tungsten carbide type. In an alternative approach, the Cs$^+$/Au$^-$ partial structure can be derived from the binary component CsAu[9] (CsCl-type), by cutting out a disk which is oriented along (101), and is of a half a face diagonal of the unit cell of CsAu in thickness. The latter description seems in this respect more suitable because gold is located rather on the faces of the trigonal-prismatic cesium polyhedra than in their centers. In addition, these prisms are completed to give cubes by cesium atoms from the Cs_3AuO_2 layer.

The two auride aurates introduced here complement the group of compounds carrying the same element in a positive, as well as a negative oxidation state by representatives being remarkably stable. In spite of the proximity in space of Au$^-$ and Au$^+$ (shortest distance $d(\mathrm{Au^+}{-}\mathrm{Au^-}) = 428$ pm), no redox lability is found.

Experimental Section

$Rb_7Au_5O_2$ and $Cs_7Au_5O_2$ were obtained as single-phase solids by reaction of the required amounts of alkali metal aurides MAu (M = Rb, Cs) with gold, and the corresponding alkali oxides under argon at $T = 425\,^\circ\mathrm{C}$ for one day. Samples of higher crystallinity were obtained by starting from alkali metal, gold, and alkali metal oxide, and by using an excess of alkali metal which is distilled off in dynamic vacuum on completion of the reaction. The alkali metals themselves were prepared by reducing the corresponding chlorides with calcium, and were distilled before usage.[10] The alkali metal monoxides were made by oxidizing the respective alkali metal with the appropriate amount of oxygen.[11] Elemental gold was precipitated by reducing tetrachloric gold acid with sodium oxalate.[12]

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[4] A. Kyeck, F. E. Wagner, A.-V. Mudring, M. Jansen, unpublished results. $Cs_7Au_5O_2$ ($Cs_3AuO_2 \cdot 4\,CsAu$): Au(+1): IS 3.21(1) mm s^{-1}, QS 7.07(1) mm s^{-1}, Au(−1): IS 5.76(1) mm s^{-1}, QS 3.48(1) mm s^{-1}. Compare with CsAuO: IS 2.54(1), QS 6.39(1) mm s^{-1}; CsAu: IS 7.00(1) mm s^{-1}.

[5] Crystallographic data of $Rb_7Au_5O_2$: orthorhombic, space group *Immm* (no. 71), $a = 567.1(1)$, $b = 930.1(2)$, $c = 1659.3(3)$ pm, $V = 875.3(3) \times 10^6$ pm^3, $\rho_{\mathrm{calcd}} = 6.128$ g cm^{-3}, $Z = 2$, $\mu\mathrm{Mo}_{K\alpha} = 61.071$ mm^{-1}, $F(000) = 1340$, $\lambda = 71.073$ pm, Enraf-Nonius CAD4 diffractometer, graphite monochromator, $T = 293$ K, $\omega/2\theta$ scan, 1014 measured reflections, 265 symmetry-independent reflections, 30 refined parameters. Empirical absorption correction (psi-scans). Structure solution (heavy atoms) with direct methods.[13] Subsequent difference Fourier analysis provided the positions of oxygen atoms. All positions can be refined anisotropically giving $R_1 = 0.043$ and $wR_2 = 0.1110$.[14]

[6] Crystallographic data of $Cs_7Au_5O_2$: orthorhombic, space group *Immm* (no. 71), $a = 599.4(1)$, $b = 960.6(3)$, $c = 1721(1)$ pm, $V = 990.8(8) \times 10^6$ pm^3, $\rho_{\mathrm{calcd}} = 6.572$ g cm^{-3}, $Z = 2$, $\mu\mathrm{Mo}_{K\alpha} = 49.54$ mm^{-1}, $F(000) = 1592$, $\lambda = 71.073$ pm, Enraf-Nonius CAD4 diffractometer, graphite monochromator, $T = 293$ K, $\omega/2\theta$ scan, 3395 measured reflections, 476 symmetry-independent reflections, 30 refined parameters. Empirical absorption correction (psi-scans). Structure solution (heavy atoms) with direct methods.[13] Subsequent difference Fourier analysis provided the positions of oxygen atoms. All positions can be refined anisotropically giving $R_1 = 0.0431$ and $wR_2 = 0.0756$. Further details on the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-411333 ($Rb_7Au_5O_2$) and CSD-411334 ($Cs_7Au_5O_2$).

