Oxidatively Induced Metal-Mediated Cycloaddition. Cyclopentene Formation via Electrocatalyzed Insertion of Alkynes into Iridacyclobutanes

Kathryn E. Schwiebert and Jeffrey M. Stryker*

Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada T6G 2G2

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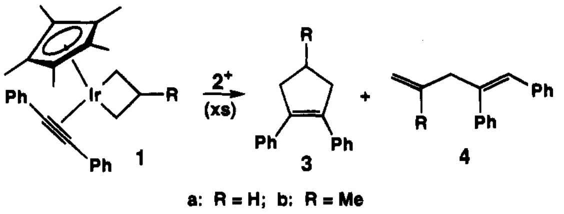
Despite reports of carbon monoxide, sulfur dioxide, and isocyanide migratory insertion in Group VIII metallacyclobutane complexes,[1] the insertion of unsautrated hydrocarbons into the metallacyclobutane framework is unprecedented. Indeed, alkyne iridacyclobutane complexes **1a**,**b**[2] are completely unreactive at temperatures up to the onset of decomposition (≥100 °C) in the presence or absence of added ligand (Me_3P, Ph_3P, CO). In this communication, however, we report that alkyne insertion is *induced* upon one-electron oxidation, providing the first examples of hydrocarbon migratory insertion in the metallacyclobutane structural class and the first report of electrocatalyzed migratory insertion reactions involving an unsaturated hydrocarbon.[3,4] The product distribution obtained from this reaction is dependent on the solvent and, surprisingly, the potential of the oxidant, leading ultimately to the selective formation of either cyclic or acyclic organic products. These data suggest that distinct reactivity patterns arise from within the odd and even-electron manifolds accessible to the substrate after the oxidatively induced migratory insertion reaction.

Treatment of the unsubstituted metallacyclobutane complex **1a** with excess $(C_5H_5)_2Fe^+BPh_4^-$ (**2a**$^+$, 2.4 equiv) in acetonitrile (0° C → room temperature, 1.5 h) results in the formation of cyclopentene **3a**, isolated in >80% yield (eq 1, Table 1).[5] No other organic products are detected in the reaction mixture. The use of greater than stoichiometric oxidant,[6] *added in one portion*, is optimal. The use of catalytic oxidant (0.3 equiv) results in a low material balance and formation of acyclic diene **4a**[5] as a byproduct (**3a**/**4a** ~ 3:1, <20%), and the slow addition of excess oxidant via syringe pump returns no organic product at all. The final disposition of the iridium remains unknown. Reduction of the crude mixture (K_2CO_3, CO or C_2H_4, EtOH, 70 °C) leads to the formation of a small amount (<20%) of $(C_5Me_5)IrL_2$ (L = CO, C_2H_4).[7] Oxidative workup (I_2, THF, −78 °C), however, returns the metal in near quantitative yield as $[(C_5Me_5)IrI_2]_2$,[8] suggesting the formation of polynuclear iridium species.



(1)

Table 1

starting complex	oxidant[a]	solvent (ligand[b])	temp (°C)	product(s) (ratio)	yield[c] (%)
1a (R = H)	**2a**$^+$	CH_3CN	0 → 15	**3a**	82
	2a$^+$	CH_3CN/C_6H_6 (1:1)[d]	RT[e]	**3a**:**4a** (6−7:1)	50−60[f]
	2a$^+$	CH_3CN (CO)	RT	**3a**:**4a** (≥10:1)	60−70
	2a$^+$	CH_2Cl_2 (CO)	RT	**4a**	40[f]
	2b$^+$	CH_3CN	RT	**3a**:**4a** (1:2)	25
1b (R = CH_3)	**2a**$^+$	CH_3CN	−7 → 20	**3b**	80
	2b$^+$	CH_3CN	RT	**4b**	43

[a] **2a**$^+$ $Cp_2Fe^+BPh_4^-$; **2b**$^+$, $Cp_2'Fe^+BPh_4^-$; Cp, cyclopentadienyl; Cp′, methylcyclopentadienyl. [b] 60 psi CO. [c] Reflects isolated yield of material purified by chromatography. [d] Deuterated solvents used. [e] Room temperature. [f] Yield determined by ^1H NMR integration.

