^{1}H NMR) of the ligand **10**; extensive work-up attempts were not undertaken due to the high cost of the starting material **9**. Complex **12** contained *ca.* 5 mol% starting material $[RuCl_2(C_6Me_6)]_2$, as assayed by ^{1}H NMR. Extensive purification attempts by recrystallization and extraction failed, and complex **12** decomposed during column chromatography.

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