ORGANOMETALLICS

Volume 23, Number 17, August 16, 2004

Communications

Nitro and Nitroso Metathesis Reactions with Monomeric Zirconium Imido Complexes

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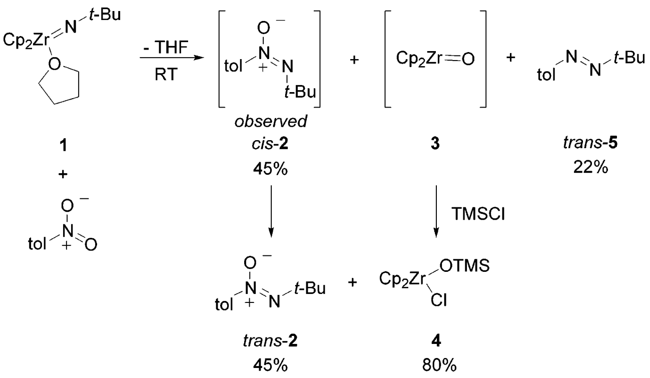
Received June 9, 2004

*Summary: The bis(cyclopentadienyl)(tert-butylimido)zirconium complex **1** undergoes ambient-temperature metathesis reactions with nitro- and nitrosoarenes, providing a rare nonphotochemical synthesis of cis-azoxy and cis-azo compounds, respectively. 2-Nitro-2-methylpropane also undergoes metathesis to give trans-(tert-butylazoxy)-2-methylpropane. This reaction was studied kinetically, and the rate was found to be first order in both **1** and substrate and inversely proportional to the concentration of tetrahydrofuran, with activation parameters* $\Delta H^{\ddagger} = 15 \pm 2$ *kcal mol*$^{-1}$ *and* $\Delta S^{\ddagger} = -26 \pm 3$ *cal mol*$^{-1}$ *K*$^{-1}$.

During our investigations of imidozirconocene-mediated epoxide opening reactions,[1] we were surprised to find that *p*-nitrostyrene oxide failed to undergo the expected epoxide opening but, rather, underwent an alternative reaction of the nitro group. We now report a more detailed study of the reaction of $\mathrm{Cp_2Zr{=}N}$-*t*-Bu(THF) (**1**)[2,3] with *p*-nitrotoluene, which has revealed a metathesis reaction between the N=O and Zr=N-*t*-Bu functionalities, generating the very reactive *cis*-(*tert*-butylazoxy)toluene (*cis*-**2**) and $[\mathrm{Cp_2Zr{=}O}]_n$ (**3**) (Scheme 1). Direct synthesis of acyclic cis azoxy compounds is challenging; therefore, the cis isomer is usually made by chemical synthesis of the trans isomer, followed by photoisomerization.[4] To our knowledge, the transformation in Scheme 1 represents a rare example of a transition-metal-mediated [2 + 2] metathesis reaction involving a nitro group and direct chemical synthesis of a cis azoxy compound. Herein we discuss the scope and mechanism of this novel process, as well as its extension to nitroso compounds.

Scheme 1. Metathesis Reaction between 1 and *p*-Nitrotoluene



The addition of imido complex **1** to *p*-nitrotoluene resulted in rapid formation of *cis*-**2** and oxozirconocene.

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[1] Blum, S. A.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 14276.

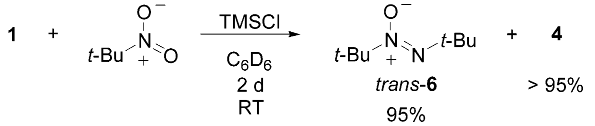
[2] Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.

[3] Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705.

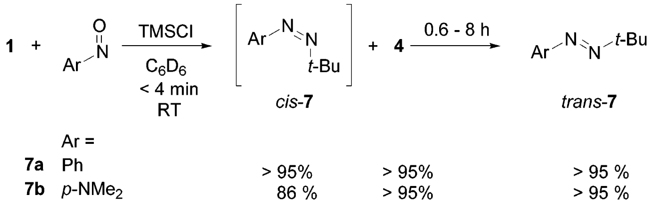
[4] Taylor, K. G.; Riehl, T. *J. Am. Chem. Soc.* **1972**, *94*, 250. An alternative method for the synthesis of *tert*-butylazoxybenzene involves addition of lithium *tert*-butylamide to nitrobenzene; however, the trans product is usually observed under those conditions.[7,8]

10.1021/om0495776 CCC: $27.50 © 2004 American Chemical Society
Publication on Web 07/16/2004

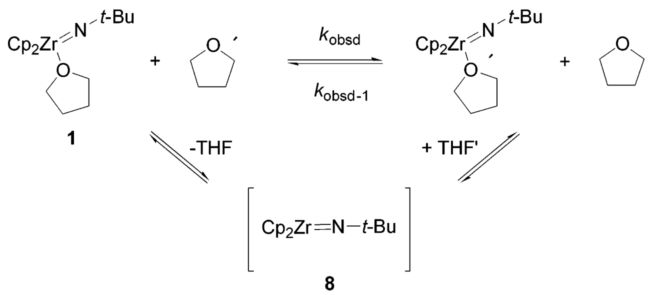
Scheme 2. Metathesis Reaction between 1 and Methyl-2-nitropropane