Consistent with these observations, cyclic voltammetry[5] of metallacycle **1a** (0.2 M $Bu_4N^+BF_4^-$, CH_3CN) shows a reversible oxidation wave at 0.03 V (vs Cp_2Fe/Cp_2Fe^+, $\Delta E_p = 0.08$ V) at scan rates from 500 to 2000 mv/s, evidence that the initial oxidation is rapid relative to the migratory insertion reaction. Scans to higher potentials reveal a second, irreversible oxidation wave at 0.47 V (vs Cp_2Fe/Cp_2Fe^+), suggesting that **1a** is subject to overoxidation by strong oxidants.[9]

The solvent is intimately involved in the postoxidation reactivity, presumably functioning to stabilize unsaturated intermediates. Solvents less coordinating than acetonitrile lead to lower yields and competitive formation of diene **4a**. The oxidation of iridacyclobutane **1a** at room temperature in 1:1 acetonitrile/benzene, for example, returns a 6−7:1 mixture of **3a** and **4a** in only 50−60% yield. Side reactions dominate the oxidation in noncoordinating solvents, yielding no identifiable products in benzene and $(C_5Me_5)Ir(\eta^5\text{-}C_5H_3Ph_2)^+BPh_4^-$ (**6**)[2] (~20%) in dichloromethane, presumably via the intermediacy of $(C_5Me_5)Ir(\eta^3\text{-allyl})(Ph_2C_2)^+BPh_4^-$.[2] In dichloromethane, however, the presence of CO (60 psi) promotes the formation of diene **4a** (40%) as the exclusive organic product. In acetonitrile, CO (60 psi) competes poorly with solvent coordination, resulting in only marginally lower yields of cyclopentene **3a**, but now accompanied by diene **4a**.

Remarkably, *the distribution of products from the electrocatalyzed insertion reaction is strongly dependent on the potential of the oxidant.* Thus, use of $(C_5H_4Me)_2Fe^+BPh_4^-$

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(1) Review: Jennings, P. W.; Johnson, L. L. *Chem. Rev.*, in press.

(2) Schwiebert, K. E.; Stryker, J. M. *Organometallics* **1993**, *12*, 600.

(3) Electrocatalyzed ligand substitution, structural isomerization, and carbon monoxide insertions into metal−alkyl bonds, both stoichiometric and catalytic in the oxidant, are well-established: Reviews: (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978. (b) Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 643. (c) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217. (d) Tyler, D. R. *Prog. Inorg. Chem.* **1988**, *36*, 125. (e) Connelly, N. G. *Chem. Soc. Rev.* **1989**, *18*, 153. (f) Trogler, W. C., Ed. *Organometallic Radical Processes*; Elsevier Science: Amsterdam, 1990. (g) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325. Recent and lead references: (h) Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1987**, *109*, 5127. (i) Diversi, P.; Iacoponi, S.; Ingrosso, G.; Laschi, F.; Lucherini, A.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1993**, 351.

(4) Other electrocatalyzed carbon−carbon bond-forming reactions: (a) Waterman, P. S.; Giering, W. P. *J. Organomet. Chem.* **1978**, *155*, C47. (b) Tsou, T. T.; Kochi, J. K.; *J. Am. Chem. Soc.* **1978**, *100*, 1634. (c) Gotzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247. (d) Geiger, W. E.; Gennett, T.; Lane, G. A.; Salzer, A.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1352. (e) Pearson, A. J.; Chen, Y.; Daroux, M. L.; Tanaka, A. A.; Zettler, M. *J. Chem. Soc., Chem. Commun.* **1987**, 155. (f) Hwang, W.; Liao, R.; Horng, Y.; Ong, C. *Polyhedron* **1989**, *8*, 479. (g) Martinez, J.; Gill, J. B.; Adams, H.; Bailey, N. A.; Saez, I. M.; Sunley, G. J.; Maitlis, P. M. *J. Organomet. Chem.* **1990**, *394*, 583. (h) Pedersen, A.; Tilset, M. *Organometallics* **1993**, *12*, 56.

(5) Experimental, electrochemical, spectroscopic, and analytical data are included as supplementary material.

