ORGANOMETALLICS

Volume 11, Number 6, June 1992

Communications

Thermal and Photochemical Reactions of Chromium Carbenes and Sulfur Ylides: An Efficient Entry to Functionalized Vinyl Ethers

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Received January 16, 1992

Summary: The photochemical reaction of pentacarbonylalkoxychromium(0) carbene complexes and stabilized sulfur ylides affords vinyl ethers with moderate stereoselectivity. The thermal reaction of the above reagents also produces vinyl ethers, but some differences in yields and stereoselectivity have been observed.

Chromium carbene (Fischer) complexes are becoming widely used reagents in organic synthesis.[1] Their rich reactivity, coupled to well-differentiated behavior patterns under thermal[2] or photochemical[3] conditions, renders these complexes useful reagents in building complex organic structures. Nevertheless, some aspects of the reactivity of these and related tungsten complexes have been scarcely investigated; among others, their reactions with ylides have been circumscribed to simple phosphorus ylides,[4] sulfoxides,[4b,5] and diazoalkanes.[6] In these Wittig-like processes the organometallic moiety behaves as an activated ester.

We have recently shown[7] that other ylides such as sulfilimines are suitable partners for Wittig-like reactions with alkoxychromium carbene complexes, and imidates were obtained in good yields upon irradiation. In this communication, we report the reaction of alkoxychromium carbenes and stabilized sulfur ylides to produce functionalized enol ethers, which in turn are not available by conventional Wittig methodology.[8]

Thus, irradiation of an equimolecular mixture of chromium complexes 1 and sulfur ylides 2 in dry acetonitrile under argon at room temperature, after air oxidation to eliminate the metallic residue, gave enol ethers 3 as E/Z mixtures in almost quantitative yields (Scheme I). Crude reaction mixtures were usually clean, which proved to be fortunate since considerable loss of material was observed upon purification of these mixtures by flash chromatography.[9] Both ester- and ketone-derived ylides gave good

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(1) For reviews, see: (a) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1990; Vol 5. (b) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1. (c) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluver Academic Publishers: Hingham, MA, 1989. (d) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 587.

(2) For some recent references on synthetic applications of chromium carbene complexes under thermal conditions, see among others: (a) Grotjahn, D. B.; Dötz, K. H. *Synlett* **1991**, 381. (b) Boger, D. L.; Jacobson, I. C. *J. Org. Chem.* **1991**, *56*, 2115. (c) Brandvold, T. A.; Wulff, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 5459. (d) Lattuada, L.; Licandro, E.; Maiorana, S.; Molinari, H.; Papagni, A. *Organometallics* **1991**, *10*, 807. (e) 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. (f) Wienand, A.; Reissig, H. *Organometallics* **1990**, *9*, 3133.

(3) For recent references on synthetic applications of chromium carbene complexes under photochemical conditions, see: (a) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 7418. (b) Hegedus, L. S.; Montgomery, J.; Narukawa, Y.; Snustad, D. C. *J. Am. Chem. Soc.* **1991**, *113*, 5784 and references therein. (c) Alcaide, B.; Domínguez, G.; Plumet, J.; Sierra, M. A. *J. Org. Chem.* **1992**, *57*, 448. (d) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 4364. (e) Söderberg, B. J.; Hegedus, L. S. *J. Org. Chem.* **1991**, *56*, 2209. (f) Hegedus, L. S.; Schwindt, M. A.; De Lombaert, S.; Imwinkelried, R. *J. Am. Chem. Soc.* **1990**, *112*, 2264.

(4) (a) Casey, C. P.; Burkhardt, T. *J. Am. Chem. Soc.* **1972**, *94*, 6543. (b) Casey, C. P.; Burkhardt, T.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127.

(5) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726.

(6) Casey, C. P.; Bertz, S. H.; Burkhardt, T. *Tetrahedron Lett.* **1973**, 1421.

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(8) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863.

