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Direct chemoselective reduction of plant oils using silane catalysed by Rh(III) complexes at ambient temperature†

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We report here a rare example of direct and chemoselective catalytic reduction of various plant oils to unsaturated fatty alcohols and glycerol. The selective reduction process is achieved using 0.5 mol% of a rhodium complex and diphenylsilane at room temperature without using any solvent producing a mixture of unsaturated fatty alcohols in yields >90%. We also observed that the selectivity of the reduction process (C=C vs. ester) depends on the nature of silane.

Sustainability spotlight

As the world pledges to achieve Net Zero by 2050, the chemical industry faces the significant challenge of rapidly developing new sustainable methods to produce chemicals, fuels and materials from renewable feedstock. Plant oils are important renewable feedstock containing olefin and ester functional groups presenting opportunities for the production of valuable feedstock. We report here a new methodology to directly transform plant oils (olive, coconut, sesame, castor, sunflower oil) to unsaturated fatty alcohols using a rhodium catalyst and silane at ambient temperature without using any solvent. In industry, this process is achieved using two steps and harsh reaction conditions (e.g. 250–350 °C and 100–200 bar). This work addresses UN SDG 12 (Responsible Consumption and Production) and SDG 13 (Climate Action).

Introduction

Plant oils are important resources produced globally at the scale of 200 million metric tons annually, more than 15% of which is used as industrial feedstock for a range of products such as biodiesel, soap, detergents, lubricants, surfactants and cosmetics.¹ With the recent drive in the circular economy, the utilisation of plant oil feedstock to produce petrochemicals has become an attractive approach to divest from fossil oil. The presence of ester and alkene groups in plant oils offers substantial opportunities for chemical manipulation. Accordingly, the transformation of plant oils using several reactions such as reduction, hydrosilylation, epoxidation, metathesis, polymerisation and hydroformylation has been developed in the past.² Reduction of plant oils and their derivatives, such as fatty acids and their esters, has been a topic of interest for the past few decades. Metal catalysed hydrogenation of double bonds (partially or fully) produces hydrogenated vegetable oils of high interest in the food industry (Pathway A, Fig. 1).³ Further

hydrogenation in the presence of a metal catalyst leads to the deoxygenative reduction by the elimination of propane and water to form a long alkane chain also known as green diesel (Pathway B, Fig. 1).⁴

Another set of products obtained from vegetable oils are fatty alcohols which have a global market size of more than £5 million and have a wide range of applications ranging from industrial/domestic cleaning products to personal care products, food and nutrition additives, plasticisers, detergents and lubricants.⁵ Unsaturated fatty alcohols can have several advantages over saturated ones as they can have lower melting points, better solubility, and can undergo functional group transformation. They are used as lubricants, additives, and feedstock in agrochemicals.⁵ The industrial production of fatty alcohols from plant oils is carried out in two steps. First, the transesterification with methanol leads to the formation of fatty acid methyl ester (FAME) which is subsequently hydrogenated to form unsaturated fatty alcohol (Pathway C, Fig. 1). Several heterogeneous and homogeneous catalysts have been reported for the latter step.⁶ Commercially, heterogeneous catalysts involving Cu/Cr are used under harsh reaction conditions (250–350 °C and 100–200 bar).⁷

Direct reduction of plant oils or fatty acids to fatty alcohols is challenging and requires corrosion-resistant materials for the reactors, acid-resistant, and glycerol-tolerant catalysts, and harsh reaction conditions producing a large amount of

