Table I. Relative Yields of 1a and 2

conditions	% ratio of 1a/2 (by GC/MS)[4]
(a) see text for conditions	77:23
(b) sample a recrystallized from hexane (−20 °C)	80:20
(c) sample b recrystallized from hexane (−20 °C)	94:6
(d) sample c recrystallized from hexane (−20 °C)	97:3
(e) conditions reported in ref 1	82:18

parison of its spectral properties with those of the minor product.[6]

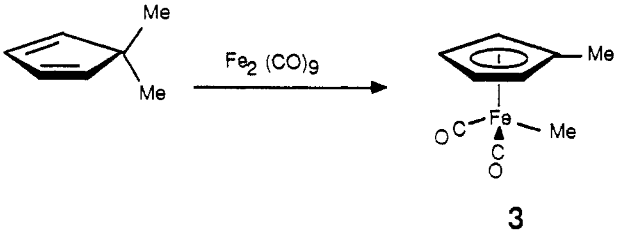
Varying the reaction temperature has little effect on the relative yields of **1a** and **2**. Carrying out the reaction under the conditions originally used by Herrmann[1] (180 °C, 13 h) resulted in an 82:18 (±3) mixture of **1a**/**2** (Table I, entry e). This reaction was repeated twice in our laboratories, and analogous GC/MS results were obtained on material prepared by using this methodology by the research group of Professor J. L. Hubbard (University of Vermont).

GC/MS analysis of a pure sample of **1a** under identical conditions[4] confirmed that **2** was not formed by degradation of **1a** during the analysis. Compound **1a** was also shown to be stable under the synthetic reaction conditions. When the reaction with $Mn_2(CO)_{10}$ was carried out in a sealed system and the product gases were subjected to FT-IR analysis, the presence of substantial quantities of methane was confirmed by comparison with an authentic sample. No IR evidence was obtained for significant quantities of other organic materials including ethane.[7] Finally heating Cp*H in the absence of metal carbonyl (180 °C, 13 h) showed no evidence for formation of degradation products. It seems clear that the mixture of **1a** and **2** is the result of competitive activation of the doubly allylic C–H and C–CH_3 bonds of Cp*H during the reaction with $Mn_2(CO)_{10}$.

In contrast the reaction of $Re_2(CO)_{10}$ with Cp*H afforded **1b** as the only organometallic product by GC/MS and NMR analysis of the crude reaction mixture, in agreement with the literature report.[2] Curiously, while no tetramethylcyclopentadienyl ligand was detected in this reaction, small traces of methane were formed as identified by FT-IR.

It is not surprising that the formation of mixtures of **1a** and **2** under these conditions was not previously noted. We have been unable to separate mixtures of **1a** and **2** efficiently by conventional column or thin-layer chromatographic methods. While successive crystallizations from hexane afforded samples increasingly enriched in **1a**, even after three such crystallizations traces of **2** were still present as revealed by GC/MS (Table I, entries b-d). Moreover, the IR spectrum (hexane solution) of the crude and recrystallized material in the CO stretching region exhibited only a single set of peaks characteristic of a tricarbonylmetal fragment of effective C_{3v} symmetry and is therefore not a good criterion of purity. Thus, the presence of **2** as a reaction product can only be detected in the ^1H or $^{13}C\{^1H\}$ NMR spectra of the crude reaction product or by GC/MS analysis.

While carbon–carbon bond activation in 5,5-disubstituted cyclopentadienes has been observed previously, affording compounds such as **3**,[8,9] our results clearly indicate that competition between C–H and C–C activation can occur under suitable circumstances. Although the mechanisms of the reactions reported here and the reasons for the differing reactivity of the Mn and Re carbonyls are not yet clearly defined, the significance of these results seems clear; it should not always be assumed that the η-C_5Me_5 ligand is the only product possible from reactions of pentamethylcyclopentadiene with metal carbonyl derivatives. Further studies of the mechanism(s) of these reactions are in progress.



3

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Air Force Office of Scientific Research (Grant AFOSR-86-0075), and to the National Science Foundation, for generous financial support of our research. Thanks are also due to Professor J. L. Hubbard (University of Vermont) for providing samples from his laboratories for GC/MS analysis.

