DOI: 10.1002/ange.200501754

Reactions of Gold(III) Oxo Complexes with Cyclic Alkenes**

Maria A. Cinellu, Giovanni Minghetti, Fabio Cocco, Sergio Stoccoro, Antonio Zucca, and Mario Manassero*

As pointed out in a recent review, metal-mediated olefin oxidation is still a subject of great interest.[1] Various classes of mechanisms have been envisaged for different metal systems. Among these, that involving metallaoxetanes (1-metalla-2-oxacyclobutanes) as a key intermediate in the oxygen-transfer reaction has been recently corroborated by experimental evidence.[2] While an oxametallacycle has been identified as the crucial surface intermediate in the ethylene epoxidation on Ag,[3] a platinaoxetane, obtained from the reaction of a platinum(II) oxo complex with norbornene, has been structurally characterized.[4] The same oxo complex has been found to stoichiometrically oxidize ethylene to acetaldehyde, thus providing a rare example of alkene oxidation by isolated late-transition-metal oxo complexes.[5] Metallaoxetanes have also been obtained from the reaction of iridium(I) and rhodium(I) alkene complexes with molecular oxygen or hydrogen peroxide.[6]

Gold oxo species are likely to be involved in oxidations catalyzed by gold supported on metal oxides,[7] as, for example, in the direct epoxidation of propene with molecular oxygen.[7d,8] As soluble oxo complexes are valuable models for species involved in heterogeneous catalytic oxidation systems, we studied the reactions of a series of gold(III) oxo complexes[9] with olefins.[10] The model reaction of $[Au_2(bipy^R)_2(\mu\text{-}O)_2](PF_6)_2$ ($bipy^R = $ 6-R-2,2′-bipyridine; see Scheme 1 for R) with styrene yielded novel cationic gold(I) alkene complexes $[Au(bipy^R)(\eta^2\text{-}CH_2{=}CHPh)](PF_6)$ and oxygenated styrene derivatives.[11,12] After these encouraging results, we searched

---

[*] Prof. M. A. Cinellu, Prof. G. Minghetti, F. Cocco, Dr. S. Stoccoro, Dr. A. Zucca
Dipartimento di Chimica
Università di Sassari
via Vienna 2, 07100 Sassari (Italy)
Fax: (+39) 079-229-559
E-mail: cinellu@uniss.it

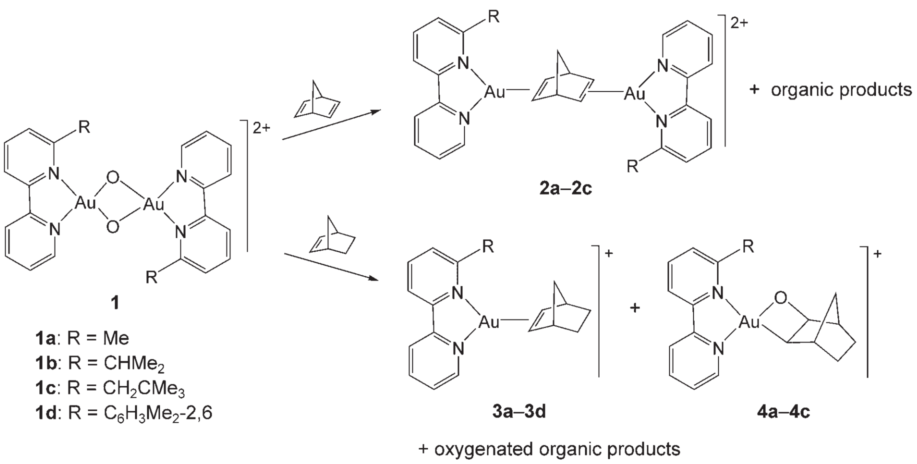
Prof. M. Manassero
Dipartimento di Chimica Strutturale e Stereochimica Inorganica
Università di Milano
Centro CNR
via Venezian 21, 20133 Milano (Italy)

[**] Support from the University of Sassari (60%) is gratefully acknowledged. We thank Mrs. E. Azara (ICB, CNR, Sassari) and Dr. A. Furesi (PMP, USSL, Sassari) for performing GC-MS and LC-MS analyses. Thanks are also due to Dr. G. A. Chelucci (Dipartimento di Chimica, Università di Sassari) for support in the organic syntheses and simulation of NMR spectra.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

for the supposed oxametallacyclic intermediate.[13] A growing number of papers have appeared on the homogeneous gold-catalyzed addition of oxygen nucleophiles to C–C multiple bonds of alkynes or alkenes.[14] Active gold–alkyne (gold–alkene) and cyclic organogold species, which have been suggested as key intermediates in the C–O bond formation,[14f,i–n,q] have never been isolated.



