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Rhodium-Catalyzed 1,1-Hydroacylation of Thioacyl Carbenes with Alkynyl Aldehydes and Subsequent Cyclization

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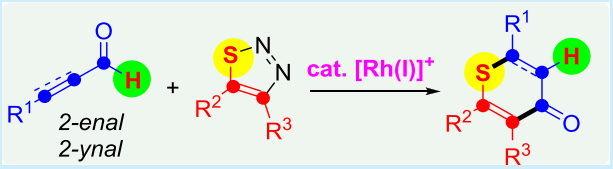
Supporting Information

ABSTRACT: A rhodium-catalyzed 1,1-hydroacylation of thioacyl carbenes with alkynyl and alkenyl aldehydes and subsequent 6-*endo*-trig/dig cyclization are realized, giving structurally diverse 4*H*-thiopyran-4-ones and 2,3-dihydro-4*H*-thiopyran-4-ones in moderate to good yields. The oxidative addition of Rh(I) to aldehydes is proposed to be the turnover-limiting step. Manipulations of estrones demonstrate the applications of our formal (3 + 3) transannulations in the structural modifications of natural products.



In 1965, Tsuji and co-workers reported the reductive decarbonylation of aldehydes with stoichiometric Wilkinson's catalyst.[1] The mechanism involved the formation of acyl rhodium hydrides as key intermediates via oxidative addition of the formyl C–H bond (Scheme 1a, i). Subsequently, in 1972, the interception of acyl rhodium hydrides was first realized by Sakai's group in an intramolecular mode, converting 4-alkenals into cyclopentanones.[2] Since then, transition-metal-catalyzed hydroacylation with aldehydes has become an important and intriguing concept, and many significant advances,[3−5] especially in the field of asymmetric catalysis,[4,5] have been reported. Nowadays, transition-metal (Rh,[3,4,5b,c] Co,[3c,e,f,h] Ir,[3c,e,f] Ni,[3e,f,5a] and Ru[3e,f,h]) catalyzed inter- and intramolecular hydroacylations of alkenes,[3,4] allenes,[3e] alkynes,[3,4] aldehydes,[5a] and ketones[4a,5b,c] are regarded as efficient, powerful, and atom-economic methods to synthesize ketones, enones, and esters (Scheme 1a, ii–iv). Despite these elegant advances, it is still of great importance to explore new kinds of partners for hydroacylations with aldehydes.

Previous hydroacylation reactions occurred across an unsaturated C=X (X = C or O) double or C≡C triple bond (1,2-hydroacylation). Out of our cabene chemistry background,[6,7] we found that reports on hydroacylation at an unsaturated carbene center (1,1-hydroacylation) are quite rare, although it provides a novel access to carbon homologation (Scheme 1a, v). It must be noted that in 2016 Yao and Lin reported the annulation between salicylaldehydes and acyl carbenes, and a 1,1-hydroacylation was proposed in the mechanism (Scheme 1b).[8a] The 1,1-hydroacylation complements the Lewis-acid catalyzed Roskamp reaction of aldehydes with active diazo compounds,[9] but the chemistries of the two kinds of reactions are distinctly different. To achieve the 1,1-hydroacylation, the following problems should be taken care of. The acyl rhodium hydrides are very susceptible to reductive decarbonylation,[8a,10] and it seems challenging to intercept them with carbenes, especially without the assistance of chelating/directing groups. On the other hand, the direct reaction between carbene precursors and rhodium catalysts will lead to undesired side products. Thus, aldehydes and carbene precursors must be well-defined. Gratifyingly, after numerous trials (see Supporting Information), the 1,1-hydroacylation of thioacyl carbenes derived from 1,2,3-thiodiazoles (**2**)[11,12] with alkynyl aldehydes (**1**) occurred to deliver thioketones (**3**), which undergo 6-*endo*-dig cyclization to give formal (3 + 3) transannulation products 4*H*-thiopyran-4-ones (**4**) as important structural subunits in a number of useful compounds.[13] Similar reactions of alkenyl aldehydes also occur to deliver useful products.[14] In a proposed mechanism for the 1,1-hydroacylation, oxidative addition of Rh(I) into aldehydes (**1**) leads to rhodium hydrides (**A**),[3−5,15] which further decompose thiodiazoles (**2**) to give carbene complexes (**B**). Migratory insertion of the hydrido into carbenic center yields (**C**),[8b] and subsequent reductive elimination regenerates catalysts and delivers 1,1-hydroacylation products (**4**).

The optimization of reaction conditions was performed by using the reaction of 1,2,3-thiadiazole (**2a**) and 3-phenylpropiolaldehyde (**1a**) as the model (Table 1 and Table S1 in Supporting Information). Under standard conditions, the desired product **4aa** was isolated in 36% yield (entry 1). The structure of **4aa** was unambiguously confirmed by the X-ray crystallography of the sulfur-dioxidized product **O-4aa** (see Table 2 and Table S2 and Figure S2 in Supporting Information). Without ligands, no reaction occurred (entry 2). Further screening of other bidentate phosphine ligands showed that no one was better than DPPF, although DPPP rendered a 36% yield (entries 3–6). Monodentate phosphine ligands gave poor results (see Table S1 in Supporting Information). The addition of Ag(I) salts did not improve the yields (entries 7–14). However, the reaction mixture with $AgSbF_6$ seemed much cleaner, as indicated by TLC analysis.

