

Carbonyl cross-metathesis via deoxygenative *gem*-di-metal catalysis

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Carbonyls and alkenes are versatile functional groups, whose reactivities are cornerstones of organic synthesis. The selective combination of two carbonyls to form an alkene – a carbonyl cross-metathesis – would be a valuable tool for their exchange. Yet, this important synthetic challenge remains unsolved. Although alkene/alkene and alkene/carbonyl cross-metathesis reactions are known, there is a lack of analogous methods for deoxygenative cross-coupling of two carbonyls. Here, we report a pair of strategies for the cross-metathesis of unbiased carbonyls, allowing an aldehyde to be chemo- and stereo-selectively combined with another aldehyde or ketone. These mild, catalytic methods are promoted by earth-abundant metal salts and enable rapid access to an unprecedentedly broad range of either *Z* or *E* alkenes by two distinct mechanisms – entailing transiently generated: (1) carbenes and ylides (via Fe catalysis) or (2) doubly nucleophilic *gem*-di-metallics (via Cr catalysis).

Given the synthetic importance of carbonyls and alkenes, mechanistically novel methods for their interchange are highly valued.¹ An important example is alkene metathesis, wherein two alkenes are structurally shuffled (**Fig. 1a**).² Although some methods enable cross-reactivity, an inherent challenge remains in differentiating the two alkenes to favor cross-selectivity over dimerization. Alkene-carbonyl metathesis provides another path by exchanging an alkene with a carbonyl, and valuable catalytic strategies exploit this inherent chemo-selectivity.^{3,6-8} Alternatively, the metathesis of carbonyls to form an alkene provides a mechanistically distinct means of differentiating a product alkene from its carbonyl precursors. Deoxygenative carbonyl dimerization has been developed using low-valent titanium (i.e., the McMurry coupling).⁹⁻¹¹ Nonetheless, cross-selectivity remains unsolved.^{4,5} Here, we present two, distinct strategies for cross-metathesis of carbonyls, entailing either: (1) carbene-to-ylide transfer or (2) *gem*-di-metalation. By these mechanistically divergent methods, an aldehyde may now be chemo- and stereo-selectively combined with another carbonyl to form either a *Z* or *E* alkene. This transform, an endothermic reverse of ozonolysis, is enabled by catalytic transformation of electrophilic carbonyls into either zwitterionic ylides or doubly nucleophilic *gem*-di-metals.

The challenge of enabling cross-selectivity in the McMurry coupling is tied to its mechanism (**Fig. 1b**).⁹ In it, Ti-mediated reduction of a carbonyl and ketyl radical coupling forms pinacol, which is subsequently deoxygenated as TiO₂ to yield an alkene. Since there is no mechanism for carbonyl selectivity in ketyl formation nor for the ensuing pinacol coupling, a statistical mixture of cross-coupling and dimerization products is inherent. The only exceptions are certain carbonyls (e.g., diaryl ketones, glyoxylates), whose double reductions to anion nucleophiles are thermodynamically biased.^{12,13} Other novel alternatives to the McMurry coupling are similarly limited to differentiation by at least one aryl carbonyl partner.¹⁴⁻¹⁷

Towards broader, chemoselective carbonyl activation, we recently developed an in situ acyl halide addition of aldehydes to form ketyl radicals by atom transfer catalysis.¹⁸ This enables

aldehyde cross-coupling with several other electrophiles.¹⁹⁻²³ However, carbonyl olefination also requires a mechanism for oxygen deletion^{24,25} (e.g. Ti to TiO₂, in the McMurry reaction). Thus, we developed a method to convert aldehydes to carbenes, wherein aldehydes are deoxygenated via transient α -benzoyl zinc intermediates (**Fig. 1b**).²⁶ Notably, we observed stereo-selective carbene dimerization to *E*-alkenes with a Co catalyst. To reverse polarity of these electrophilic carbenes and combine them with another carbonyl, we included sulfide co-catalysts to access sulfonium ylide reactivity.²⁷ Yet, this strategy affords epoxides rather than alkenes (i.e., only one carbonyl is deoxygenated).²⁶ Instead, to promote carbonyl metathesis, double deoxygenation of two carbonyls is necessary.