Scheme 3. Metathesis Reaction between 1 and Nitrosoarenes



Scheme 4. Exchange of Bound and Free THF



The product *cis*-**2** was initially identified by the distinctive upfield resonances of its ortho protons in the ^{1}H NMR spectrum (45% NMR yield).[5] Over several hours *cis*-**2** isomerized quantitatively to *trans*-**2**. The oxozirconocene coproduct formed through this metathesis was efficiently trapped under the reaction conditions with chlorotrimethylsilane (TMSCl) to give complex **4**.[6]

Interestingly, the reduced *trans*-*tert*-butylazotoluene (**5**) is formed as a byproduct (22% ^{1}H NMR yield), with no *cis*-**5** observed. (Alkylazo)aryl compounds have been observed previously as byproducts in the synthesis of (alkylazoxy)aryl compounds by the reaction of Grignard reagents with nitroaromatic compounds.[7,8] We considered the possibility that imido complex **1** reacted with the newly formed azoxy compound **2** to form **5**. Azoxy compound **2**, however, was found to be stable to the presence of excess imido complex **1** on the time scale of the reaction. Therefore, it seemed that another pathway accounted for formation of **5**, possibly through the intermediacy of nitroso or azodioxy (nitroso dimer) compounds (vide infra).

Further investigation showed that imido complex **1** also underwent metathesis with 2-methyl-2-nitropropane to give *trans*-(*tert*-butylazoxy)-2-methylpropane (*trans*-**6**; 95% ^{1}H NMR yield) (Scheme 2). This reaction was notably slower than the reactions with nitroarenes, requiring 2 days to reach complete conversion at ambient temperature. In this case, no cis intermediate was observed.[9]

The more reactive nitroso group displayed metathesis reactivity similar to that of the nitro group. Transition-metal-mediated metathesis reactions of nitroso compounds are known, involving both alkylidene[10] (CR_2 transfer) and imido (NR transfer) complexes.[11] However, while several of these alkylidene reactions proceed from isolable complexes, prior to this account a metathesis reaction proceeding from a fully characterized imido complex had not been studied. Nitrosobenzene reacted cleanly with imido complex **1** to give *cis*-(*tert*-butylazo)benzene (*cis*-**7**) (Scheme 3). The compound *cis*-**7a** was identified by the distinctive upfield resonances of its ortho protons in the ^{1}H NMR spectrum[5] and its isomerization to *trans*-**7a** over several hours (>95% NMR yield). The electron-rich *p*-(dimethylamino)nitrosobenzene also reacted cleanly (>95% NMR yield). In this case, the cis to trans isomerization proceeded rapidly, with 13% *trans*-**7b** already present at the earliest monitoring time (4 min) and with quantitative isomerization after 40 min. Addition of imido complex **1** to 2-nitroso-2-methylpropane in the presence of TMSCl led to formation of **3**, identified by its trapping product **4**; however, the expected 2,2′-azobis(2-methylpropane) coproduct was not observed.[12]

The reaction of **1** with 2-methyl-2-nitropropane to give *trans*-**6** and **4** was studied kinetically under pseudo-first-order conditions. The disappearance of starting complex **1** and appearance of both *trans*-**6** and **4** were monitored by ^{1}H NMR spectroscopy over the temperature range 45.0−74.5 °C. The reaction exhibited first-order kinetics with respect to both **1** and 2-methyl-2-nitropropane. We report rate constants k_{obsd}, independent of the concentrations of 2-methyl-2-nitropropane and THF, which were used in excess to establish flooding conditions: $k_{obsd} = 0.000\,43$ s^{-1} (45.0 °C), $k_{obsd} = 0.000\,76$ s^{-1} (56.0 °C), $k_{obsd} = 0.0016$ s^{-1} (64.5 °C), $k_{obsd} = 0.0034$ s^{-1} (74.5 °C).[13] The rate was zero order in the concentration of trapping agent [TMSCl] and was inversely proportional to the concentration of THF. Furthermore, *trans*-**6** and **4** formed at equal rates, concomitant with the disappearance of imido complex **1**, which precludes the possibility that the concentration of an intermediate builds up significantly. Rates measured over this temperature range gave activation parameters $\Delta H^\ddagger = 15 \pm 2$ kcal mol^{-1} and $\Delta S^\ddagger = -26 \pm 3$ cal mol^{-1} K^{-1}, corresponding to a free energy of activation $\Delta G^\ddagger = 24 \pm 3$ kcal mol^{-1} at 60.5 °C.