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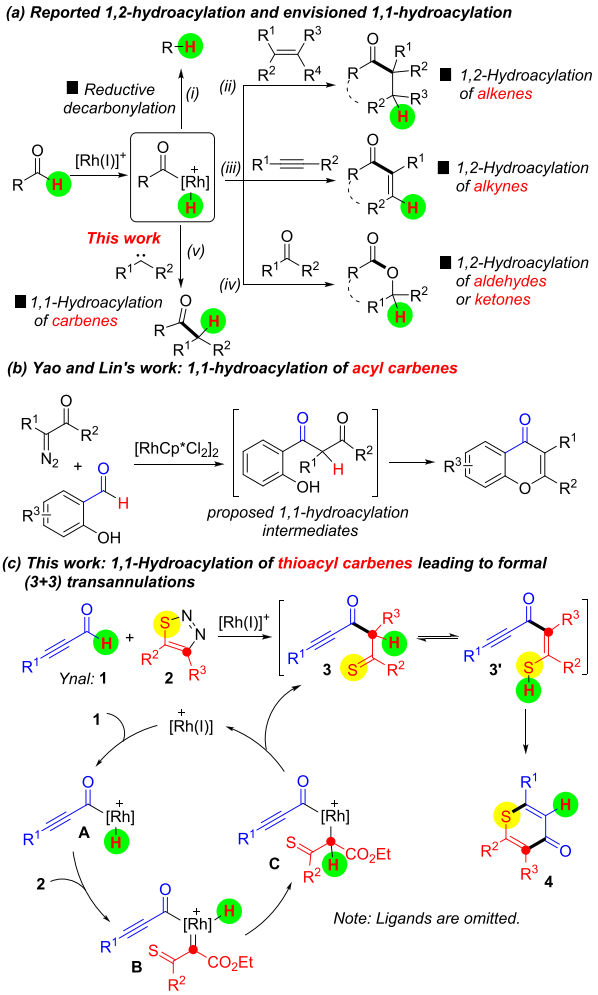
Scheme 1. 1,2- and 1,1-Hydroacylations and Our Work

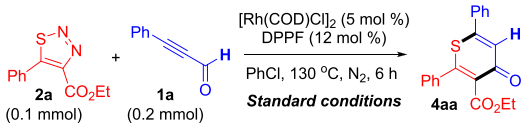


Although addition of AgOAc delivered the highest yield, the purification of **4aa** by column chromatography seemed tougher, due to the generation of unidentified impurities. With 10 mol % of $[Rh(COD)Cl]_2$, 24 mol % of DPPF, and 24 mol % of $AgSbF_6$, the reactions for 24 and 48 h gave 61% and 60% yields, respectively (entries 15 and 16). Thus, the conditions listed in entry 12 were selected as optimum.

With the optimal conditions, different alk-2-ynals were tested (Scheme 2). The reactions of a variety of arylpropiolaldehydes with electron donors (**4ab**, **4ac**, **4ad**, and **4ae**), halogens (**4af**, **4ag**, **4ah**, and **4ai**), electron acceptors (**4ak**, **4al**, and **4am**), fused, or hetero rings (**4an**, **4ao**) gave the desired products in satisfactory 45−70% yields, expect for 4-iodophenylpropiolaldehyde (**4aj**). Possibly, the aromatic $C(sp^2)$−I bond was not well tolerated. Hept-2-ynal and hex-2-ynal underwent the formal (3 + 3) transannulation to deliver 4*H*-thiopyran-4-ones **4ap** and **4aq** in 70% and 68% yields, respectively. 4,4-Dimethylpent-2-ynal (**4ar**) and 3-cyclopropylpropiolaldehyde (**4as**) gave moderate 39% and 40% yields, respectively, probably because of the large steric hindrance of *tert*-butyl in the former and the severe ring strain of cyclopropyl in the latter. Good yields were obtained when cyclopentyl and cyclohexylpropiolaldehydes were used (**4at** and **4au**).

Alkenyl aldehydes (**5**) were also viable substrates for the rhodium-catalyzed formal (3 + 3) transannulations, with lower