(6) The requirement for excess oxidant is due at least partly to the instability of **2a**$^+$ in CH_3CN: Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892. The reduced reaction temperature minimizes the excess necessary for complete conversion. For comparison to the remaining data in Table 1, the use of 1.1 equiv of **2a**$^+$ at room temperature affords **3a** exclusively in 58% yield; with 2.6 equiv of **2a**$^+$ at room temperature, an 87% yield of **3a** is isolated.[5]

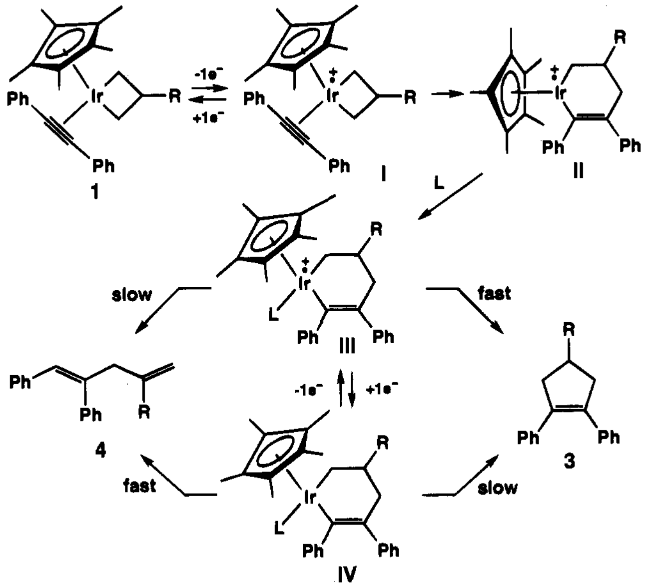
(7) (a) L = CO: Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. (b) L = C_2H_4: Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc. A* **1970**, 2875.

(8) Gill, D. S.; Maitlis, P. M. *J. Organomet. Chem.* **1975**, *87*, 359.

(9) Treatment of metallacycle **1a** with stronger oxidants, such as AgOTf or acetylferrocenium, results in complete consumption of starting material with no formation of identifiable organic products.

0002-7863/94/1516-11570$04.50/0

Scheme 1



($2b^+$) (1.1 equiv, room temperature,[10] 12 h), an approximately 0.1 V weaker oxidant than the parent ferrocenium $2a^+$, favors the formation of diene **4a** over cyclopentene **3a** (**3a**/**4a** ~ 1:2, 20–25% combined yield, no starting material recovered). The reactivity of β-methyliridacyclobutane complex **1b** confirms this unusual dichotomy: use of the stronger oxidant $2a^+$ results in exclusive formation of methylcyclopentene **3b**[5] in high yield, while use of the weaker oxidant $2b^+$ returns only diene **4b**[5] in attenuated isolated yield (Table 1). All attempts to reproduce this reactivity manifold and confirm the outer-sphere character of the oxidation by using bulk electrolysis at controlled potential fail, yielding no organic fraction.[11]

On the assumption that both oxidants function by an initial outer-sphere electron transfer,[12] a mechanistic rationale consistent with these results can be proposed (Scheme 1). The product distribution is determined after the alkyne insertion, we propose, *by the rate and extent of back reduction to the even electron manifold* (**III** → **IV**). The partition between cyclization and diene formation thus arises from inherent differences in the activation barriers to reductive elimination and β-hydride elimination from within the odd and even-electron manifolds. In the oxidized manifold, reductive elimination from the electron-deficient iridacyclohexene **III** is apparently more facile than β-hydride transfer,[4b,h,13] while in the relatively electron-rich even-electron manifold, iridacyclohexene **IV** undergoes selective β-elimination, the more conventional reactivity pattern.[14] In the electrocatalyzed alkyne insertion, back-reduction (**III** → **IV**) is mediated by the conjugate of the original oxidant. Thus, for ferrocene, the weaker reductant, the reaction is maintained in the odd-electron manifold, selectively producing cyclopentene, while 1,1′-dimethylferrocene more efficiently mediates the reduction back to the even-electron manifold, where the partitioning favors diene formation. This mechanistic hypothesis is consistent with the observed solvent and ligand effects: coordination of the donor acetonitrile ligand stabilizes the radical cation **III** (L = CH_3CN), maintaining the reaction in the oxidized manifold. Replacement of the donor solvent with π-acidic CO in a noncoordinating solvent destabilizes **III** (L = CO), leading to more facile reduction to the even-electron manifold and, as observed, selective diene formation. This proposal is also consistent with the requirement for rapid, stoichiometric oxidation to obtain cyclopentene selectively: using catalytic oxidant, slow addition techniques, or bulk electrolysis, the remaining neutral iridacyclobutane can function as the reductant for highly electron-deficient complex **II** and/or ring-expanded complex **III**, leading to destructive overoxidation or return to the even-electron manifold (and diene formation), respectively. The lower yields invariably obtained from reactions leading to the diene can be attributed both to slower oxidation with the weaker oxidant and to unfavorable partitioning in the presumed oxidative process that releases the diene from a substitutionally inert[7b] Ir(I) intermediate.[15]

