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Efficient Synthetic Strategy

A Catalytic Approach to (*R*)-(+)-Muscopyridine with Integrated "Self-Clearance"**

Alois Fürstner* and Andreas Leitner

The chemist's ability to make molecules of utmost complexity^[1] must not hide the fact that the practicability of many such syntheses is still low. The arithmetic demon inherent to any linear sequence constitutes one of the major hurdles in this regard. To overcome this obstacle new methodology and improved retrosynthetic logic are called for which allow more than one bond-making event to be integrated into a single synthetic operation.^[2] The approaches to the odoriferous alkaloid (*R*)-(+)-muscopyridine (1), derived from the animal kingdom, and its naturally occurring nor-analogue 2 outlined below tackle this theme and illustrate how priority can be given to the "economy of steps"^[3] by a highly orchestrated catalysis-based process. Following its isolation by Ruzicka and Prelog,^[4] the unusual *meta*-pyridinophane derivative 1 has



been repeatedly targeted.^[5-7] Despite its rather simple structure, however, none of the reported syntheses is fully satisfactory, being either unduly lengthy and/or poor yielding.^[8]

Our approach to the alkaloid **1** takes advantage of the favorable application profile of an iron-catalyzed alkyl–aryl cross-coupling reaction recently developed in our laboratory as a powerful alternative to established organopalladium chemistry; in the present case the iron–salen complex **3** was applied.^[9,10] The method not only allows one to replace expensive precious metal complexes by cheap iron salts, but it is also distinguished by unprecedentedly high reaction rates even at or below room temperature. While aryl chlorides as



[*] Prof. A. Fürstner, Dipl.-Ing. A. Leitner Max-Planck-Institut für Kohlenforschung 45470 Mülheim an der Ruhr (Germany) Fax: (+49) 208-306-2994 E-mail: fuerstner@mpi-muelheim.mpg.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft (Leibniz program) and the Fonds der Chemischen Industrie. well as aryl sulfonates qualify as the substrates, the latter are usually distinctly more reactive. This chemoselectivity pattern constitutes a major design element of the synthesis depicted in Scheme 1.

Specifically, reaction of the commercially available bromo alcohol **4** with H₂C=CHMgBr in the presence of catalytic amounts of CuI affords the rather volatile alkene (X = OH),^[11] which is immediately converted without further purification into tosylate **5** to minimize losses during workup



Scheme 1. Synthesis of (*R*)-(+)-muscopyridine (1): a) $H_2C=CHMgBr$, Cul (5 mol%), THF, 0°C; b) tosyl chloride, pyridine, CH_2Cl_2 , 65% (over two steps); c) LiBr, acetone, reflux, 81%; d) triflic anhydride, pyridine, 97%; e) Mg, THF, bromide **6**; f) complex **3** (5 mol%), THF/ NMP, 0°C; g) 6-heptenylmagnesium bromide, complex **3** (5 mol%), 80% (combined yield, **11**:10 \approx 4:1); h) HCl, Et₂O; i) complex **13** (10 mol%), CH₂Cl₂, reflux, *c* = 0.006 м, 14 h; then *c* = 0.13 м, 12 h; j) H₂ (50 atm), 70°C; k) aqueous saturated NaHCO₃, 57% (over steps h)–k)) NMP=*N*-methylpyrrolidinone.

(65% over both steps). Subsequent treatment with LiBr in acetone affords the corresponding bromide 6. The enantiomerically pure Grignard reagent derived therefrom is then added by syringe to a solution of the difunctional pyridine derivative 7 and the iron-salen complex 3 (5 mol %) in THF/ NMP at 0°C. Monitoring of the reaction by TLC reveals that substrate 7 is completely consumed after 20 min; compound 9 forms selectively by reaction at the triflate site, together with small amounts of the dialkylation product 10. However, rather than taking recourse to workup and purification at this point, a solution of 6-heptenylmagnesium bromide and additional 3 (5 mol%) were introduced and stirring was continued for 30 min at 0°C. The ensuing second ironcatalyzed cross-coupling reaction affords the desired diene 11, which is contaminated with compound 10 formed in the first step (80% combined yield, $11:10 \approx 4:1$). Again, no attempt was made to separate these products that are indistinguishable by TLC; instead, a much more convenient chemical "self-clearance" occurs as an integral part of the subsequent metathesis cascade.