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Unusual C–H···Se=C Interactions in Aldols of Chiral *N*-Acyl Selones Detected by Gradient-Selected ^{1}H–^{77}Se HMQC NMR Spectroscopy and X-ray Crystallography[**]

Ryszard Michalczyk, Jürgen G. Schmidt, Eddie Moody,
Zizhong Li, Ruilian Wu, R. Bruce Dunlap,
Jerome D. Odom, and Louis A. "Pete" Silks III*

During the past decade we have been exploring the uses of the selenocarbonyl group both as an analytical tool to interrogate chiral centers[1] (using ^{77}Se NMR spectroscopy) and as a platform for the development of new asymmetric chemical methods associated with selone-based chiral derivatizing agents (CDAs). In the course of these studies, we have uncovered a new type of aldol reaction using chiral *N*-acyl selone reagents (Scheme 1), in which the selenocarbonyl group plays a pivotal role in the stereoselectivity of these reactions.[2] An unexpected observation in the aldol products was proton couplings to the selenium atom of the CDA.

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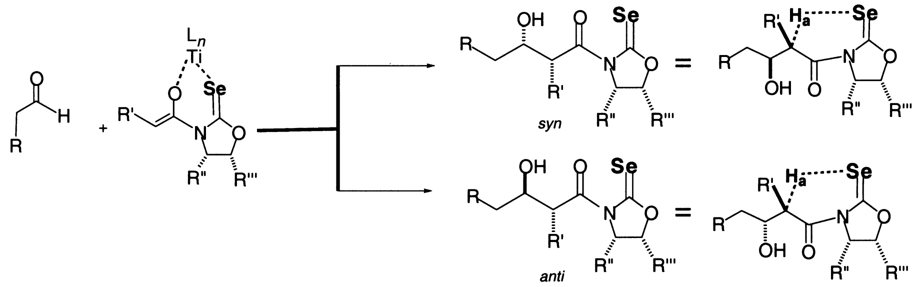
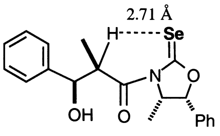


Scheme 1. $TiCl_4$-mediated stereoselective aldol reactions of chiral *N*-acyl selones. R = alkyl, alkenyl, aryl, NHFmoc (Fmoc = 9-fluorenylmethoxycarbonyl), OBn; R′ = Me, OBn; R″ = Me, *i*Pr, Bn; R‴ = H, Ph.

Intrigued by this observation, we systematically examined these aldol structures by gradient-selected ^{1}H–^{77}Se HMQC NMR spectroscopy, X-ray crystallography, and modeling calculations. While these structural investigations were initially undertaken to gain insight into the orientation and the high selectivities shown for these selone aldol reactions, they ultimately led to the observation of C–H···Se=C hydrogen bonds in all of the aldol products.

Though controversial, C–H···O,N hydrogen bonds are generally classified as weak interactions.[3] The observation of the corresponding C–H···S,Se interactions[4] is very rare, and the C–H···Se=C interaction, to the best of our knowledge, is reported here for the first time. Single-crystal X-ray analysis of three of the aldols (**1**–**3**) indicated C–H···Se distances of 2.63, 2.71, and 2.72 Å (Figure 1); these values are smaller than the sum of the van der Waals radii. The chemical shifts of the aldol H$_a$ protons of $\delta = 5.2-6.9$ indicate significant deshielding of this proton. To date, we have observed $J_{^1\text{H-}^{77}\text{Se}}$ couplings for all of the aldols we have investigated. For the *syn*-aldols, we observed an apparent unique doublet in each 1D proton-coupled (H$_a$) selenium spectrum ($J_{^1\text{H-}^{77}\text{Se}} = 5-6$ Hz) indicating that the *β*-hydroxy group is not significantly hydrogen bonding to the selenium center as we had initially expected. The proton resonance signals were unambiguously assigned and the J_H values were determined from ^{1}H–^{1}H DQF-COSY spectra for both *anti*-**3** and *syn*-**4**. The gradient-selected ^{1}H–^{77}Se HMQC spectra of *syn*-**4** and *anti*-**3** are illustrated in Figure 2.[5] The *syn*-**4** selenium interacts with three proton spin systems. The strongest interaction arises from the H$_a$. Minor interactions are observed for the oxazolidine ring methyl and *α*-methyl groups. For the *anti*-aldols, the 1D proton-coupled ^{77}Se spectra exhibited more than one spin system interacting with the selenium atom. The gradient-selected ^{1}H–^{77}Se HMQC spectrum of *anti*-**3** confirmed the interactions of four different spin systems with the selenium atom (Figure 3). The major H···Se interactions arose from both the *α*-methine (H$_a$) and *β*-hydroxy hydrogen (H$_c$), while weak, but clearly observable, interactions resulted from the *β*-methine hydrogen (H$_b$) and one of the methyl groups on the CDAs isopropyl group (H$_d$).