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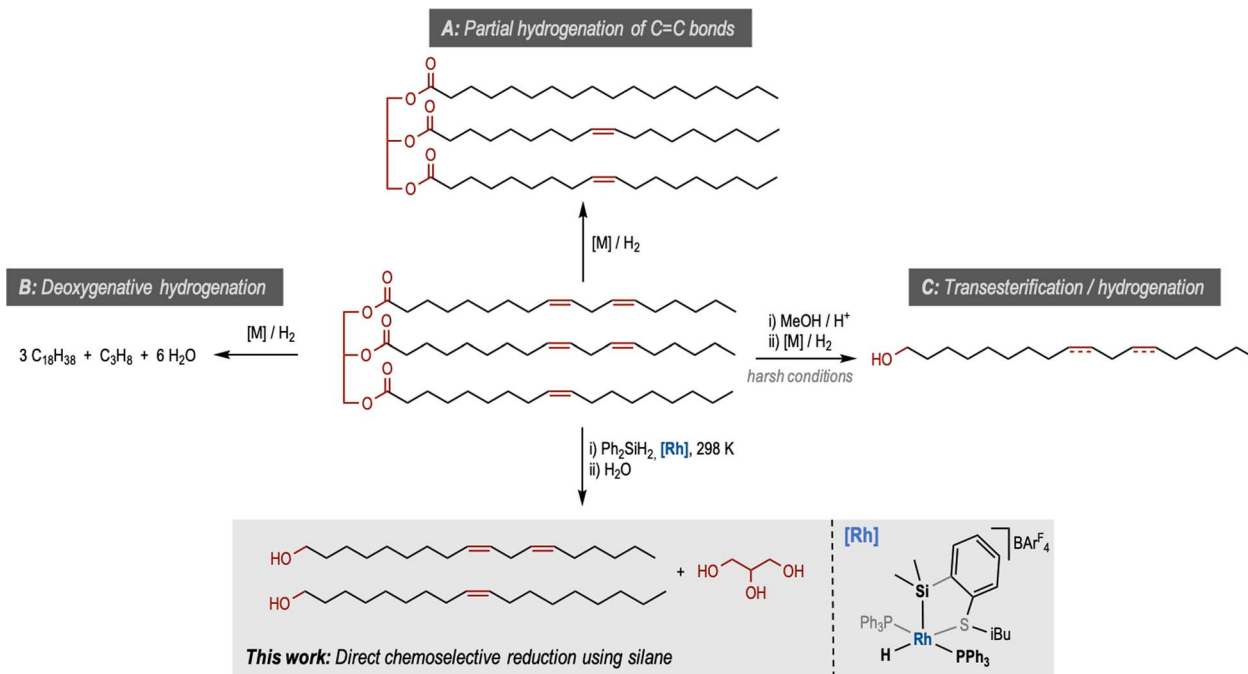


Fig. 1 Different pathways for the reduction of plant oils and the structure of the $[\text{Rh}(\text{SiS}^i\text{Bu})]$ complex used in this study.

hydrocarbon by-products.⁵ For example, a patent application claimed the demonstration of this process at 20 to 300 bar H_2 and 160 to 250 °C.⁸ Recently, Zhang and co-workers have reported the direct hydrogenation of Jatropha oil to fatty alcohol using a cobalt-based catalyst.⁹ However, the reaction conditions were harsh (190 °C, and 40 bar H_2) and the major product was the saturated alcohol. Elsevier and de Bruin also reported an example of the hydrogenation of a triglyceride to fatty alcohol using a cobalt-triphos-based homogeneous catalyst at milder conditions (100 °C, 80 bar H_2). However, also in this case the saturated alcohol was obtained as the product.¹⁰ To the best of our knowledge, the direct reduction of plant oils to unsaturated fatty alcohols is not known in peer-reviewed literature.

We hypothesise that the reason for the lack of selectivity in the direct reduction of plant oils to unsaturated fatty alcohols is the high temperatures required for the ester reduction. To circumvent this issue, we propose the use of a silane-based reducing agent for this process. Silanes have been used for the reduction of esters to produce ethers,¹¹ arenes (from aryl esters)¹² and aldehydes,¹³ using transition metal catalysts. The reduction of esters to alcohols using silanes has also been reported in the presence of rhodium,¹⁴ ruthenium,¹⁵ molybdenum,¹⁶ iron,¹⁷ titanium,¹⁸ cobalt¹⁹ and zinc.²⁰ Recently, silanes have also been used for the reductive depolymerisation of polyesters using iridium,²¹ molybdenum,²² and zinc-based²³ catalysts to make diols, and for the hydrosilylation of plant oils or fatty acid esters to make silylated esters with potential applications in lubricants.²⁴

We herein report a direct and selective reduction of fatty acid esters and plant oils at ambient temperature using silane as the reducing agent.