To enable synergistic deoxygenation of a second carbonyl, we have now developed two distinct catalytic strategies to access either a *Z* or *E* alkene stereoselectively (**Fig. 1c**). The first approach is inspired by a modified Wittig mechanism.¹ In this case, the ensuing deoxygenation is enabled by converting a transient carbene to a phosphonium ylide. This method complements pioneering approaches by Carreira, Lebel, and Aggarwal entailing carbene transfer from diazo reagents,²⁸⁻³⁰ by now permitting the use of enolizable alkyl aldehydes as carbene precursors. And for comparison with other modern ylide-based approaches, Silvi recently intercepted the Wittig reaction by decarboxylative radical addition of α -stabilized acids to vinyl phosphoniums,³¹ and Ott developed a P=P reagent to promote a double Wittig of aryl aldehydes.¹⁶ Yet, in our proposal, we expected this chemoselective conversion of aldehydes to ylides to now enable catalytic coupling of unbiased, alkyl aldehydes. Moreover, this base-free olefination is expected to be stereoselective – affording *Z*-alkenes, in contrast with diazo-mediated *E*-olefinations.²⁸⁻³⁰

To test our first proposal (**Table 1**), we converted unbiased, enolizable, alkyl aldehyde **A** to its stable α -benzyloxy bromide by in situ BzBr addition with a ZnBr₂ catalyst. This intermediate may be purified by column chromatography or

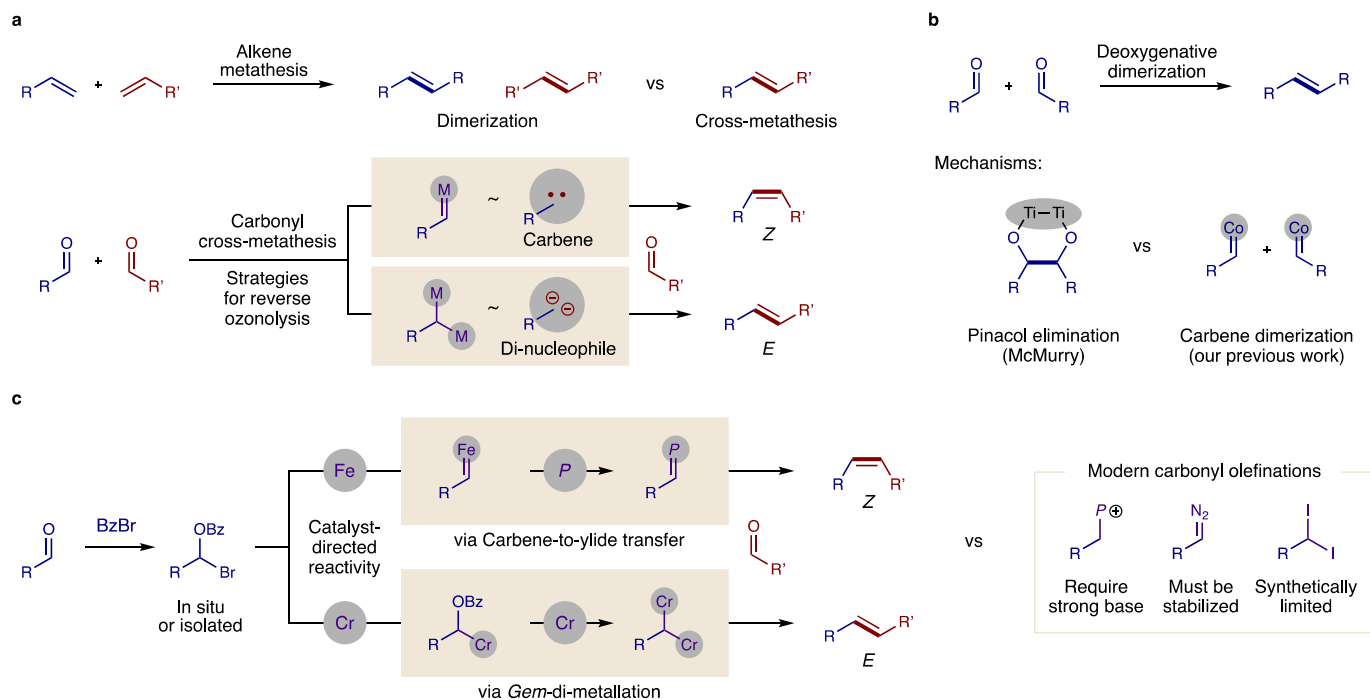
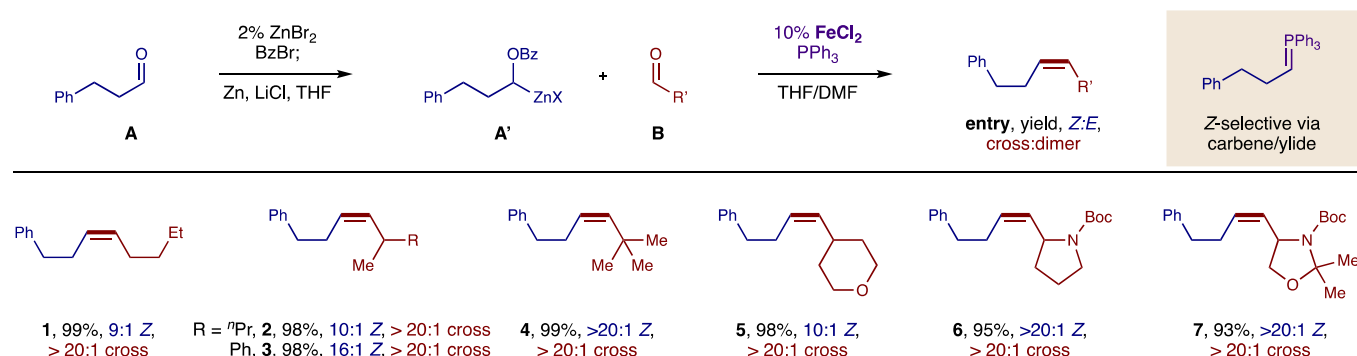