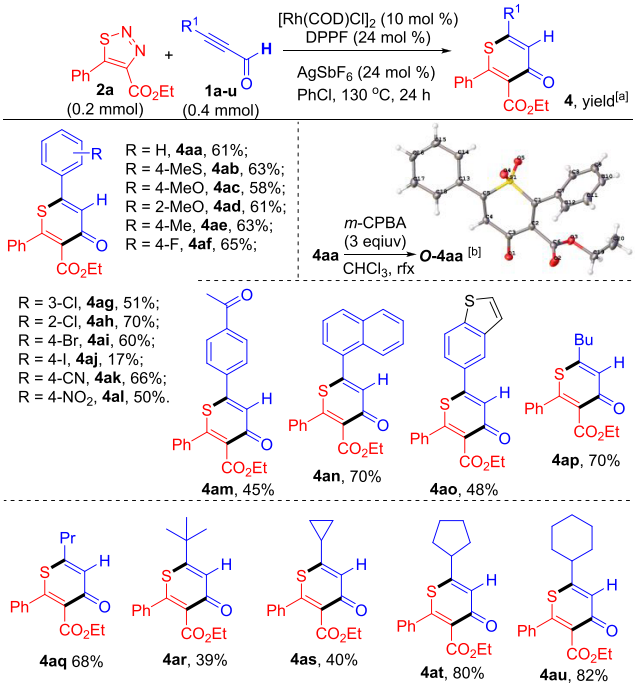
Table 1. Selected Optimization of the Reaction Conditions



entry	variation of standard conditions	yield (%)[a]
1	none	36
2	No DPPF	0
Variations of Ligands (instead of DPPF)		
3	DPPM	0
4	DPPE	10
5	DPPP	36
6	DPPPenta	30
Additions of Ag^+ Salts (12 mol)		
7	$AgNO_3$	5
8	AgOAc	42
9	Ag_2O	20
10	$AgSbF_6$	30
11	CF_3SO_3Ag	21
12	$AgBF_4$	trace
13	NaBARF	14
14	$AgNTf_2$	17
Variations of Time (10 mol % of $[Rh(COD)Cl]_2$, 24 mol % of DPPF, 24 mol % of $AgSbF_6$)		
15	*24 h*	*61[b] (40)[c]*
16	48 h	60[b]

[a]The yields were determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yields after column chromatography. [c]Yield of 1 mmol scale reaction (for details, see Supporting Information).

Scheme 2. Reactions of Different Alkynyl Aldehydes



[a]Isolated yields after column chromatography. [b]Oxidation of **4aa** was carried out on a 0.5 mmol scale for 4 h, and the X-ray crystallography was simplified for clarity (for details, see Supporting Information).

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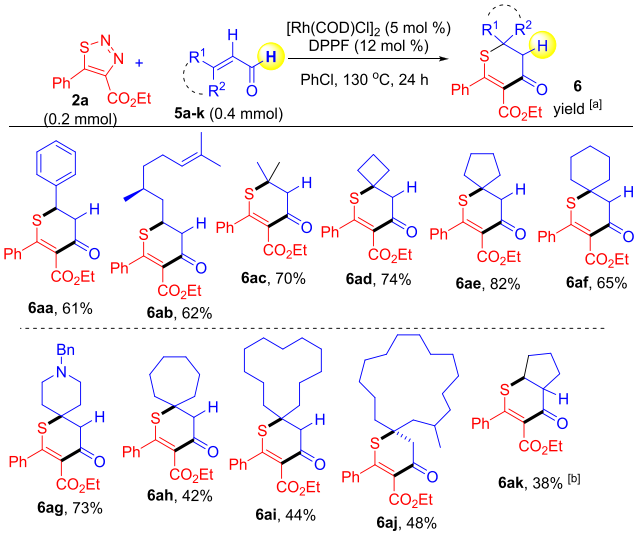
levels of catalysts and ligands in the absence of siver salts (Scheme 3). The reason for the high activity of alkenyl

Scheme 3. Reactions of Different Alkenyl Aldehydes

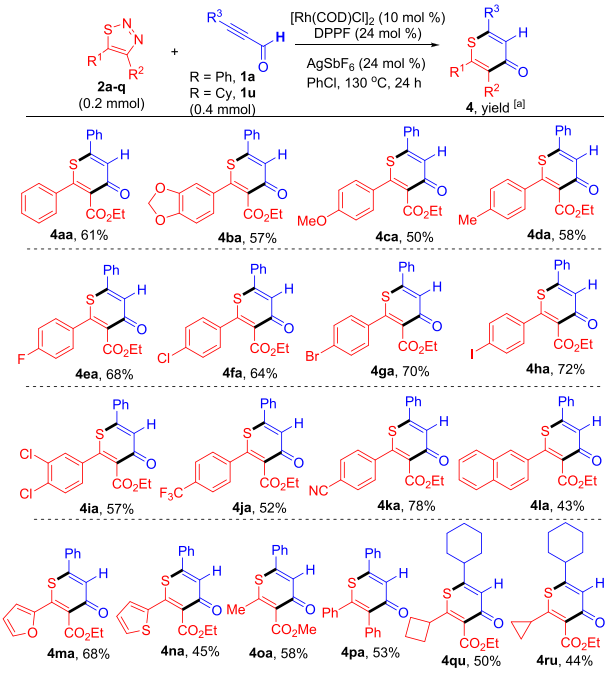


[a]Isolated yields after column chromatography. [b]0.6 mmol of **5j** was used.

aldehydes was obscure. Cinnamaldehyde (**5a**) and 2-citronylacrylaldehyde (**5b**) were transformed to 2,3-dihydro-4*H*-thiopyran-4-ones (**6aa**) and (**6ab**) in 61% and 62% yields, respectively. 3-Methylbut-2-enal (**5c**), with two *β*-methyls, was also susceptible to the transannulation, affording the desired product **6ac** in 70% yield. Next, we sought to synthesize spiro 2,3-dihydro-4*H*-thiopyran-4-ones. Spiro products (**6ad**, **6ae**, **6af**, and **6ag**) with 4-, 5-, and 6-membered rings were prepared in 65−82% yields, while those (**6ah**, **6ai**, and **6aj**) bearing 7-, 12-, and 15-membered rings were synthesized in 42−48% yields. Bridged bicyclic product **6ak** was accessed through the (3 + 3) transannulation in 38% yield.