Results and discussion

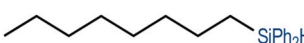
We have recently reported cationic unsaturated hydrido-silyl-rhodium(III) complexes bearing Si,S bidentate ligands as catalysts for the tandem isomerisation-hydrosilylation of alkenes to make linear silanes under mild reaction conditions (room temperature and solvent-free).²⁵ Our studies also demonstrated that ligands with larger steric bulk on the thioether facilitate this process, with the cationic rhodium(III) complex $\{\text{Rh}(\text{H})[\text{SiMe}_2(o\text{-C}_6\text{H}_4\text{Si}^i\text{Bu})](\text{PPh}_3)_2\}[\text{BARF}_4]$ ($[\text{Rh}(\text{SiS}^i\text{Bu})]$) being the most efficient one from the series.^{25b} We therefore decided to use this complex to study its activity and selectivity in the reduction of fatty acid esters and plant oils.

We started our investigation by screening the reactivity using simple model substrates (alkenes and esters). Initially, we studied the reactivity of a terminal (1-octene) and an internal (*cis*-2-octene) alkene towards silanes in the presence of $[\text{Rh}(\text{SiS}^i\text{Bu})]$ catalyst (0.5 mol%) at room temperature for 2 hours under neat conditions.^{25b} These have been used as standard reaction conditions in this study. As described in Table 1, using Et_3SiH , both substrates transformed into triethyl(octyl)silane with good yields (Table 1, entries 1 and 2).^{25b} However, when Ph_3SiH was used, no conversion towards hydrosilylated products was observed (Table 1, entries 3 and 4). Interestingly, when Ph_2SiH_2 was used, 1-octene was hydrosilylated to form octyldiphenylsilane in >99% yield (Table 1, entry 5) but no hydrosilylation of *cis*-2-octene was observed (Table 1, entry 6).

To analyse the ability of this system to catalyse the reduction of an ester, we used ethyl acetate as a model substrate. Aiming for a full reduction of the ester, we used two equivalents of the different hydrosilanes, under standard conditions. When tertiary silanes were used (Et_3SiH or Ph_3SiH), no conversion was



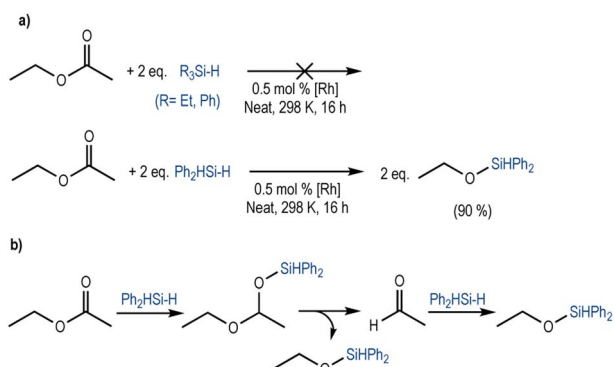
Table 1 Hydrosilylation of 1-octene and *cis*-2-octene with Et₃SiH, Ph₃SiH and Ph₂SiH₂ using [Rh(SiSⁱBu)] as a catalyst^a

Octene + R ₃ Si-H $\xrightarrow[\text{Neat, 298 K, 2 h}]{0.5 \text{ mol \% [Rh]}}$ 			
Entry	Silane	Alkene	Hydrosilylated product (yield) ^b
1	Et ₃ SiH	1-Octene	 (78%)
2 ^c	Et ₃ SiH	<i>cis</i> -2-Octene	 (85%)
3	Ph ₃ SiH	1-Octene	0%
4	Ph ₃ SiH	<i>cis</i> -2-Octene	0%
5	Ph ₂ SiH ₂	1-Octene	 (>99%)
6	Ph ₂ SiH ₂	<i>cis</i> -2-Octene	0%

^a Reaction conditions: alkene (0.25 mmol), R₃SiH (0.25 mmol), catalyst 0.5 mol%, solvent-free, 298 K, 2 h. ^b Yields were calculated based on ¹H NMR (CDCl₃) analysis using 1,2-dichloroethane (0.0625 mmol) as an internal standard. ^c Results from previous work.^{25b}

observed. Instead, Ph₂SiH₂ led to the formation of two equivalents of ethoxydiphenylsilane in 90% yield (Scheme 1a). Additionally, a trace amount of acetaldehyde was observed (Fig. S12, ESI†). We suggest that the reduction occurs in a stepwise manner; after the initial 1,2-hydrosilylation of the ester to form the silyl-protected acetal²⁶ (1-ethoxyethoxy)diphenylsilane, C–O bond cleavage results in a first equivalent of ethoxydiphenylsilane and acetaldehyde. The latter is further hydrosilylated to form a second equivalent of ethoxydiphenylsilane (Scheme 1b).²⁶