Scheme 1. Oxo complexes **1**-(PF$_6$)$_2$ (only the *trans* isomer is depicted; **1a** and **1b** are mixtures of the *cis* and *trans* isomer) and products of the reaction with 2,5-norbornadiene, **2**-(PF$_6$)$_2$, and with norbornene, **3**-PF$_6$ and **4**-PF$_6$.

Herein we describe the reaction of [Au$_2$(bipy^R)$_2$(μ-O)$_2$](PF$_6$)$_2$ [**1**-(PF$_6$)$_2$: R = Me (**1a**), CHMe$_2$ (**1b**), CH$_2$CMe$_3$ (**1c**), C$_6$H$_3$Me$_2$-2,6 (**1d**)] with the strained cyclic alkenes norbornene (nb) and 2,5-norbornadiene (nbd) to give alkene complexes and unprecedented metallaoxetanes (Scheme 1).[15] A dinuclear complex [Au$_2$(bipy^R)$_2$(μ-η^2,η^2-nbd)](PF$_6$)$_2$ [**2**-(PF$_6$)$_2$: R = Me (**2a**), CHMe$_2$ (**2b**), CH$_2$CMe$_3$ (**2c**)] with a bridging nbd ligand is the main product of the reaction as shown by NMR spectra and other analytical data; signals attributable to trace amounts of a second species are sometimes observed in the ^{1}H NMR spectra.

In the case of the nb derivatives, the ^{1}H NMR spectra indicate the presence of two species, the ratio of which depends on the preparative conditions and the nature of the substituent of the bipyridine ligand. The main product is the alkene complex [Au(bipy^R)(nb)](PF$_6$) [**3**-PF$_6$: R = Me (**3a**), CHMe$_2$ (**3b**), CH$_2$CMe$_3$ (**3c**), C$_6$H$_3$Me$_2$-2,6 (**3d**)]. When signals from the minor species, **4**, are not observed in the ^{1}H NMR spectrum, as in the case of the 6-(2,6-xylyl)-2,2′-bipyridine derivative, **4** is detected in the mass spectrum in which, besides the molecular ion, M^+, corresponding to the nb complex (**3d**), a peak of low to medium intensity is found at $[M+16]^+$. Under comparable preparative conditions, significant amounts of the latter species are obtained from **1a**-(PF$_6$)$_2$.[15] To separate the two species, different methods were employed in the case of the 6-methyl-2,2′-bipyridine (bipy^{Me}) derivatives **3a**-PF$_6$ and **4a**-PF$_6$. Crystals of **3a**-PF$_6$ and **4a**-PF$_6$, obtained by slow diffusion of diethyl ether into an acetonitrile solution of the mixture, were separated and subjected to X-ray diffraction analyses. Although full refinement of the structure of **3a**-PF$_6$ has not been accomplished, the main feature of the coordination geometry has been established.[16] The second species, **4a**-PF$_6$, proved to be the auraoxetane, [Au(bipy^{Me})(κ^2-*O*,*C*-2-oxynorbornyl)](PF$_6$).[17]

