To our knowledge, these reactions are the first examples of a single-site oxidative addition of a vinyl group yielding a stable σ-vinyl cationic complex. The reaction appears to be general in that a broad range of vinyl triflates including mono-, di-, and trisubstituted as well cyclic ones readily undergo reaction yielding products in excellent isolated yields. These novel complexes may also serve as useful model compounds in the vinyl triflate coupling reactions. Further work is in progress and will be the subject of future reports.

Acknowledgment. We are grateful to the NSF (CHE-8419099) for financial support and the NSF and DOD instrumentation grants used for acquisition of the 300-MHz NMR used in this study.

Registry No. 1, 28075-50-5; **2**, 53282-30-7; **3**, 53282-32-9; **4**, 24541-32-0; **5**, 32363-21-6; **6**, 104549-11-3; **7**, 104549-13-5; **8**, 104549-15-7; **9**, 104549-17-9; **10**, 104549-19-1; **11**, 104549-20-4; **12**, 104549-21-5; Pt(PPh$_3$)$_4$, 14221-02-4; 1-iodocyclohexene, 17497-53-9.

Transition-Metal-Catalyzed Carbon–Carbon Bond Forming Reactions: Regio- and Chemoselective Iron(0)-Catalyzed Diene to Olefin Cross-Coupling Reactions

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Summary: The iron(0)-catalyzed cross coupling of certain allylic ethers to 2,3-disubstituted 1,3-butadienes results in either a formal [4 + 4] ene reaction across the diene or in the net 1,4-insertion of the diene unit into the C–H bond at the 2-position of the allylic ether. The course of the reaction is determined by the ligands attached to the iron(0) catalyst. The active catalyst can be generated in situ, and reactions proceed catalytic in iron(0) at or near ambient temperatures. These new coupling reactions generate synthetically useful functionality (stereodefined olefin and an allylic ether or a protected carbonyl) on either side of the newly formed carbon–carbon bond. The results of deuterium-labeling experiments suggest a catalytic cycle which involves initial oxidative coupling of the diene and allyl ether in the mechanism of these reactions.

The design of new catalytic transition-metal-mediated carbon–carbon bond constructions, which are of utility in the course of organic synthesis, remains an important challenge.[1,2] We wish to report our observations on the previously unpublished chemistry of iron(0)-catalyzed 1:1 cross couplings of 1,3-dienes to allylic ethers.[3] These reactions proceed with unusual regio- and chemoselectivities which are highly dependent upon the ligands attached to the iron(0) catalyst. In certain cases the products of these reactions are the net result of a thermally forbidden [4 + 4] ene reacton, wherein the allylic ether serves as the enophile and the 1,3-diene as the ene component. Thus these iron-catalyzed reactions enable a previously inacessible bond construction to be performed. In other cases the reaction products are the result of a previously unreported 1,4-hydrovinylation of the diene.

Soluble iron(0) complexes can be conveniently prepared in situ via the reduction of Fe(II) or Fe(III) salts (usually the chlorides or acetyl acetonates) by grignard or trialkylaluminum reagents.[4] Reduction of Fe(acac)$_3$ by 3.1 equiv of Et$_3$Al in the presence of 2,3-dimethyl-1,3-butadiene and 1.1 equiv of 2,2′-bipyridine (bpy) yields a solution of the catalytically active "bpy·Fe(0)·diene" complex.[5] Allyl benzyl ether reacts with 2,3-dimethylbutadiene in the presence of 5–10 mol % of this catalyst (benzene, 25 °C, 8 h) to give a 95:5 ratio of two isomeric 1:1 coupling products **1** and **2** in 80% chemical yield based on consumed allyl benzyl ether (eq 1).[6,7] A small amount (5–10%) of *cis*/*trans*-1-(benzyloxy)-1-propene (**3**), which

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[†] This paper is dedicated to the memory of Mr. Wayne F. Devroy.

(1) (a) Scheffold, R. *Modern Synthetic Methods*; Wiley: New York, 1983; Vol. 3. (b) Davies, S. G. *Organotransition Metal Chemistry*: Application *to Organic Synthesis*; Pergamon: New York, 1982. (c) Colquhoun, H. M.; Horton, J.; Thompson, D. J.; Twigg, M. V. *New Pathways for Organic Synthesis*: *Practical Application of Transition Metals*; Plenum: New York, 1984. For examples illustrating the synthetic utility of organoiron chemistry see: (d) Semmelhack, M. F.; Le, H. T. M. *J. Am. Chem. Soc.* **1985**, *107*, 1455–1457. (e) Pearson, A. J.; Ong, C. W. *J. Org. Chem.* **1982**, *47*, 3780–3782. (f) Rosenblum, M.; Bucheister, A.; Chang, T. C. T.; Cohen, M.; Marsi, M.; Samuels, S. B.; Scheck, D.; Sofen, N.; Watkins, J. C. *Pure Appl. Chem.* **1984**, *56*, 129–136. (g) Wright, M. E.; Nelson, G. O.; Glass, R. S. *Organometallics* **1985**, *4*, 245–250.

(2) For examples illustrating transition-metal-mediated olefin cross-coupling reactions see: (a) Trost, B. M.; Chung, J. Y. L. *J. Am. Chem. Soc.* **1985**, *107*, 4586–4588. (b) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1985**, *107*, 1781–1783. (c) Kende, A. S.; Roth, B.; Sanfilippo, P. J.; Blacklock, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 5808–5810. (d) Overman, L. E.; Renaldo, A. F. *Tetrahedron Lett.* **1983**, *24*, 2235–2238. (e) Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P.-C. *J. Am. Chem. Soc.* **1985**, *107*, 1060–1062. (f) Berris, B. C.; Hovakeemian, G. H.; Lai, Y.-H.; Mestdagh, H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1985**, *107*, 5670–5687. (g) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120–126. (h) Buono, G.; Peiffer, C. S. G.; Triantaphycides, C.; Denis, P.; Mortreux, A.; Petit, F. *J. Org. Chem.* **1985**, *50*, 1782–1784. (i) Brun, P.; Tenaglia, A.; Waegell, B. *Tetrahedron Lett.* **1983**, *24*, 385–388. (j) Lehmkuhl, H.; Tsien, Y. L. *Chem. Ber.* **1983**, *116*, 2437–2446.

(3) A preliminary account of this work was presented at the 189th National Meeting of the American Chemical Society Miami, Florida, April 1985 (Division of Organic Chemistry Abs No. 158).

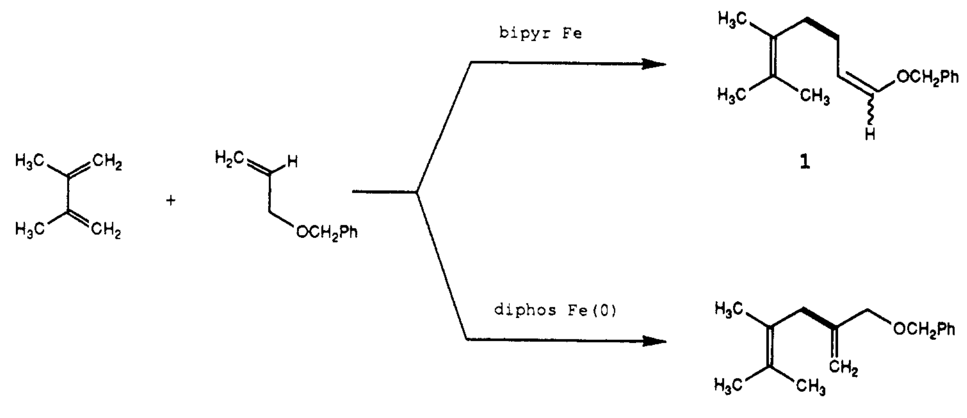
(4) Such catalyst preparations are known in the literature to mediate a variety of interesting carbon–carbon bond forming reactions: (a) Carbonaro, A.; Greco, A.; Dall'Asta, G. *J. Organomet. Chem.* **1969**, *20*, 177–186. (b) Hata, G.; Aoki, D. *J. Org. Chem.* **1967**, *32*, 3754–3758. (c) Su, A. C. L. *Adv. Organomet. Chem.* **1979**, *17*, 269–318. (d) Tolstikov, G. A.,; Dzhemilev, U. M.; Khusnutdinov, R. I. *J. Org. Chem., USSR (Engl. Transl.)* 1979, *15*(4), 618–621. (e) Carbonaro, A.; Greco, A.; Dall'Asta, G. *J. Org. Chem.* **1968**, *33*, 3948–3950. (f) Dieck, H. tom; Diercks, R. *Angew Chem., Int. Ed. Engl.* **1983**, *22*, 778–779. (g) Genet, J. P.; Ficini, J. *Tetrahedron Lett.* **1979**, *20*, 1499–1502 (h) Heck, R. F. *Organotransition Metal Chemistry*: *A Mechanistic Approach*; Academic: New York, 1974.

(5) An efficient catalyst requires reduction of the Fe(acac)$_3$ by a minimum of 3.0 equiv of Et$_3$Al. Addition of Et$_3$Al in excess of 3.0 equiv has no apparent effect on the course of the reaction, however, reduction of Fe(acac)$_3$ by 2.0 equiv or less produces an iron complex which is catalytically inactive. Coupling of allyl benzyl ether to 2,3-dimethylbutadiene is not effected by Et$_3$Al (or Et$_2$AlCl) in the absence of Fe(acac)$_3$. Similarly the 1:1 stoichiometry of bipyridine:Fe is critical to the success of this chemistry. In the presence of 2.2 equiv of bipyridine, a catalytically inactive iron(0) complex is formed. The reduction of FeCl$_3$ by 3.1 equiv of *i*-PrMgBr in the presence of 1.1 equiv of 2,2′-bipyridine and 2,3-dimethylbutadiene also yields an active catalyst.

(6) Compound 1 is formed as a 60:40 cis/trans mixture of enol ethers. The minor component 2 in this reaction is formed as a 70:30 mixture of 1,4- and 1,2-insertion products. The ratio of isomeric products does not change with the degree of conversion. Conversions are typically 60–100% over 8 h at 25 °C. The cyclooligomerization of 2,3-dimethylbutadiene is competitive with the coupling reaction. No attempt to optimize the catalyst or reaction conditions with respect to this side reaction was made. Typically a 3–5-fold excess of 1,3-diene is employed.

(7) A similar product distribution is observed when Fe(acac)$_3$ is reduced in the presence of 1 equiv of pyridine or in the absence of added ligand. In the latter "ligand-free" catalyst excess diene, olefin, or solvent is assumed to occupy the remaining coordination sites on Fe(0).

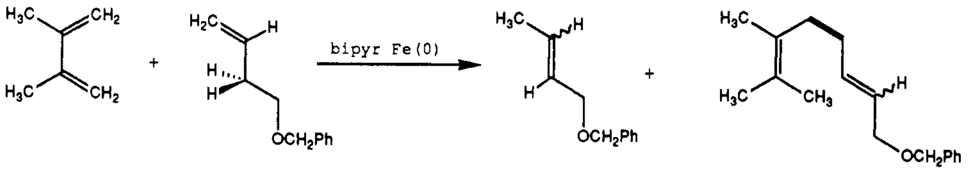
0276-7333/86/2305-2395$01.50/0



1

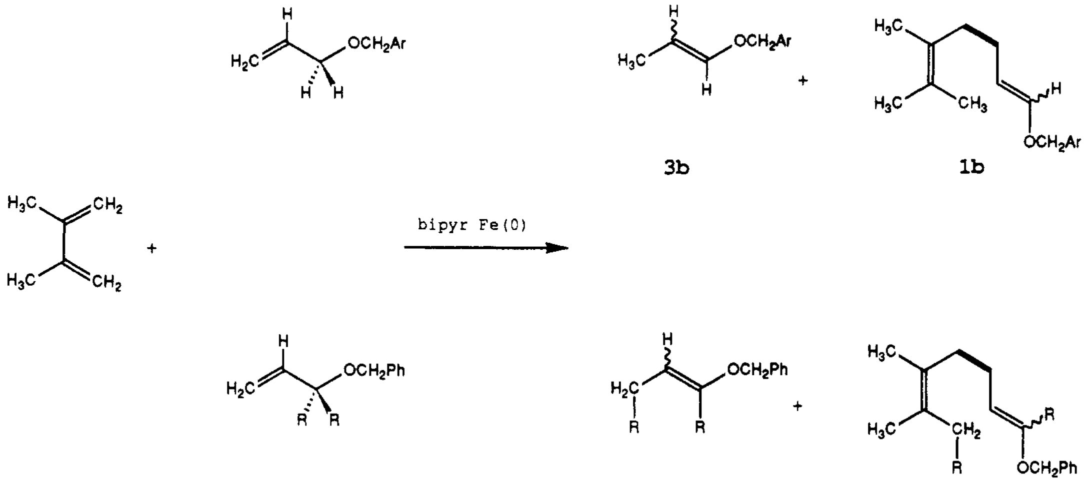
2

(1)



chemical yield: 20% <5%

(2)



3b 1b

3a 1a

(3)

arises from the known iron(0)-catalyzed isomerization of allyl ethers to enol ethers, is also isolated.[8]

The nature of the ligand is critical in determining the regiochemical course of carbon–carbon bond formation with respect to allyl benzyl ether. We have investigated a series of bidentate nitrogen- and phosphine-containing ligands. In contrast to the bipyridine reaction discussed above, reaction of allyl benzyl ether with 2,3-dimethylbutadiene in the presence of "dppe·Fe(0)·diene" (dppe = 1,2-bis(diphenylphosphino)ethane, benzene, 60 °C, 8 h) yields a mixture of coupled products (50%) favoring >95% of the 1,4-hydrovinylation product **2**, wherein carbon–carbon bond formation has occurred at the more substituted carbon of the olefin (eq 1). Phosphine-containing catalysts, however, do not exclusively prefer the hydrovinylation pathway. For example, coupling catalyzed by "dmpe·Fe(0)·diene" (dmpe = 1,2-bis(dimethylphosphino)ethane) yields a 90:10 mixture of **1**:**2**. Our data to date suggests that the origin of this unusual regioselectivity is related to the steric demand of the coordinated ligand.[9]

We have investigated the details of the [4 + 4] ene bond construction reaction at some length. The "bpy·Fe(0)" catalyzed reaction exhibits unusual chemoselectivity toward allylic ethers.[10] Certain other olefinic substrates fail to give any appreciable amounts of coupled products in the presence of catalysts which we have examined. Allyl benzoate rapidly and stoichiometrically decomposes the "bpy·Fe(0)·diene" catalyst, apparently by a mechanism involving C–O bond insertion. Competition experiments

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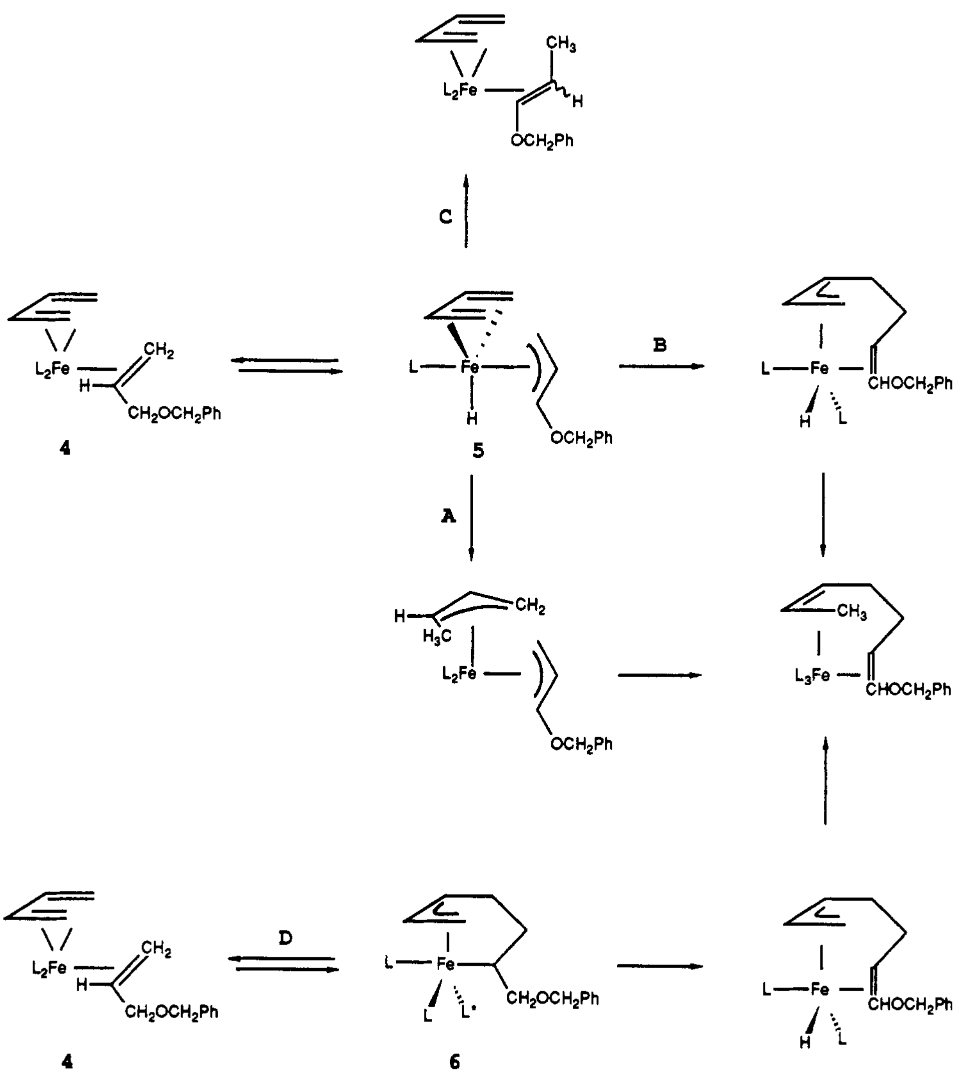
[8] (a) Hubert, A. J.; Georis, A.; Warin, R.; Teyssie, P. *J. Chem. Soc., Perkin Trans. 2* **1972**, 366–370. (b) Jolly, P. W.; Stone, F. G. A.; Machenzie, K.; *J. Chem. Soc.* **1965**, 6416–6420.

[9] We find that the ratio of ene:hydrovinylation coupling products in the reaction of allyl benzyl ether with isoprene catalyzed by "L·Fe(0)·diene" also varies as a function of the steric demand of L.

[10] The benzyl ether appears to be optimal. The chemical yields with other allylic ethers, $CH_2{=}CHCH_2OR$ (R = phenyl, 2-phenylethyl, 1-phenylethyl, cyclohexylmethyl, or 2-tetrahydropyranyl), tend to be 10–30% lower than for R = benzyl. In part, these poorer isolated yields reflect an unusual dependence of the reaction rate on the ether substituent, R.

Scheme I



between equimolar quantities of allyl benzoate and allyl benzyl ether yield less than 2% of the coupled product **1**. Simple terminal olefins are relatively unreactive toward these catalysts. For example, attempted coupling of 2,3-dimethylbutadiene to benzyl 3-butenyl ether in the presence of "bpy·Fe(0)·diene" (benzene, 25 °C, 12 h) yields approximately 20% of *cis*- and *trans*-crotyl benzyl ether via isomerization and less than 5% of the product from diene to olefin cross coupling (eq 2).

Understanding the origin of the unusual reaction selectivities and the applications of these bond constructions in organic synthesis will be greatly facilitated if a good model for the catalytic cycle can be deduced. Three reasonable catalytic cycles leading to coupling product **1**, each proceeding via initial formation of an iron(0) diene–olefin complex **4**, can be written which account for the observations cited above (illustrated for 1,3-butadiene reacting with allyl benzyl ether in Scheme I).[11] Two of the pathways (Scheme I, pathways A and B) involve initial C–H bond insertion to yield the π-allyl iron hydride complex **5**. Complex **5** could lead to the observed product by either of two modes of ligand coupling, followed in each case by reductive elimination. Such a process is consistent with the isomerization of allyl benzyl ether to *cis*/*trans*-1-propenyl ether **3**, which is observed as a minor side product in the coupling reaction (Scheme I, pathway C).[8,13] The third coupling pathway illustrated (Scheme I, pathway D) involves initial oxidative coupling of complex **4** to yield a chelated π-allyl iron(II) σ-bonded complex **6**. Such a pathway is consistent with the isolation and/or spectroscopic characterization of structurally analogous iron carbonyl complexes obtained via the oxidative coupling of 1,3-dienes to methylacrylate, fluoroalkenes, and acetylenes.[14]

The following experiments help to elucidate the fate of complex **4**. Reaction of 2,3-dimethylbutadiene with an equimolar mixture of allyl benzyl ether and allyl *p*-

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[11] The following double labelling experiment eliminates those possible mechanisms which are initiated by an iron(I) hydride complex. Such an intermediate has previously been proposed to account for other iron-catalyzed cross-coupling reactions.[4d] Coupling of 2,3-dimethyl-1,3-butadiene to an equimolar mixture of 1,1-dideuterio-2-propenyl benzyl ether[12] and 1,1-diprotio-2-propenyl *p*-methylbenzyl ether catalyzed by the "bpy·Fe(0)·diene" catalyst yields a 1:1 mixture of coupling products **1a** and **1b** (eq 3, R = ^{2}H). Analysis of the isotope distribution shows no scrambling of deuterium between the two sets of products.

[12] The synthesis of this compound follows from the work of Bartlett and Tate: Bartlett, P. D.; Tate, F. A. *J. Am. Chem. Soc.* **1953**, *75*, 91–98.

[13] The isomerization reaction is irreversible under the reaction conditions. A competition of "bpy·Fe(0)·diene" catalyzed coupling of 2,3-dimethylbutadiene to an equimolar mixture of allyl *p*-methylbenzyl ether and *cis*/*trans*-1-(benzyloxy)-1-propene (**3**) yields only the coupled product **1** derived from the *p*-methylbenzyl ether. No products are observed into which the benzyl enol ether **3** has been incorporated.

[14] (a) Green, M.; Lewis, B.; Daly, J. J.; Sanz, F. *J. Chem. Soc., Dalton Trans.* **1975**, 1118–1137. (b) Grevels, F.-W.; Schneider, K. *Angew. Chem., Int. Engl.* **1981**, *20*, 410–411. (c) Akiyama, T.; Grevels, F.-W.; Reuvers, J. G. A.; Ritterskamp, P. *Organometallics* **1983**, *2*, 157–160.

methylbenzyl ether in the presence of the bpy·Fe(0) catalyst gives a mixture of isomerized and coupled products, the components of which can be fully resolved by capilliary gas chromatography (eq 3, R = H, Ar = p-$CH_3C_6H_4$). Analysis of the reaction mixture after short reaction times shows that the benzyl and p-methylbenzyl groups are incorporated into each of the observed products with identical facility. Repeating the above experiment with an equimolar mixture of 1,1-dideuterio-2-propenyl benzyl ether and allyl p-methylbenzyl ether allows us to determine the overall isotope effects (k_H/k_D) for the isomerization and the coupling reactions by measuring the relative abundances of benzyl and p-methylbenzyl products, **3a**:**3b** and **1a**:**1b**, respectively (eq 3, R = ^2H, Ar = p-$CH_3C_6H_4$).[11] Carrying out such a competition experiment through approximately two turnovers of the "bpy·Fe(0)" catalyst shows an isotope effect for the isomerization process k_H/k_D of 1.5 ± 0.1, a value which is consistent with literature data.[15] In contrast, the observed ene product distribution (**1b**:**1a**) gives a ratio k_H/k_D of 1.0 ± 0.1 for the coupling process.[16]

The data demonstrate that coupling and isomerization do not involve rate-determining formation of a common intermediate through hydrogen transfer. The lack of a kinetic isotope effect fully supports pathway D as the mechanism of coupling. A mechanism similar to that outlined in Scheme I can be written to account for the formation of allylic ether product **2**. In this latter case, one role of the bulky dppe ligand might be to direct oxidative coupling toward the more substituted carbon of the allylic ether so as to form the least sterically congested metal carbon σ-bond. Further studies on the utility of these novel cross-coupling reactions are in progress.

Acknowledgment. We wish to thank the National Institutes of Health (GM 34927), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Utah Research Committee for generous support of this work. Mass spectra were obtained by using instruments purchased with funds provided by the National Science Foundation and the Universty of Utah Institutional Funds Committee. NMR spectra were obtained by using 300-MHz spectrometers purchased with funds provided by the National Science Foundation and the Department of Defense Instrumentation Grants.

Registry No. **1**, 104693-23-4; **1b**, 104693-28-9; **2**, 104693-24-5; *cis*-**3**, 32426-80-5; *trans*-**3**, 32426-79-2; *cis*-^{3}b, 104693-26-7; *trans*-**3b**, 104693-27-8; $(CH_3)_2C{=}C(CH_3)CH_2CH_4CH{=}CHCH_2OCH_2Ph$, 104693-25-6; p-$CH_3C_6H_4CH_2OCH_2CH{=}CH_2$, 42463-79-6; D_2, 7782-39-0; $Fe(acac)_3$, 14024-18-1; bpy·Fe(0)·diene, 104714-94-5; dppe·Fe(0)·diene, 104693-29-0; dmpe·Fe(0)·diene, 104693-30-3; benzyl 3-butenyl ether, 70388-33-9; *cis*-crotyl benzyl ether, 27299-31-6; Trans-crotyl benzyl ether, 27299-30-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; allyl benzyl ether, 14593-43-2; allyl benzoate, 583-04-0.

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[15] Chrisope, D. R.; Beak, P. *J. Am. Chem. Soc.* **1986**, *108*, 334–335 and references herein.

[16] Similar kinetic isotope effects are observed with the "ligand free" Fe(0) catalyst (see ref 7).

Additions and Corrections

Serge Attali, Francoise Dahan, and René Mathieu*: Reaction of $[P(C_6H_5)_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CHCH_2)]$ with $[RhCl(CO)_2]_2$. Synthesis of a Triiron–Dirhodium Cluster Anion Containing a $CH_3C{=}C{=}CH_2$ Allenyl Ligand with an Unusual μ_4-η^3 Mode of Bonding, $[P(C_6H_5)_4][Fe_3Rh_2(CO)_{10}(\mu\text{-}CO)_3(\mu_4\text{-}\eta^3\text{-}CH_3C{=}C{=}CH_2)]$. **1986**, *5*, 1376.

The correct title is published above. The title was incorrectly published as "Reaction of $[P(C_6H_5)_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CHCH_2)]$ with $[RhCl(CO)_2]_2$. Synthesis of a Triiron–Dirhodium Cluster Anion Containing a $CH_3C{=}C{=}CH_2$ Triiron–Dirhodium Ligand with an Unusual μ_4-η^3 Mode of Bonding, $[P(C_6H_5)_4][Fe_3Rh_2(CO)_{10}(\mu\text{-}CO)_3(\mu_4\text{-}\eta^3\text{-}CH_3C{=}C{=}CH_2)]$".

D. Ewan Smith and Alan J. Welch*: Indenylmetallacarboranes. 1. The 18-Valence-Electron Complex 3-(η^5-C_9H_7)-3,1,2-$CoC_2B_9H_{11}$ and Comparative Molecular Structures of This Complex and 3-(η^5-C_5H_5)-3,1,2-$CoC_2B_9H_{11}$. **1986**, *5*, 760.

On p 761 we erroneously described 3-(η^5-C_5H_5)-3,1,2-$FeC_2B_9H_{11}$ as the first reported metallacarborane. In fact the ions $Fe(C_2B_9H_{11})_2^{2-}$ and $Fe(C_2B_9H_{11})_2^{-}$ predate the Cp complex by several months (Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 1818).