Registry No. **1a**, 34807-89-1; **2**, 104215-32-9; $Mn_2(CO)_{10}$, 10170-69-1; $MnBr(CO)_5$, 14516-54-2; Cp*H, 41539-64-4; lithium tetramethylcyclopentadienide, 82061-21-0.

---

(5) The use of tetramethylcyclopentadiene and its anion have been reported (Scholtz, H. J.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, C8–C12. Jutzi, P.; Dickbreder, R. *Chem. Ber.* **1986**, *119*, 1750–1754), but no synthetic details were given. We prepared the diene by a modification of the Cp*H synthesis[3] using ethyl formate rather than ethyl acetate. The Li salt was prepared by reaction of the diene with BuLi. To a solution of this salt in THF was added $MnBr(CO)_5$, and the mixture was refluxed overnight, cooled and evaporated to dryness. Chromatography on silica (hexane) afforded **2** in 20% yield.[6]

(6) **2**: mp 88–90 °C; ^1H NMR ($CDCl_3$) δ 1.88 (br s, 12 H, Me), 4.33 (s, 1 H, CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 10.23 (Me), 12.03 (Me), 79.96 (*C*H), 97.15 (*C*Me), 97.25 (*C*Me), 226.43 (CO); IR (hexane) ν_{CO} 2010, 1930 cm^{-1}; MS, *m/e* 260 (M^+), 204 ($M^+ - 2CO$), 176 ($M^+ - 3CO$), 121 ($M^+ - Mn(CO)_3$), 55 (Mn). Anal. Calcd for $C_{12}H_{13}MnO_3$: C, 55.40; H, 5.04. Found: C, 55.34; H, 4.98.

(7) Herzberg, G. In *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*; Litton Educational Publishing: New York, 1945; Chapter 3.

(8) Eilbracht, P.; Dahler, P. *Chem. Ber.* **1980**, *113*, 542–554.

(9) A number of variations of this reaction have been reported, including the reactions of spirocyclic analogues of 5,5-dimethylcyclopentadiene (see ref 8 and Eilbracht, P.; Mayser, U. *Chem. Ber.* **1980**, *113*, 2211–2220) and reactions of acetylpentamethylcyclopentadiene (King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1972**, *94*, 3773–3779). In the latter case apparently selective activation of the acetyl–ring bond was observed.

Stable, Four-Coordinate, σ-Vinyl Platinum(II) Complexes[†]

Mark H. Kowalski and Peter J. Stang*

Department of Chemistry, The University of Utah
Salt Lake City, Utah 84112

Received March 11, 1986

Summary: The single site oxidative addition reactions of $Pt(PPh_3)_4$ and a series of vinyl triflates are described. The products obtained are stable, crystalline *16*-electron Pt(II) complexes containing a σ-vinyl ligand and the noncoordinating triflate anion.

[†] Dedicated to Professor Cheves Walling on the occasion of his 70th Birthday.