The structure consists of the packing of **4a** cations and PF$_6$ anions in the molar ratio of 1:1 with normal van der Waals contacts. The molecular structure of **4a** is shown in Figure 1. The gold atom has a square-planar coordination environment with a slight square-pyramidal distortion; maximum deviations from the best plane are +0.024(8) and −0.027(1) Å for O and Au atoms, respectively. Carbon atom C13 lies in the metal coordination plane, and the oxametallacycle is strictly planar, as reported for other late-transition-metal metallaoxetanes.[18] The Au–O bond length of 1.967(7) Å is very similar to the Au–O bond lengths of 1.971(4) and 1.960(6) Å found in [Au(bipy)(OMe)$_2$](PF$_6$),[19] and the Au–C12 separation of 2.055(8) Å is comparable with the Au–C bond length of 2.028(7) Å found in [Au{N$_2$C$_{10}$H$_7$(CMe$_2$CH$_2$)-6}Cl]$^+$ (**5**), in which N$_2$C$_{10}$H$_7$(CMe$_2$CH$_2$)-6 is a cyclometalated 6-*tert*-butyl-2,2′-bipyridine ligand.[20] The Au–N1 and Au–N2 bonds (2.026(6) and 2.183(6) Å, respectively) can be compared with corresponding interactions in **5** (1.976(5) and 2.151(5) Å, respectively).

As the isolation of oxametallacycles is unprecedented in the chemistry of gold, we tried to synthesize **4a**-PF$_6$ in better yields in order to study its reactivity.[21] In

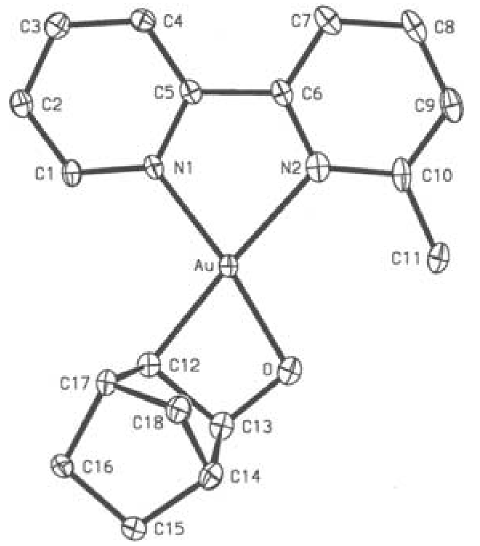
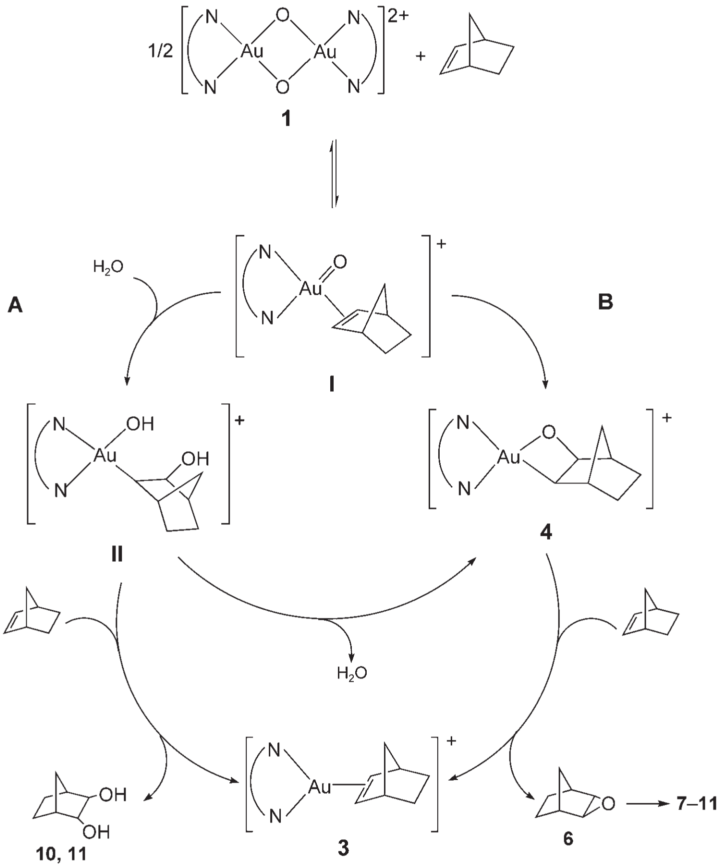


Figure 1. Molecular structure (ORTEP) of cation **4a**. Ellipsoids are drawn at the 30% probability level. Principal bond lenghts [Å] and angles [°]: Au–N1 2.026(6), Au–N2 2.183(6), Au–O 1.967(7), Au–C12 2.055(8), C12–C13 1.550(14), C13–O 1.433(12); N1-Au-N2 78.2(3), N1-Au-C12 103.9(3), N1-Au-O 172.9(3), N2-Au-O 108.2(3), N2-Au-C12 177.7(3), C12-Au-O 69.6(3), Au-C12-C13 91.2(5), C12-C13-O 100.7(7), C13-O-Au 98.5(6).