On the other hand, different 1,2,3-thiadiazoles were tested in the reactions with 3-phenylpropiolaldehyde (**1a**) (Scheme 4). Thiadiazoles with electron-rich 5-aryls readily underwent the formal (3 + 3) transannulations, giving desired products **4ba**−**4da** in 50−58% yields. Halogens on the phenyl ring were well tolerated under the rhodium catalysis. The transannulations of thiadiazoles with halogen-substituted phenyls gave the corresponding 4*H*-thiopyran-4-ones (**4ea**−**4ia**) in 57−72% yields. Electron-deficient 4-trifluoromethylphenyl and 4-cyanophenylthiadiazoles transannulated with ynal **1a** to afford thiopyran-4-ones (**4ja**) and (**4ka**) in 52% and 78% yields, respectively. 2-Naphthalenyl, 2-furyl, and 2-thiophenyl thiopyran-4-ones (**4la**, **4ma**, and **4na**) were prepared in 43%, 68%, and 45% yields, respectively. In addition, 5-methylthiadiazole was converted to the desired product **4oa** in 58% yield. In the above synthesis, an electron-withdrawing ester group was located at the 4-position of thiadiazoles to ensure its decomposition into the corresponding carbenes when exposed to rhodium catalysts. But the ester group was not mandatory. For example, the reaction of 4,5-diphenyl-1,2,3-thiadiazole (**2p**) readily produced 2,3,6-triphenyl-4*H*-thiopyran-4-one (**4pa**) in 53% yield. The reaction of 5-cyclobutyl (**2q**) and 5-cyclopropyl thiadiazole (**2r**) with 3-phenylpropiolaldehyde (**1a**) afforded no desired products; however, their reactions

Scheme 4. Reactions of Different Thiodiazoles with 2-ynals

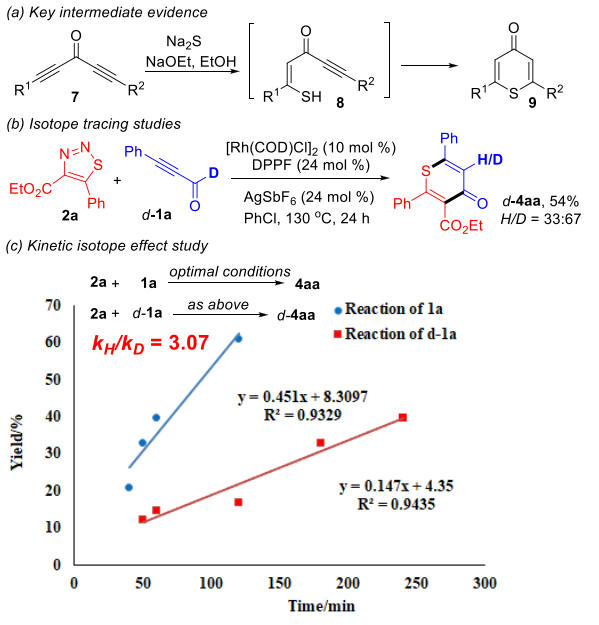


[a]Isolated yield after column chromatography.

with 3-cyclohexylpropiolaldehyde (**1u**) gave **4qu** and **4ru** in 50% and 44% yields, respectively. This means that, to guarantee the feasibility of the transannulations, the electronic properties of thiodiazoles and 2-ynals must be well matched.

Several reports have disclosed that treating dialkynyl ketones (**7**) with Na_2S in protic solvents led to 4*H*-thiopyran-4-ones (**9**), and the intermediates were enthiols (**8**) (Scheme 5a).[13] In the isotope tracing experiment, the reaction of 3-phenylpropiolaldehyde-*d* (*d*-**1a**) with thiadiazole (**2a**) under standard conditions gave *d*-**4aa** in 54% yield with 33:67 H/D ratio (Scheme 5b), revealing that the proton at the 5-position of