Conversion of the product mixture of **11** and **10** to the corresponding hydrochloride salts^[12] followed by treatment with the readily available ruthenium–indenylidene complex **13** $(10 \text{ mol }\%)^{[13,14]}$ under high dilution conditions leads to the selective cyclization of



diene 11 to the *meta*-pyridinophane 12 ($E,Z \approx 1.8:1$), while the hydrochloride of compound 10 remains unchanged. This reflects the greater ease of formation of the 13-membered ring as compared to the kinetically and thermodynamically handicapped 11-membered analogue that would derive from 10 by ring-closing metathesis (RCM).^[15,16] After most of the solvent has been distilled off, however, residual 10 is forced to polymerize by acyclic diene metathesis (ADMET)^[17] and thereby completely disappears from the GC trace while the macrocycle persists. Evidently, the indenylidene catalyst 13 does not lead to any noticeable reopening of the cyclic olefin 12 once it is formed, although RCM is a priori a reversible transformation.^[18] Therefore this transformation constitutes a noteworthy illustration for selectivity by catalyst tuning which allows one to rigorously distinguish between terminal and disubstituted double bonds.

At this point, workup is further postponed and advantage is taken from the multifaceted behavior of the ruthenium catalyst **13**. Thus, the crude mixture containing the cyclic monomer **12**, the ADMET-polymer, and the still intact metathesis catalyst is transferred into an autoclave and is stirred under H₂ (50 atm) overnight. Thereby, the carbene complex converts into a ruthenium hydride species, which acts as an efficient hydrogenation catalyst.^[19] Passing the mixture through a short pad of silica suffices to give analytically pure (*R*)-(+)-muscopyridine **1** in 57 % yield, while the polymeric by-product is retained on top of the column. This streamlined approach to enantiopure **1** together with the most convenient workup outperforms all previous approaches to this natural musk by virtue of its brevity and highly integrated character.

The adaptation of this concept to the synthesis of the achiral nor-analogue 2 is straightforward (Scheme 2). Treatment of substrate 7 with an excess of 5-hexenylmagnesium

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Scheme 2. Synthesis of normuscopyridine **2**: a) 5-hexenylmagnesium bromide, complex **3** (10 mol%), THF/NMP, 0°C, 75%; b) HCl, Et₂O; c) complex **13** (10 mol%), CH₂Cl₂, reflux, 14 h; d) H₂ (50 atm), 70°C; e) aqueous saturated NaHCO₃, 68% (over steps b)–e)).

bromide^[20] in the presence of catalytic amounts of complex **3** as the precatalyst provides the dialkylation product **14** in 75% yield after a reaction time of only 20 min. Exposure of the corresponding hydrochloride to the ruthenium–indenylidene complex **13** in a dilute CH_2Cl_2 solution delivers cycloalkene **15**. Subsequent hydrogenation (50 atm H₂) of the crude product affords the targeted 10-[2,6]-pyridinophane **2** in 68% overall yield.

In summary, these syntheses feature several notable aspects: They show the exceptional performance of the emerging iron-catalyzed alkyl-aryl cross-coupling method, which enables the construction of polysubstituted arenes by serial "three-component coupling" in one pot at unusually high reaction rates. Moreover, the syntheses of 1 and 2 illustrate several ways in which one can benefit from the subtleties of olefin metathesis chemistry: not only is it possible to rigorously distinguish between medium-sized rings and macrocycles as well as between terminal and internal double bonds, but it is also possible to perform "tandem catalysis" events (RCM/ADMET + hydrogenation) with a single ruthenium-carbene complex as the catalytically competent precursor.^[19] Finally, the muscopyridine case study exemplifies an unprecedented "chemical" self-clearance routine that exploits the complementarity between RCM and ADMET. Further work aimed at a rational use of these and related aspects is underway.

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Gaseous Gold Dihalides



Gold Dichloride and Gold Dibromide with Gold Atoms in Three Different Oxidation States**

Detlef Schröder,* Reuben Brown, Peter Schwerdtfeger, Xue-Bin Wang, Xin Yang, Lai-Sheng Wang, and Helmut Schwarz

Dedicated to Professor Roald Hoffmann on the occasion of his 65th birthday

While the most common oxidation states of gold are 0, I, and III, gold(II) compounds are also known to exist in the condensed phase and generally contain Au–Au bonds.^[1,2] However, genuine gold(II) chloride, AuCl₂, is not known in the condensed phase.^[3] Compounds such as CsAuCl₃ or

[*]	Dr. D. Schröder, Prof. Dr. H. Schwarz Institut für Chemie Technische Universität Berlin Strasse des 17. Juni 135, 10623 Berlin (Germany) Fax: (+49) 30-314-21102 E-mail: df@www.chem.tu-berlin.de
	Dr. R. Brown, Prof. Dr. P. Schwerdtfeger, Dr. X. B. Wang Department of Chemistry University of Auckland Private Bag 92019, Auckland (New Zealand)
,	Dr. X. Yang, Prof. Dr. L. S. Wang Department of Physics Washington State University 2710 University Drive, Richland, WA 99352 (USA) and W. R. Wiley Environmental Molecular Science Laboratory Pacific Northwest National Laboratory P. O. Box 999, Richland, WA 99352 (USA)

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Herein, we report an experimental and theoretical study of gaseous gold dihalides $AuX_2^{-/0/+}$ (X = Cl, Br) bearing three different charges, that is, the AuX_2^- ions (formally containing gold(i)), neutral AuX_2 species (formally gold(II)), and the corresponding AuX_2^+ ions (formally gold(II)), provided that the latter species can still be described as ionized gold dihalides (see below).