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

reactions using different ratios of nb to **1a**-$(PF_6)_2$ and at different concentrations of **1a**-$(PF_6)_2$, in both CH_3CN and in CH_3CN/H_2O, we established a general trend.[22] During the reaction of *trans*-[**1c**-$(PF_6)_2$] (the most soluble complex) with nb in CD_3CN, we observed by ^{1}H NMR spectroscopy that the ratio of **3** to **4** remains unchanged. Signals for **3c**-PF_6 and **4c**-PF_6 were detected after about 40 h (**3c**-PF_6/**4c**-PF_6 = 2:1); a resonance at $\delta = 9.58$ ppm (d, $J_{H-H} = 1.9$ Hz), which is typical of an aldehyde proton, appeared at the same time. Isolation of the organic fraction obtained from the same reaction in MeCN identified *exo*-2,3-epoxynorbornane (**6**)[23] as the main product accompanied by at least three aldehydes, **7**, **8,** and **9**.[24] The main aldehyde species was cyclopentane-1,3-dicarbaldehyde (**7**, M^+ 126)[25], the others were likely to be 3-methylene-cyclopentane carbaldehyde (**8**, M^+ 110)[26] and 3-methyl-2-cyclopentene carbaldehyde (**9**, M^+ 110). The epoxide and the dialdehyde were also the main products of the same reaction in MeCN in the presence of a small amount of water (3%). When a larger amount was added (≥10%), a 6:1 mixture of *cis-endo*-2,3-norbonanediol (**10**) and *trans*-2,3-norbonanediol (**11**) is obtained. GC–MS and LC–MS analyses showed peaks of $M^+ = 128$, which correspond to $C_7H_{12}O_2$.

Formation of the epoxide in solution and direct loss of a $C_7H_{10}O$ fragment from the molecular ion of $[Au(bipy^{Me})(C_7H_{10}O)]^+$ in the gas phase—shown by the FAB mass spectrum of **4a**—point to the oxaauracycle **4** being the origin of both the oxygenated products and the olefin complex **3**. Accordingly, the olefin complex **3a**-PF_6, 2,3-epoxynorbornane (**6**), and small amounts of aldehydes **8** and **9** were slowly formed when a MeCN solution of **4a**-PF_6 was treated with excess nb.[27] To the best of our knowledge, elimination of an epoxide from an isolated oxametallacycle has never been previously observed.[1,2b] Aldehydes or ketones are formed by isolated Rh^{III} and Ir^{III} 2-metalla-oxetanes.[6e,f,28] Plausible reaction pathways for the formation of the auraoxetane, **4**, and the alkene complex, **3**, are given in Scheme 2.



Scheme 2. Proposed reaction pathways for the formation of **3**, **4**, and oxygenated organic products **6**–**11**: A) in MeCN/H_2O and B) in MeCN. **I** and **II** are supposed intermediates.

Attempts to obtain **4a** by reaction of **3a** with O_2[6a] or H_2O_2[6b–d] in neutral MeCN solution were unsuccessful: partial decomposition of the alkene complex was observed in both cases.

Complexes **4a**–**4c** are the first isolated auraoxacyclobutanes. Their formation by the reaction of gold oxo complexes with alkenes may lead to a better understanding of the oxidation of olefins mediated by late-transition-metal complexes. Moreover, both the gold(I) alkene complex and the auraoxetane provide evidence for intermediates in the gold-catalyzed addition of oxygen nucleophiles to alkenes and alkynes.

Received: May 20, 2005
Revised: July 28, 2005
Published online: October 5, 2005

Keywords: alkene ligands · gold · oxidation · oxo ligands

[1] B. de Bruin, P. H. M. Budzelaar, A. W. Gal, *Angew. Chem.* **2004**, *116*, 4236–4251; *Angew. Chem. Int. Ed.* **2004**, *43*, 4142–4156.

