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Hydroxymethylation beyond Carbonylation: Enantioselective Iridium-Catalyzed Reductive Coupling of Formaldehyde with Allylic Acetates via Enantiotopic π-Facial Discrimination

Victoria J. Garza and Michael J. Krische*

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, United States

Supporting Information

ABSTRACT: Chiral iridium complexes modified by SEGPHOS catalyze the 2-propanol-mediated reductive coupling of branched allylic acetates **1a**−**1o** with formaldehyde to form primary homoallylic alcohols **2a**−**2o** with excellent control of regio- and enantioselectivity. These processes, which rely on enantiotopic π-facial discrimination of σ-allyliridium intermediates, represent the first examples of enantioselective formaldehyde C−C coupling beyond aldol addition.

Enantiotopic facial discrimination of electrophilic allylmetal species is well established in asymmetric allylic alkylation (W,[1a] Pd,[1b] Mo,[1c] Ir[1d]) (Scheme 1, eq 1). However, despite nearly four decades of work on enantioselective carbonyl allylation,[2−8] this mode of enantioselection is unknown in the context of nucleophilic allylmetal species, where work has focused exclusively on asymmetric additions to aldehydes or ketones to form chiral α-stereogenic secondary or tertiary alcohols, respectively (Scheme 1, eq 2). Nucleophilic allylations of formaldehyde to form chiral β-stereogenic primary homoallylic alcohols have not been described. Indeed, the only catalytic enantioselective C−C couplings of formaldehyde reported, to date, involve asymmetric aldol addition.[9,10]

Merging the chemistry of transfer hydrogenation and carbonyl addition,[7] formaldehyde (or methanol)[11b] mediated hydrohydroxymethylations of diverse π-unsaturated reactants (allenes,[11a−c] dienes[11d,e] and alkynes[11f]) were developed.[11−13] While these processes are efficient and regioselective in contexts where carbonylation/hydroformylation is not, enantioselective variants have not been established nor has the hydroxymethylation of allylic acetates been explored. Here, we apply a chiral iridium catalyst to the enantioselective reductive coupling of allylic acetates with formaldehyde to form chiral β-stereogenic primary homoallylic alcohols via enantiotopic π-facial discrimination of σ-allyliridium intermediates (Scheme 1, eq 3). These processes constitute the first examples of enantioselective formaldehyde C−C coupling beyond aldol addition.

The use of paraformaldehyde as an electrophilic partner in asymmetric nucleophilic allylation poses several challenges. First, high levels of enantioselectivity require intervention of a single geometrical isomer of the σ-allylmetal species in the carbonyl addition event. As our collective data are consistent with a catalytic mechanism wherein carbonyl addition occurs by way of a closed chair-like transition structure,[7,8] competition between chair-like vs boat-like transition structures, which inverts the enantiotopic nucleophile π-face undergoing addition, presents an additional challenge. This issue figures prominently in mechanistically related aldol additions.[14] Finally, in the presence of group 9 metals, paraformaldehyde will transform to synthesis gas,[15] which can promote a variety of side reactions and act as a catalyst poison.

Cognizant of these potential obstacles, initial optimization experiments were undertaken. Gratifyingly, it was found that the indicated π-allyliridium *C,O*-benzoate complex modified by (*S*)-SEGPHOS promotes reductive coupling of the 4-bromophenyl-substituted allylic acetate **1a** (150 mol %) with paraformaldehyde (100 mol %) to provide the desired product, the primary homoallylic alcohol **2a**, in 54% yield and 94% ee as a single regioisomer (Table 1). It was postulated that synthesis gas

Scheme 1. Enantiotopic π-Facial Discrimination in Electrophilic and Nucleophilic Allylation