Fig. 1: Carbonyl metathesis strategies are rare and cross-selectivity mechanisms must be developed. **a**, Reactivity and selectivity challenges are shown. Cross-selective, alkene metathesis is rare, yet synthetically valuable. Carbonyl cross-metathesis (a reverse ozonolysis of an unsymmetric alkene) is unknown. **b**, State of the art methods for deoxygenative olefination of carbonyls only yield dimeric products. **c**, Two complementary strategies to access cross-selective reactivity are presented via either (1) Fe-catalyzed carbene/ylide or (2) Cr-catalyzed *gem*-di-metal mechanisms. Synthetic advantages of these approaches include mild (base-, diazo-, and dihalo- free) conditions that employ unbiased, enolizable aldehydes and yield robust, divergent (*Z* or *E*) stereoselectivity.

recrystallization, and stored cold indefinitely or may be used directly without purification. Upon its Zn-insertion to form alkyl zinc carbenoid, **A'** (mediated by LiCl), an iron catalyst (10% FeCl₂), phosphine (Ph₃P), and acceptor aldehyde **B** were added to the mixture and let stir at room temperature. In support of our mechanistic hypothesis, the product alkenes **1-7** are formed with complete cross-selectivity (>20:1 by ¹H NMR) since the phosphonium ylide is exclusively generated from aldehyde **A**, and the ylide does not dimerize, but only reacts with aldehyde **B**. The high efficiency and cross-selectivity observed also indicates that transfer of the iron carbene to Ph₃P

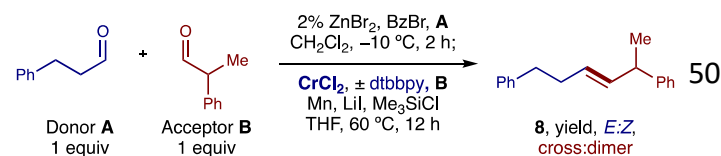
outpaces dimerization. To our delight, *Z*-alkene formation is also highly stereoselective (up to >20:1 with LiCl in THF/DMF) in contrast to diazo variants.²⁸⁻³⁰ The cross-coupling of two linear *n*-alkyl aldehydes (**1**) yields 9:1 *Z*:*E* selectivity, and trapping with α -branched (alkyl or aryl) aldehydes affords even higher stereo-selectivity (**2**, 10:1 *Z* and **3**, 16:1 *Z*). Further steric hindrance is also well-tolerated (and more stereoselective), as in the case of pivaldehyde (**4**, >20:1 *Z*) and heterocyclic aldehydes (**5-7**, >20:1 *Z*).

Table 1: Discovery and synthetic scope of an Fe-catalyzed, carbonyl cross-metathesis (*Z*-selective).



