J. Am. Chem. Soc. 1992, 114, 10667-10669 10667

Sequential Benzannulation/Nucleophilic Aromatic Addition Reactions Mediated by Chromium(0)†

Steven Chamberlin[1a] and William D. Wulff*

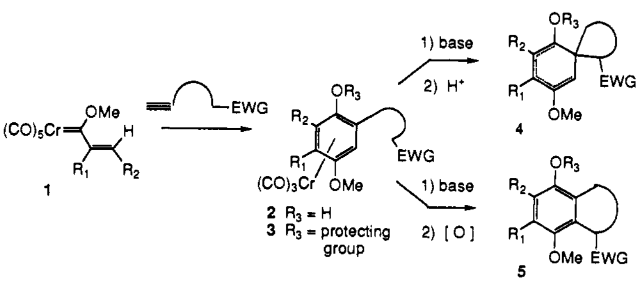
*Department of Chemistry, Searle Chemistry Laboratory
The University of Chicago, Chicago, Illinois 60637*

Received May 4, 1992

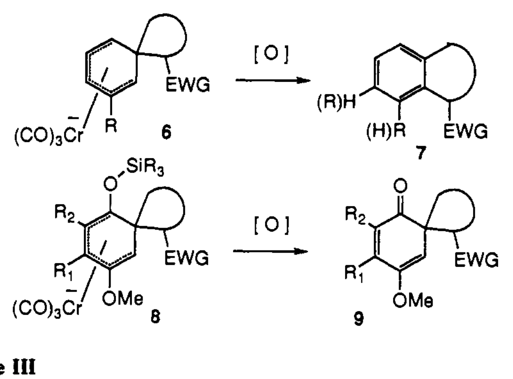
It can be argued that the two most important reactions of organochromium compounds in organic synthesis are the benzannulation reactions of Fischer carbene complexes[2] and aromatic nucleophilic substitution/addition reactions on (arene)chromium tricarbonyl complexes.[3,4] It is remarkable that although the products of the benzannulation reactions are (arene)chromium tricarbonyl complexes, they have never been utilized as substrates for aromatic nucleophilic substitution/addition reactions. The products from the benzannulation reaction are phenols of the type **2**, and the use of a base strong enough to generate a carbanion on the side chain of **2** would be expected to first generate a phenolate complex, which would be unlikely to suffer nucleophilic addition. Thus, one of the reasons that complexes of the type **2** have never been used as substrates for nucleophilic addition is that all attempts to protect the phenol functionality while at the same time retaining the $Cr(CO)_3$ group have failed.[5,6]

In principle, the strategy of employing a tandem benzannulation/aromatic nucleophilic addition could lead to direct routes to synthetic intermediates useful for the preparation of spirobicyclic compounds such as acorenone,[7] a spirobicyclic sesquiterpene, or to fused bicyclic products such as the anthracycline antitumor antibiotics[8] if conditions could be found to control ipso versus vicinal intramolecular nucleophilic attack in complex **3**. While vicinal products such as **5** can be directly obtained by oxidative induced loss of hydride, current methodology in nucleophilic additions to (arene)chromium tricarbonyls requires that spiro products be generated as dienes by protonation of intermediates of the type **6**, which can lead to mixtures of olefin isomers (i.e., **4** in Scheme I).[9] Oxidative workup of spirocyclic anionic intermediates of the type **6** leads to isomeric mixtures of fused products by a presumed Wagner–Meerwein shift when a cationic form of **6** is reached in the oxidation.[10] We report here the first successful development of methods for the protection of the phenol

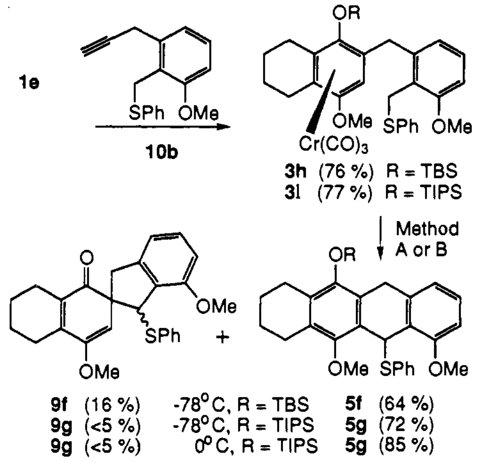
Scheme I



Scheme II



Scheme III



---

† This paper is dedicated to Professor E. O. Fischer, who was the first to describe the preparation of both chromium carbene complexes and (arene)chromium tricarbonyl complexes.

