Ruthenium-Catalyzed trans-Hydroalkynylation and trans-Chloroalkynylation of Internal Alkynes

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ABSTRACT: [Cp*RuCl]₄ catalyzes the addition of iPr₂SiC≡CX (X = H, Cl) across internal alkynes with formation of 1,3-enzyme or 1-chloro-1,3-enzyme derivatives, respectively; the reaction follows an unorthodox trans-addition mode. The well-balanced affinities of the different reaction partners to the ruthenium catalyst ensure that crossed addition prevails over homodimerization of the individual components, as can be deduced from spectroscopic and crystallographic data of various intermediates; this includes a dinuclear complex in which an internal alkyne bridges two [Cp*RuCl] fragments.

The addition of a terminal alkyne across an internal triple bond is a conceptually appealing yet highly challenging approach to 1,3-enynes (Scheme 1). For such a hydroalkynylation reaction to become useful, competing homodimerization, oligomerization, and/or cyclotrimerization of either alkynylation reaction partners to the ruthenium catalyst ensure that crossed addition prevails over homodimerization of the individual components, as can be deduced from spectroscopic and crystallographic data of various intermediates; this includes a dinuclear complex in which an internal alkyne bridges two [Cp*RuCl] fragments.

Scheme 1. Challenge of Crossed Hydro(chloro)alkynylation

The addition of a terminal alkyne across an internal triple bond is a conceptually appealing yet highly challenging approach to 1,3-enynes (Scheme 1).1,2 For such a hydroalkynylation reaction to become useful, competing homodimerization, oligomerization, and/or cyclotrimerization of either partner must be suppressed and regiocontrol be imposed when working with unsymmetrical substrates (R¹ ≠ R³). The stereoechemical course of the reaction is therefore usually less of an issue in that cis-hydroalkynylation is observed,1,2 except for special cases: a notable exception employs biased N-sulfonyl ynamides, which resulted in net trans-hydroalkynylation.1,2,3,4 Even more demanding are related halo-alkynylations.5 The fact that the C–X bond of the resulting haloenzyme product might react with the catalyst used for its preparation poses an additional challenge; unsurprisingly, perhaps, the few known examples uniformly follow a cis-addition mode.6

Outlined below are an efficient trans-hydroalkynylation of unbiased internal alkynes and the first trans-chloroalkynylation reactions ever. Since 1,3-enynes in general serve as valuable building blocks,1,2 the new entry is enabling. This is particularly true for chloroenynes of type A (X = Cl), as they comprise adjacent electrophilic and nucleophilic sites amenable to orthogonal activation. Their dual reactivity can be harnessed in small-molecule synthesis and material science alike: the benzannulation strategy leading to polysubstituted arenes by cycloisomerization/cross-coupling (see below)7,8 and the preparation of π-conjugated oligomers with valuable optoelectronic properties,9 are deemed representative.

Following up on our investigations into ruthenium-catalyzed trans-hydrogenation10,11 and trans-hydrometallation12–19 catalyzed by [Cp*RuCl]₄ or related complexes, we reasoned that the reactivity pattern manifested in these unorthodox transformations might be further extended.20 For their activated C–H bonds, terminal alkynes were deemed promising candidates; the desirable “crossed” addition mode seemed possible because [Cp*RuCl] readily forms heteroleptic complexes comprising two different π-ligands.5

To test this hypothesis, various terminal alkynes were screened (see the SI), but only trisopropylsilylacetylene (1a) gave good results (Scheme 2).23 In the presence of catalytic [Cp*RuCl]₄, 1a reacts with internal dialkylalkynes to form the corresponding trans-addition products; the Z:E ratios are generally excellent. The stereochemistry was assigned by NMR and confirmed for product 9 by X-ray diffraction (see the SI). As expected, the functional group tolerance is high, in that ketones, esters, unprotected alcohols, acetals, aryl and alkyl halides, as well as cyclopropyl rings, remain intact. Aromatic substrates, however, react less well, likely because [Cp*RuCl] tends to form kinetically stable π-arene adducts that may sequester the catalyst (cf. 6; for further examples, see the SI); this limitation has precedent in the trans-hydrometallation reactions cited above.10–20

Unsymmetrical substrates usually afford mixtures of regioisomers (see the SI), but propargyl alcohols of type 10 provide a handle to control the outcome (Table 1): [Cp*RuCl]₄ favors “proximal delivery” to give the α-trans...
addition product, whereas cationic \([\text{Cp}^*\text{Ru(}\text{MeCN})_3\text{]}\text{SbF}_6\) leads to the regio-complementary outcome, although the overall selectivity is lower. As previously shown for analogous trans-hydrometallations, proximal delivery is caused by interligand hydrogen bonding between the \([\text{Ru-Cl}]\) group and the propargylic \(-\text{OH}\) substituent.\(^{18,19}\) The selectivity can be further improved by using the bulkier complex \(12\) in combination with \(\text{nBu}_4\text{NCl}\),\(^{24}\) even though the reaction proceeds more slowly. This result holds the promise that more systematic ligand tuning will allow for further optimization.

