maintains. This leads to the conjecture that the functional vanadium-containing species is in fact the vanadophore vacuole, or perhaps the entire vanadocyte, and not some smaller molecular unit.

Acknowledgments. We thank Patrick Frank for numerous helpful discussions and experimental assistance and Donald P. Abbott for help in the various biological aspects of this study. Partial support for R.M.K.C. was provided by NIH Grant GM 06840 to Carl Djerassi. The research was supported by the National Science Foundation through Grant PCM 79-0495 and the synchrotron beam time was provided by the Stanford Synchrotron Radiation Laboratory supported by National Science Foundation Grant DMR-77-27489 in cooperation with the Stanford Linear Accelerator Center and the U.S. Department of Energy.

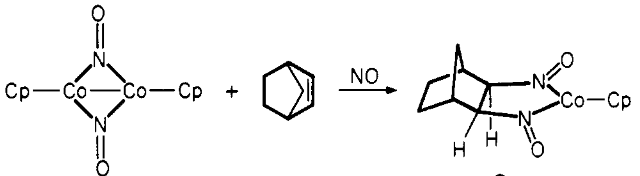
Communications to the Editor

A New Method for 1,2-Diamination of Alkenes Using Cyclopentadienylnitrosylcobalt Dimer/NO/LiAlH$_4$

Sir:

We report a new cobalt-based reagent for vicinal diamination of alkenes. This is the first general method for the direct conversion of olefins into primary vicinal diamines; because of this, and the fact that it works satisfactorily for terminal, *E* and *Z* di-, tri-, and at least some tetrasubstituted alkenes, it appears to circumvent the problems of scope encountered with reagents developed earlier.[1-3]

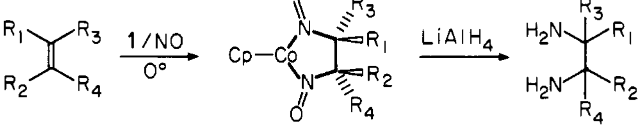
Our work utilizes some organometallic cobalt nitrosyl chemistry discovered by Brunner and Loskot.[4] These workers reported that the cobalt nitrosyl dimer **1**, easily prepared[5] by nitrosating



1 **2**

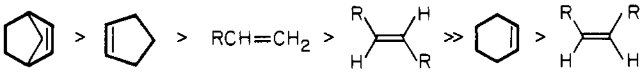
CpCo(CO)$_2$ (Cp = η^5-C$_5$H$_5$), reacted (in the presence of additional NO) with moderately strained bicyclic alkenes such as norbornene to give cis-exo complexes of general structure **2**. In the norbornene case, Bernal and his co-workers ultimately confirmed this structure by X-ray diffraction.[6] Brunner and Loskot noted that **2** reacted with both LiAlH$_4$ and I$_2$; however, the products of these reactions were not reported. They also observed the formation of cobalt alkylnitroso complexes similar to **2** when **1** was allowed to react with ethylene or cyclohexene and NO, but attempts to purify these materials were unsuccessful.

We have now observed that the reaction of **1** with ordinary alkenes is quite general, and the alkylnitroso complexes **3** so generated can be stabilized (at least in solution) by performing the reactions at 0 °C rather than at room temperature. More significantly, in lieu of isolation, solutions of these adducts may be treated directly with LiAlH$_4$, leading on workup to primary vicinal diamines (**4**) in adequate to excellent *isolated* yield (Table I).[7]



3 **4**

Scheme I



The relative reactivity of alkenes toward dimer **1** increases with increasing ring strain. Interestingly, the relative reactivity of cis and trans isomers of a given alkene appears to parallel the palladium- and osmium-based reactions,[1,2] except that in our system the cis stereoisomers react rapidly enough to obtain product. A qualitative scale of reaction rates for a series of common alkenes is shown in Scheme I. This reactivity parallels the apparent thermal stability of the corresponding alkylnitroso complexes (**3**), the stereoselectivity of the LiAlH$_4$ reduction (see below), and the diamine yield.

The formation of pure cis-exo adduct **2** from norbornene suggested that the overall diamination might be stereospecific. Addition of the adduct solution *to* a suspension of LiAlH$_4$ in THF with rapid stirring gave reasonable stereoselectivity. In refluxing THF, the cis-exo diamine made up 84% of the mixture, and 10% and 6% of the other two isomers were found; reduction at −65 °C gave a 90:4:6 ratio.[8] Similarly, some stereoselectivity was observed with the other alkenes investigated by using this addition sequence (Table I).

The mechanism of this reaction is presently unclear, although the requirement for NO in the adduct-forming step suggests that CpCo(NO)$_2$ may be the initially formed intermediate. We have also found that treatment of **2** with 2 mol of I$_2$ in THF gives a complex whose structure is as yet unknown; however, when hydrolyzed with saturated aqueous NaCl/Na$_2$S$_2$O$_3$ solution, this material gives 2,3-dioxonorbornane dioxime in 60% yield. We are currently investigating the generality of this reaction.

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(1) J. Bäckvall, *Tetrahedron Lett.* **2**, 163 (1978).

(2) A. Chong, K. Oshima, and K. B. Sharpless, *J. Am. Chem. Soc.*, **99**, 3420 (1977).

(3) (a) V. Gomez Aranda, J. Barluenga, and F. Aznar, *Synthesis*, 504 (1974); (b) J. Barluenga, L. Alonso-Cires, and G. Asencio, *ibid.*, 962 (1979).

(4) (a) H. Brunner and S. Loskot, *Angew. Chem., Int. Ed. Engl.*, **10**, 515 (1971); (b) *J. Organomet. Chem.*, **61**, 401 (1973).

(5) H. Brunner, *J. Organomet. Chem.*, **12**, 517 (1968).

(6) G. Evrard, R. Thomas, B. Davis, and I. Bernal, *J. Organomet. Chem.*, **124**, 59 (1977).

(7) The diamines are surprisingly easy to handle. They are quite volatile and may be purified by distillation or vapor-phase chromatography, and can be stored neat without very much decomposition over time. In most cases, diastereomeric diamines could be resolved by VPC (33 ft × 1/4 in. 10% DC 710 on Chrom W + 5% KOH 60–80 mesh); cf.: E. D. Smith and R. D. Radford, *Anal. Chem.*, **33**, 1160 (1961).

(8) This order of addition consistently gave the stereoselectivity indicated. Addition of LiAlH$_4$ *to* the solution of adduct **2**, however, has given more erratic stereochemical results. The ratios obtained in these experiments were sometimes reminiscent of those obtained on LiAlH$_4$ reduction of 2,3-dioxonorbornane dioxime. At the suggestion of a referee, we have carried out the reduction of **2** with LiAlD$_4$. Mass spectral analysis of the products showed substantial deuterium incorporation at the α-amino positions (for the *cis-exo*-diamine, we observed 52% d_0, 41% d_1, and 7% d_2 species; the two minor isomers, analyzed as a mixture, showed somewhat increased amounts of d_2 and decreased amounts of diamine-d_0. This indicates that at least part of the conversion to diamine (even in the cis-exo case) takes place after alkylnitroso → oxime isomerization of at least one of the C–N functionalities. It may be that some batches of LiAlH$_4$ contain Lewis acid species capable of promoting such rearrangement.

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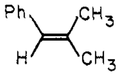
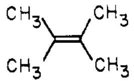
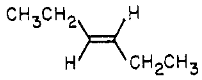
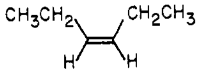
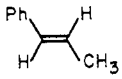
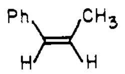
Table I. Conversion of Alkenes to 1,2-Diamines Using $[CpCoNO]_2$

alkene	alkene, mmol	$[CpCoNO]_2$, mmol	ν_{NO} of adduct, cm^{-1}	reaction time, min[a]	yield, %	ratio of diastereomers(%)
	3.33	2.48	1355, 1420	60[b]	80	4:6:90
	3.35	2.50	1355, 1420	40	70	30:70
	3.35	2.50	1365, 1387, 1430	120	78[d]	
	3.35	2.50	1358, 1388, 1425, 1434	85	66[d]	
	2.90	2.20	1362, 1427	75 (120)[c]	61 (80)[c]	90:10
	3.30	2.49	1370, 1418	150 (140)[c]	43 (62)[c]	34:66
$C_4H_9CH{=}CH_2$	3.33	2.48	1370, 1427	60	79	
	3.39	2.50	1378, 1425	120	47	32:68
	3.35	2.53	1359, 1371, 1428	90	90	85:15
	3.30	2.47	1354, 1378, 1428	120	74[d]	28:72

[a] Refers to time required for formation of adduct 3 from 1 and alkene. [b] This reaction not monitored by GC; reaction time not optimized in this case. [c] Times and yields in parentheses are those obtained by adding a second 2.5 mmol of dimer 3 after 30 min. [d] Yield of product isolated after conversion to cyclic urea derivative.

A typical diamination procedure is the following: a three-neck 25-mL pear-shaped flask equipped with stir bar, rubber septum, gas-inlet bubbler, and dry ice condenser was charged with 0.765 g (2.49 mmol) of $[CpCoNO]_2$ under a positive pressure of argon.[9] Freshly distilled, oxygen-free THF (10 mL) was added via cannula, and 423 μL (3.37 mmol) of degassed (nitrogen was bubbled through the neat liquid) *trans*-3-hexene was added via syringe. The resulting dark green solution was cooled to 0 °C in an ice bath, and the condenser was cooled to −78 °C to prevent loss of the olefin by evaporation. Argon was bubbled through the mixture for 10 min. Nitric oxide gas was then allowed to purge the tubing before being bubbled through the solution.[10] The gas was bubbled *very slowly* (<3 mL/min) through the reaction mixture.[11] The disappearance of *trans*-3-hexene was monitored by GC, and the disappearance of $[CpCoNO]_2$ was followed by TLC on silica gel.

After 75 min, the solution was degassed for 5 min by bubbling with argon to remove excess NO, diluted to a total volume of 20 mL with THF (added via cannula), and cooled to −65 °C.

The resulting dark red solution was added dropwise, via cannula, over a 15-min period to a 250-mL three-neck round-bottom flask fitted with a reflux condenser and rubber septum and containing 1.70 g (42.6 mmol) of $LiAlH_4$ magnetically stirred in 50 mL of THF at −70 °C under a nitrogen atmosphere. The red reaction mixture became dark green in color as the temperature rose to between −55 and −60 °C. The initial-reaction vessel was rinsed with 20 mL of THF, and the solution was added in the same manner to the $LiAlH_4$ mixture. The dry-ice bath was allowed to warm to room temperature, and the solution was stirred overnight. The mixture was brought to reflux for 1 h, then cooled to −60 °C, and the excess $LiAlH_4$ was destroyed by sequential dropwise addition of 1.70 mL of H_2O, 1.70 mL of 15% NaOH, and 5.10 mL of H_2O.[12,13] After the mixture was warmed to room temperature and stirred for 4 h, it was filtered, and the precipitate was washed with 2 × 30 mL of THF. The filtrate was dried over K_2CO_3 and filtered, and the solvent was removed under vacuum to give a dark yellow oil. This was distilled under reduced pressure at <5 μm and room temperature into a liquid nitrogen cooled trap yielding 0.232 g (60%) of a clear, pale yellow oil that was 98% pure by GC, IR, and ^1H NMR data.[14] Removal of the minor impurities by preparative GC gave analytically pure diamine.

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(9) The dimer $[CpCoNO]_2$ is air stable in the solid state, but decomposes in solution. To minimize surface oxidation over long storage periods, we recommend storage of the reagent under an inert atmosphere.

(10) In the presence of oxygen, nitric oxide reacts instantaneously to give nitrogen dioxide, which produces unwanted side reactions.

(11) Slow bubbling of NO is crucial to obtaining a good yield of diamine. We have found that if NO is allowed to bubble through a solution of $[CpCoNO]_2$ for prolonged periods of time, and/or at excessive rates, an intractable brown solid results. The decomposition is most probably due to the presence of small amounts of NO_2 (0.05 mol %) in the NO gas.

(12) For every x g of $LiAlH_4$ used, add dropwise x mL of H_2O, x mL of 15% NaOH, and $3x$ mL of H_2O in that order: L. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley-Interscience, New York, 1967, p 584.

(13) We have found that quenching $LiAlH_4$ by using the Fieser and Fieser technique results in an excess of H_2O so that large amounts of K_2CO_3 were required to dry the solution. This problem was circumvented by limiting the final dropwise addition of H_2O to $2.7x$ instead of $3x$.

(14) For diamines containing more than seven carbons, distillation was carried out at elevated temperatures.

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