Scheme 5. Mechanistic Studies



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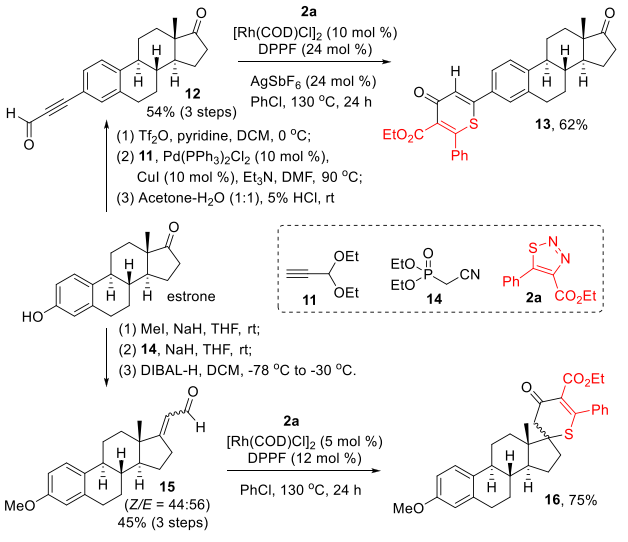
product primarily came from the formyl proton of 2-ynal. The incomplete D-incorporation indicated that an acid proton might be involved. Control experiments were also conducted. Decompostions of thiodiazole (**2a**)[11] and 2-ynal (**1a**) occurred, when they were individually treated with catalysts (see Schemes S11 and S12 in the Supporting Information). According to Gevorgyan's and Lee's reports, an alternative mechanism in which the decomposition of 1,2,3-thiodiazoles occurs prior to oxidative addition to 2-ynals is also possible. However, according to published results on Rh-catalyzed hydroacylations,[3−5,8a] we prefer a somewhat different one in which the oxidative addition to 2-ynal takes place first (Scheme 1c).

To gain more mechanistic details, we performed the kinetic isotope effect (KIE) study by the initial rate method using two parallel reactions of ynals **1a** and *d*-**1a** with thiodiazole **2a** (Scheme 5c and Scheme S15, Figures S3 and S4, Table S2 in the Supporting Information). A primary KIE of 3.07 was observed. In several cases of Rh(I)-catalyzed hydroacylations of ketones[16a] and alkenes[16b,c] in which KIEs of 2.4−2.9 were measured, the direct oxidative cleavage of aldehyde C−H bond with Rh(I) catalysts was also proposed to be turnover-limiting.[16] Assuming that oxidative addition is turnover-limiting, Madsen et al. calculated out a KIE of 2.85 for Rh-catalyzed aldehyde decarbonylation.[15] Our KIE result is consistent with those reported; thus, the mechanism proposed in Scheme 1c is more reasonsable, and the irreversible oxidative addition of Rh(I) into formyl C−H bond to form acyl rhodium hydride **A** is suggested to constitute the turnover-limiting step. Previous reports also revealed that KIEs of 1.4−1.7 for other hydroacylation reactions were indicative of migratory insertion or reductive elimination as a turnover-limiting step.[17]

Our 1,1-hydroacylation/cyclization sequence is useful in the structural modifications of natural products (Scheme 6).[18] For example, submission of estrone (**10**) to a sequence of triflation, Sonogashira coupling, and deketalization afforded alkynal (**12**), which was transformed to 4*H*-thiopyran-4-one (**13**) in 62% yield by the rhodium-catalyzed formal (3 + 3) transannulation with thiodiazole **2a**. O-Methylation of estrone, followed by Horner−Wadsworth−Emmons olefination with phosphonate (**14**) and reduction with DIBAL-H, delivered enal (**15**). Spiro 2,3-dihydro-4*H*-thiopyran-4-one (**16**) was easily constructed in 75% yield by our rhodium-catalyzed transannulation.

Scheme 6. Structural Modifications of Estrone



In summary, we have realized a rhodium-catalyzed 1,1-hydroacylation of thioacyl carbenes with alkynyl and alkenyl aldehydes to generate thioketone intermediates, which undergo an intramolecular cyclization to complete formal (3 + 3) transannulations. 1,2,3-Thiodiazoles are used as thioacyl carbene precursors. Structurally diverse 4*H*-thiopyran-4-ones and 2,3-dihydro-4*H*-thiopyran-4-ones are prepared in moderate to good yields from 2-enals and 2-ynals, respectively. In the mechanistic proposal, acylrhodium hydrides are key intermediates, and their formation via oxidative addition is the turnover-limiting step. The 1,1-hydroacylation/cyclization protocol is demonstrated to be useful in structural modifications of naturally occurring products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01003.

Experimental details, compound characterization, and spectra (PDF)

Accession Codes

CCDC 1895642 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Tsuji, J.; Ohno, K. Organic Syntheses by Means of Noble Metal Compounds XXI. Decarbonylation of Aldehydes using Rhodium Complex. *Tetrahedron Lett.* **1965**, *6*, 3969−3971.

(2) Sakai, K.; Ide, L.; Oda, O.; Nakamura, N. Synthetic Studies on Prostanoids 1 Synthesis of Methyl 9-Oxoprostanoate. *Tetrahedron Lett.* **1972**, *13*, 1287−1290.