At this point, however, the search for yet other substrates amenable to trans-addition was given priority. Gratifyingly, (chloroethyl)triisopropylsilane (1b) also reacts well, resulting in trans-chloroalkynylation of internal alkyne partners (Scheme 3);\(^{25,26}\) to the best of our knowledge, this transformation is unprecedented and the selectivity remarkably high. The stereochemical outcome was ascertained by NMR (see the SI). The structure of 21 in the solid state confirmed the assignment (Figure 1).\(^{27}\)

The scope is significantly broader than that of the trans-hydroalkynylation in that good results were obtained in many cases even for aromatic and/or unsymmetrical substrates (Scheme 4). This is particularly true for propynylated arenes, which gave excellent yields and notably high \(E/Z\)-ratios, independent of whether electron-withdrawing or -donating substituents were placed on the aromatic ring. Likewise, propynylated pyridine or thiophene reacted well despite the heteroatom donor sites. Tolane, in contrast, was the only alkyne investigated so far in which cis-chloroalkynylation was truly competitive (23, \(E/Z = 45:55\)). Collectively, these examples illustrate the scope and notable functional group compatibility of the reaction, which matches the experiences previously made with various other ruthenium-catalyzed trans-addition processes.\(^{20}\)

The trans-chloroalkynylation of 3-hexyne was also carried out on 12.2 mmol scale with a reduced catalyst loading of 1.25 mol%. While the yield of 13 remained unchanged (92%),\(^{28}\) the \(E/Z\)-ratio was slightly improved (\(\geq 95:5\) versus 93:7 at 2.5 mol % \([\text{Cp}^*\text{RuCl}_4]\)); this observation is consistent with the mechanistic insights outlined below. Likewise, chloroenyne

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**Scheme 2. trans-Hydroalkynylation**

3-hexyne + \([\text{Cp}^*\text{RuCl}_4\text{(2.5 mol%)}]\), 1,2-dichloroethane, 80°C, 83%, \(E/Z = 93:7\)

1a (1.2 equiv.)

**Scheme 3. trans-Chloroalkynylation of Symmetrical Alkynes**

3-hexyne + \([\text{Cp}^*\text{RuCl}_4\text{(cat.)}}\), 1,2-dichloroethane, 80°C

1b (1.2 equiv.)

**Table 1. Catalyst-Dependent Regioselectivity**

| Nr | Catalyst | \(R^1\) | \(R^2\) | Yield (%) |
|----|----------|--------|--------|-----------|
| 1  | \([\text{Cp}^*\text{Ru(}\text{MeCN})_3\text{]}\text{SbF}_6\) | Me, Me | 66 | 10:59:31 |
| 2  | \([\text{Cp}^*\text{Ru(}\text{MeCN})_3\text{]}\text{SbF}_6\) | Me, Me | 76 | 75:10:15 |
| 3  | \([\text{Cp}^*\text{RuMeCl}])\text{SbF}_6\) | Me, Me | 84 | 84:10:6 |
| 4  | \([\text{Cp}^*\text{RuMeCl}])\text{SbF}_6\) | Me, Me | 84 | 74:10:16 |
| 5  | \([\text{Cp}^*\text{RuMeCl}])\text{SbF}_6\) | Et, Me | 82 | 72:10:16 |
| 6  | \([\text{Cp}^*\text{RuCl}_4\text{(cat.)}}\) | Me, \(\text{C}_9\text{H}_{12}\) | 62 | 83:11:6 |
| 7  | \([\text{Cp}^*\text{RuCl}_4\text{(cat.)}}\) | H, Pr | 65 | 65:6:0 |

\(^{a}\)In the presence of \(\text{nBu}_4\text{NCl}\) (10 mol %). \(^{b}\)The remainder is the \(\alpha\)-cis isomer.
was formed on gram scale; after recrystallization, the material was almost isomerically pure.

The chloroalkenes thus formed are relevant in that they bring stereodefined tetrasubstituted alkenes into reach, as illustrated by the iron-catalyzed formation of the polyfunctionalyzed product 30 (Scheme 5).\textsuperscript{29} The π-acid-catalyzed cycloisomerization of 31 derived from 25c showcases a very different application: Catalytic PtCl\textsubscript{2} affords the corresponding naphthalene derivative 32, retaining a chloride substituent for further manipulation;\textsuperscript{30,31} its iron-catalyzed borylation with formation of 33 represents just one such possibility.\textsuperscript{32} The many other ways of engaging a halide into all sorts of cross-coupling bring innumerable arene derivatives into reach with substitution patterns that are difficult to make otherwise.\textsuperscript{33,34} Equally important is the fact that the concept underlying this new benzannulation is also applicable to the heterocyclic series, as illustrated by the formation of chlorobenzothiophene 37. Further flexibility is gained by the possibility of interchanging the order of cycloisomerization/cross-coupling, as demonstrated by the two sequences leading to 35. These enabling virtues are subject to further study.

The fact that the “crossed” addition prevails over homodimerization (oligomerization) of either reaction partner speaks for a well-orchestrated coordination chemistry, especially since neither substrate has to be used in large excess. To gain insights, we first studied the interaction of the individual components with the catalyst (Scheme 6). Addition of [Cp*RuCl]\textsubscript{4} (0.25 equiv) to 1a in CD\textsubscript{2}Cl\textsubscript{2} at −50 °C leads to a cherry-red solution containing some unbound 1a and a single new species. Based on the diagnostic deshielding of the alkyne C-atoms (135.7/137.5 ppm; compare: 85.9/94.8 ppm in 1a) and the “olefinic” character of the alkyne proton (\(\delta\textsubscript{H} = 8.64\text{ ppm};\) compare 2.43 ppm in 1a), this species can be safely assigned as the corresponding π-complex 38.\textsuperscript{18,19} Its structure in the solid state (Figure 2) shows the substantial elongation of the C\textsubscript{1}−C\textsubscript{2} (1.265(3) Å) bond, together with the notable bending of the alkyne away from linearity (H1−C1−C2 144.5(4)°; C1−C2−Si 153.0(2)°) as the result of substantial electron back-donation from the filled metal d-orbitals into the π*-orbitals of the bound alkyne.\textsuperscript{19} The silyl group is oriented toward the chlorine ligand, which is favorable on steric as well as electronic grounds: 36 attractive interligand interactions between a polarized [Ru-Cl] unit and a silyl substituent have previously been invoked to explain the outcome of various mechanistically different transformations.\textsuperscript{18,19,37} The fact that only a single molecule of 1a is coordinated to the 14-electron fragment [Cp*RuCl]\textsubscript{4} is of particular relevance, as it leaves a vacant site for uptake of the reaction partner as necessary for formation of 33.
crossed addition. It is here that the size of the TIPS group is thought to come into play: slim Me3SiC≡CH in lieu of 1a is rapidly consumed by homocyclodimerization and is therefore no suitable substrate for trans-hydroalkynylation. Although 1a will eventually also homodimerize upon warming, the reaction is slow enough to leave the desired crossed addition time to proceed.

Chloroalkyne 1b shows a similar coordination behavior, as indicated by the massive downfield shifts of the alkyne C-atoms (141.1/150.6 ppm; compare: 70.9/79.5 ppm in 1b). Complex 39 also comprises only one alkyne ligand (Figure 3), featuring the typical signs of partial rehybridization. When replacement of 3-hexyne by 1-bromo-4-(prop-1-yn-1-yl)-benzene was met with success. In the resulting dinuclear complex 43, one massively elongated alkyne (C2–C3 1.332(5) Å) and the two chlorine atoms bridge the two Ru centers (Figure 4).

With all individual complexes identified, a 1:1:1 mixture of [Cp*RuCl]₄, chloroalkyne 1b, and 3-hexyne was investigated with the hope of identifying the heteroleptic bis-alkyne complex resulting in crossed chloroalkynylation. When mixed at −50 °C in CD₂Cl₂, the hexyne-derived complexes 40 and 41 were the major species, whereas the chloroalkyne adduct 39 was minor. Upon gradual warming to room temperature, the speciation changes in that 40 and 41 disappear and 39 is the only complex left (product formation commences). Signs of a mixed complex have not be detected at any point. Re-cooling of the equilibrated sample to −50 °C does not restore the original product distribution. Therefore, we conclude that binding of 3-hexyne is kinetically favored, but the chloroalkyne complex 39 is thermodynamically more stable.