0276-7333/86/2305-2392$01.50/0

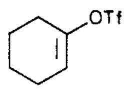
Table I

complex	yield, %	mp, °C dec	IR,[a] cm^{-1}	^{1}H NMR,[b] ppm	^{13}C NMR,[c] ppm	^{31}P NMR, ppm
6	97	195–197	3059 (m), 1605 (w), 1588 (w), 1572 (w), 1480 (m), 1433 (s), 1270 (vs), 1141 (s), 1091 (s), 1029 (s), 745 (s), 695 (s), 635 (s)	0.10 (m, CH$_2$, 2 H), 0.21 (m, CH$_2$, 2 H), 1.18 (m, CH$_2$, 2 H), 1.72 (m, CH$_2$, 2 H), 5.53 (br d, J_{PH} = 10 Hz, J_{PtH} = 37 Hz, 1 H), 7.0–7.8 (aromatics, 45 H)	22.0 (s, CH$_2$), 25.4 (s, Pt$_{sat}$ = 36 Hz, CH$_2$), 30.6 (d, J_{CP} = 9 Hz, Pt$_{sat}$ = 50 Hz, CH$_2$), 37.8 (s, CH$_2$), 122.4 (q, J_{CF} = 320 Hz, CF$_3$SO$_3^-$), 129.5 (m, C$_5$, C$_9$), 131.0 (d, J_{CP} = 56 Hz, C$_7$), 131.0 (t, J_{CP} = 28 Hz, C$_3$), 131.9 (s, C$_{10}$), 132.1 (s, C$_6$), 135.7 (d, J_{CP} = 11 Hz, C$_4$), 136.2 (t, J_{CP} = 5 Hz, C$_8$), 146.7 (dt, $J_{CPtrans}$ = 85 Hz, J_{CPcis} = 12 Hz, C$_1$)	20.6 (d, J_{pp} = 19.5 Hz, J_{Pt-P} = 3139 Hz, P$_{cis}$), 18.6 (t, J_{pp} = 19.5 Hz, J_{Pt-P} = 1692 Hz, P$_{trans}$)
7	87	244–245	3060 (m), 1588 (w), 1573 (w), 1482 (m), 1435 (s), 1270 (vs), 1143 (s), 1092 (s), 1027 (s), 742 (s), 695 (s), 635 (s)	0.67 (br s, CH$_3$, 3 H), 0.97 (br s, CH$_3$, 3 H), 5.39 (m, 1 H), 7.1–7.7 (aromatics, 45 H)	26.5 (s, Pt$_{sat}$ = 83 Hz, CH$_3$), 29.4 (d, J_{CP} = 10 Hz, Pt$_{sat}$ = 61 Hz, CH$_3$), 122.4 (q, J_{CF} = 320 Hz, CF$_3$SO$_3^-$), 129.7 (t, J_{CP} = 5 Hz, C$_5$), 130.0 (d, J_{CP} = 10 Hz, C$_9$), 131.6 (t, J_{CP} = 27 Hz, C$_3$), 131.6 (d, J_{CP} = 54 Hz, C$_7$), 132.4 (s, C$_6$, C$_{10}$), 136.0 (d, J_{CP} = 10 Hz, C$_8$), 136.3 (t, J_{CP} = 5 Hz, C$_4$), 139.0 (br s, C$_1$)	19.8 (overlapping dt, $J_{Pt-P_{cis}}$ = 2952 Hz, $J_{Pt-P_{trans}}$ = 1901 Hz, J_{pp} = 18.4 Hz)
8	79	251–254	3060 (m), 1589 (w), 1573 (w), 1482 (m), 1435 (s), 1269 (vs), 1143 (s), 1021 (s), 1027 (s), 744 (s), 695 (s), 635 (s)	0.70 (m, CH$_2$, 2 H), 0.91 (m, CH$_2$, 2 H), 1.05 (m, CH$_2$, 4 H), 1.81 (m, CH$_2$, 2 H), 4.82 (m, 1 H), 7.1–7.7 (aromatics, 45 H)	26.8 (s, CH$_2$), 27.2 (s, CH$_2$), 27.3 (s, CH$_2$), 36.7 (s, Pt$_{sat}$ = 32 Hz, CH$_2$), 41.2 (d, J_{CP} = 12 Hz, Pt$_{sat}$ = 51 Hz, CH$_2$), 122.4 (q, J_{CF} = 320 Hz, CF$_3$SO$_3^-$), 129.5 (t, J_{CP} = 5 Hz, C$_5$), 129.6 (d, J_{CP} = 10 Hz, C$_9$), 131.0 (d, J_{CP} = 58 Hz, C$_7$), 131.0 (t, J_{CP} = 29 Hz, C$_3$), 132.1 (s, C$_6$, C$_{10}$), 135.8 (d, J_{CP} = 11 Hz, C$_8$), 136.1 (t, J_{CP} = 6 Hz, C$_4$), 143.6 (br s, C$_1$)	18.7 (d, J_{pp} = 19.5 Hz, J_{Pt-P} = 2982 Hz, P$_{cis}$), 19.2 (t, J_{pp} = 19.5 Hz, J_{Pt-P} = 1914 Hz, P$_{trans}$)
9	88	175–178	3059 (m), 1588 (w), 1584 (w), 1571 (w), 1480 (m), 1432 (s), 1268 (vs), 1141 (s), 1092 (s), 1023 (s), 742 (s), 693 (s), 631 (s)	0.99 (br d, CH$_3$, J_{PH} = 5.5 Hz, J_{PtH} = 28 Hz, 3 H), 4.85 (dd, J_{PH} = 8.4 Hz, J_{gem} = 1.5 Hz, J_{PtH} = 39 Hz, 1 H), 5.04 (dd, J_{PH} = 19 Hz, J_{gem} = 1.5 Hz, J_{PtH} = 83 Hz, 1 H), 7.1–7.7 (aromatics, 45 H)	30.6 (br s, CH$_3$), 122.4 (q, J_{CF} = 320 Hz, CF$_3$SO$_3^-$), 123.4 (br s, C$_2$), 129.5 (m, C$_5$, C$_8$), 130.6 (d, J_{CP} = 56 Hz, C$_9$), 130.6 (t, J_{CP} = 28 Hz, C$_3$), 132.0 (s, C$_6$), 132.3 (s, C$_{10}$), 135.6 (d, J_{CP} = 12 Hz, C$_8$), 136.3 (t, J_{CP} = 6 Hz, C$_4$), 156.3 (dt, $J_{CPtrans}$ = 85 Hz, J_{CPcis} = 11 Hz, C$_1$)	19.7 (d, J_{pp} = 19.6 Hz, J_{Pt-P} = 3054 Hz, P$_{cis}$), 18.4 (t, J_{pp} = 19.6 Hz, J_{Pt-P} = 1718 Hz, P$_{trans}$)
10	85	194–196	3057 (m), 1585 (w), 1572 (w), 1479 (m), 1432 (s), 1269 (vs), 1141 (s), 1090 (s), 1025 (s), 742 (s), 694 (s), 632 (s)	0.03 (m, CH$_2$, 2 H), 0.25 (m, CH$_2$, 2 H), 1.07 (m, CH$_2$, 2 H), 1.90 (m, CH$_2$, 2 H), 1.90 (br s, CH$_3$, 3 H), 7.0–7.6 (aromatics, 45 H)	22.0 (s, CH$_2$), 24.8 (br s, CH$_2$), 30.2 (d, J_{CP} = 6 Hz, Pt$_{sat}$ = 50 Hz, CH$_2$), 35.6 (br d, J_{CP} = 8 Hz, CH$_3$), 40.4 (s, CH$_2$), 122.4 (q, J_{CF} = 320 Hz, CF$_3$SO$_3^-$) 129.2 (m, C$_5$, C$_9$), 131.2 (d, J_{CP} = 54 Hz, C$_7$) 131.2 (t, J_{CP} = 27 Hz, C$_3$), 131.7 (s, C$_{10}$), 132.3 (s, C$_6$), 136.0 (d, J_{CP} = 11 Hz, C$_8$), 136.3 (t, J_{CP} = 6 Hz, C$_4$), 141.8 (dt, $J_{CPtrans}$ = 84 Hz, J_{CPcis} = 10 Hz, C$_1$)	19.2 (d, J_{pp} = 17.5 Hz, J_{Pt-P} = 3145 Hz, P$_{cis}$), 15.6 (t, J_{pp} = 17.5 Hz, J_{Pt-P} = 1583 Hz, P$_{trans}$)

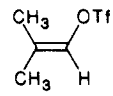
[a] KBr pellet. [b] ^{1}H NMR and ^{13}C NMR referenced to CD$_3$NO$_2$; ^{31}PNMR to external 85% H$_3$PO$_4$. [c] C$_1$ = α-vinyl C; C$_3$, C$_4$, C$_5$, C$_6$ = C$_{ipso}$, C$_{ortho}$, C$_{meta}$, C$_{para}$, on cis phosphines; C$_7$, C$_8$, C$_9$, C$_{10}$ the same on the trans phosphine.

There has been considerable recent interest in transition-metal-mediated vinyl–vinyl coupling reactions and, in paticular, those using vinyl triflates as vinyl cation equivalents.[1] $Pd(PPh_3)_4$ appears to be a very efficient catalyst in these reactions. Existing evidence indicates oxidative addition of the vinyl triflate early in the catalytic cycle. However, to date no simple vinyl triflate addition products have been isolated.[2] While the oxidative addition reactions with saturated alkyl halides and nickel triad zerovalent compounds are ubiquitous,[3] data for vinyl substrate reactions are relatively scarce.[4] All known reactions are limited solely to vinyl substrates with "activating" substituents such as halogens or aromatic groups. There are two modes of addition possible with these "activated" vinyl substrates. The first is net oxidative addition in which σ-vinyl bonds are formed. The other is π-addition in which stable π-complexes are formed. In some cases the π-complex can be converted to the σ-complex by addition of a polar solvent, thus giving an indication of the likely mechanism of these oxidative additions.[5] Initiated by our interest in the reactivity of vinyl triflates with organometallic nucleophiles, we wish to report on the stoichiometric reaction between a series of vinyl triflates and $Pt(PPh_3)_4$.

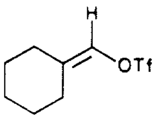
The reaction of $Pt(PPh_3)_4$ with a threefold excess of vinyl triflates 1–4 in toluene at room temperature occurs from within a few minutes to 12 h, yielding complexes 6–9 in high yields (eq 1). Reaction of the fully substituted triflate 5 with $Pt(PPh_3)_4$ required a reaction time of 10 h at 80 °C, yielding complex 10. Recrystallization of complexes 6–10 from toluene/hexanes gives stable pale yellow microcrystals. Spectral (Table I), and physical, elemental analysis[6] data are consistent with loss of 1 mol of triphenylphosphine and metal insertion between the vinyl carbon and triflate oxygen.



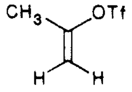
1



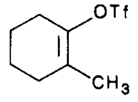
2



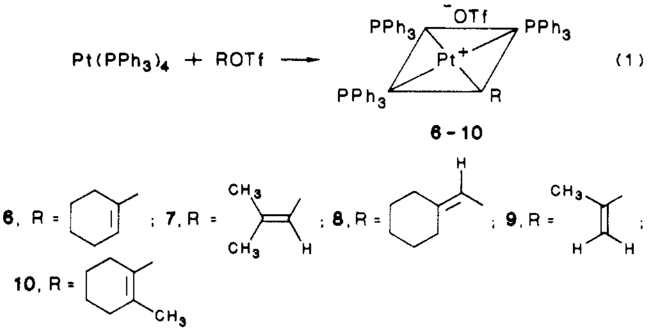
3



4



5

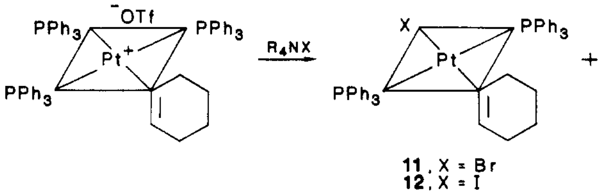


(1)

Data for compound 6 are representative. In particular the ^{1}H NMR spectrum shows resonances and integration consistent with loss of PPh_3 and incorporation of the vinyl ligand. The $^{31}P\{^{1}H\}$ NMR at 121 MHz was key to identification. The spectrum includes a doublet and triplet with $^{2}J_{P_{cis}-P_{trans}} = 19.5$ Hz, ^{195}Pt satellites, and the expected integration of 2:1, respectively. Infrared absorptions characteristic of an anionic triflate[7] group ($^{-}OSO_2CF_3$) at 1270 and 635 cm^{-1}, a ^{19}F NMR resonance at −77.43 ppm (reference $CFCl_3$ in CD_3NO_2), and conductance of 85 $cm^2\ \Omega^{-1}\ mol^{-1}$ in CH_3NO_2 support the ionic formula $[RPt(PPh_3)_3]^{+}\cdot{}^{-}OSO_2CF_3$.[8] ^{13}C data are complicated, especially in the aromatic region, but the presence of alkyl carbons is clearly established and the expected virtual coupling of the mutually trans phosphines is apparent. The C_1 vinyl carbons were assigned by off-resonance decoupling experiments. The C_2 carbons were uniformly obscured by the aromatic carbons, except for complex 9 (see Table I).