The origin of the rate acceleration for migratory insertion processes in the odd-electron manifold has been the subject of extensive discussion.[3] In general, the high reactivity has been attributed to the rapid coordination of an additional ligand to the 17e$^-$ complex, forming a 19e$^-$ species which (despite marginal stabilization[3g]) undergoes facile migratory insertion in order to reduce the electron count at the metal.[3f] In the present case, it is interesting to consider that the transformation from 17e$^-$ to 19e$^-$ intermediates can be accomplished internally, by conversion of the alkyne coordination mode from 2e$^-$ to 4e$^-$ donation, rather than by the addition of an external ligand.

One-electron oxidation of the otherwise unreactive iridacyclobutane complexes **1a**,**b** thus provides a rich and complicated reactivity manifold in which the distribution of products appears to be determined by the partitioning between odd- and even-electron manifolds and by differences in the inherent reactivity on each energy surface. Despite this complexity, either manifold can be accessed selectively, with the odd-electron domain providing an unprecedented cyclopentene synthesis. The oxidation not only reduces the kinetic barrier to alkyne migratory insertion but also shifts the preferred reactivity pattern from β-hydride elimination to reductive cyclization. Continued investigations are focused on mechanistic issues and electrocatalyzed insertion processes on other iridacyclobutane templates.

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Supplementary Material Available: Experimental procedures with complete spectroscopic and analytical data for **3a**,**b** and **4a**,**b** (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(10) Oxidations mediated by the weaker 1,1′-dimethylferrocenium salt proceed too slowly to go to completion at reduced temperature.

(11) Because electrochemical oxidation is limited by diffusion at the electrode, the oxidation necessarily proceeds a little at a time, yielding results that parallel those obtained from slow addition of the oxidant.

(12) Given the modest steric profile of ferrocenium salts $2a^+$ and $2b^+$, inner-sphere mechanisms for the observed transformations cannot be conclusively excluded, despite the common assumption of outer-sphere electron transfer for such oxidations.[3b] For two such structurally similar oxidants, however, it is difficult to rationalize how such distinct reactivity patterns could arise from direct oxidant/substrate interactions. In a preliminary investigation, the stoichiometric oxidation of iridacyclobutane complex **1a** using the sterically more encapsulated oxidant $[Co(phen)_3]^{3+}(PF_6)_3$ (phen = 1,10-phenanthroline) leads to exclusive formation of cyclopentene **3a**, while the β-methyl iridacyclobutane **1b** gives mixtures of cyclopentene **3b** and diene **4b** (Moore, M. R.; Stryker, J. M., unpublished results).

(13) Sixteen-electron Cr(II) alkyl complexes undergo β-H elimination faster than ethylene insertion, whereas the 15e$^-$ Cr(III) analogue undergoes rapid multiple ethylene insertions: Thomas, B. J.; Noh, S. K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc* **1991**, *113*, 893.

(14) (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521. Barabotti, P.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Nuti, F. *J. Chem. Soc., Dalton. Trans.* **1984**, 2517. (b) Analogous β-elimination is observed in a related iridabenzocycloheptene: McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246.

(15) Control experiments reveal that diene **4** is itself reasonably stable to the oxidation conditions.