Reaction conditions: Aldehyde **A** (0.2 mmol, 1 equiv), ZnBr₂ (2 mol%), BzBr (1.2 equiv) in CH₂Cl₂ (0.6 mL) at -10 °C for 2 h; α -OBzBr of **A** (2 equiv), LiCl (2 equiv), Zn (3 equiv) in THF (1 mL) at r.t. for 8 h; carbenoid **A'** (2 equiv), FeCl₂ (10 mol%), Ph₃P (2 equiv), aldehyde **B** (1 equiv) in THF/DMF (2 mL/0.5 mL) at r.t. for 12 h. Isolated yields. Cross- and Stereo- selectivity measured by ¹H NMR. THF, tetrahydrofuran; DMF, *N,N*-dimethylformamide.

Table 2: Discovery of a Cr-catalyzed cross-metathesis of aldehydes (*E*-selective).



Entry	CrCl ₂	dtbbpy	Yield 8	<i>E</i> : <i>Z</i>	Cross
1	100%	—	90%	>20:1	>10:1
2	0%	10%	0%	—	—
3	25%	10%	79%	10:1	8:1
4	50%	10%	95%	>20:1	>10:1
5	100%	10%	91%	>20:1	>10:1

5 Reaction conditions: Aldehyde **A** (0.2 mmol, 1 equiv), ZnBr₂ (2 mol%), BzBr (1.2 equiv) in CH₂Cl₂ (0.2 mL) at -10 °C for 2 h; then add to aldehyde **B** (1 equiv), CrCl₂ (X mol%), dtbbpy (Y mol%), Mn (2 equiv), LiI (3 equiv), Me₃SiCl (2 equiv) in THF (2.5 mL) at 60 °C for 4–12 h. Isolated yields. Cross- and Stereo-selectivity measured by ¹H NMR. THF, tetrahydrofuran; dtbbpy, 4,4'-di-*t*-butyl-2,2'-bipyridyl.

We next sought to develop a parallel strategy to access *E*-alkenes via a distinct deoxygenation mechanism (Fig. 1c). Here, we were inspired by the Takai reaction, wherein *gem*-dimetals stereoselectively olefinate aldehydes.^{32,33} In this phosphine-free approach, *gem*-diiodides are converted to dizinc or dichromium intermediates by insertion of either Zn or Cr reductants.³⁴ Like the reagents developed by Nysted or Tebbe, metal oxide formation drives alkene generation and carbonyl deoxygenation in these cases.¹ Yet, advantages of the Cr-based method include high *E*-selectivity and broad reactivity with either aryl or alkyl aldehydes, including base-sensitive, enolizable ones. Still, the need for unstable *gem*-diiodides, or related precursors, remains a major synthetic limitation since harsh iodination conditions and the potential for elimination typically limit generality and accessibility.^{35,36} Motherwell and Boland have each extended this reaction to employ other carbonyl derivatives as the *gem*-di-metal precursor.^{37,38} However, neither approach is cross-selective, catalytic, or exhibits the wide synthetic scope of the Takai method. In contrast, we anticipated chemoselective in situ aldehyde preactivation and catalytic stereocontrol could enable a broadly useful carbonyl cross-metathesis.

To examine our proposed *E*-selective cross-metathesis (Table 2), aldehyde **A** was converted to its α-OBz bromide and added to aldehyde **B** and CrCl₂ in a 1:1:1 ratio. In this preliminary stoichiometric example, we were pleased to see complete cross-selectivity (>10:1) and stereoselectivity (>20:1) in the formation of alkene **8**. Toward a catalytic variant, we were inspired by how Fürstner rendered the Nozaki–Hiyama–Kishi reaction catalytic in Cr by incorporating a Mn reductant and chlorosilane.³⁹ Recent examples have also shown the value of bipyridyl ligands and coordinating solvents to enable reductive catalytic turnover of Cr.^{40–42} We investigated several ligands and reductants and found the combination of Mn, LiI, Me₃SiCl, and 4,4'-*di-t*-butyl-bipyridyl ligand (dtbbpy) to be most effective. Upon inclusion of 10% dtbbpy in THF, Cr catalyst loading may be reduced to 25% CrCl₂. Yet, while product **8** forms efficiently (79%) in this case, cross- (8:1) and stereo-

(10:1 *E*) selectivity are diminished for this dichromium-mediated reaction. Thus, 50% CrCl₂ was selected to enable broad, robust efficiency (>90% yield) and selectivity (>10:1 cross; >20:1 *E*:*Z*).