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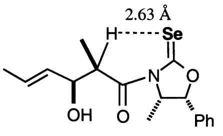

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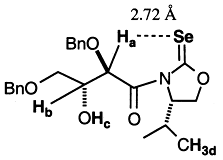

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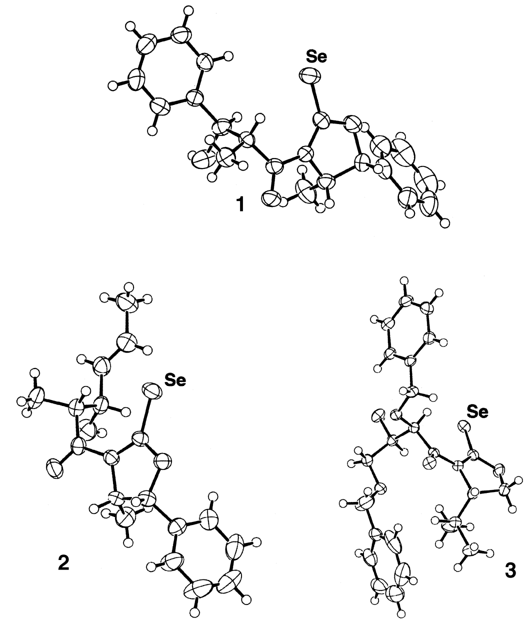


Figure 1. Structures of **1**–**3** (ORTEP representation).[11]

To analyze the energetics of the observed C–H···Se=C interactions we have performed molecular mechanics and ab initio calculations on model system **5**.[6] The structural data of

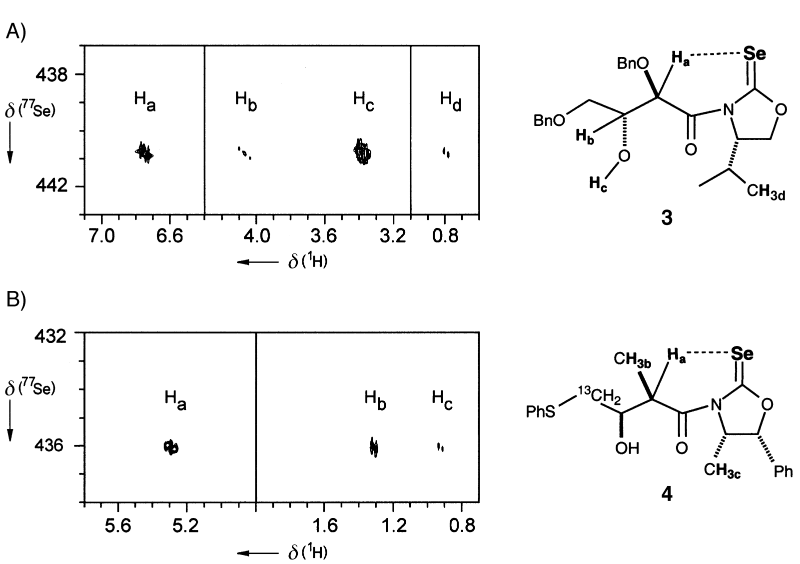


Figure 2. Gradient-selected ^{1}H–^{77}Se HMQC spectra for **3** (A; right panel is fifty times greater) and **4** (B; right panel is 40 times greater) in $CDCl_3$.

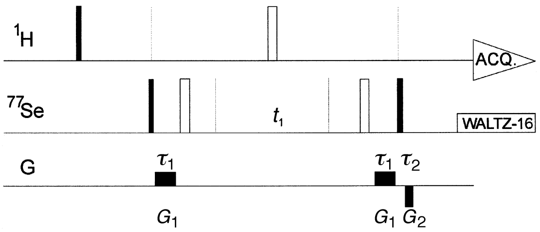
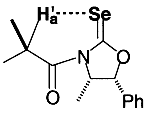


Figure 3. Pulse sequence used for $^1H-^{77}Se$ HMQC experiment. Black, open, and shaded rectangles represent 90°, 180°. Rectangles on line G designate gradient pulses. ACQ = acquisition; WALTZ-16 $^1H-^{77}Se$ decoupling.