[2] a) K. B. Sharpless, A. Y. Teranishi, J.-E. Bäckvall, *J. Am. Chem. Soc.* **1977**, *99*, 3120–3128; b) K. A. Jørgensen, B. Schiøtt, *Chem. Rev.* **1990**, *90*, 1483–1506.

[3] S. Linic, H. Piao, K. Adib, M. A. Barteau, *Angew. Chem.* **2004**, *116*, 2978–2981; *Angew. Chem. Int. Ed.* **2004**, *43*, 2918–2921.

[4] E. Szuromi, H. Shan, P. R. Sharp, *J. Am. Chem. Soc.* **2003**, *125*, 10522–10523.

[5] T. Hosokawa, M. Takano, S.-I. Murahashi, *J. Am. Chem. Soc.* **1996**, *118*, 3990–3991.

[6] a) V. W. Day, W. G. Klemperer, S. P. Lockledge, D. J. Main, *J. Am. Chem. Soc.* **1990**, *112*, 2031–2033; b) B. de Bruin, M. J. Boerakker, J. J. J. M. Donners, B. E. C. Christiaans, P. P. J. Schlebos, R. de Gelder, J. M. M. Smits, A. L. Spek, *Angew. Chem.* **1997**, *109*, 2153–2157; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2064–2067; c) B. de Bruin, J. A. Brands, J. J. J. M. Donners, M. P. J. Donners, R. de Gelder, J. M. M. Smits, A. W. Gal, A. L. Spek, *Chem. Eur. J.* **1999**, *5*, 2921–2936; d) T. C. Flood, M. Iimura, J. M. Perotti, A. L. Rheingold, T. E. Concolino, *Chem. Commun.* **2000**, 1681–1682; e) B. de Bruin, M. J. Boerakker, J. A. W. Verhagen, R. de Gelder, A. W. Gal, *Chem. Eur. J.* **2000**, *6*, 298–312; f) B. de Bruin, J. A. W. Verhagen, C. H. J. Schouten, A. W. Gal, D. Feichtinger, D. A. Plattner, *Chem. Eur. J.* **2001**, *7*, 416–422.

[7] a) M. Haruta, *Gold Bull.* **2004**, *37*, 27–36; b) G. C. Bond, D. T. Thompson, *Gold Bull.* **2000**, *33*, 41–50; c) H. H. Kung, M. C.

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Kung, C. K. Costello, *J. Catal.* **2003**, *216*, 425–432; d) J. R. Monnier, *Appl. Catal. A* **2001**, *221*, 73–91.

[8] A. K. Sinha, S. Seelan, S. Tsubota, M. Haruta, *Angew. Chem.* **2004**, *116*, 1572–1574; *Angew. Chem. Int. Ed.* **2004**, *43*, 1546–1548.

[9] M. A. Cinellu, G. Minghetti, M. V. Pinna, S. Stoccoro, A. Zucca, M. Manassero, M. Sansoni, *J. Chem. Soc. Dalton Trans.* **1998**, 1735–1741.

[10] D. Rais, Dissertation, Università di Sassari, **1998**.

[11] M. A. Cinellu, G. Minghetti, S. Stoccoro, A. Zucca, M. Manassero, *Chem. Commun.* **2004**, 1618–1619.

[12] Analogous alkene complexes are likewise obtained with other 1-alkenes, whereas no reaction occurs with linear internal alkenes; a small amount of an oxygenated gold species is also detected by ^{1}H NMR spectroscopy and FAB-MS of the α-methylstyrene derivative. Oxygenated organic products were characterized. Styrene derivatives: phenylacetaldehyde (main product) and benzaldehyde, reaction in MeCN; phenylacetaldehyde dimethyl acetal, reaction in MeCN/MeOH; styrene glycol, reaction in MeCN/H_2O. α-Methylstyrene derivatives: acetophenone, reaction in MeCN; 2-phenyl-1,2-propanediol, reaction in MeCN/H_2O; this diol converts almost completely into methylbenzylketone after a prolonged reaction time.

[13] Part of this work was presented in oral form: M. A. Cinellu, F. Cocco, G. Minghetti, S. Stoccoro, A. Zucca, M. Manassero, *III Euchem Conference on Nitrogen Ligands in Organometallic Chemistry and Homogeneous Catalysis*, Camerino, Italy, September 8–12, **2004**, O3.