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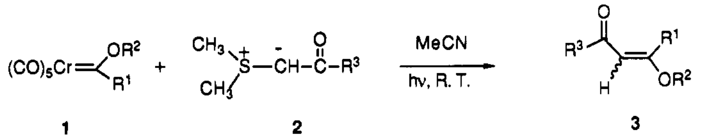
Scheme I



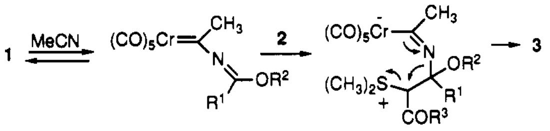
						Yield (%)[a]	E/Z (hν)	E/Z (Δ)
1a $R^1 = CH_3$ $R^2 = CH_3$	**2a** $R^3 = OCH_3$	**3a**	$R^1 = CH_3$	$R^2 = CH_3$	$R^3 = OCH_3$	65	2.3 : 1	2.3 : 1
1b $R^1 = CH_3$ $R^2 = CH_2Ph$	**2b** $R^3 = OBu^t$	**3b**	$R^1 = Ph$	$R^2 = CH_3$	$R^3 = OCH_3$	70	4.0 : 1	1.0 : 3
1c $R^1 = Ph$ $R^2 = CH_3$	**2c** $R^3 = Ph$	**3c**	$R^1 = CH_3$	$R^2 = CH_2Ph$	$R^3 = OCH_3$	60	5.6 : 1	1.4 : 1[b]
		3d	$R^1 = CH_3$	$R^2 = CH_3$	$R^3 = OBu^t$	73	4.0 : 1	4.0 : 1
		3e	$R^1 = CH_3$	$R^2 = CH_3$	$R^3 = Ph$	81	100[c]	
		3f	$R^1 = Ph$	$R^2 = CH_3$	$R^3 = Ph$	90	4.6 : 1	4.6 : 1

[a] Yields of pure, isolated *E*/*Z* mixtures of compound **3**, obtained under photochemical conditions. [b] Extensive hydrolysis was observed under thermal conditions. [c] *E* isomer was exclusively formed, under both thermal and photochemical conditions.

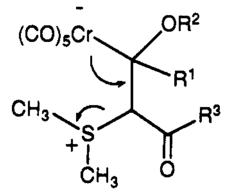
yields of the desired vinyl ethers. It is noteworthy that complexes bearing alkyl substituents at the carbene carbon form smoothly the corresponding enol ethers, in clear contrast with the analogous reaction of phosphorus ylides, for which competitive deprotonation renders the reaction useless for vinyl ether synthesis.[6] However, all attempts to use nonstabilized sulfur ylides resulted in total disappearance of the starting material to give a pale yellow solution, from which we were unable to isolate any identifiable organic product. This is again in contrast with the phosphorus ylide approach to vinyl ethers,[4] which makes use of nonstabilized ylides. Spectroscopic data for compounds **3** were fully consistent with their enol ether nature.[10]

On the other hand, when the reaction between compounds **1** and **2** was carried out at room temperature, in the dark, the stereochemical outcome was in most cases analogous to that observed under photochemical conditions, except for the reaction of complex **1c** and ylide **2a**, where a clear inversion of the stereochemistry was found, and for complex **1b** and ylide **2a**, where loss of stereoselectivity was observed. Although yields of crude product were essentially the same for both the thermal and the photochemical processes, shorter reaction times and cleaner crude mixtures were obtained when photochemical conditions were used.[11] Both thermal and photochemical conditions show a stereochemical bias for the *E* isomer, which is complete in the case of compound **3e**. The observed selectivity may be of steric origin, both in the carbene complex and in the ylide. This is suggested when selectivities observed in the reactions of **1a** and **1b** with **2a** (*E*/*Z* 2.3/1 vs 5.6/1, respectively), and of **2a** and **2b** with **1a** (*E*/*Z* 2.3/1 vs 4.1/1), are compared. However, at this time, it is difficult to explain the complete selectivity obtained in the preparation of **3e** and the inversion of stereochemistry observed in some cases by changing from photochemical to thermal conditions. Equilibration between isomers during the long reaction times required in thermal reactions may account for the observed change in the stereochemical outcome.