These preliminary studies on simple substrates suggest that the reactivity of different substrates (internal or terminal alkenes and esters) towards hydrosilylation and/or reduction is strongly dependent on the nature of the silane. Apparently,

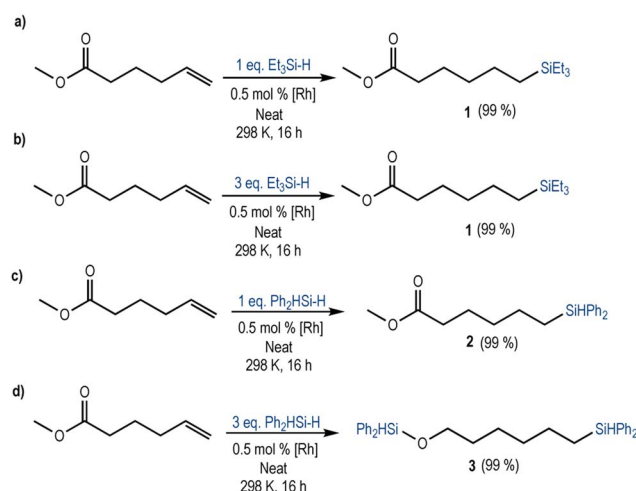


Scheme 1 (a) Reaction of ethyl acetate (0.25 mmol) with hydrosilanes (0.5 mmol) using a [Rh(SiSⁱBu)] complex (0.5 mol%) at 298 K (neat, 16 h). Yields were calculated based on ¹H NMR (CDCl₃) analysis using 1,2-dichloroethane (0.0625 mmol) as an internal standard. (b) Proposed reaction pathways for the reduction of ethyl acetate using Ph₂SiH₂.

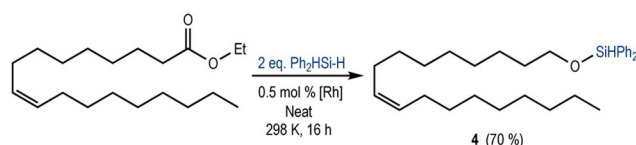
regardless of the silane used, anti-Markovnikov hydrosilylation of terminal alkenes always occurs. On the other hand for internal alkenes, the formation of the terminal alkyl silane by the tandem isomerisation-hydrosilylation reaction only occurs when using triethylsilane. Finally, ester reduction appears to occur only when diphenylsilane is used. Therefore, a judicious selection of the hydrosilane can be used to control the chemo-selectivity in more complex substrates containing both functional groups (*i.e.* vegetable oils), using [Rh(SiSⁱBu)] as a catalyst.

To test this hypothesis, we investigated the reactivity of a terminal alkene containing an ester functional group using different loadings of the most reactive silanes (Et₃SiH and Ph₂SiH₂). The reaction of methyl 5-hexenoate with Et₃SiH in the presence of 0.5 mol% [Rh(SiSⁱBu)] led to the complete and selective anti-Markovnikov hydrosilylation of the terminal alkene independently of the amount of hydrosilane used (Scheme 2a and b, Fig. S14 and S15 in the ESI†). Accordingly, the ¹H NMR spectrum of the crude reaction mixture showed the formation of compound 1 and unreacted Et₃SiH, when an excess (3 equivalents) of triethylsilane was used. This result is consistent with the reactivity pattern described before for the simpler substrates.

Interestingly, when Ph₂SiH₂ was used as a reducing agent, which was previously shown to be reactive to both terminal



Scheme 2 Reaction of methyl 5-hexenoate (0.25 mmol) with Et₃SiH (a, 0.25 mmol; b, 0.75 mmol) and Ph₂SiH₂ (c, 0.25 mmol; d, 0.75 mmol). Yields were calculated based on ¹H NMR (CDCl₃) analysis using 1,2-dichloroethane (0.0625 mmol) as an internal standard.