(1) (a) American Chemical Society Organic Division American Cyanamid Fellow, 1991-1992. (b) A preliminary account of this work was presented at the ACS National Meeting in New York, Aug 25-30, 1991, ORG 221.

(2) For reviews on the synthetic applications of Fischer carbene complexes, see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Casey, C. P. *React. Intermed.* **1985**, 3. (d) Dötz, K. H. In *Organometallics in Organic Synthesis: Aspects of a Modern Interdisciplinary Field*; tom Dieck, H., de Meijere, A., Eds.; Springer: Berlin, 1988. (e) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (f) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Boston, 1989. (g) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1. (h) *Transition Metals in Total Synthesis*; Harrington, P. J., Ed.; John Wiley: New York, 1990; pp 346-399. (i) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5, pp 1065-1113.

(3) For recent reviews, see: (a) Semmelhack, M. F. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 4, pp 517-549. (b) Kündig, E. P. *Pure Appl. Chem.* **1985**, *57*, 1855.

(4) For recent articles, see: (a) Dickens, M. J.; Gilday, J. P.; Mowlem, T. J.; Widdowson, D. A. *Tetrahedron* **1991**, *47*, 8621. (b) Rose-Munch, F.; Aniss, K.; Rose, E.; Vaisserman, J. *J. Organomet. Chem.* **1991**, *415*, 223. (c) Kündig, E. P.; Inage, M.; Bernardinelli, G. *Organometallics* **1991**, *10*, 2921. (d) Uemura, M.; Minami, T.; Shinoda, Y.; Mishimura, H.; Shiro, M.; Hayashi, Y. *J. Organomet. Chem.* **1991**, *406*, 371. (e) Kündig, E. P.; Bernardinelli, G.; Liu, R.; Ripa, A. *J. Am. Chem. Soc.* **1991**, *113*, 9676. (f) Kündig, E. P.; Amurrio, D.; Liu, R.; Ripa, A. *Synlett* **1991**, 657. (g) Persson, M.; Hacksell, U.; Csoregh, I. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1453. (h) Yang, S. S.; Dawson, B. T.; Rieke, R. D. *Tetrahedron Lett.* **1991**, *32*, 3341. (i) Chaari, M.; Henhi, A.; Lavergne, J. P.; Viallefont, P. *Tetrahedron* **1991**, *47*, 4619. (j) Kündig, E. P.; Grivet, C.; Wenger, E.; Bernardinelli, G.; Williams, A. *Helv. Chim. Acta* **1991**, *74*, 2009. (k) Djukic, J. P.; Geysermans, P.; Rose-Munch, R.; Rose, E. *Tetrahedron Lett.* **1991**, *32*, 6703. (l) Djukic, J. P.; Rose-Munch, F.; Rose, E. *J. Chem. Soc., Chem. Commun.* **1991**, 1634. (m) Rose-Munch, F.; Mignon, L.; Souchez, J. P. *Tetrahedron Lett.* **1991**, *32*, 6323. (n) Uemura, M.; Nishimura, H.; Minami, T.; Hayashi, Y. *J. Am. Chem. Soc.* **1991**, *113*, 5402. (o) Davies, S. G.; Edwards, A. J.; Shipton, M. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1009. (p) Davies, S. G.; Shipton, M. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 757. (q) Rose-Munch, F.; Bellot, O.; Mignon, L.; Semra, A.; Robert, R.; Jeannin, Y. *J. Organomet. Chem.* **1991**, *402*, 1.

(5) (a) Yamashita, A.; Toy, A. *Tetrahedron Lett.* **1986**, 3471. (b) Yamashita, A.; Scahill, T. A.; Toy, A. *Tetrahedron Lett.* **1985**, 2969. (c) Boger, D. L.; Jacobsen, I. C. *J. Org. Chem.* **1991**, *56*, 2115. (d) McCallum, J. S.; Kunng, F. A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346.

(6) Wulff, W. D.; Chamberlin, S. Manuscript in preparation.

(7) (a) Semmelhack, M. F.; Yamashita, A. *J. Am. Chem. Soc.* **1980**, *102*, 5924. (b) Uemura, M.; Kobayashi, T.; Isobe, K.; Minami, T.; Hayashi, Y. *J. Org. Chem.* **1986**, *51*, 2859.

(8) (a) Wulff, W. D.; Xu, Y. C. *J. Am. Chem. Soc.* **1988**, *110*, 2312. (b) Dötz, K. H.; Popall, M. *Chem. Ber.* **1988**, *121*, 665. (c) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. (d) Dötz, K. H.; Popall, M. *Tetrahedron* **1985**, *41*, 5797. (e) Wulff, W. D.; Tang, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 434.

(9) (a) Semmelhack, M. F.; Yoshifuji, M.; Clark, G. *J. Am. Chem. Soc.* **1976**, *98*, 6387. (b) Semmelhack, M. F.; Harrison, J. J.; Thebtaranonth, Y. *J. Org. Chem.* **1979**, *44*, 3275.

(10) (a) Semmelhack, M. F.; Harrison, J. J.; Thebtaranonth, Y. *J. Org. Chem.* **1979**, *44*, 3275. (b) Semmelhack, M. F.; Thebtaranonth, Y.; Keller, L. *J. Am. Chem. Soc.* **1977**, *99*, 959.

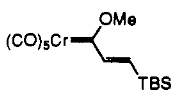
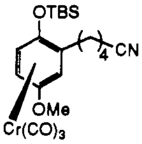
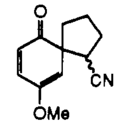
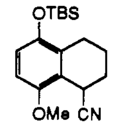
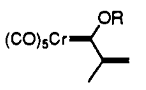
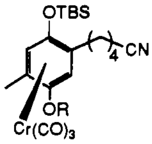
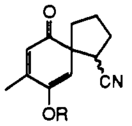
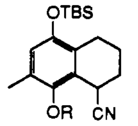
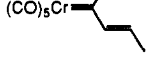
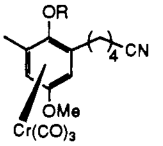
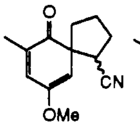
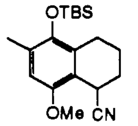
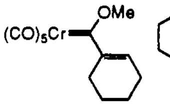
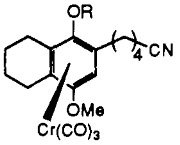
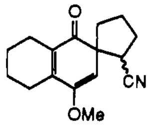
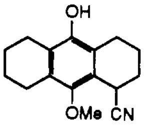
0002-7863/92/1514-10667$03.00/0

complexes **2**, the controlled nucleophilic additions to the arene complexes **3** to give either spirocyclic or fused bicyclic products, and the development of an oxidative method for the generation of spirocyclic products that relies on the ability of the silicon in **8** to arrest Wagner–Meerwein shifts by intercepting cations generated in the oxidation of **8** (Scheme II).

The protected (phenol)chromium tricarbonyl complexes **3** can be generated in situ by carrying out the reaction in the presence of a silyl triflate and 2,6-lutidine or by a silyl-transfer strategy if a silyl substituent is incorporated into the β-position of carbene complex **1** ($R_2 = SiR_3$).[11] The phenol complexes **3** can be isolated as their silyl ethers in good yields (69–77% yield) from the reactions of a number of carbene complexes with either 6-cyano-1-hexyne (**10a**) or the alkyne **10b** and are stable to silica gel as their *tert*-butyldimethylsilyl or triisopropylsilyl derivatives (Scheme III). In each case the silylated phenol complex was produced in a yield at least as good as (and often better than) the yield of the corresponding quinone if an oxidative workup was employed.[12c]

The regioselectivity of the benzannulation step is highly selective as expected,[12] and the regioselectivity of the aromatic nucleophilic addition is dependent on both the nature and positions of the substituents on **3** and on whether the reaction is carried out under kinetic or thermodynamic control.[3,13–15] The regioselectivity for nucleophilic addition in these reactions is surprising, since although in simple systems intramolecular nucleophilic additions to arene $Cr(CO)_3$ complexes are selective, this is lost in more functionalized examples.[7] In the case of the complex **3a**, the closure can give exclusively either the spirocyclic adduct **9a**, when the reaction is quenched with iodine at −78 °C, or the fused aromatic product **5a**, when the reaction is quenched at 0 °C (Table I). A comparison of the reactions carried out under kinetic control (method A) reveals a correlation between the nature of the aryl substituents and the regioselectivity of the addition that is similar to that which has been generally established.[3,15,16] The two oxygen substituents appear to be largely offsetting since either product can be obtained in the reaction of **3a**, and in the reaction of the methyl-substituted complexes **3b** and **3d**, the kinetic addition is meta to the methyl groups whereas normally a methoxyl will dominate a methyl group in controlling the addition.

Table I. Sequential Benzannulation/Aromatic Nucleophilic Substitutions

carbene complex	benzannulation product ^{a,b}	method ^{c}	nucleophilic aromatic substitution products ^{b,d}	
				
1a (55 %) ^{e}	**3a** (69 %)	A	**9a** (73 %)	
		B		**5a** (67 %)
				
1b R = methyl	**3b** (73 %)	A	**9b** (<5 %)	**5b** (62 %)
(72 %) ^{e}	**3c** (75 %)	B	**9b** (<5 %)	**5b** (52 %)
1c R = cyclohexyl		A	**9c** (<5 %)	**5c** (18 %)
(55 %) ^{e}				
				
1d (67 %) ^{f}	**3d** (73 %)	A	**9d** (73 %)	
	R = TBS	B		**5d** (13 %)
	3e (68 %)	A	**9d** (48 %)	
	R = TIPS			
				
1e (65 %) ^{f}	**3f** (72 %)	A	**9e** (72 %)	
	R = TBS	B	(<5 %) ^{g}	**5e** (<5 %) ^{g}
	3g (76 %)	A		(62 %)
	R = TIPS			

^{a}Reactions run in CH_2Cl_2, 0.05 M in **1b–e** with 1.5 equiv of **10a** or 1.3 equiv of **10b**, 1.5 equiv of TBS- or TIPS-OTf, and 2.5 equiv of 2,6-lutidine, 50–65 °C, 15–24 h. Reactions with **1a** are the same except that the silyl triflate and lutidine were omitted. ^{b}All yields are for isolated products purified by silica gel chromatography in air. ^{c}Reactions run in THF, 0.02–0.05 M in **3**: (A) 1.2 equiv of LDA, −78 °C, 1.5 h, then 7–8 equiv of I_2, −78 °C, 1 h; then 25 °C, 1–3 h; (B) 1.2 equiv of LDA, −78 °C, 10 min, then 0 °C, 1 h, followed by addition of 7–8 equiv of I_2 at 0 °C, then 25 °C, 2–4 h. ^{d}**9a–e** isolated as ca. 2:1 mixtures of separable diastereomers; **9f** isolated as a ca. 2:1 mixture of inseparable diastereomers (Scheme III). ^{e}Reference 22. ^{f}Reference 24. ^{g}Crude ^1H NMR revealed the absence of **9e** and **5e** and the presence of two compounds (~30% each), one of which was identified as the decomplexed arene **3f**.

In an effort to extend this methodology to the tetracyclic carbon skeleton of anthracyclines,[8] we sought to include an arene ring in the tether to the carbanion-stabilizing group. Since the pK_a of the carbanion needs to be $\geq\sim 25$ for optimal nucleophilic closure,[3,17] we chose the sulfide-substituted complexes **3h** and **3i** as target precursors which could be efficiently generated from alkyne **10b**.[18] The advantage of the benzannulation reaction is evident for the preparation of **3h** and **3i** (and also complexes from 6-cyano-1-hexyne) since their generation from the free arene could lead to coordination of $Cr(CO)_3$ to any of the three arene rings or to the sulfide group (or nitrile group). In comparing the positions of attack in complexes **3f** and **3h** it is clear that the inclusion of the two sp^2-carbons in the tether biases the attack toward fused-ring products. The reaction gives only the fused tetracyclic product **5g**[20] in 85% yield if the triisopropylsilyl complex **3i** is employed. It is not clear whether the difference in the siloxy groups in **3h** and **3i** (also **3f** and **3g**) is due to a steric impact on the nucleophile or to an effect on the conformation of the $Cr(CO)_3$ group, but if there is a steric effect, it is not expressed in the reactions of **3d** and **3e**.[4n,14,15,21]

---

(11) (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7565. (b) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, 5813.

(12) (a) Wulff, W. D.; Tang, P. C.; McCallum, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 7677. (b) Dötz, K. H.; Muhlemeier, J.; Schubert, U.; Orama, O. *J. Organomet. Chem.* **1983**, *247*, 187. (c) Wulff, W. D.; Chan, K. S.; Tang, P. C. *J. Org. Chem.* **1984**, *49*, 2293. (d) Yamashita, A.; Toy, A. *Tetrahedron Lett.* **1986**, *27*, 3471.

(13) (a) Kündig, E. P.; Desobry, V.; Simmons, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 6962. (b) Kündig, E. P.; Desobry, V.; Simmons, D. P.; Wenger, E. *J. Am. Chem. Soc.* **1989**, *111*, 1804. (c) Kündig, E. P.; Cunningham, A. F., Jr.; Paglia, P.; Simmons, D. P. *Helv. Chim. Acta* **1990**, *73*, 386.

(14) (a) Ohlsson, B.; Ullenius, C. *J. Organomet. Chem.* **1984**, *267*, C34. (b) Ohlsson, B.; Ullenius, C. *J. Organomet. Chem.* **1988**, *350*, 35. (c) Semmelhack, M. F.; Wulff, W. D.; Garcia, J. L. *J. Organomet. Chem.* **1982**, *240*, C5.

(15) Ohlsson, B.; Ullenius, C.; Jagner, S.; Grivet, C.; Wegner, E.; Kündig, E. P. *J. Organomet. Chem.* **1989**, *365*, 243.

(16) (a) Semmelhack, M. F.; Clark, G. *J. Am. Chem. Soc.* **1977**, *99*, 1675. (b) Semmelhack, M. F.; Clark, G. R.; Farina, R.; Saeman, M. *J. Am. Chem. Soc.* **1979**, *101*, 217. (c) Semmelhack, M. F.; Garcia, J. L.; Cortes, D.; Farina, R.; Hong, R.; Carpenter, B. K. *Organometallics* **1983**, *2*, 467.

(17) Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; Druker, G. E.; Gerhold, J.; McCollum, G. J.; Van Der Puy, M.; Vanier, N. R.; Matthews, W. S. *J. Org. Chem.* **1977**, *42*, 326.

(18) Alkyne **10b** was prepared in nine steps in 40% overall yield from 3-methoxyphenol (see supplementary material).

(19) Semmelhack, M. F.; Yamashita, A. *J. Am. Chem. Soc.* **1980**, *102*, 5924.

(20) The fused product **5f** was isolated exclusively as tetrahydronaphthacene **11f** resulting from the loss of benzenethiol, and **5g** was isolated as a variable mixture with tetrahydronaphthacene **11g**, where **5g** was favored with smaller excesses of iodine. (See supplementary material.)

The tandem benzannulation/nucleophilic aromatic addition permits synthetic strategies for direct access to either spirobicyclic or fused bicyclic intermediates. It also obviates many of the tactical problems that have been encountered previously in the intramolecular application of aromatic nucleophilic additions to chromium arene complexes, which may be transferable to intermolecular examples as well.

Acknowledgment. This work was supported by a grant from the National Institutes of Health (PHS-CA 32974). We thank the Organic Division of the American Chemical Society for a predoctoral fellowship sponsored by American Cyanamid Company. Some of the mass spectral data were obtained at the Midwest Center for Mass Spectrometry, an NSF Regional Instrument Facility (CHE-8211164). The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program.

Supplementary Material Available: Spectral data for all new compounds and general procedures for the benzannulation and aromatic nucleophilic substitution reactions and the preparation of **10b** (11 pages). Ordering information is given on any current masthead page.

---

(21) (a) van Meurs, F.; van der Toorn, J. M.; van Bekkum, H. *J. Organomet. Chem.* **1976**, *113*, 341, 353. (b) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (c) Albright, T. A.; Carpenter, B. K. *Inorg. Chem.* **1980**, *19*, 3092. (d) Solladie-Cavallo, A.; Wipff, G. *Tetrahedron Lett.* **1980**, 3047. (e) Solladie-Cavallo, A.; Suffert, J. *Org. Magn. Reson.* **1980**, *14*, 426. (f) Boutonnet, J. C.; Mordenti, L.; Rose, E.; LeMartret, D.; Precigoux, G. *J. Organomet. Chem.* **1981**, *221*, 147. (g) Jackson, W. R.; Rae, I. D.; Wong, M. G.; Semmelhack, M. F.; Garcia, J. L. *J. Chem. Soc., Chem. Commun.* **1982**, 1359. (h) Rogers, R. D.; Atwood, J. L.; Albright, T. A.; Rausch, M. D. *Organometallics* **1984**, *3*, 263. (i) Solladie-Cavallo, A. *Polyhedron* **1985**, *4*, 901. (j) Jackson, W. R.; Rae, I. D.; Wong, M. G. *Aust. J. Chem.* **1986**, *39*, 303.

(22) Yields for complexes **1b** and **1c** prepared from the metal acylate[26] methyl triflate or acetyl bromide[27]/cyclohexanol. Complex **1a** (ref 6).

(23) (a) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642. (b) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hydahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9.

(24) Complexes **1d** (ref 23a). Complex **1e** (ref 23b).

(25) Jones, T. K.; Denmark, S. E. *Helv. Chim. Acta* **1983**, *66*, 2397.

(26) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445.

(27) Hegedus, L. S.; Schwindt, M. A.; De Lombaert, D.; Imwinkelried, R. *J. Am. Chem. Soc.* **1990**, *112*, 2264.

New Polymetallic Ruthenium Carbonyl Halide Complexes: Exotic Combinations of Electron Deficient Skeletons with Electron Rich Anions. Their Potential Interest in Ethylene Hydroesterification

Guy Lavigne* and Noël Lugan

Laboratoire de Chimie de Coordination du CNRS
associé à l'Université Paul Sabatier et à
l'Institut National Polytechnique
205, route de Narbonne, 31077 Toulouse Cedex, France

Philippe Kalck, Jean Marc Soulié, and Olivier Lerouge

Ecole Nationale Supérieure de Chimie de Toulouse
Institut National Polytechnique
118, route de Narbonne, 31077 Toulouse Cedex, France

Jean Yves Saillard and Jean François Halet

Laboratoire de Chimie du Solide et
Inorganique Moléculaire, Université de Rennes I
Avenue du Général Leclerc, 35042 Rennes Cedex, France

Received August 10, 1992

In connection with the observation that mixtures of $Ru_3(CO)_{12}$ and [PPN]Cl are good catalyst precursors in the hydroesterification of ethylene by methyl formate[1] to produce methyl propionate (eq 1),[2,3] we attempted to trace the transformation of preformed ruthenium carbonyl halide species $[PPN][Ru_3(Cl)(CO)_{12-n}]$ (**1-3**) (n = 1, 2, 3)[4-6] under catalytic conditions.

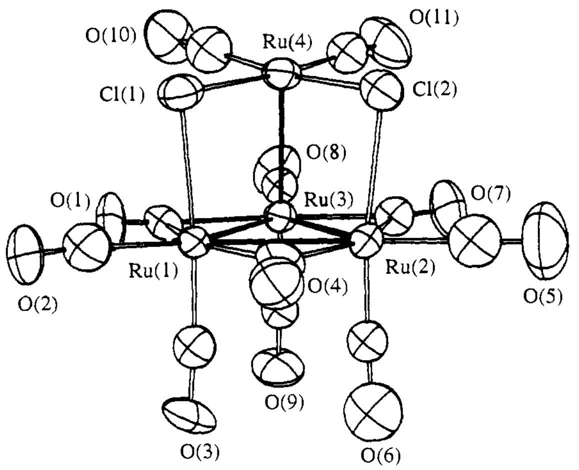


Figure 1. Perspective view of the dianionic unit of complex **4**. Selected interatomic distances (Å): Ru(1)-Ru(3) = 2.812 (2); Ru(2)-Ru(3) = 2.806 (2); Ru(1)-Ru(2) = 2.870 (1); Ru(3)-Ru(4) = 2.766 (2); Ru(1)⋯Ru(4) = 3.502 (2); Ru(2)⋯Ru(4) = 3.463 (2); Ru(1)-Cl(1) = 2.536 (4); Ru(2)-Cl(2) = 2.534 (4); Ru(4)-Cl(1) = 2.417 (4); Ru(4)-Cl(2) = 2.416 (4).

$$H_2C{=}CH_2 + HC(O)OCH_3 \xrightarrow[160\ ^\circ C,\ 12\ h,\ 100\%\ conversion]{Ru_3(CO)_{12}/[PPN]Cl,\ dimethylformamide} CH_3CH_2C(O)OCH_3 \quad (1)$$

99% selectivity, turnover = 339

During the course of preliminary experiments aimed at evaluating the optimum Ru/halide ratio, we were led to discover that $[PPN][Ru_3(\mu_3\text{-}Cl)(CO)_9]$ (**3**)[5h] reacts cleanly with [PPN]Cl under a stream of inert gas to provide a unique dianionic species $[PPN]_2[Ru_4(\mu\text{-}Cl)_2(CO)_{11}]$ (**4**) according to eq 2.[3]

$$\underset{\mathbf{3}}{4[PPN][Ru_3(\mu_3\text{-}Cl)(CO)_9]} + 2[PPN]Cl \xrightarrow[THF,\ 60\ ^\circ C,\ 1\ h]{argon\ stream} \underset{\mathbf{4}}{3[PPN]_2[Ru_4(\mu\text{-}Cl)_2(CO)_{11}]} + 3CO \quad (2)$$

The red complex **4**, insoluble in THF, was isolated by filtration, recrystallized in 70% yield, and characterized by X-ray analysis.[3,7]

---

(1) For reviews on methyl formate as a versatile intermediate, see: (a) Röper, M. *Erdöl Kohle, Erdgas, Petrochem.* **1984**, *37* (11), 506-511. (b) Lee, J. S.; Kim, J. C.; Kim, Y. G. *Appl. Catal.* **1990**, *57*, 1-30.

(2) Catalytic runs performed in a 100-mL autoclave; HCOOMe, 0.081 mol; DMF, 15 mL; ethylene, 20 bar (at 25 °C); T = 160 °C; time = 12 h. Catalyst precursor: $Ru_3(CO)_{12}$/[PPN]Cl (1/1); substrate/catalyst molar ratio, 345. Turnover = 339 (moles of formate converted per mole of catalyst). The only side product is 3-pentanone (<1%).[3]

(3) Full details and provided in the supplementary material.

(4) For known Ru-based catalytic systems involving halide promoters, see: (a) Dombek, B. D. *J. Organomet. Chem.* **1989**, *372*, 151-161 and references therein. (b) Knifton, J. *J. Mol. Catal.* **1988**, *47*, 99-116 and references therein. (c) Knifton, J. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Reidel: Dordrecht, The Netherlands, 1988; Vol. 6, pp 1-58 and references therein. (d) Yoshida, S.-I.; Mori, S.; Kinoshita, H.; Watanabe, Y. *J. Mol. Catal.* **1987**, *42*, 215-227. (e) Cenini, S.; Crotti, C.; Pizzotti, M.; Porta, F. *J. Org. Chem.* **1988**, *53*, 1243-1250 and references therein.

(5) For fundamental reactions of anion-promoted species, see: (a) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647-4648. (b) Zuffa, J. L.; Blohm, M. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 552-553. (c) Zuffa, J. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 4669-4671. (d) Han, S.-H.; Geoffroy, G. L.; Dombek, B. D.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 4355-4361. (e) Han, S.-H.; Song, J. S.; Macklin, P. D.; Nguyen, S. T.; Geoffroy, G. L. *Organometallics* **1989**, *8*, 2127-2138. (f) Chin-Choy, T.; Harrison, W. T. A.; Stucky, G. D.; Keder, N.; Ford, P. C. *Inorg. Chem.* **1989**, *28*, 2028-2029. (g) Rivomanana, S.; Lavigne, G.; Lugan, N.; Bonnet, J.-J.; Yanez, R.; Mathieu, R. *J. Am. Chem. Soc.* **1989**, *111*, 8959-8960. (h) Rivomanana, S.; Lavigne, G.; Lugan, N.; Bonnet, J.-J. *Organometallics* **1991**, *10*, 2285-2297. (i) Ramage, D. L.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1992**, *11*, 1242-1255.

(6) For a recent review, see: Lavigne, G. In *The Chemistry of Metal Clusters*; Shriver, D., Adams, R. D., Kaesz, H. D., Eds.; VCH: New York, 1990; Chapter 5, pp 201-303 and references therein.

0002-7863/92/1514-10669$03.00/0