Scheme II



Formation of enol ethers **3** may occur through the zwitterionic intermediate **4** related to that previously proposed by Casey,[4] and by us[7] in related Wittig-like processes of metal carbene complexes and ylides.[12]



4

A general experimental procedure for the preparation of compounds **3** follows: Chromium alkoxy carbene **1** (1 mmol) was placed in a Pyrex test tube, which was sealed with a rubber septum, evacuated, and purged with argon (three cycles). Degassed MeCN (5 mL) and ylide **2** (1 mmol) in MeCN (5 mL) were added with a syringe. The resulting solution was irradiated (450-W medium-pressure mercury lamp, Pyrex well) in a water bath until complete disappearance (TLC) of the starting carbene. The solvent was removed under reduced pressure, the brown residue was dissolved in methyl acetate, and the resulting solution was filtered through Celite, diluted with 1 volume of pentane, and air-oxidized in a light box[13] (9 × 20 W fluorescent bulbs) until a clear colorless solution with a brown precipitate was obtained. Filtration of the brown precipitate (Celite) and removal of the solvent gave almost pure product **3** as an inseparable mixture of *E*/*Z* stereoisomers. Pure compounds **3** were obtained by flash

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(9) Compounds 3 are unstable, are very easily hydrolyzed, and are in some cases volatile. Considerable loss of material and extensive hydrolysis were observed when standard flash chromatography was used for purification of the crude reaction mixtures. Best results were obtained by using short deactivated ($NaHCO_3$) silica gel columns and short chromatography times. Use of pentane–methyl acetate mixtures as eluent prevents loss of material by evaporation during solvent elimination under reduced pressure.

(10) The ratio of *E*/*Z* isomers was determined by integration of well-resolved signals (usually olefinic protons and when possible methyl groups) in the ^1H NMR spectra of crude reaction mixtures. Assignment of *E*/*Z* stereochemistry was made by comparison of ^1H and ^{13}C NMR spectra with those of previously reported analogous vinyl ethers. See: Brower, H.; Stothers, J. B. *Can. J. Chem.* **1972**, *50*, 601 and references therein. For full spectroscopic data, see the supplementary material.

(11) This behavior is analogous to that observed in the reaction of alkoxychromium carbene complexes and sulfilimines.[7]

(12) The alternative reaction pathway sketched in Scheme II, involving MeCN insertion into the Cr–carbene bond followed by conjugated ylide attack leading to a zwitterionic intermediate related to 4, has been proposed by a reviewer. This interesting mechanism may be operative, as either a main or secondary pathway, although it has been reported that nitrile insertion occurs at temperatures higher or reaction times longer than those used in this work. See: Yang, D. C.; Dragisich, V.; Wulff, W. D.; Huffman, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 307. We thank the reviewer for this suggestion, which will be taken into consideration in our future work.

(13) In order to reduce the possibility of hydrolysis of unstable compounds 3, short oxidation times are desirable.

chromatography through a short path of deactivated silica gel.[9] Thermal reactions were carried out by following the same procedure but strictly excluding light.

In summary, a new stereoselective approach to vinyl ethers **3** starting from chromium carbenes having both alkyl and aryl substituents at the carbene carbon and stabilized sulfur ylides has been developed. This novel reaction provides an alternative strategy for constructing 2-acyl enol ethers directly in enolized form, in a process which formally results in the totally *site*-selective enolization of a β-keto ester or a β-diketone. Compounds **3** are in turn not available by using standard Wittig methodology, and the stereoselectivity of the process may be steric in nature. Efforts to extend this methodology to other chromium carbene complexes and to control the stereochemistry in the formation of compounds **3** are now in progress.

Acknowledgment. Support for this work under Grant PB90-0047 from the DGICYT (MEC-Spain) is gratefully acknowledged. We thank Prof. Joaquin Plumet for fruitful discussions and Dr. Fernández de la Pradilla for his help during the preparation of this paper.