Scheme 3 Catalytic hydrosilylation of ethyl oleate (0.25 mmol) using 0.50 mmol of Ph₂SiH₂. Yields were calculated based on ¹H NMR (CDCl₃) analysis using 1,2-dichloroethane (0.065 mmol) as an internal standard.



Table 2 Reduction of plant oils catalysed by $[\text{Rh}(\text{SiS}^i\text{Bu})]^a$

$\text{Plant Oil} + 6 \text{ eq. Ph}_2\text{HSi-H} \xrightarrow[\text{Neat, 289 K, 16 h}]{0.5 \text{ mol \% [Rh]}} \text{Aldehydes} + \text{Silyl ethers}$			
Entry	Plant oil	Aldehydes (% yield)	Silyl ethers (% yield)
1	Olive	13	65
2	Coconut	28	51
3	Castor	22	65
4	Sesame	24	71
5	Sunflower	25	64

^a Reaction conditions: oil (0.1 mmol), Ph_2SiH_2 (0.2 mmol), catalyst 0.5 mol%, solvent-free, at room temperature. The amount of products (16 hours) is estimated based on ^1H NMR (CDCl_3) analysis using 0.05 mmol of 1,1,2,2-tetrachloroethane as an internal standard.

alkenes and esters, the main reaction product depended on the equivalents of hydrosilane employed. When 1 equivalent was used, the ^1H NMR spectrum of the crude reaction mixture showed the chemo- and regio-selective hydrosilylation of the terminal alkene (forming compound 2). The ester group remained unreacted (Scheme 2c, Fig. S16 in the ESI[†]). Instead, when 3 equivalents of diphenylsilane were used, compound 3 was obtained (Scheme 2d, Fig. S17 in the ESI[†]). 3 results from the hydrosilylation of the terminal alkene and the double hydrosilylation of the ester. Accordingly, an equimolecular amount of methoxydiphenylsilane and a small amount of the intermediate aldehyde (<1%) were also present in the ^1H NMR spectrum of the crude reaction mixture. These results suggest that, when Ph_2SiH_2 was used, the hydrosilylation occurred through a stepwise process: first the hydrosilylation of the terminal alkene followed by the reduction of the ester (Fig. S17 in the ESI[†]).

Increasing the complexity of the substrate, we studied the reactivity of the $[\text{Rh}(\text{SiS}^i\text{Bu})]$ towards the reduction of a fatty acid ester (ethyl oleate) containing an internal alkene. As

expected, using Ph_2SiH_2 (2 equivalents), the chemoselective reduction of ester towards the silyl ether 4 was observed in 70% yield (Scheme 3). The ^1H NMR spectrum of the crude reaction mixture (Fig. S19 in the ESI[†]) also showed the presence of a small amount of aldehyde (4%) and silyl-protected acetal (8%). These results suggest a mechanism analogous to that proposed for the reduction of ethyl acetate (Scheme 1b).

We decided to apply this catalytic protocol towards the chemoselective reduction of plant oils, as most of them contain internal C=C bonds and ester functional groups. We initially explored the use of olive oil as a substrate. Olive oil is mainly formed by triglyceride esters of linoleic, palmitic and oleic acid, the latter being the most abundant one. Olive oil was reacted with 6 equivalents of Ph_2SiH_2 under standard conditions. Interestingly, the ^1H NMR spectra of the reaction crude after 16 h showed ~78% conversion of olive oil to a mixture of aldehydes (~13%), and silyl ethers (~65%) originating from the three triglyceride chains (Table 2, entry 1; Fig. S21 in the ESI[†]). As expected, the C=C bond was found to be unreacted and the selectivity towards silyl ether was found to be 100%. When the reaction time was extended to 72 h, the ^1H NMR spectrum of the crude reaction mixture in CDCl_3 showed an almost complete consumption of the olive oil, and the formation of the corresponding silyl ethers in quantitative yields (Fig. 2 and S22 in the ESI[†]). Hydrolysis of these silyl ethers under basic conditions resulted in the formation of the desired fatty alcohols as well as glycerol in quantitative yields (Fig. 2, S23 and S24 in the ESI[†]).