5

the molecule **2** were used as a starting point for the calculations. The large side chain ($-CH(OH)-CH=CH-CH_3$) was replaced with a methyl group to give structure **5** which significantly reduced the calculation time. MM+ structural optimization was carried out exclusively for the relaxation of the three protons of the newly introduced methyl group. All other single-point calculations were carried out on the obtained preoptimized coordinates at the RHF or ROHF level with a SBKJC basis set using the GAMESS program package.[7] These calculations indicate that the $Se\cdots H_a'$ interaction has an energy equivalent to $-1.488\ kcal\,mol^{-1}$. This additional stabilization could potentially originate from the interactions with the carbonyl oxygen atom. However, the distance from H_a' to the carbonyl oxygen atom is more than 4 Å, and we found no electron overlap from the "α-carbon radical" to the carbonyl oxygen atom; whereas the distance from H_a' to the Se atom is only 2.63 Å. In addition, the Se and H_a' have an overlap of 0.0212 electrons; this strongly suggests that stabilization is a result of the $C-H_a'\cdots Se=C$ hydrogen bond.

Numerous reports of $C-H\cdots O$ interactions have not only been found and characterized in organometallic and organic structural chemistry, but also in biological systems such as oligomeric nucleic acids and proteins.[8] The importance of these weak interactions has become increasingly evident in providing structural elements to macromolecular systems and in playing a dominant role in the stereoselectivity of chemical reactions. However, there are few reports of $C-H\cdots S$ interactions,[4a] and only three reports of $C-H\cdots Se$ interactions. Tomoda and co-workers[4b] reported the shortest $C-H\cdots Se$ distance of 2.94 Å, while Vij and co-workers[4b] have reported distances of 2.98 and 3.26 Å for their sapphyrin molecules.

Our results indicate that we have uncovered a fundamental new type of non-opportunistic hydrogen bond in the aldols investigated.[9] In addition, we have for some time been puzzling over the reasons our chiral selones have the ability to interrogate remotely disposed chiral centers by ^{77}Se NMR spectroscopy, especially when there are no intervening aromatic or vinyl groups to facilitate the communication. An explanation for the remarkable ability of the selenium atom to report on the status of a chiral center up to eight bonds removed from the observing selenium nucleus[10] is provided by the $C-H\cdots Se$ interaction. This interaction allows both the necessary conformational amide rigidity and the critical truncation in the communication pathway between the chiral center and the "observing" selenium atom.

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[5] The 2D $^1H-^{77}Se$ correlation was recorded at ambient temperature on a Bruker DPX300 NMR spectrometer using a previously described pulse sequence[12] (see Figure 3). Transmitter offset was chosen to 4.0 ppm in ^1H dimension (f2) and 435 ppm in ^{77}Se dimension (f1). The spectrum was obtained with 4096 points in f2, 128 increments in f1, and 32 scans per t_1 increment with spectral width of 9.0 ppm in f1 and 8.0 ppm in f2. Recycle delay was 3.76 s, delay Δ was set to 70 ms, corresponding to $J_{H,Se}$ of ~7 Hz and WALTZ-16 ^{77}Se decoupling during acquisition was employed. Rectangular gradients were applied along z axis with field strength $G_1 = 24\ G\,cm^{-1}$ and $G_2 = -24.4\ G\,cm^{-1}$ and duration of $\tau_1 = 525\ \mu s$ and $\tau_2 = 196\ \mu s$, respectively, to fulfill condition (1) (γ_H and γ_{Se} are the gyromagnetic coefficients for ^1H and

$$\frac{2G_1\tau_1}{G_2\tau_2} = \frac{\gamma_H}{\gamma_{Se}} = 5.245 \qquad (1)$$

^{77}Se, respectively). The spectra were processed by using Bruker XWIN-NMR software. The data were zero-filled to a 4096 × 512 matrix and exponential line broadening of 1 Hz in f2 and 2 Hz in f1 was applied before Fourier transform.

[6] All ab initio calculations were preformed with the GAMESS program using a SBKJC basis set. See: M. W. Schmidt, K. K. Baldridge, J. A. Boatz, J. H. Jensen, S. Koseki, N. M. Matsunaga, M. S. Gordon, K. A. Nguyen, S. Su, T. L. Windus, S. T. Elbert, *J. Comput. Chem.* **1993**, *14*, 1347. Molecular mechanics calculations on the methyl hydrogens were performed with HyperChem5.01 using the MM+ force field.