To evaluate the synthetic utility of this Cr-catalyzed carbonyl cross-metathesis (Fig. 2a), a diverse range of aldehydes were investigated as the donor (**A**) and acceptor (**B**) components. Both were shown to have broad scope and generality. For example, acceptor **B** may consist of linear (**9–12**) and branched (**13–20**) aldehydes, including isotopes of formaldehyde (**9**), *d*-acetaldehyde (**10**), and citronellal (**12**), as well as medically relevant, small rings and heterocycles (**14–18**). Large sterics are also well-tolerated (**19–20**). In each of these cases (**8**, **13–20**), high chemo- and stereo- selectivity is observed (>10:1 cross; >20:1 *E*:*Z*). Conversely, aryl and heteroaryl aldehydes are also efficient and cross-selective but lack stereoselectivity (**21–27**). Notably, ketones may also be employed as acceptors (**28–34**) with their efficiency illustrating the robustness of this dichromium reactivity.

To probe the mildness and unique tunability of the aldehyde activation, the donor component **A** of this cross-metathesis was also varied (Fig. 2b). These experiments show a similarly broad scope. For example, formaldehyde (**35**) may be employed, as well as aldehydes containing reactive functional groups, such as alkenes (**36**) or halides (**37**). Moreover, sterically hindered, α-branched and enolizable aldehydes are tolerated (**38–40**) – overcoming significant limitations of the Wittig reaction.¹ Complex aldehydes were also coupled to form a heteroatom-rich alkene (**41**) and showcase the synthetic utility of this mild, catalytic protocol (Fig. 2c). Finally, ring-closing metathesis was performed on a molecule bearing an aldehyde and ketone to generate α-pinene **42**.

To benchmark the unprecedented cross-selectivity of these two new strategies, we evaluated the metathesis of aldehydes using other current state-of-the-art methods. First, our previous Co-catalyzed carbene dimerization method (Fig. 3a) yields a 4:1 mixture of dimers (**43** and **44**) to cross-coupled alkene **8** since there is no mechanism for cross-selectivity. Surprisingly, the Ti-mediated McMurry coupling does not afford any alkene when two alkyl aldehydes (**A** and **C**) are employed (Fig. 3b). Yet, if a more easily reduced aryl aldehyde **D** is combined with aldehyde **A**, then a 1:1 mixture of **D–D** dimerization (**45**) and **A–D** cross-coupling (**21**) is observed. In this case, although there is a method for differentiating Ti-ketyl radical generation (favoring **D** > **A**), there is no selectivity mechanism for its cross-coupling.

Since we have already shown selective formation of these two products (**3**, **8**, **21**) with >10:1 cross-selectivity, we next sought to evaluate the rate of reactivity between aldehyde and ketone acceptors in our Cr-catalyzed method (Fig. 3c). In this case, when donor aldehyde **A** (1 equiv.) is subjected to two acceptors, aldehyde **C** and ketone **E** (1 equiv. each), the aldehyde partners are exclusively coupled with >20:1 aldehyde:ketone selectivity and >20:1 cross-selectivity. When aryl aldehyde **D** and ketone **F** (1 equiv. each) are employed as acceptors in this three-component competition, the same >20:1 aldehyde:ketone chemoselectivity is observed.

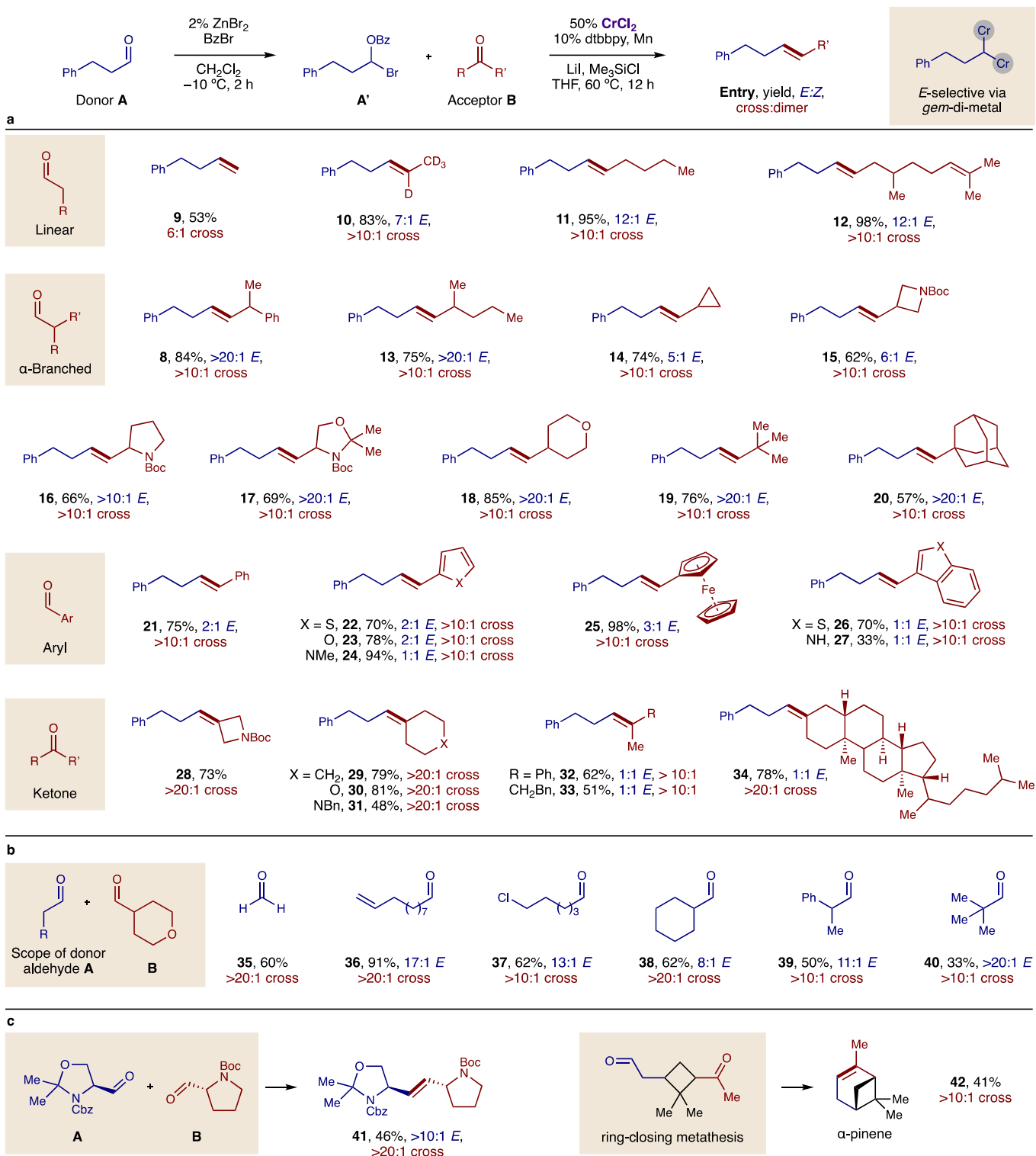


Fig. 2: The Cr-catalyzed carbonyl metathesis has wide scope with robust *E*- and cross-selectivity. **a**, Acceptor **B** may be a linear or branched, alkyl or aryl aldehyde, as well as a ketone. **b**, Donor **A** may be a wide range of aldehydes, including the 5 smallest formaldehyde or most hindered, pivaldehyde. **c**, Complex molecule applications show the utility of this olefination. See Table 2 for conditions.

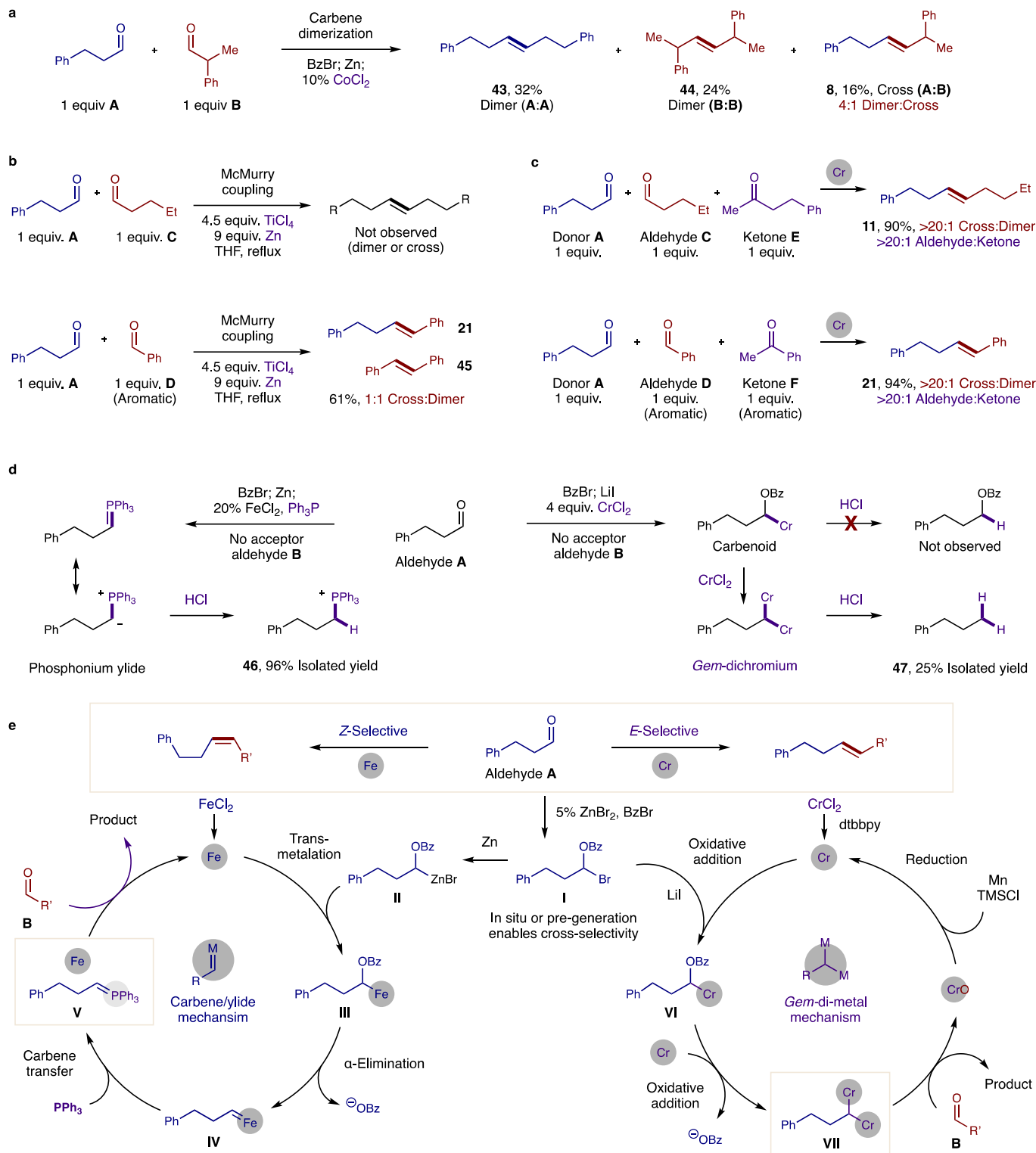


Fig. 3: Cross-metathesis: selectivity probes and mechanism. No cross-selectivity is observed via previous methods, including: **a**, Co-catalyzed carbene dimerization, or **b**, Ti-mediated McMurry coupling with either alkyl or aryl aldehyde acceptors. **c**, In contrast, Cr-catalysis affords cross- and chemo- selectivity, even in three-component competitions with aldehyde and ketone acceptors. **d**, In the absence of an aldehyde acceptor, key proposed intermediates were isolated to support each mechanism, including phosphonium **46** by ylide protonation and doubly reduced **47** by *gem*-dichromium protodemetalation. **e**, Proposed mechanisms for each strategy are shown. Cross-selectivity is ensured by transient formation of **I** from aldehyde **A**. *Z*-selectivity (left catalytic cycle) occurs by Zn-insertion of **I** to **II**, followed by transmetalation to an FeCl₂ catalyst. Upon α -elimination of **III** to alkyl carbene **IV**, carbene transfer to PPh₃ affords catalyst turnover and ylide **V**, which enables *Z*-selective olefination of **B**. In contrast, *E*-selectivity (right catalytic cycle) occurs by double Cr-insertions of **I** to **VI** to **VII**. This catalytically generated

gem-dichromium arises from two oxidative additions of a L-CrCl_2 catalyst to the α -oxy carbon of **I**, in a net deoxygenation of carbonyl **A**. Upon *E*-selective olefination of **B** by doubly nucleophilic organometal **VII**, CrO reduction permits catalyst turnover.