To this end, two complementary experimental techniques are combined: photoelectron spectroscopy (PES)[8] and sector-field mass spectrometry using charge-reversal (CR) and neutralization reionization (NR) techniques in conjunction with the related neutral-and-ion decomposition difference (NIDD) method.^[9,10] Both types of experiments start from the corresponding mass-selected AuX2- ions as precursors. In the PES study, the AuX_2^- ions (X = Cl, Br, I) are generated by electrospray ionization of diluted AuX solutions in water/methanol.^[11] In the sector experiments,^[12,13] fastatom bombardment (FAB) of aqueous slurries of AuX₃ is used to generate AuX_2^- ions; this method does not work for X = I, because reduction of AuI₃ to metallic gold occurs upon contact of the metallic probe tip with the sample. Likewise, no gold-fluoride ions could be generated by FAB of an AuF₃ slurry, because of the rapid hydrolysis of gold fluorides.

The photodetachment spectra of AuX_2^- ions (X = Cl, Br, I) indicate substantial electron affinities for the corresponding neutral species (Figure 1). Thus, the vertical detachment energies amount to $VDE(AuCl_2) = 4.74 \pm 0.05 \text{ eV},$ $VDE(AuBr_2^{-}) = 4.61 \pm 0.05 \text{ eV}, \text{ and } VDE(AuI_2^{-}) = 4.28 \pm 0.05 \text{ eV}, \text{ and } VDE(AuI_2^{-}) = 4.28 \pm 0.05 \text{ eV}, \text{ and } VDE(AuI_2^{-}) = 4.28 \pm 0.05 \text{ eV}, \text{ and } VDE(AuI_2^{-}) = 4.28 \pm 0.05 \text{ eV}, \text{ and } VDE(AuI_2^{-}) = 4.28 \pm 0.05 \text{ eV}, \text{ and } VDE(AuI_2^{-}) = 4.28 \pm 0.05 \text{ eV}, \text{ and } VDE(AuI_2^{-}) = 4.28 \pm 0.05 \text{ eV}, \text{ and } VDE(AuI_2^{-}) = 4.28 \pm 0.05 \text{ eV}, \text{ and } VDE(AuI_2^{-}) = 4.28 \pm 0.05 \text{ eV}, \text{ eV}, \text{ and } VDE(AuI_2^{-}) = 4.28 \pm 0.05 \text{ eV}, \text{ and } VDE(AuI_2^{$ 0.05 eV. Adiabatic detachment energies, that is, the electron affinities (EAs) of the corresponding neutral species, can be estimated by linear extrapolation of the onsets of the first features to the baseline. This analysis leads to the values $EA(AuCl_2) = 4.60 \pm 0.07 \text{ eV},$ $EA(AuBr_2) = 4.46 \pm 0.07 \text{ eV},$ and $EA(AuI_2) = 4.18 \pm 0.07$ eV. The relatively small differences ($\leq 0.15 \text{ eV}$) between the vertical and adiabatic transitions indicate similar geometries for the anionic and neutral $AuX_2^{-/0}$ species. Further, the PE spectra show several bands at higher energy which are assigned to the formation of electronically excited states in neutral AuX₂; these features will be analyzed in a forthcoming article. Here, we focus on the ground-state properties of the $AuX_2^{-/0/+}$ systems and in particular for X = Cl.

Upon collisional activation of mass-selected AuCl₂⁻ ions in the sector-field experiments, only the AuCl⁻ ion is detected as an anionic fragment. If the analyzer is switched to positive ions, the corresponding CR spectrum (Figure 2a) is dominated by the AuCl⁺ fragment (100%) along with a significant recovery signal for AuCl₂⁺ as well as the atomic Au⁺ ion; a weak signal from the Cl⁺ ion is detected at highest sensitivity (<1%, not visible in Figure 2a). The NR spectrum of the AuCl₂⁻ ion is also dominated by AuCl_n⁺ ions (n = 0-2), but the relative yield of AuCl⁺ is reduced significantly (Figure 2b).^[14]