FAB mass spectra[9] show molecular ions and isotope patterns resulting from polyisotopic platinum, consistent with predictions. The most stable fragment in all cases corresponds to [vinyl $Pt(PPh_3)_2]^{+}$, resulting from the loss of PPh_3 from the molecular cation.

Treatment of 6 with Et_4NBr or Bu_4NI yields the neutral trans square-planar products 11 and 12, respectively, evidently due to the labilization of the unique phosphine by the trans effect of the vinyl group (eq 2). Complex 12 can be prepared independently by reaction of $Pt(PPh_3)_4$ with 1-iodocyclohexene, while complex 11 cannot be prepared under similar conditions with the bromide even after 2 days.[10]



11, X = Br
12, X = I

R_4NOTf (2)

Compounds 6–10 are of an unique structural type owing to the noncoordinating ability of triflate. Analogous alkyl and hydride complexes are known. Meek[10] prepared the methyl derivative by the reaction of CH_3OSO_2F with $Pt(PPh_3)_3$. The reactions of strong inorganic acids yield the cationic Pt(II) hydrides.[11] In contrast to oxidative additions with halogen compounds, which usually give oxidative addition products with trans stereochemistry in the square-planar products, these reactions give *16-electron* species in which the extra phosphine is needed to stabilize the complex.

---

[1] Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630. Crisp, G. T.; Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7500. Wulff, W. D.; Peterson, G. A.; Bauta, W. E.; Chan, K. S.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem.* **1986**, *51*, 277.

[2] Stille, J. K., personal communication.

[3] Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386. Ugo, R. *Coord. Chem. Rev.* **1968**, *3*, 319. Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434.

[4] Fitton, P.; McKeon J. E. *J. Chem. Soc. D* 4. Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc. A* **1971**, 2667. Johnson, B. F. G.; Lewis, J.; Jones, J. D.; Taylor, K. A. *J. Chem. Soc., Dalton. Trans.* **1974**, 34. Rajaram, J.; Pearson, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 2103.

[5] Bland, W. J.; Kemmitt, R. D. W. *Nature (London)* **1966**, *221*, 963. Bland, W. J.; Kemmitt, R. D. W. *J. Chem. Soc. A* **1968**, 127. Nelson, J. H.; Jonassen, H. B. *Coord. Chem. Rev.* 1971, *6*, 27 and references therein.

[6] Elemental analysis (C, H, P) for complexes 6–10 are satisfactory.

[7] Wechsberg, M.; Bulliner, P. A.; Sladky, F. O.; Mews, R.; Bartlett, N. *Inorg. Chem.* **1972**, *12*, 3063.

[8] All new complexes have an ^{19}F resonance at −77.43 ± 0.02 ppm (CD_3NO_2) and conductance data in support of a 1:1 electrolyte.

[9] Examined by + Ve FAB mass spectrometry using *m*-nitrobenzyl alcohol as the matrix.

[10] Compound 12 was prepared by reacting 0.200 mmol of $Pt(PPh_3)_4$ with 2.00 mmol of 1-iodocyclohexene in 25 mL of degassed toluene at room temperature overnight, quenching with hexane, and filtering, yielding 121 mg (65%). The cyclic vinyl triflate reacts at room temperature in less than 2 h, yielding complex 6.

[11] Person, J. L.; Nappier, T. E.; Meek, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 8195.

[12] Cariati, F.; Ugo, R.; Bonati, F. *Inorg. Chem.* **1966**, *5*, 1128.

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

James M. Takacs,* Lawrence G. Anderson, G. V. Bindu Madhavan, Mark W. Creswell, Franklin L. Seely, and Wayne F. Devroy[†]

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received May 7, 1986

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

---

[†] 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).