(3) For selected reviews, see: (a) Guo, R.; Zhang, G. Recent Advances in Intermolecular Hydroacylation of Alkenes with Aldehydes through Rhodium Catalysis. *Synlett* **2018**, *29*, 1801−1806. (b) Kim, D.-S.; Park, W.-J.; Jun, C.-H. Metal-Organic

DOI: 10.1021/acs.orglett.9b01003
Org. Lett. XXXX, XXX, XXX−XXX

Cooperative Catalysis in C−H and C−C Bond Activation. *Chem. Rev.* **2017**, *117*, 8977−9015. (c) Ghosh, A.; Johnson, K. F.; Vickerman, K. L.; Walker, J. A.; Stanley, L. M. Recent Advances in Transition Metal-Catalysed Hydroacylation of Alkenes and Alkynes. *Org. Chem. Front.* **2016**, *3*, 639−644. (d) Oonishi, Y. Development of Novel Cyclizations via Rhodacycle Intermediate and its Application to Synthetic Organic Chemistry. *Chem. Pharm. Bull.* **2015**, *63*, 397−407. (e) Willis, M. C. Hydroacylation of Alkenes, Alkynes, and Allenes. *Comprehensive Organic Synthesis II.* **2014**, *4*, 961−983. (f) Leung, J. C.; Krische, M. J. Catalytic Intermolecular Hydroacylation of C−C π-Bonds in the Absence of Chelation Assistance. *Chem. Sci.* **2012**, *3*, 2202−2209. (g) Tanaka, K. Rhodium- Catalyzed Annulation Reactions of 2-Alkynylbenzaldehydes and 2-Vinylbenzaldehyde with Unsaturated Compounds. *Yuki Gosei Kagaku Kyokaishi* **2012**, *70*, 1134−1144. (h) Willis, M. C. Transition Metal Catalyzed Alkene and Alkyne Hydroacylation. *Chem. Rev.* **2010**, *110*, 725−748. (i) Jun, C.-H.; Jo, E.-A.; Park, J.-W. Intermolecular Hydroacylation by Transition-Metal Complexes. *Eur. J. Org. Chem.* **2007**, *2007*, 1869−1881.

(4) For selected reviews see: (a) Xua, Q.; You, S. *Asymmetric Hydroacylation Reactions in Asymmetric Functionalization of C−H Bonds*, RSC Catalysis Series No. 25.; You, S., Ed.; RSC: Cambridge, UK, 2015; Vol. *8*, pp358−383. (b) Murphy, S. K.; Dong, V. M. Enantioselective Hydroacylation of Olefins with Rhodium Catalysts. *Chem. Commun.* **2014**, *50*, 13645−13649. (c) González-Rodríguez, C.; Willis, M. C. Rhodium-Catalyzed Enantioselective Intermolecular Hydroacylation Reactions. *Pure Appl. Chem.* **2011**, *83*, 577−585. (d) Fu, G. C. Recent Advances in Rhodium(I)-Catalyzed Asymmetric Olefin Isomerization and Hydroacylation Reactions. *Modern Rhodium-Catalyzed Organic Reactions*; Evans, P. A., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2005; pp 79−91. (e) Tanaka, M.; Sakai, K.; Suemune, H. Asymmetric Rhodium-Catalyzed Intramolecular Hydroacylation for Five-Membered Ring Ketone Formation. *Curr. Org. Chem.* **2003**, *7*, 353−367.

(5) (a) Hoshimoto, Y.; Ohashi, M.; Ogoshi, S. Catalytic Transformation of Aldehydes with Nickel Complexes through η^2 Coordination and Oxidative Cyclization. *Acc. Chem. Res.* **2015**, *48*, 1746−1755. (b) Coulter, M. M.; Dong, V. M. Enantioselective Synthesis of Lactones via Rh-Catalyzed Ketone Hydroacylation. In *Asymmetric Synthesis: More Methods and Applications*, 1st ed.; Christmann, M., Bräse, St., Eds.; Wiley-VCH: Weinheim, Germany, 2012; pp 279−284. (c) Willis, M. C. Catalytic Intramolecular Ketone Hydroacylation: Enantioselective Synthesis of Phthalides. *Angew. Chem., Int. Ed.* **2010**, *49*, 6026−6027.

(6) (a) Yang, Z.; Xu, J. Synthesis of Benzo-γ-Sultams via the Rh-Catalyzed Aromatic C−H Functionalization of Diazosulfonamides. *Chem. Commun.* **2014**, *50*, 3616−3618. (b) Huang, P.; Yang, Z.; Xu, J. Specific Intramolecular Aromatic C-H Insertion of Diazosulfonamides. *Tetrahedron* **2017**, *73*, 3255−3265. (c) Liu, J.; Tu, J.; Yang, Z.; Pak, C.; Xu, J. Improved Buchner Reaction Selectivity in the Copper-Catalyzed Reactions of Ethyl 3-Arylmethylamino-2-Diazo-3-Oxopropanoates. *Tetrahedron* **2017**, *73*, 4616−4626.