Registry No. **1a**, 20540-69-6; **1b**, 117041-03-9; **1c**, 27436-93-7; **2a**, 18915-90-7; **2b**, 79261-11-3; **2c**, 5633-34-1; (*E*)-**3a**, 4525-28-4; (*Z*)-**3a**, 22157-30-8; (*E*)-**3b**, 60456-20-4; (*Z*)-**3b**, 40203-51-8; (*E*)-**3c**, 140853-75-4; (*Z*)-**3c**, 140853-76-5; (*E*)-**3d**, 82481-16-1; (*Z*)-**3d**, 140853-77-6; (*E*)-**3e**, 50487-01-9; (*E*)-**3f**, 101009-45-4; (*Z*)-**3f**, 101009-48-7.

Supplementary Material Available: Text describing the syntheses and giving full characterization and spectral data (^{1}H NMR, ^{13}C NMR, IR, and analytical data) for compounds **3a–f** (4 pages). Ordering information is given on any current masthead page.

OM920027U

Unexpected Carbon–Carbon Coupling between Organic Cyanides and an Isopropyl β-Carbon in a Hafnium Ene Diamide Complex

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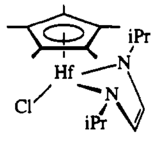
Received February 24, 1992

Summary: A reaction sequence involving two hydrogen transfers and a C–C coupling on the β-carbon of an isopropyl group leads to formation of a new dianionic tridentate ligand in the reaction of the ene diamide complex $Cp^*Hf(\sigma^2,\pi$-*i*Pr-DAB)Cl (**1**; $Cp^* = \eta^5$-C_5Me_5, *i*Pr-DAB = 1,4-diisopropyl-1,4-diaza-1,3-butadiene) with organic cyanides. The product $Cp^*Hf[$*i*PrNCH=CHNC(Me)=CHC(*t*Bu)=NH]Cl was structurally characterized (*Pbca*, $a = 13.454$ (1) Å, $b = 11.470$ (1) Å, $c = 31.297$ (2) Å, 100 K). The reaction sequence is probably initiated by the transfer of the *i*Pr α-H atom to a coordinated cyanide. Such a hydrogen transfer was observed in the reaction of **1** with ketones, producing the ene imine alkoxide complexes $Cp^*Hf[$*i*PrNCH=CHN=$CMe_2](OCHR_2)Cl$, which were identified by NMR spectroscopy.

One of the most interesting and useful aspects of transition-metal centers in organometallic chemistry is that they can induce unusual transformations in coordinated organic ligands. C–C bond-forming reactions and reactions involving C–H bonds have attracted special attention in this respect and have found application in metal-directed organic synthesis.[1] Here we wish to report a unique sequence of consecutive C–H activation and C–C coupling on an *i*Pr group in an ene diamide ligand observed in the reaction of a hafnium ene diamide complex with organic cyanides.

Recently we reported the use of 1,4-diisopropyl-1,4-diaza-1,3-butadiene (*i*Pr-DAB) as an ancillary ligand for early-transition-metal centers to prepare various organohafnium complexes of the type Cp^*Hf(*i*Pr-DAB)R ($Cp^* = \eta^5$-C_5Me_5; R = Cl (**1**), Me, C≡CMe, C(O)Me, H).[2] In these complexes the ligand assumed a nonplanar σ^2,π ene diamide structure and acted in preliminary reactivity studies as an inert ancillary ligand, yielding thermally robust compounds. The π-donation from the nitrogen lone-pair electrons makes the metal center in these complexes significantly less electron-deficient than in the isostructural 14-electron butadiene complex $Cp^*Hf(\sigma^2,\pi$-2,3-dimethyl-1,3-butadiene)Cl (**2**).[3]



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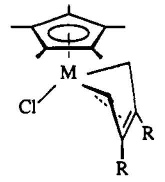

2

Despite this relative electron richness, complex **1** still exhibits some Lewis-acidic behavior and forms isolable

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