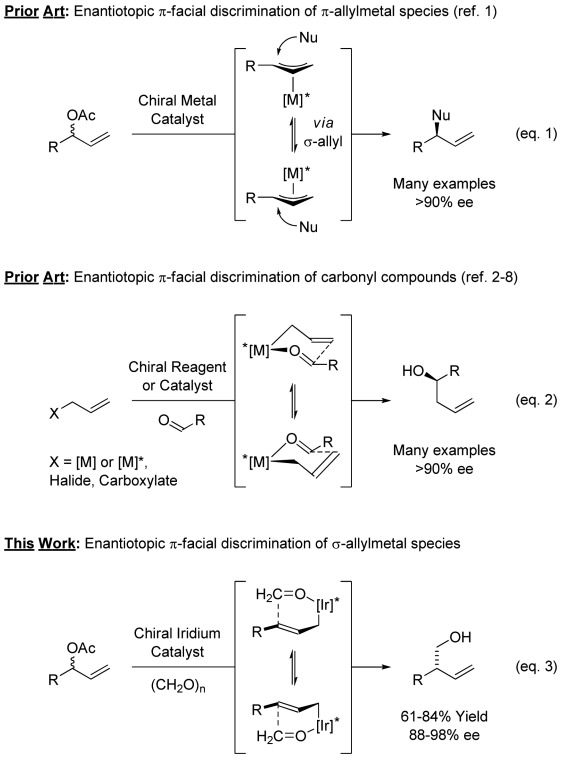

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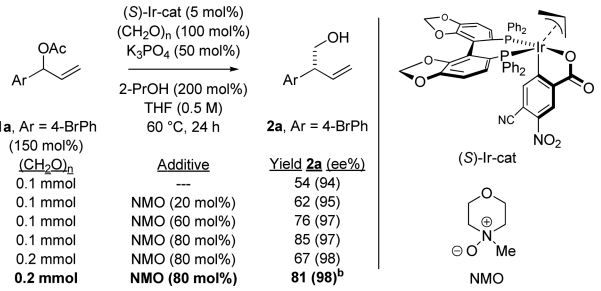
Table 1. Selected Optimization Experiments in the Enantioselective Iridium-Catalyzed Reductive Coupling of Allylic Acetate 1a with Formaldehyde Illustrating the Importance of NMO[a]

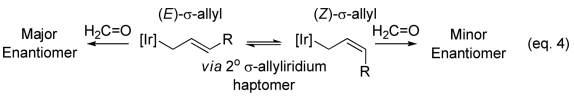


(150 mol%) (CH2O)n	Additive	Yield 2a (ee%)
0.1 mmol	---	54 (94)
0.1 mmol	NMO (20 mol%)	62 (95)
0.1 mmol	NMO (60 mol%)	76 (97)
0.1 mmol	NMO (80 mol%)	85 (97)
0.2 mmol	NMO (80 mol%)	67 (98)
0.2 mmol	**NMO (80 mol%)**	**81 (98)**[b]

[a]Yields are of material isolated by silica gel chromatography. Enantioselectivities were determined by chiral stationary phase HPLC analysis. See Supporting Information (SI) for further experimental details. [b]Microwave heating, 6 h.

generated upon decomposition of paraformaldehyde[15] might contribute to the formation of catalytically inactive iridium carbonyl complexes. This hypothesis was corroborated by the observance of absorptions at 2125 cm^{-1} in IR spectra taken from aliquots of crude reaction mixtures.[16] Hence, *N*-methyl morpholine oxide (NMO), which is commonly used for the oxidative removal of carbonyl ligands,[17] was employed as an additive. As hoped, the addition of NMO proved to be beneficial, allowing homoallylic alcohol **2a** to be isolated in 85% yield and 97% ee. However, this yield could not be reproduced on a larger scale due to solubility issues involving both paraformaldehyde and NMO. Fortunately, it was found that microwave heating largely restored the isolated yield of **2a** with the advantage of significantly shortened reaction times.