(7) For selected recent reviews carbene transannulations, see: (a) Chattopadhyay, B.; Gevorgyan, V. Transition Metal Catalyzed Denitrogenative Transannulation: Converting Triazoles into Other Heterocyclic Systems. *Angew. Chem., Int. Ed.* **2012**, *51*, 862−872. (b) Shu, X.-Z.; Shu, D.; Schienebeck, C. M.; Tang, W. Rhodium-Catalyzed Acyloxy Migration of Propargylic Esters in Cycloadditions, Inspiration from the Recent "Gold Rush. *Chem. Soc. Rev.* **2012**, *41*, 7698−7711. (c) Gulevich, A. V.; Gevorgyan, V. Versatile Reactivity of Rhodium-Iminocarbenes Derived from N-Sulfonyl Triazoles. *Angew. Chem., Int. Ed.* **2013**, *52*, 1371−1373. (d) Xu, X.; Doyle, M. P. The [3 + 3]-Cycloaddition Alternative for Heterocycle Syntheses: Catalytically Generated Metalloenolcarbenes as Dipolar Adducts. *Acc. Chem. Res.* **2014**, *47*, 1396−1405. (e) Davies, H. M. L.; Alford, J. S. Reactions of Metallocarbenes Derived from N-sulfonyl-1,2,3-Triazoles. *Chem. Soc. Rev.* **2014**, *43*, 5151−5162. (f) Burtoloso, A. C. B.; Dias, R. M. P.; Bernardim, B. α,β-Unsaturated Diazoketones as Useful Platforms in the Synthesis of Nitrogen Heterocycles. *Acc. Chem. Res.* **2015**, *48*, 921−934. (g) Xia, Y.; Qiu, D.; Wang, J. Transition-Metal-Catalyzed Cross-Couplings through Carbene Migratory Insertion. *Chem. Rev.* **2017**, *117*, 13810−13889.

(8) (a) Sun, P.; Gao, S.; Yang, C.; Guo, S.; Lin, A.; Yao, H. Controllable Rh(III)-Catalyzed Annulation between Salicylaldehydes and Diazo Compounds: Divergent Synthesis of Chromones and Benzofurans. *Org. Lett.* **2016**, *18*, 6464−6467. For a 1,1-hydroacylation of carbenes via palladium-catalyzed carbonylation followed by acyl migratory insertion in the presence of aryl iodides, CO, and triethylsilane, see: (b) Zhang, Z.; Liu, Y.; Gong, M.; Zhao, X.; Zhang, Y.; Wang, J. Palladium-Catalyzed Carbonylation/Acyl Migratory Insertion Sequence. *Angew. Chem., Int. Ed.* **2010**, *49*, 1139−1142.

(9) For a review, see: (a) Liu, X.; Lin, L.; Feng, X. Chiral *N,N'*-Dioxides: New Ligands and Organocatalysts for Catalytic Asymmetric Reactions. *Acc. Chem. Res.* **2011**, *44*, 574−587. (b) Zhang, Y.; Wang, J. Recent Development of Reactions with α-Diazocarbonyl Compounds as Nucleophiles. *Chem. Commun.* **2009**, 5350−5361.

(10) (a) Allen, C. L.; Williams, J. M. J. Ruthenium-Catalyzed Alkene Synthesis by the Decarbonylative Coupling of Aldehydes with Alkynes. *Angew. Chem., Int. Ed.* **2010**, *49*, 1724−1725. (b) Dermenci, A.; Dong, G. B. Decarbonylative C−C Bond Forming Reactions Mediated by Transition Metals. *Sci. China: Chem.* **2013**, *56*, 685−701.

(11) (a) Kurandina, D.; Gevorgyan, V. Rhodium Thiavinyl Carbenes from 1,2,3-Thiadiazoles Enable Modular Synthesis of Multisubstituted Thiophenes. *Org. Lett.* **2016**, *18*, 1804−1807. (b) Seo, B.; Kim, Y. G.; Lee, P. H. Synthesis of Isothiazole via the Rhodium-Catalyzed Transannulation of 1,2,3-Thiadiazoles with Nitriles. *Org. Lett.* **2016**, *18*, 5050−5053. (c) Son, J.-Y.; Kim, J.; Han, S. H.; Kim, S. H.; Lee, P. H. Regioselective Synthesis of Dihydrothiophenes and Thiophenes via the Rhodium-Catalyzed Transannulation of 1,2,3-Thiadiazoles with Alkenes. *Org. Lett.* **2016**, *18*, 5408−5411. (d) Kim, J. F.; Lee, J.; Yun, H.; Baek, Y.; Lee, P. H. Rhodium-Catalyzed Intramolecular Transannulation Reaction of Alkynyl Thiadiazole Enabled 5,*n*-Fused Thiophenes. *J. Org. Chem.* **2017**, *82*, 1437−1447. (e) Seo, B.; Kim, H.; Kim, Y. G.; Baek, Y.; Um, K.; Lee, P. H. Synthesis of Bicyclic Isothiazoles through an Intramolecular Rhodium-Catalyzed Transannulation of Cyanothiadiazoles. *J. Org. Chem.* **2017**, *82*, 10574−10582.

(12) For our work on 1,2,3-thiodiazoles, see: (a) He, W.; Zhuang, J.; Yang, Z.; Xu, J. Sterically Controlled Diastereoselectivity in Thio-Staudinger Cycloadditions of Alkyl/Alkenyl/Aryl-Substituted Thioketenes. *Org. Biomol. Chem.* **2017**, *15*, 5541−5548. (b) He, W.; Zhuang, J.; Du, H.; Yang, Z.; Xu, J. Stereochemistry and Mechanistic Insights in the $[2^t + 2^i + 2^i]$ Annulations of Thioketenes and Imines. *Org. Biomol. Chem.* **2017**, *15*, 9424−9432.

(13) For some examples, see: (a) Chen, C. H.; Reynolds, G. A.; Van Allan, J. A. Synthesis of 4*H*-Thiopyran-4-Ones. *J. Org. Chem.* **1977**, *42*, 2777−2778. (b) Chen, C. H.; Reynolds, G. A. Synthesis of Unsymmetrical DELTA 4,4'-2,6-Diphenyl-4-(Thiopyranyl)-4*H*-Pyrans. *J. Org. Chem.* **1980**, *45*, 2449−2453. (c) Belfield, K. D.; Bondar, M. V.; Morales, A. R.; Frazer, A.; Mikhailov, I. A.; Przhonska, O. V. Photophysical Properties and Ultrafast Excited-State Dynamics of a New Two-Photon Absorbing Thiopyranyl Probe. *J. Phys. Chem. C* **2013**, *117*, 11941−11952.

(14) For some examples, see: (a) Rosiak, A.; Müller, R. M.; Christoffers, J. Synthesis of 2,3-Dihydrothiopyran-4-ones from 3-Oxo-1-pentene-4-ynes. *Monatsh. Chem.* **2007**, *138*, 13−26. (b) Pieroni, M.; Dimovska, M.; Brincat, J. P.; Sabatini, S.; Carosati, E.; Massari, S.; Kaatz, G. W.; Fravolini, A. From 6-Aminoquinolone Antibacterials to 6-Amino-7-thiopyranopyridinylquinolone Ethyl Esters as Inhibitors of Staphylococcus Aureus Multidrug Efflux Pumps. *J. Med. Chem.* **2010**, *53*, 4466−4480.

(15) For a mechanism for Rh-catalyzed decarbonylation, see: Fristrup, P.; Kreis, M.; Palmelund, A.; Norrby, P.-O.; Madsen, R. The Mechanism for the Rhodium-Catalyzed Decarbonylation of Aldehydes: A Combined Experimental and Theoretical Study. *J. Am. Chem. Soc.* **2008**, *130*, 5206−5215.

(16) (a) Kou, K. G. M.; Le, D. N.; Dong, V. M. Rh(I)-Catalyzed Intermolecular Hydroacylation: Enantioselective Cross-Coupling of

DOI: 10.1021/acs.orglett.9b01003
Org. Lett. XXXX, XXX, XXX−XXX

Aldehydes and Ketoamides. *J. Am. Chem. Soc.* **2014**, *136*, 9471−9476. (b) Murphy, S. K.; Bruch, A.; Dong, V. M. Mechanistic Insights into Hydroacylation with Non-Chelating Aldehydes. *Chem. Sci.* **2015**, *6*, 174−180. (c) Guo, R.; Zhang, G. Expedient Synthesis of 1,5-Diketones by Rhodium-Catalyzed Hydroacylation Enabled by C−C Bond Cleavage. *J. Am. Chem. Soc.* **2017**, *139*, 12891−12894.

(17) (a) Moxham, G. L.; Randell-Sly, H.; Brayshaw, S. K.; Weller, A. S.; Willis, M. C. Intermolecular Alkene and Alkyne Hydroacylation with *β*-S-Substituted Aldehydes: Mechanistic Insight into the Role of a Hemilabile P−O−P Ligand. *Chem. - Eur. J.* **2008**, *14*, 8383−8397. (b) Shen, Z.; Dornan, P. K.; Khan, H. A.; Woo, T. K.; Dong, V. M. Mechanistic Insights into the Rhodium-Catalyzed Intramolecular Ketone Hydroacylation. *J. Am. Chem. Soc.* **2009**, *131*, 1077−1091. (c) Chaplin, A. B.; Hooper, J. F.; Weller, A. S.; Willis, M. C. Intermolecular Hydroacylation: High Activity Rhodium Catalysts Containing Small-Bite-Angle Diphosphine Ligands. *J. Am. Chem. Soc.* **2012**, *134*, 4885−4897. (d) Pernik, I.; Hooper, J. F.; Chaplin, A. B.; Weller, A. S.; Willis, M. C. Exploring Small Bite-Angle Ligands for the Rhodium-Catalyzed Intermolecular Hydroacylation of *β*-S-Substituted Aldehydes with 1-Octene and 1-Octyne. *ACS Catal.* **2012**, *2*, 2779−2786. (e) Prades, A.; Fernández, M.; Pike, S. D.; Willis, M. C.; Weller, A. S. Well-Defined and Robust Rhodium Catalysts for the Hydroacylation of Terminal and Internal Alkenes. *Angew. Chem., Int. Ed.* **2015**, *54*, 8520−8524.

(18) For our recent work on steroidal structure modification, see: Li, J.; Tang, W.; Ren, D.; Xu, J.; Yang, Z. Iridium-Catalysed Highly Selective Reduction−Elimination of Steroidal 4-En-3-ones to 3,5-Dienes in Water. *Green Chem.* **2019**, *21*, 2088−2094.

DOI: 10.1021/acs.orglett.9b01003
Org. Lett. XXXX, XXX, XXX−XXX