[14] For selected reviews on homogeneous catalysis by gold, see: a) A. Hoffmann-Röder, N. Krause, *Org. Biomol. Chem.*, **2005**, *3*, 387–391; b) A. S. K. Hashmi, *Gold Bull.* **2004**, *37*, 51–65; c) A. S. K. Hashmi, *Gold Bull.* **2003**, *36*, 3–9; d) G. Dyker, *Angew. Chem.* **2000**, *112*, 4407–4409; *Angew. Chem. Int. Ed.* **2000**, *39*, 4237–4239; selected examples of alkyne transformations: e) Y. Fukuda, K. Utimoto, *J. Org. Chem.* **1991**, *56*, 3729–3731; f) J. H. Teles, S. Brode, M. Chabanas, *Angew. Chem.* **1998**, *110*, 1475–1478; *Angew. Chem. Int. Ed.* **1998**, *37*, 1415–1418; g) A. S. K. Hashmi, T. M. Frost, J. W. Bats, *Org. Lett.* **2001**, *3*, 3769–3771; h) E. Mizushima, K. Saro, T. Hayashi, M. Tanaka, *Angew. Chem.* **2002**, *114*, 4745–4747; *Angew. Chem. Int. Ed.* **2002**, *41*, 4563–4565; i) R. Casado, M. Contel, M. Laguna, P. Romero, S. Sanz, *J. Am. Chem. Soc.* **2003**, *125*, 11925–11935; j) T. Yao, X. Zhang, R. C. Larock, *J. Am. Chem. Soc.* **2004**, *126*, 11164–11165; k) A. S. K. Hashmi, J. P. Weyrauch, W. Frey, J. W. Bats, *Org. Lett.* **2004**, *6*, 4391–4394; l) V. Mamane, T. Gress, H. Krause, A. Fürstner, *J. Am. Chem. Soc.* **2004**, *126*, 8654–8655; m) A. S. K. Hashmi, P. Sinha, *Adv. Synth. Catal.* **2004**, *346*, 432–438; n) A. S. K. Hashmi, M. Rudolf, J. P. Weyrauch, M. Wölfle, W. Frey, J. W. Bats, *Angew. Chem.* **2005**, *117*, 2858–2861; *Angew. Chem. Int. Ed.* **2005**, *44*, 2798–2801; selected examples of alkene transformations: o) A. S. K. Hashmi, L. Schwarz, J.-H. Choi, T. M. Frost, *Angew. Chem.* **2000**, *112*, 2382–2385; *Angew. Chem. Int. Ed.* **2000**, *39*, 2285–2288; p) S. Kobayashi, K. Kakumoto, M. Sugiura, *Org. Lett.* **2002**, *4*, 1319–1322; q) C.-G. Yang, C. He, *J. Am. Chem. Soc.* **2005**, *127*, 6966–6967.

[15] For full experimental data on the synthesis, spectroscopy, and elemental analysis of complexes **2a**–**2c**, **3a**–**3d**, **4a**–**4c** and for spectroscopic characterization of organic compounds **6**–**11** see Supporting Information.

[16] Crystal data for **3a**-PF_6: $C_{18}H_{20}AuF_6N_2P$, $M_r = 606.30\ \mathrm{g\,mol^{-1}}$, orthorhombic, space group $Pna2_1$ (no. 33), $a = 16.480(4)$, $b = 16.662(3)$, $c = 6.911(2)$ Å, $V = 1897.7(7)$ Å^3.