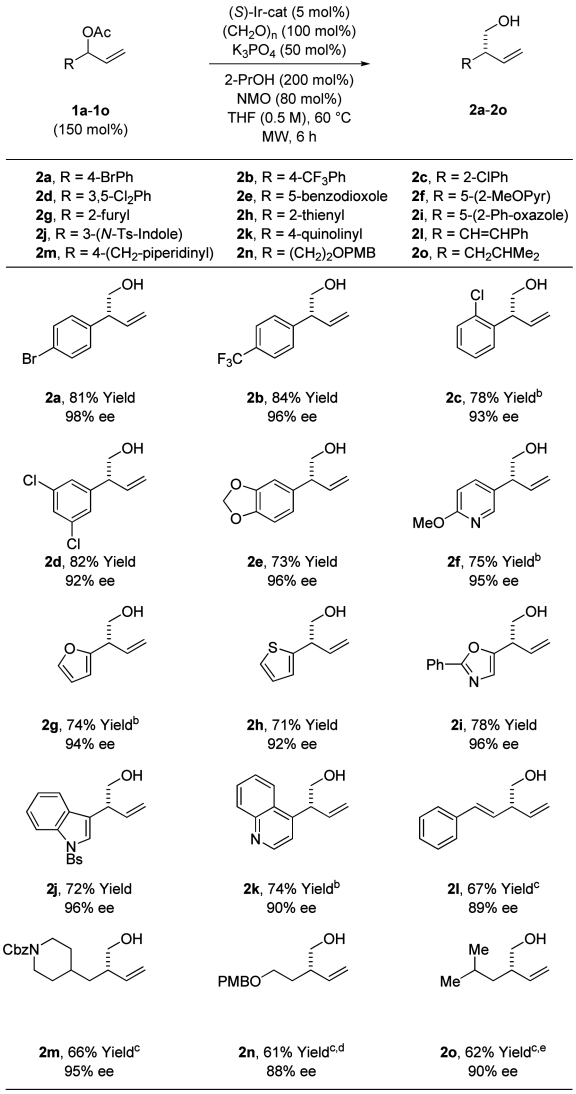
To assess scope, optimized conditions were applied to the reductive coupling of paraformaldehyde with diverse branched allylic acetates **1a**–**1o** (Table 2). As illustrated in the formation of primary homoallylic alcohols **2a**–**2e**, a variety of substituted aryl groups are tolerated, including *ortho*-substituted aryl moieties (**2c**). The formation of compounds **2f**–**2k** establishes the tolerance of these conditions toward *N*-, *S*-, and *O*-bearing heterocycles. In each case, aryl- and heteroaryl-substituted products **2a**–**2k** are formed in good yield with uniformly high levels of enantioselectivity, consistent with good partitioning of (*E*)- and (*Z*)-σ-allyliridium isomers in the carbonyl addition event (eq 4). Even in the case of branched allylic acetates



substituted by styryl groups (**1l**) or alkyl chains (**1m**–**1o**), high levels of enantioselectivity are retained. In all cases, complete levels of branch regioselectivity are observed. Attempted redox-neutral hydroxymethylations wherein methanol serves dually as reductant and formaldehyde precursor were inefficient due to transesterification and transfer hydrogenation of the terminal olefin of the allylic acetate.

The products of reductive coupling serve as useful building blocks in chemical synthesis (Scheme 2). For example, rhodium catalyzed hydroformylation[18] of adduct **2a** provides a lactol, which upon treatment with pyridinium chlorochromate is converted to the enantiomerically enriched δ-lactone **3a** (Scheme 2, eq 5). The absolute stereochemistry of **3a** was

Table 2. Enantioselective Iridium-Catalyzed Reductive Coupling of Branched Allylic Acetates 1a–1o with Formaldehyde to Form Primary Homoallylic Alcohols 2a–2o[a]



[a]Yields are of material isolated by silica gel chromatography. Enantioselectivities were determined by chiral stationary phase HPLC analysis. **2k**, 8 h. **2l**, 10 h. See SI for further experimental details. [b]80 °C. [c]70 °C. [d]The catalyst modified by (*S*)-DM-SEGPHOS was used. [e]Isolated as the 4-nitrobenzoate due to volatility.

determined by single crystal X-ray diffraction and is the basis for the stereochemical assignments of compounds **2a**–**2o**. Conversion of alcohol **2a** to the corresponding acrylic ester, followed by ring-closing metathesis, delivers the α,β-unsaturated δ-lactone **4a** (Scheme 2, eq 6). Amination of the alcohol moiety of **2a** by way of the *p*-toluene sulfonate was challenging due to competing elimination. However, treating the *p*-toluene sulfonate derived from **2a** with sodium azide in DMF delivered the primary azide in good yield. Reduction of the azide provided the amine, which was isolated as the *N*-Boc carbamate **5a** (Scheme 2, eq 7).