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-81.035 kcal mol^{-1} and the average energy necessary to break a C–H bond is 80.841 kcal mol^{-1}. The extent of covalent versus electrostatic contributions to hydrogen bonding have been the subject of numerous discussions in the chemical literature (see, for example, J. J. Dannenberg, L. Haskamp, A. Masunov, *J. Phys. Chem. A.* **1999**, *103*, 7083, and references therein) and depend on the particular system studied. Calculated Mulliken partial charges are $+0.077$ for H_a' and -0.13 for Se indicating an attractive interaction. The difference between an average bond order of C–H bonds (0.904; this value is less than the expected due to the destabilization of C–H bond by the oxazoline ring system) and of the C–H_a' bond (0.888) directly gives the destabilization by 0.016 bond orders and therefore the C–H_a' bond is destabilized by 1.293 kcal mol^{-1} (C–H = 80.841 kcal mol^{-1}).[6] The Se$\cdots H_a'$ interaction is equal to the total stabilization of the system (-0.194 kcal mol^{-1}) minus the destabilization of the C$\cdots H_a'$ bond (1.293 kcal mol^{-1}), that is, 1.487 kcal mol^{-1}.

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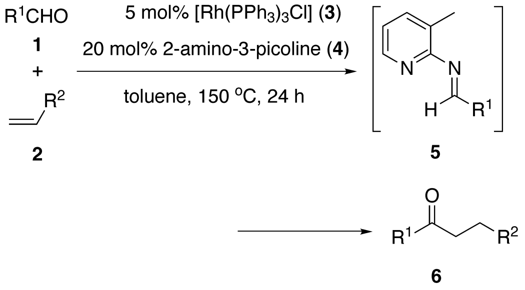
A Highly Active Catalyst System for Intermolecular Hydroacylation**

Chul-Ho Jun,* Dae-Yon Lee, Hyuk Lee, and Jun-Bae Hong

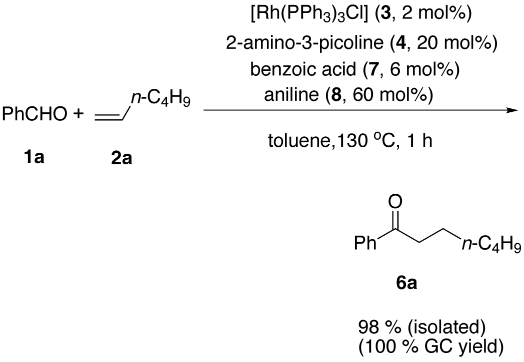
Hydroacylation[1–3] is a useful synthetic method for obtaining ketones from aldehydes and olefins by using C–H bond activation by transition metal complexes. Although the intramolecular hydroacylation of 4-pentenals has been extensively studied,[1] only a few successful intermolecular reactions have been reported.[2a–f] To effect intermolecular hydroacylation, ethylene,[2a,b] carbon monoxide,[2c] or vinylsilanes with a Co^I catalyst[2d,e] have been used to suppress the decarbonylation that results in catalytically inactive metal carbonyl species. We have developed a general intermolecular hydroacylation of 1-alkenes by using an Rh^I complex and 2-amino-3-picoline as cocatalyst, whereby aldimine **5** is assumed to be a key intermediate that suppresses decarbonylation and permits C–H bond activation [Eq. (1)].[3] Herein we report an efficient intermolecular hydroacylation for which a catalyst system was designed to ensure facile formation of the intermediate aldimine.



(1)

Recently, we found that the reactivity in the hydroacylation depicted in Equation (1) improved when benzaldehyde (**1a**) contaminated by benzoic acid (**7**)[4] was used as the substrate.[5] Benzoic acid was assumed to catalyze the condensation of aldehydes **1** with **4** to generate **5**; this may be the rate-determining step of the reaction (see below). This observation prompted us to search for a way to facilitate the formation of **5**, and we found a remarkable enhancement of the reactivity occurred when aniline (**8**), as well as **3**, **4**, and **7**, was used as an additive.

In our experiment **1a** was treated with 1-hexene (**2a**) at 130 °C for 1 h in the presence of 2 mol % of [Rh(PPh$_3$)$_3$Cl](**3**), 20 mol % of **4**, 6 mol % of **7**, and 60 mol % of **8** as cocatalysts to give heptanophenone (**6a**) in 98 % yield after chromatographic separation [Eq. (2)]. A significant decrease in reactivity was observed when the reaction was performed under the same conditions but without **7** and **8** (Figure 1). For example, while the reaction was complete (100 % GC yield) after 1 h when both **7** and **8** were added, only a 9 % yield of **6a** was obtained when the reaction was performed without additives. The yield increased to 28 % with the addition of **7**.



(2)

The postulated mechanism is depicted in Scheme 1. Cycle A represents the mechanism for the catalyst system consisting of **3** and **4**. The first step is believed to be the formation of aldimine **9** from **1a** and **4**. Aldimine **9** reacts with **2a** to yield ketimine **10** by hydroiminoacylation.[6] The resulting ketimine **10** is hydrolyzed by H_2O, generated from

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