This methodology was extended to the reduction of other plant oils (castor, sesame, and sunflower oil) including an unsaturated plant oil (coconut oil). The results obtained are presented in Table 2. Interestingly, in all the cases good conversions were achieved in 16 h, producing the corresponding silyl ethers as major products (Fig. S26, S28, S30 and S32 in the ESI[†]). An attempt to reuse the catalyst after reduction of olive oil for 24 h as per the conditions described in Table 2, entry 1 was not successful. The reaction using the recovered catalyst did not lead to the production of any fatty alcohol (see ESI, Section 7[†]).

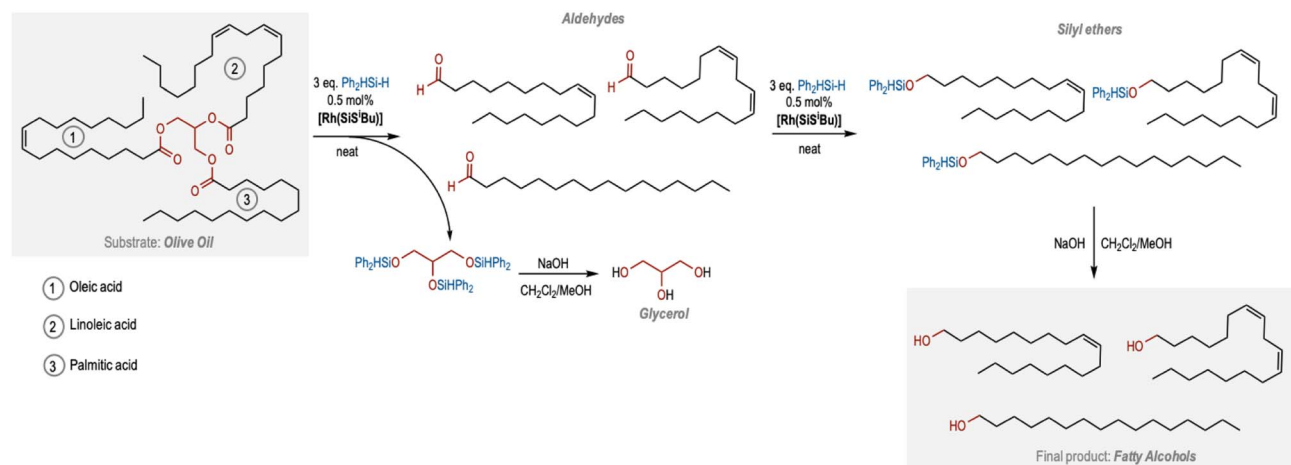


Fig. 2 Proposed pathway to produce fatty alcohols from plant oils.



Based on these studies, we have outlined a pathway to produce unsaturated fatty alcohols from plant oils (Fig. 2). We suggest that the three equivalents of silanes first cleave the triglyceride esters to produce three aldehyde molecules derived from the corresponding fatty acid esters along with the silyl ether of glycerol that upon hydrolysis leads to the formation of glycerol. The three saturated/unsaturated aldehydes undergo the second C=O reduction to form the three silyl ether chains that upon hydrolysis lead to the formation of fatty alcohols (Fig. 2). Remarkably, the internal fatty acid unsaturations remain intact throughout the process.

Moreover, we speculate that both the steric and electronic factors of silanes are important in the selectivity of the reaction. A detailed study to elucidate a catalytic cycle involving organo-metallic intermediates is currently ongoing.

Conclusion

In conclusion, we report here the effect of silanes (nature and amount) on the selectivity of reduction of esters and C=C bonds. For example, (a) triethylsilane performs hydrosilylation of both terminal and internal alkenes but doesn't reduce an ester group, (b) triphenylsilane is unreactive towards both alkenes (terminal or internal) and esters whereas (c) diphenylsilane reduces an ester to alcohol and performs hydrosilylation of a terminal alkene but not of an internal alkene. We have utilised this reactivity to demonstrate a rare example of the direct and chemoselective reduction of plant oils to unsaturated fatty alcohols under mild reaction conditions (298 K under neat conditions). This was achieved using 0.5 mol% rhodium catalyst and Ph₂SiH₂ (6 equivalents relative to plant oil, two for the reduction of each carbonyl bond).

Data availability

The research data supporting this publication can be accessed at <https://doi.org/10.17630/17b8990a-2901-4d90-aa94-6786412a3c21>.

Conflicts of interest

There are no conflicts to declare.

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