A catalytic mechanism and stereochemical model have been proposed (Chart 1). Entry into the catalytic cycle occurs via protonolytic cleavage of the π-allyliridium *C*,*O*-benzoate complex mediated by 2-propanol to furnish the indicated iridium 2-propoxide complex. β-Hydride elimination with loss of acetone

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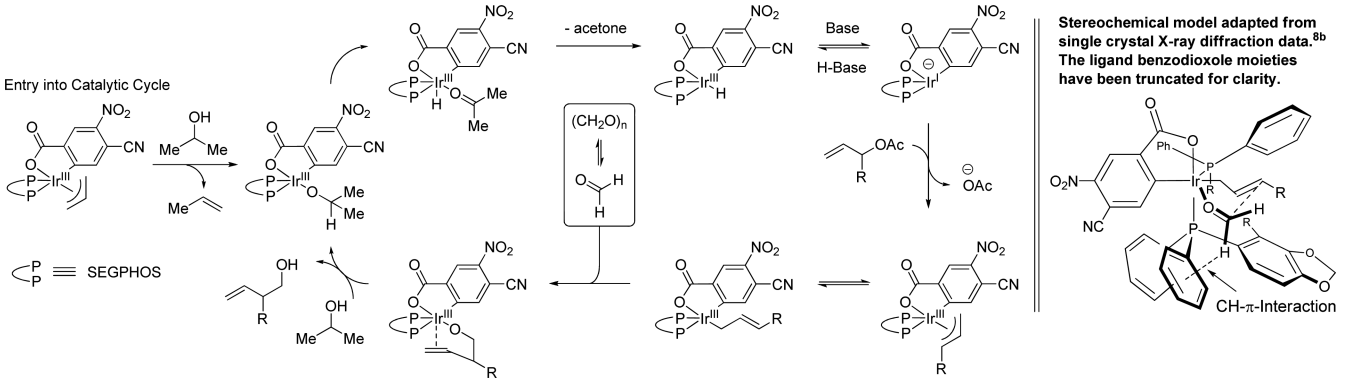
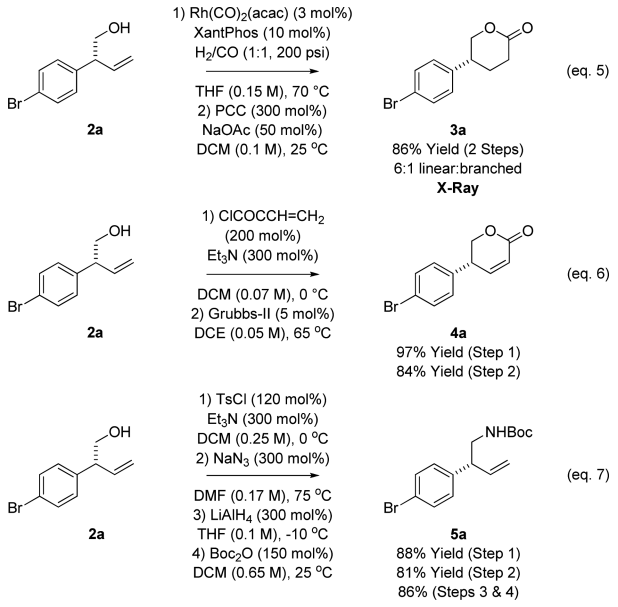
Chart 1. General Catalytic Mechanism and Stereochemical Model



generates an iridium hydride, which upon deprotonation forms an anionic iridium(I) species. Ionization of the allylic acetate delivers the monosubstituted π-allyliridium complex. Complete levels of branch regioselectivity accompanied by high levels of enantioselectivity suggest formaldehyde addition occurs predominantly by way of the primary (E)-σ-allyliridium haptomer through a closed 6-centered transition structure.[7,8] Protonolytic cleavage of the resulting homoallylic alkoxide mediated by 2-propanol regenerates the iridium 2-propoxide complex to close the catalytic cycle. The absolute stereochemical course of the carbonyl addition event is consistent with our previously proposed stereochemical model.[8b] Allylic acetate recovered from the reaction is racemic, indicating kinetic resolution does not occur in the ionization event.

In summary, we report the first enantioselective formaldehyde C−C couplings beyond aldol addition. Specifically, chiral iridium complexes modified by SEGPHOS catalyze the 2-propanol-mediated reductive coupling of branched allylic acetates **1a−1o** with formaldehyde to form primary homoallylic alcohols **2a−2o** with complete control of regioselectivity and uniformly high levels of enantioselectivity. This process provides access to products of hydroxyalkylation that are inaccessible using classical carbonylative methods[11,12] and supports the feasibility of related transformations, including the noncarbonylative aminomethylation[19] of branched allylic acetates.

Scheme 2. Elaboration of Adduct 2a and Assignment of Absolute Stereochemistry[a]



[a]Yields are of material isolated by silica gel chromatography.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b01078.

Single crystal X-ray diffraction data for compound **3a** (CIF)

Experimental details and data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*mkrische@mail.utexas.edu

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For seminal examples of enantiotopic facial discrimination in electrophilic π-allyl complexes based on W, Pd, Mo, and Ir, respectively, see: (a) Lloyd-Jones, G. C.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 462. (b) Trost, B. M.; Krische, M. J.; Radinov, R.; Zanoni, G. *J. Am. Chem. Soc.* **1996**, *118*, 6297. (c) Janssen, J. P.; Helmchen, G. *Tetrahedron Lett.* **1997**, *38*, 8025. (d) Trost, B. M.; Hachiya, I. *J. Am. Chem. Soc.* **1998**, *120*, 1104.

(2) For selected reviews on enantioselective carbonyl allylation, see: (a) Ramachandran, P. V. *Aldrichimica Acta* **2002**, *35*, 23. (b) Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763. (c) Kennedy, J. W. J.; Hall, D. G. *Angew. Chem., Int. Ed.* **2003**, *42*, 4732. (d) Yu, C.-M.; Youn, J.; Jung, H.-K. *Bull. Korean Chem. Soc.* **2006**, *27*, 462. (e) Marek, I.; Sklute, G. *Chem. Commun.* **2007**, 1683. (f) Hall, D. G. *Synlett* **2007**, *2007*, 1644. (g) Lachance, H. Hall, D. G. *Organic Reactions*; John Wiley & Sons, Inc.: Hoboken, NJ, 2008; Vol. 73, p 1 (h) Yus, M.; González-Gómez, J. C.; Foubelo, F. *Chem. Rev.* **2011**, *111*, 7774.

(3) For selected examples of enantioselective carbonyl allylation using chirally modified allylmetal reagents, see: (a) Herold, T.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 768. (b) Hoffmann, R. W.; Herold, T. *Chem. Ber.* **1981**, *114*, 375. (c) Hayashi, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4963. (d) Brown, H. C.; Jadhav, P. K. *J. Am. Chem. Soc.* **1983**, *105*, 2092. (e) Roush, W. R.; Walts,

DOI: 10.1021/jacs.6b01078
J. Am. Chem. Soc. 2016, 138, 3655−3658

A. E.; Hoong, L. K. *J. Am. Chem. Soc.* **1985**, *107*, 8186. (f) Reetz, M. T. *Pure Appl. Chem.* **1988**, *60*, 1607. (g) Short, R. P.; Masamune, S. *J. Am. Chem. Soc.* **1989**, *111*, 1892. (h) Corey, E. J.; Yu, C.-M.; Kim, S. S. *J. Am. Chem. Soc.* **1989**, *111*, 5495. (i) Seebach, D.; Beck, A. K.; Imwinkelzied, R.; Roggo, S.; Wonnacott, A. *Helv. Chim. Acta* **1987**, *70*, 954. (j) Riediker, M.; Duthaler, R. O. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 494. (k) Panek, J. S.; Yang, M. *J. Am. Chem. Soc.* **1991**, *113*, 6594. (l) Kinnaird, J. W. A.; Ng, P. Y.; Kubota, K.; Wang, X.; Leighton, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 7920. (m) Hackman, B. M.; Lombardi, P. J.; Leighton, J. L. *Org. Lett.* **2004**, *6*, 4375. (n) Burgos, C. H.; Canales, E.; Matos, K.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 8044.

(4) For selected examples of enantioselective carbonyl allylation using achiral allylmetal reagents in combination with chiral catalysts, see: (a) Furuta, K.; Mouri, M.; Yamamoto, H. *Synlett* **1991**, *1991*, 561. (b) Costa, A. L.; Piazza, M. G.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Am. Chem. Soc.* **1993**, *115*, 7001. (c) Keck, G. E.; Tarbet, K. H.; Geraci, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 8467. (d) Denmark, S. E.; Coe, D. M.; Pratt, N. E.; Griedel, B. D. *J. Org. Chem.* **1994**, *59*, 6161. (e) Denmark, S. E.; Fu, J. *J. Am. Chem. Soc.* **2001**, *123*, 9488. (f) Lachance, H.; Lu, X.; Gravel, M.; Hall, D. G. *J. Am. Chem. Soc.* **2003**, *125*, 10160. (g) Wada, R.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2004**, *126*, 8910. (h) Rauniyar, V.; Hall, D. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2426. (i) Rauniyar, V.; Zhai, H.; Hall, D. G. *J. Am. Chem. Soc.* **2008**, *130*, 8481. (j) Lou, S.; Moquist, P. N.; Schaus, S. E. *J. Am. Chem. Soc.* **2006**, *128*, 12660. (k) Barnett, D. S.; Moquist, P. N.; Schaus, S. E. *Angew. Chem., Int. Ed.* **2009**, *48*, 8679. (l) Jain, P.; Antilla, J. C. *J. Am. Chem. Soc.* **2010**, *132*, 11884.

(5) For selected reviews on enantioselective carbonyl allylation via Nozaki–Hiyama–Kishi coupling, see: (a) Avalos, M.; Babiano, R.; Cintas, P.; Jiménez, J. L.; Palacios, J. C. *Chem. Soc. Rev.* **1999**, *28*, 169. (b) Bandini, M.; Cozzi, P. G.; Umani-Ronchi, A. *Chem. Commun.* **2002**, 919. (c) Hargaden, G. C.; Guiry, P. J. *Adv. Synth. Catal.* **2007**, *349*, 2407.

(6) For selected reviews covering carbonyl allylation via umpolung of π-allyls, see: (a) Masuyama, Y. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, 1994, Vol. 3, p 255. (b) Tamaru, Y. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; E.-i. Negishi, A. de Meijere, Eds.; Wiley: New York, 2002, Vol. 2, pp 1917. (c) Tamaru, Y. In *Perspectives in Organopalladium Chemistry for the XXI Century*; Tsuji, J., Ed.; Elsevier: Amsterdam, 1999; pp 215. (d) Kondo, T.; Mitsudo, T.-A. *Curr. Org. Chem.* **2002**, *6*, 1163. (e) Tamaru, Y. *Eur. J. Org. Chem.* **2005**, *2005*, 2647. (f) Zanoni, G.; Pontiroli, A.; Marchetti, A.; Vidari, G. *Eur. J. Org. Chem.* **2007**, *2007*, 3599.

(7) For a recent review on enantioselective carbonyl allylation via transfer hydrogenation, see: Ketcham, J. M.; Shin, I.; Montgomery, T. P.; Krische, M. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 9142.

(8) For selected examples of catalytic enantioselective redox-triggered carbonyl allylations employing allylic carboxylates as pronucleophiles, see: (a) Kim, I. S.; Ngai, M.-Y.; Krische, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 6340. (b) Kim, I. S.; Ngai, M.-Y.; Krische, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 14891. (c) Kim, I. S.; Han, S. B.; Krische, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 2514. (d) Gao, X.; Townsend, I. A.; Krische, M. J. *J. Org. Chem.* **2011**, *76*, 2350. (e) Schmitt, D. C.; Dechert-Schmitt, A.-M. R.; Krische, M. J. *Org. Lett.* **2012**, *14*, 6302. (f) Dechert-Schmitt, A.-M. R.; Schmitt, D. C.; Krische, M. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 3195. (g) Shin, I.; Wang, G.; Krische, M. J. *Chem. - Eur. J.* **2014**, *20*, 13382.

(9) For catalytic enantioselective Mukaiyama aldol additions of formaldehyde, see: (a) Ozasa, N.; Wadamoto, M.; Ishihara, K.; Yamamoto, H. *Synlett* **2003**, 2219. (b) Manabe, K.; Ishikawa, S.; Hamada, T.; Kobayashi, S. *Tetrahedron* **2003**, *59*, 10439. (c) Ishikawa, S.; Hamada, T.; Manabe, K.; Kobayashi, S. *J. Am. Chem. Soc.* **2004**, *126*, 12236. (d) Kobayashi, S.; Ogino, T.; Shimizu, H.; Ishikawa, S.; Hamada, T.; Manabe, K. *Org. Lett.* **2005**, *7*, 4729. (e) Kokubo, M.; Ogawa, C.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 6909.

(10) For catalytic enantioselective direct aldol additions of formaldehyde, see: (a) Kuwano, R. *Chem. Commun.* **1998**, 71. (b) Torii, H.; Nakadai, M.; Ishihara, K.; Saito, S.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 1983. (c) Casas, J.; Sundén, H.; Córdova, A. *Tetrahedron Lett.* **2004**, *45*, 6117. (d) Fukuchi, I.; Hamashima, Y.; Sodeoka, M. *Adv. Synth. Catal.* **2007**, *349*, 509. (e) Mouri, S.; Chen, Z.; Matsunaga, S.; Shibasaki, M. *Chem. Commun.* **2009**, 5138. (f) Mase, N.; Inoue, A.; Nishio, M.; Takabe, K. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 3955. (g) Boeckman, R. K., Jr.; Miller, J. R. *Org. Lett.* **2009**, *11*, 4544. (h) Pasternak, M.; Paradowska, J.; Rogozińska, M.; Mlynarski, J. *Tetrahedron Lett.* **2010**, *51*, 4088. (i) Shirakawa, S.; Ota, K.; Terao, S. J.; Maruoka, K. *Org. Biomol. Chem.* **2012**, *10*, 5753. (j) Yasui, Y.; Benohoud, M.; Sato, I.; Hayashi, Y. *Chem. Lett.* **2014**, *43*, 556. (k) Meninno, S.; Fuoco, T.; Tedesco, C.; Lattanzi, A. *Org. Lett.* **2014**, *16*, 4746.

(11) For catalytic hydrohydroxymethylation of allenes (a,b,c), dienes (d,e), and alkynes (f,g) to paraformaldehyde via C–C bond forming transfer hydrogenation, see: (a) Ngai, M.-Y.; Skucas, E.; Krische, M. J. *Org. Lett.* **2008**, *10*, 2705. (b) Moran, J.; Preetz, A.; Mesch, R. A.; Krische, M. J. *Nat. Chem.* **2011**, *3*, 287. (c) Sam, B.; Montgomery, T. P.; Krische, M. J. *Org. Lett.* **2013**, *15*, 3790. (d) Smejkal, T.; Han, H.; Breit, B.; Krische, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 10366. (e) Köpfer, A.; Sam, B.; Breit, B.; Krische, M. J. *Chem. Sci.* **2013**, *4*, 1876. (f) Bausch, C. C.; Patman, R. L.; Breit, B.; Krische, M. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 5687.

(12) For reviews encompassing use of paraformaldehyde and methanol as C1-feedstocks in metal-catalyzed C–C coupling, see: (a) Wu, L.; Liu, Q.; Jackstell, R.; Beller, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 6310. (b) Sam, B.; Breit, B.; Krische, M. J. *Angew. Chem., Int. Ed.* **2015**, *54*, 3267.

(13) For methanol-mediated Guerbet-type aldol reactions, see: (a) Chan, L. K. M.; Poole, D. L.; Shen, D.; Healy, M. P.; Donohoe, T. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 761. (b) Shen, D.; Poole, D. L.; Shotton, C. C.; Kornahrens, A. F.; Healy, M. P.; Donohoe, T. J. *Angew. Chem., Int. Ed.* **2015**, *54*, 1642.

(14) Evans, D. A.; Nelson, J. V.; Taber, T. *Top. Stereochem.* **1982**, *13*, 1.

(15) Fuentes, J. A.; Pittaway, R.; Clarke, M. L. *Chem. - Eur. J.* **2015**, *21*, 10645 and references cited therein.

(16) The absorption at 2125 cm^{-1} in IR is consistent with an iridium(III) carbonyl complex: (a) Vaska, L.; DiLuzio, J. W. *J. Am. Chem. Soc.* **1961**, *83*, 2784. (b) Vaska, L. *J. Am. Chem. Soc.* **1966**, *88*, 4100.

(17) Shen, J.-K.; Gao, Y.-C.; Shi, Q.-Z.; Basolo, F. *Coord. Chem. Rev.* **1993**, *128*, 69 and references cited therein.

(18) For impact of large bite-angle ligands on regioselectivity in hydroformylation, see ref (a). For seminal use of XantPhos in linear regioselective hydroformylation, see ref (b): (a) Casey, C. P.; Whiteker, G. T.; Melville, M. G.; Petrovich, L. M.; Gavney, J. A., Jr.; Powel, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 5535. (b) Kranenburg, M.; van der Burgt, Y. E. M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K. G.; Fraanje, J. *Organometallics* **1995**, *14*, 3081.

(19) (a) Oda, S.; Sam, B.; Krische, M. J. *Angew. Chem., Int. Ed.* **2015**, *54*, 8525. (b) Oda, S.; Franke, J.; Krische, M. J. *Chem. Sci.* **2016**, *7*, 136.

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J. Am. Chem. Soc. 2016, 138, 3655–3658