The contribution of the initial dissociation of THF from imido complex **1** to the overall activation energy was examined next. The rate of exchange of bound and free THF (Scheme 4) was measured by ^{1}H NMR

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(5) (a) Ege, S. N.; Sharp, R. R. *J. Chem. Soc. B* **1971**, 2014. (b) Snyder, J. P.; Bandurco, V. T.; Darack, F.; Olsen, H. *J. Am. Chem. Soc.* **1974**, *96*, 5158.

(6) Hanna, T. A.; Baranger, A. M.; Bergman, R. G. *J. Org. Chem.* **1996**, *61*, 4532.

(7) Shepelev, E. V.; Kostikova, N. N.; Dzhetigenov, B. A.; Kalinin, A. V. *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1991**, *40*, 1291; *Izv. Akad. Nauk SSSR Ser. Khim.* **1991**, *6*, 1452.

(8) Apasov, E. T.; Dzhetigenov, B. A.; Strelenko, Y. A.; Kalinin, A. V.; Tartakovskii, V. A. *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1991**, *40*, 1234; *Izv. Akad. Nauk SSSR Ser. Khim.* **1991**, *6*, 1394.

(9) The reactions of imido complex **1** with nitromethane, 2-nitropropane, and β-nitrostyrene generated a variety of products, none corresponding to the desired metathesis pathway.

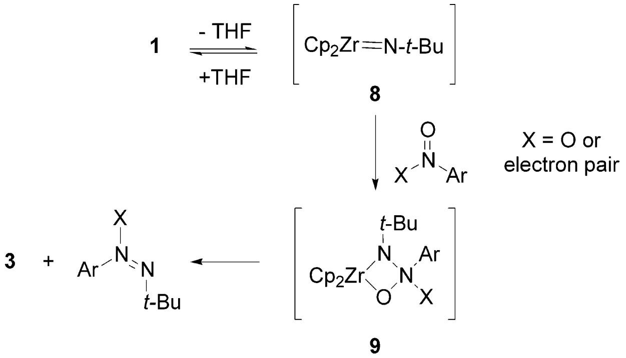
(10) Pilato, R. S.; Williams, G. D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 3665.

(11) Herndon, J. W.; McMullen, L. A. *J. Organomet. Chem.* **1989**, *368*, 83.

(12) Azo-2-methylpropane was found to be stable in the presence of excess **1**, implying that azo-2-methylpropane likely does not form and then decompose by reaction with **1**.

(13) We estimate the error to be ±0.0001 s^{-1} at 64.5 °C, on the basis of a triplicate run.

Scheme 5. Proposed Mechanism of Metathesis Reactions



spectroscopy, revealing $k_{obsd} = 240\ s^{-1}$ at 60.5 °C, which corresponds to a free energy of activation $\Delta G^{\ddagger} = 16$ kcal mol^{-1}. This value is consistent with the establishment of a rapid equilibrium between imido complex **1** and coordinatively unsaturated imido complex **8**, which, in the presence of 2-methyl-2-nitropropane, undergoes rate-limiting metathesis.

A competition experiment between *p*-(dimethylamino)nitrosobenzene and nitrosobenzene provided further mechanistic insight. When 1 equiv of imido complex **1** was allowed to react with a mixture of 2 equiv of *p*-(dimethylamino)nitrosobenzene and 2 equiv of nitrosobenzene at ambient temperature, formation of **7b** was favored modestly over formation of **7a** (**7b**:**7a** = 69:31). This modest preference is consistent with low activation barriers for reaction with either substrate, in contrast to the higher barrier observed for the reaction of **1** with 2-methyl-2-nitropropane.

On the basis of the [2 + 2] reactivity of imido complex **1** with alkenes and alkynes to give isolable metallacyclobutane and -butene complexes,[3] respectively, and with aldehydes to give likely oxametallacyclobutane intermediates,[14] we consider that the nitro and nitroso metatheses may also proceed through [2 + 2] cycloadditions, in this case to give diazaoxametallacyclobutanes (**9**) (Scheme 5). Retrocycloaddition in the opposite sense then leads to the observed products.

In conclusion, imido complex **1** undegoes metathesis reactions with arylnitro and arylnitroso compounds to give *cis*-azoxy and *cis*-azo compounds, respectively. 2-Methyl-2-nitropropane also undergoes metathesis, yielding *trans*-(*tert*-butylazoxy)butane. This represents a rare transition-metal-mediated [2 + 2] metathesis reaction of nitro compounds and a rare example of a transition-metal-mediated metathesis reaction of nitroso compounds that proceeds from a fully characterized imido complex. Mechanistic credence is therefore lent to the presence of imido complexes as intermediates in other known nitroso metathesis reactions.

Acknowledgment. This work was supported by the NIH through Grant No. GM-25459. The Center for New Directions in Organic Synthesis is supported by Bristol-Meyers Squibb as a Sponsoring Member and Novartis as a Supporting Member.

Supporting Information Available: Text and figures giving experimental procedures, kinetic data, and analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0495776

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(14) Lee, S. Y.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 6396.