Next, we sought to support our mechanistic hypotheses by isolating key intermediates of each method (**Fig. 3d**). When aldehyde **A** is subjected to the *Z*-selective conditions in the absence of an acceptor aldehyde **B**, the phosphonium ylide is expected to be present stoichiometrically, even with 20% Fe catalyst. In fact, quenching with HCl yields alkyl phosphonium **46** in >95% isolated yield – validating the intermediacy of an ylide in this *Z*-selective reaction. In parallel, aldehyde **A** was subjected to the *E*-selective reaction, albeit with stoichiometric CrCl_2 to isolate a transient organometallic intermediate. If α -OBz-Cr-carbenoid (via only one Cr reduction) predominates, then HCl quenching should yield the reduced benzoate ester. However, this product was not observed. Instead, acidic quenching yields a fully deoxygenated product **47**, which results from the doubly reduced *gem*-dichromium intermediate. Since LiI accelerates this stoichiometric CrCl_2 reaction, we expect it also plays a role in activating the α -OBz species for reduction by Cr.

Given these observations, we propose the following two mechanisms (**Fig. 3e**). For the Fe-catalyzed carbene/ylide strategy (shown on the left), in situ activation of aldehyde **A** by BzBr (with ZnBr_2 catalyst) yields α -OBz bromide **I**. Next, Zn insertion of **I** affords carbenoid **II**. Transmetalation with the Fe catalyst then yields α -OBz organoiron **III**, which may rapidly α -eliminate the OBz anion to generate Fe-carbene **IV**. Upon carbene transfer to Ph_3P , phosphonium ylide **V** is formed (as observed by its protonated analog **46**), which can chemoselectively combine with aldehyde **B** to form *Z*-alkene while recycling the Fe catalyst. Conversely, in the *gem*-di-metal, Cr-catalyzed mechanism (shown on right), α -OBz bromide **I** may be directly and chemoselectively reduced by Cr(II) to Cr-carbenoid **VI** – accelerated by LiI, and in the presence of acceptor aldehyde **B**. A second Cr-mediated reduction yields the key *gem*-dichromium **VII**, which enables deoxygenative olefination of aldehyde **B** to afford the *E*-alkene and a chromium oxide. By combination of Mn, LiI, and TMSCl , this CrO_n is reduced back to Cr(II) to turn over the Cr catalytic cycle.

In conclusion, two catalytic methods have been developed for the chemo- and stereo- selective cross-metathesis of carbonyls. These deoxygenative strategies enable the reverse of modern ozonolysis reactions^{43,44} by combining two carbonyls to form an alkene – a valuable addition to the synthetic toolkit.

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Author contributions.

L.Z. and D.A.N. designed these strategies and wrote the manuscript. L.Z. performed all experiments and analysis.

Competing interests.

The authors declare no competing interests.

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Methods.

Cr-catalyzed cross-metathesis (E-selective): To ZnBr_2 (5 mol%) in a dry vial, was added CH_2Cl_2 (0.2 mL) and BzBr (1.2 equiv.). Next, aldehyde **A** (0.2 mmol, 1 equiv.) was added slowly and stirred at -10°C for 2 h, then purified by chromatography or recrystallization, or used crude. Separately, to a dry vial of CrCl_2 (50 mol%), dtbbpy (10 mol%), Mn (2 equiv.), LiI (3 equiv.), Me_3SiCl (2 equiv.), THF (1 mL), and a stir bar, was added aldehyde **B** (1 equiv.). The aldehyde **A** mixture was then added with THF (1.5 mL), stirred at 60°C for 4–12 h, then quenched and purified by chromatography to afford the E-alkene product.

Fe-catalyzed cross-metathesis (Z-selective): To ZnBr_2 (2 mol%) in a dry vial, was added CH_2Cl_2 (0.6 mL) and BzBr (1.2 equiv.). Aldehyde **A** (0.2 mmol, 1 equiv.) was added slowly and stirred at -10°C for 2 h, then purified by chromatography. Next, this α -OBz bromide (2 equiv.) in THF (1 mL) was slowly added to a dry vial of LiCl (2 equiv.) and Zn dust (3 equiv.), then stirred at room temperature for 8 h. The filtrate of this alkyl zinc carbenoid solution was then transferred to FeCl_2 (10 mol%), Ph_3P (2 equiv.), aldehyde (1 equiv.), THF/DMF (2 mL/0.5 mL), and then stirred at room temperature for 12 h. Purification by chromatography affords the Z-alkene product.

Data availability.

The data supporting the findings of this study are included in the Supplementary Information.