Table II. Chromium Hydride pK_a and BDE Data in Acetonitrile

metal hydride (M-H)	BDE(M-H)[a,b]	pK_a(M-H)[c]	$\Delta(pK_a)$ = pK_a(M-H) - pK_a(M-H$^{\bullet+}$)[d]	Δ(BDE) = BDE(M-H) - BDE(M-H$^{\bullet+}$)[b,e]
$CpCr(CO)_2(P(OMe)_3)H$	62.7	21.1	23.5	11
$CpCr(CO)_2(PPh_3)H$	59.8	21.8[f]	23.9	10
$CpCr(CO)_2(PEt_3)H$	59.9	25.8	25.5	9
$Cp^*Cr(CO)_3H$	62.3	16.1	23.3	8

[a] From ref 10. [b] In kilocalories/mole. [c] $pK_a(M-H) = (BDE(M-H) - FE°_{ox}(M^-) - 59.5)/2.301RT$ (ref 5b) unless otherwise noted. [d] $pK_a(M-H) - pK_a(M-H^{\bullet+}) = F(E°_{ox}(M-H) - E°_{ox}(M^-))/2.301RT$ (ref 5c). [e] From eq 1. [f] From equilibrium measurements (ref 5b).

for which the corresponding radicals $CpCr(CO)_2(PR_3)^\bullet$ (**2a-c**) and $Cp^*Cr(CO)_3^\bullet$ (**2d**) are stable enough for their oxidation potentials to be measured.[10] In conjunction with the pertinent Cr-H BDEs which have been calorimetrically determined,[11] the oxidation potentials for $CpCr(CO)_2(PR_3)^-$ (**3a-d**) and $Cp^*Cr(CO)_3^-$ (**3d**) give access to the respective Cr-H pK_a values.[5a,b]

Figure 1 shows cyclic voltammograms for the oxidation of **3a**·Et_4N.[12] The reversible oxidation of **3a** is observed at -1.11 V (taken as the midpoint between the anodic (O1) and cathodic (R1) waves) vs the ferrocene/ferricinium (Fc) couple. An irreversible wave (O2) of the same intensity as O1 is observed at -0.21 V vs Fc. A product resulting from the reaction of the species generated at O2 is observed as reduction wave R3 at -1.48 V vs Fc and is assumed to be $CpCr(CO)_2(P(OMe)_3)(NCMe)^+$ (**4a**). The disappearance of **3a** and the appearance of **4a** were monitored during a constant-current coulometry experiment, and it was revealed that R3 did not emerge until **3a** had been completely oxidized to **2a**. The **3a**/**2a** couple vanished after the passage of 2 faraday/mol, generating a solution of **4a** (IR (dichloromethane) ν_{CO} 2000, 1930 cm^{-1}).

The metal anion, radical, and hydride oxidation potentials are summarized in Table I. Table II lists the BDE and calculated pK_a values for the neutral metal hydrides and the BDE and pK_a changes caused by their oxidation.

The $\Delta(pK_a)$ estimates represent minimum numbers due to the kinetic potential shifts caused by the irreversible nature of the M-H oxidation waves.[14] The activation of the Cr-H bonds toward heterolysis, $-\Delta\Delta G_{het} = 2.3RT\Delta(pK_a)$, amounts to at least 32-35 kcal/mol.[15] The irreversibility of the M$^\bullet$ and M-H oxidation waves introduces some uncertainty into the 8-11 kcal/mol estimates for the homolytic activation, $-\Delta\Delta G_{hom} = \Delta$(BDE), but these potential shifts will cancel in part. Despite these uncertainties, the data leave little doubt that the activation toward heterolysis by far exceeds the homolytic activation. In fact, the equations (Table II, footnotes *c* and *d*) that lead to $\Delta\Delta G_{het}$ and $\Delta\Delta G_{hom}$ may be combined and rearranged to give $(\Delta\Delta G_{het} - \Delta\Delta G_{hom}) = F(E_{ox}(M^-) - E_{ox}(M^\bullet)$, which implies that the heterolytic activation will be greater than the homolytic activation if $E_{ox}(M^\bullet) > E_{ox}(M^-)$. This condition should be fulfilled unless significant structural changes occur when the anion is oxidized to the radical.[16]

It has been discussed previously whether metal hydride cation radicals react via initial H^+ or $H^\bullet$ transfer,[5c,17,18] the former being supported by experimental evidence in most cases. The data presented here provide a quantitative and sound rationale for the observed behavior.

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Supplementary Material Available: IR (ν_{CO}) and elemental analysis data for compounds **3a**·Et_4N, **3b**·Et_4N, **3c**·Et_4N, and **3d**·$(Ph_3P)_2N$ (1 page). Ordering information is given on any current masthead page.

(9) Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5.

(10) (a) Goh, L.-Y.; D'Aniello, M. J., Jr.; Slater, S.; Muetterties, E. L.; Tavanaiepour, I.; Chang, M. I.; Fredrich, M. F.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 192. (b) Cooley, N. A.; Watson, K. A.; Fortier, S.; Baird, M. C. *Organometallics* **1986**, *5*, 2563. (c) Jaeger, T. J.; Baird, M. C. *Organometallics* **1988**, *7*, 2074. (d) Cooley, N. A.; MacConnachie, P. T. F.; Baird, M. C. *Polyhedron* **1988**, *7*, 1965. (e) O'Callaghan, K. A. E.; Brown, S. J.; Page, J. A.; Baird, M. C.; Richards, T. C.; Geiger, W. E. *Organometallics* **1991**, *10*, 3119.

(11) Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D. *J. Am. Chem. Soc.* **1990**, *112*, 5657.

(12) Et_4N^+ (**3a-c**) or $(Ph_3P)_2N^+$ (**3d**) salts were prepared by treating **1a-d** with *t*-BuOK in THF, followed by cation exchange. IR (ν_{CO}) and elemental analysis data are given in the supplementary material.

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(14) Characteristics of the oxidation wave for **1a** are representative: $E_p - E_{p/2} = 76$ mV at $\nu = 1.0$ V/s (cf. 68 mV for ferrocene); no observable return wave for $\nu < 100$ V/s.

(15) The pK_a differences are comparable with those reported for other metal hydrides[5c,d] and also fall in the range estimated for neutral/cation radical acidities in many organic systems.[4a,d]

(16) Astruc, D.; Lacoste, M.; Toupet, L. *J. Chem. Soc., Chem. Commun.* **1990**, 558.

(17) (a) Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 208. (b) Detty, M. R.; Jones, W. D. *J. Am. Chem. Soc.* **1987**, *109*, 5666. (c) Westerberg, D. E.; Rhodes, L. F.; Edwin, J.; Geiger, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 1107.

(18) $H^\bullet$ transfer has been reported from Sn, Ge, and Si hydride cations to the tetracyanoethylene radical anion: Klingler, R. J.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6626.

Functionalization of the β-Lactam Ring: Diastereoselective Azide Transfer and N-O Bond Reduction on C_4-Substituted *N*-Hydroxy β-Lactams in One Step

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While investigating new methods for the synthesis of the carbacephem class of β-lactam antibiotics,[1] we serendipitously discovered a fascinating transformation on *N*-hydroxy β-lactams which effected simultaneous azide transfer to the C_3 position diastereoselectively with cleavage of the *N*-hydroxy bond.

This conversion was effected during attempted diazotization[2] of racemic β-keto ester **2** (Scheme I). Compound **2** was obtained

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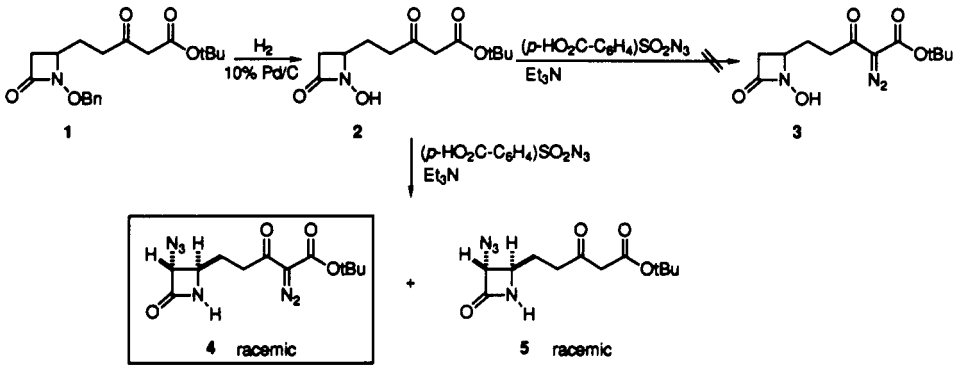
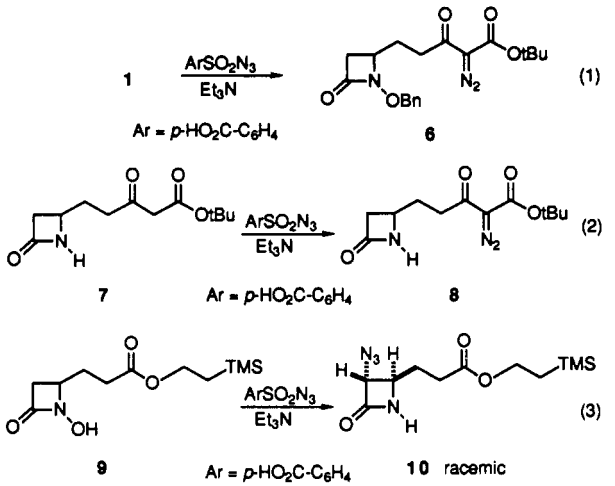
Scheme I



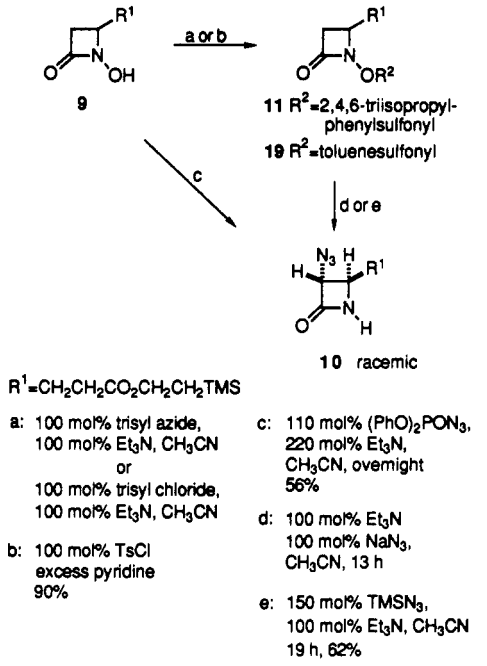
from β-lactam **1**[3] by hydrogenation in the presence of 10% Pd/C and was used immediately to avoid the precedented rearrangement to the 1,2-oxazolidin-5-one.[3a,4] Instead of forming the expected α-diazo-β-keto ester **3**, reaction of **2** with 330 mol % of (p-$HO_2CC_6H_4$)SO_2N_3[5] and 550–630 mol % of Et_3N in anhydrous CH_3CN with stirring at room temperature led to the formation of β-lactam **4** in up to 60% crude yield, after an aqueous workup consisting of washes with weak acid and weak base. Subsequent to chromatography and recrystallization, which allowed unambiguous structure determination by X-ray crystallography, **4** was isolated in 27% overall yield. β-Lactam **4** is an immediate precursor to the carbacephem framework, which can be obtained by rhodium(II)-catalyzed N–H bond insertion of the diazo-generated carbenoid.[1]

In order to test the structural requirements for this novel conversion, several control reactions were done. For example, when 110 mol % of (p-$HO_2CC_6H_4$)SO_2N_3 and 330 mol % of Et_3N were employed in the reaction of N-hydroxy β-lactam **2**, low yields of both **4** and **5** were isolated. Furthermore, three related substrates were subjected to the same conditions employed to yield only **4** and gave **6**, **8**, and **10**, respectively (eqs 1–3).[6] Examination of

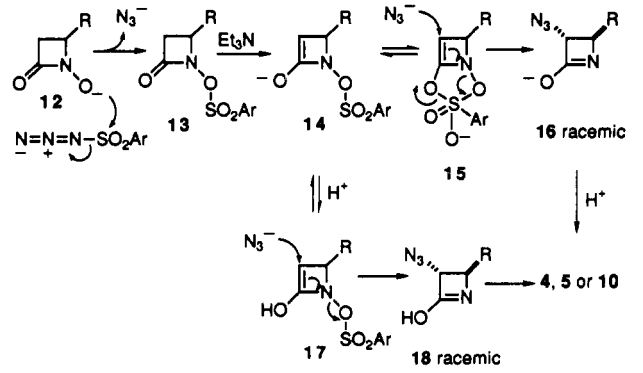


the products suggested that, although diazo transfer on the β-keto ester could occur according to the mechanism recorded by Regitz[7] independent of functional group changes on the β-lactam ring, diastereoselective azide transfer and N–O bond reduction might occur simultaneously. These two transformations about the β-lactam ring itself were intriguing and deserved additional inquiry.[8]

Scheme II



Scheme III



Azide transfer to the C_3 position of 1,4-dimethylazetidin-2-one by tosyl azide had been demonstrated originally by Kühlein and Jensen. Unlike our transformation, which was effected with Et_3N, their procedure required strong base (LDA).[9]

Additional experimentation has been done which has helped us formulate a mechanism for this novel reaction. Substitution

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of 2,4,6-triisopropylbenzenesulfonyl azide (trisyl azide)[10] for (*p*-$HO_2CC_6H_4)SO_2N_3$ in the production of compound **4** has shown that the structure of the arylsulfonyl azide apparently is not significant. A slight decrease to 30% yield of **4** after partial purification was observed, which was likely due to the somewhat more difficult chromatographic separation of product **4** from the reaction byproducts.

Studies with *N*-hydroxy β-lactam **9** and trisyl azide illustrated that *only 1 equiv* (100 mol %) of arylsulfonyl azide and *2 equiv* (200 mol %) of base were required for facile conversion into product **10** (eq 3, 62% yield after chromatographic purification with no aqueous workup). However, use of 1 equiv of base (100 mol % of Et_3N) with **9** led to the isolation of intermediate β-lactam **11** (conditions a, Scheme II). β-Lactam **11** could also be obtained by reaction of **9** with trisyl chloride and Et_3N. Furthermore, reaction of **11** with a nucleophilic source of azide effected partial conversion to product **10** (conditions d, Scheme II, ratio of starting material to product was 4 to 5).

On the basis of these results, a plausible mechanism for the azide transfer and N–O bond cleavage of β-lactams **2** and **9** can be proposed (Scheme III). In the presence of base, oxy anion **12** could form (pK_a's of *N*-hydroxy β-lactams similar to **2** and **9** are 6–9)[11] and subsequently attack the arylsulfonyl azide such that azide would be released to yield *N*-arylsulfonyloxy β-lactam **13**. The electron-withdrawing moiety on the β-lactam nitrogen of **13** could facilitate formation of enolate **14**, which might be stabilized as **15** or in enol form **17**. Thus, the negative charge of **14** would be sufficiently distanced from the C_3 position (or be a minor component in equilibrium with **17**) to allow the previously released azide anion to attack, thereby effecting azide transfer *trans* to the pendant C_4 substituent and N–O bond reduction via **15** or **17** in one step. Literature precedent in support of this mechanism was grounded in studies on the solvolysis of α-mesyl or α-triflyl ketones; enolization was determined to be the rate-determining step.[12,13]

Indeed, preliminary studies are consistent with prior sulfonylation followed by azide attack (Scheme III). In fact, it appears that *any* nucleophilic source of azide could be employed to facilitate azide attack on a suitably activated *N*-hydroxy β-lactam. For example, reaction of preformed *N*-tosyloxy β-lactam **19** with trimethylsilyl azide resulted in production of **10** (conditions b and e, Scheme II). Likewise, activation and azide transfer were accomplished just as effectively when diphenylphosphoryl azide[14] was substituted for an arylsulfonyl azide (conditions c, Scheme II).

In summary, diastereoselective azide transfer and N–O bond reduction can be effected by appropriate activation of the *N*-hydroxy moiety of an *N*-hydroxy β-lactam in the presence of base and a nucleophilic source of azide. This remarkable conversion has been accomplished not only sequentially by reaction with an arylsulfonyl chloride and then trimethylsilyl azide (or sodium azide) but also simultaneously with diphenylphosphoryl azide or an arylsulfonyl azide. Diazo transfer can also occur with the latter reagent when the substrate *N*-hydroxy β-lactam structure includes a β-keto ester-containing side chain (Scheme I). Application of these three simultaneous conversions allows the preparation of a fully functionalized β-lactam suitable for elaboration to important carbacephems and related antibiotics.[1,15] *Thus, it appears that substitution of any suitable nucleophile at C_3 may be possible.* Synthetic applicability of the transformation is under current investigation, and additional details are forthcoming.

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Supplementary Material Available: Experimental procedures for the synthesis of all compounds mentioned in the text and tables of X-ray crystallographic data for compound **4** (22 pages); listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Pure Gold Cluster of 1:9:9:1:9:9:1 Layered Structure: A Novel 39-Metal-Atom Cluster $[(Ph_3P)_{14}Au_{39}Cl_6]Cl_2$ with an Interstitial Gold Atom in a Hexagonal Antiprismatic Cage

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With only a few exceptions (e.g., Mn), nearly all pure metals crystallize in one of the three basic close-packing structures: face-centered cubic (fcc), hexagonal close-packing (hcp), and body-centered cubic (bcc).[1] In the "cluster phase", constraints of the infinite lattice are lifted such that the metal arrangements can adopt any one of the close-packing structures[2-6] or some combination and/or variant thereof (such as pentagonal or icosahedral packing), depending upon the electronic and stereochemical requirements of the metal core and the ligand environment.[7,8] For example, $[Rh_{13}(CO)_{24}H_{5-q}]^{q-2}$ has a 3:7:3 layered hcp structure, whereas $[Pt_{38}(CO)_{44}]^{2-3}$ has a 7:12:12:7 layered fcc structure. $[Rh_{15}(CO)_{27}]^{3-4}$ and $[Rh_{22}(CO)_{37}]^{4-}$,[5] on the other hand, have mixed bcc/hcp and fcc/hcp structures, respectively. We wish to report here a novel pure gold cluster $[(Ph_3P)_{14}Au_{39}Cl_6]^{2+}$ (**1**) which has an unprecedented 1:9:9:1:9:9:1 layered hcp/hcp′ structure (Figure 1a). Cluster **1** represents the largest structurally characterized pure gold cluster known to date.[9]

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