The finding that an ordinary alkyne can bind two catalyst fragments simultaneously raised the question as to whether complex 40 or the [2:1] adduct 41 accounts for product formation. Variable time normalization analysis proved that the formation of the trans-chloroalkynylation product (E)-13 is first-order in [Ru] (Figure 5, top), whereas the formation of the minor cis-isomer shows a second-order dependence (see SI Figure S28). The unexpected finding that the trans- and the cis-addition follow different rate laws readily explains why the E/Z-ratio depends on the catalyst concentration (Figure 6). In this context we reiterate the observation made during scale-up that lowering of the catalyst loading improved the selectivity to ≥95:5; for comparison, the stoichiometric control experiment furnished 13 with a poor E/Z-ratio of 64:36.

Furthermore, the consumption of 3-hexyne and the formation of the trans-addition product 13 show first-order dependence on the concentration of complex 39. Hence, 39 likely represents the resting state of the catalytic process before the turnover-limiting step (Figure 5, bottom).

Since a “loaded” complex carrying two different alkynes has not been observed experimentally, we are currently not in the position to rigorously exclude an outer-sphere process, in which only the chloroalkyne is activated by coordination to ruthenium and is then attacked by 3-hexyne. Although indirect...
evidence speaks for an inner-sphere mechanism,47 the final answer must await further study. In summary, we demonstrate herein that ruthenium-catalyzed alkyne trans-addition chemistry can be expanded beyond trans-hydrogenation and trans-hydrometalations. The ease with which \( iPr_3SiC\equiv CX \) (X = H, Cl) add across internal alkynes in a highly selective trans-mode is remarkable and suggests that further extensions of this unorthodox reactivity paradigm might be possible.48 This aspect is subject to ongoing studies in this laboratory.

Figure 5. Variable time normalization analysis of NMR data. Formation of (E)-13 shows first-order dependence in [Ru] (top) as well as in the chloroalkyne adduct 39 (bottom); in contrast, formation of (Z)-13 shows second-order dependence in [Ru] (cf. Figure S28).

Figure 6. E/Z-ratio of 13 as a function of catalyst loading.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c08582.

Experimental section including characterization data, NMR spectra of new compounds, and supporting X-ray crystallographic data (PDF)
X-ray crystallographic data for 9 (CIF)
X-ray crystallographic data for 21 (CIF)
X-ray crystallographic data for 38 (CIF)
X-ray crystallographic data for 39 (CIF)
X-ray crystallographic data for 43 (CIF)

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Notes
The authors declare no competing financial interest.

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(40) Again, the short contact between the TIPS group and the [Ru-Cl] unit in 39 speaks for an attractive interligand interaction: as for complex 38 (see ref 36), the Cl1⋯Si1 (3.45 Å) distance as well as the distances between Cl and the H-atoms directed toward it (3.04–3.13 Å) are notably short; in this case, however, the C–Si–C angles deviate only slightly from the ideal tetrahedral geometry (105.1, 110.1, 110.5°).

(41) Identified by comparison with an authentic sample; for details, see the SI.

(42) This composition was suggested by the integrals over the H NMR signals; at 20 °C, the monomeric and the dimeric complexes are in exchange on the NMR time scale.

(43) The closest analogue to 43 is a triruthenium cluster, in which trimethylsilylacetylene bridges two of the three metal atoms in a similar manner, serving as a 4e-donor ligand. See: Campion, B. K.; Heyn, R. H.; Tilley, T. D. Reactions of Alkynes with Coordinatively Unsaturated (η2-C5H5Me)Ru Derivatives. X-ray Crystal Structures of (η2-C5H5Me)ClRu(η2:η1-C5H5Me) and (η2-C5H5Me)ClRu(μ2:μ1-C5H5Me). *Organometallics* 1990, 9, 1106–1112.

(44) Another binuclear complex was observed, likely as a byproduct, in trans-additions to 1,3-diyne substrates: in this case, one of the Cp* rings was transformed into a fulvene by interligand hydride transfer. See: Mo, X.; Letort, A.; Rosca, D.-A.; Higashida, K.; Fürstner, A. Site-Selective trans-Hydrostannation of 1,3- and 1,1-Diynes: Application to the Total Synthesis of Typhonosides E and F, and a Fluorinated Cerebroside Analogue. *Chem. - Eur. J.* 2018, 24, 9667–9674.