[17] Crystal data for **4a**-PF_6: $C_{18}H_{20}AuF_6N_2OP$, $M_r = 622.30\ \mathrm{g\,mol^{-1}}$, triclinic, space group $P\bar{1}$ (no. 2), $a = 6.466(1)$, $b = 8.822(1)$, $c = 17.548(1)$ Å, $\alpha = 103.45(1)$, $\beta = 90.38(1)$, $\gamma = 100.97(1)°$, $V = 954.4(2)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 2.165\ \mathrm{g\,cm^{-3}}$, $T = 150$ K, $\mu(\mathrm{Mo_{K\alpha}}) = 78.4\ \mathrm{cm^{-1}}$, $F(000) = 596$. Reflections measured 19839, independent 5795 with $R_{\mathrm{int}} = 0.043$. Final R_2 (F^2, all reflections) = 0.113, w$R_2 = 0.165$, conventional $R_1 = 0.052$ for 262 variables. Bruker SMART CCD area detector, $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71073$ Å), ω-scan mode, $\theta_{\mathrm{min}} = 3°$, $\theta_{\mathrm{max}} = 26°$. Structure solved by direct methods and refined by full-matrix least squares. The program used to refine the structure was Personal SDP. CCDC-272640 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[18] A. A. Zlota, F. Frolow, D. Milstein, *J. Am. Chem. Soc.* **1990**, *112*, 6411–6413; M. J. Calhorda, A. M. Galvão, C. Ünaleroglu, A. A. Zlota, F. Frolow, D. Milstein, *Organometallics* **1993**, *12*, 3316–3325; and references therein.

[19] M. A. Cinellu, G. Minghetti, M. V. Pinna, S. Stoccoro, A. Zucca, M. Manassero, *J. Chem. Soc. Dalton Trans.* **2000**, 1261–1265.

[20] M. A. Cinellu, G. Minghetti, S. Stoccoro, A. Zucca, M. Manassero, M. Sansoni, *J. Chem. Soc. Dalton Trans.* **1996**, 4217–4225.

[21] **4a**-PF_6 was isolated in low yield after elaborate workup of the mixture. **4a**-BPh_4 which conversely can be obtained in fairly good yields, is not stable enough in solution for carrying out a reactivity study.[15]

[22] General trend: 1) high **1a**-$(PF_6)_2$ conversions (high **3a** + **4a** yields) require a long reaction time (at least 15 days) a temperature of 10–15 °C and high nb/**1a** ratio (20:1–30:1) both in MeCN and in MeCN/H_2O. 2) Under the same preparative conditions the overall yield (**3a** + **4a**) is only slightly higher in MeCN/H_2O; nevertheless, the **3a**/**4a** ratios are remarkably different: 6.5:1 (averaged) in MeCN and 1.5:1 in MeCN/H_2O. 3) Under the same nb/**1a** ratio and time conditions higher **4a** yields are obtained from concentrated solutions; the overall yield (**3a** + **4a**) was slightly lower than that from dilute solutions.

[23] Signals of the epoxide could not be detected in the spectrum of the reaction mixture (CD_3CN) as they overlapped with those of **1c**, **3c**, and **4c**.

[24] ^{1}H NMR spectra were recorded soon after workup of the reaction mixture. Aldehyde signals ($CDCl_3$): **7**: 9.64 (d, 2.0 Hz; 2H); **8** or **9**: 9.63 (d, 2.4 Hz; 1H); **9** or **8**: 9.62 ppm (d, 2.4 Hz; 1H). Intensities: $\mathbf{7} \geq (\mathbf{8} + \mathbf{9})$; $\mathbf{7} \leq \mathbf{6}$ (molar ratio based on CH*H*-7 of the epoxide at $\delta = 0.70$ ppm).

[25] ^{1}H NMR and GC-MS spectra were compared to those of an authentic sample prepared according to: S. Göksu, R. Altundas, Y. Sütbeyaz, *Synth. Commun.* **2000**, *30*, 1615–1621.

[26] Oxidation of nb with N_2O to give 3-methylenecyclopentane carbaldehyde (and norbornanone) has recently been reported: E. V. Starokon, K. A. Dubkov, D. E. Babushkin, V. N. Parmon, G. I. Panov, *Adv. Synth. Catal.* **2004**, *346*, 268–274. In default of ^{1}H NMR data for these aldehydes, the experimental spectra have been compared to the simulated ones obtained by ChemDraw 9.0 (CambridgeSoft).

[27] Complex **3a** and **6** also form upon addition of nb and a catalytic amount (5 %) of $HBF_4 \cdot Et_2O$ to **4a**; in this case small amounts of diols **10** and **11** are formed.

[28] D. Milstein, J. C. Calabrese, *J. Am. Chem. Soc.* **1982**, *104*, 3773–3774.

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim