cysteine-containing dipeptides in high yield and without significant loss of chirality at the C2-exomethine carbon atom. Finally, the application of this method to one-pot tandem dehydrocyclizations afforded a thiazole–thiazoline product in good overall yield and with excellent stereocontrol.

Experimental Section

General procedure for synthesis of thiazolines: Trifluoromethanesulfonic anhydride (50 μL, 0.3 mmol) was added slowly to a solution of triphenylphosphane oxide (167 mg, 0.6 mmol) in dry CH_2Cl_2 (2 mL) at 0 °C. The reaction mixture was stirred for 10 min at 0 °C and then adjusted to the desired reaction temperature, followed by addition of the fully protected cysteine *N*-amide (0.2 mmol). The reaction progress was monitored by TLC. The reaction mixture was quenched with 10 % aqueous $NaHCO_3$ solution. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The resultant crude product was purified by flash chromatography with EtOAc/hexanes. More details and characterization data of the products can be found in the Supporting Information.

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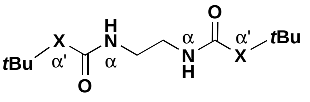
H-Bond-Supported Oxo Bridges

Hydrogen Bonds around $M(\mu\text{-}O)_2M$ Rhombs: Stabilizing a $\{Co^{III}(\mu\text{-}O)_2Co^{III}\}$ Complex at Room Temperature[**]

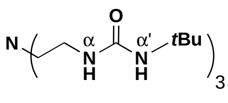
*Peter L. Larsen, Terry J. Parolin,
Douglas R. Powell, Michael P. Hendrich, and
A. S. Borovik[*]*

Species with $\{M(\mu\text{-}O)_2M\}$ rhombs containing late 3d transition metal ions are proposed as key intermediates in biological and chemical processes.[1–4] Studies on metalloenzymes suggest that noncovalent interactions between the protein-derived active-site structures and the $\{M(\mu\text{-}O)_2M\}$ cores are often necessary for function.[1b,5] These types of interactions, such as hydrogen bonds (H-bonds), are often difficult to replicate in synthetic systems,[6] which may partially explain the thermal instability of many complexes containing $\{M(\mu\text{-}O)_2M\}$ cores: reported examples that contain Co^{III}, Ni^{III}, and Cu^{III} ions are only stable at temperatures below −20 °C. Herein we describe the preparation and characterization of $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$, which is stable at room temperature, in part, because of intramolecular H-bonds that form with the bridging oxo ligands of the $\{Co^{III}(\mu\text{-}O)_2Co^{III}\}$ core. These results add to the growing body of evidence that demonstrates the importance of noncovalent interactions in regulating the properties of metal–oxo complexes.



$H_4\mathbf{1}$ X = NH

$H_2\mathbf{2}$ X = O



$H_6\mathbf{3}$

We have recently shown that monomeric Fe^{III} and Mn^{III} complexes with a terminal oxo or hydroxo ligand can be isolated by confining the $\{M^{III}\text{–}O(H)\}$ units within rigid H-bond cavities.[7] These complexes were prepared with the

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[*] Prof. Dr. A. S. Borovik, P. L. Larsen, Dr. D. R. Powell
Department of Chemistry
University of Kansas
2010 Malott Hall, 1251 Wescoe Dr., Lawrence, KS 66045-7582 (USA)
Fax: (+1) 785-864-5396
E-mail: aborovik@ku.edu

T. J. Parolin, Prof. Dr. M. P. Hendrich
Department of Chemistry
Carnegie Mellon University
Pittsburgh, PA 15213 (USA)

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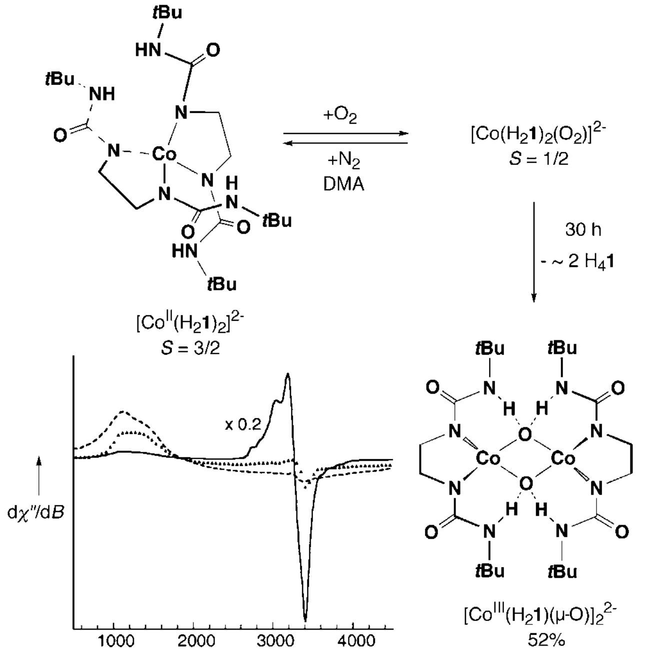
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

tripodal ligand $[H_3\mathbf{3}]^{3-}$, which uses monodeprotonated *N*-ethylene-*N'*-*tert*-butyl-urea groups as a scaffold for the H-bond cavity. While useful to generate these unique monomeric complexes, $[H_3\mathbf{3}]^{3-}$ has yet to yield polynuclear species with single-atom bridges. In contrast, $[H_2\mathbf{1}]^{2-}$ has a less constrained H-bond framework that could support complexes with bridging groups, such as oxo ligands. Deprotonation of the urea α-NH groups in $H_4\mathbf{1}$ generate N^- sites, which bind to metal ions. The α'-NH groups remain protonated and serve as H-bond donors to other coordinated ligands. Intramolecular H-bonds are expected because thermodynamically favored six-membered rings are formed. Because urea groups have been successfully used to promote the formation of H-bonds to terminal M–O units, we anticipated that a similar type of intramolecular interaction would aid in the isolation of complexes with $\{M(\mu\text{-}O)_2M\}$ rhombs.

The preparation of $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ is outlined in Scheme 1. Bubbling dry O_2 through a solution of the four-coordinate $[Co^{II}(H_2\mathbf{1})_2]^{2-}$[8] complex ($E_{1/2} = -0.33$ V versus a saturated calomel electrode (SCE)) in *N*,*N*-dimethylacetamide (DMA) at room temperature produces observable changes in the optical and EPR spectra. In the presence of excess O_2, $[Co^{II}(H_2\mathbf{1})_2]^{2-}$ (λ_{max} (ε_M) = 292 (2100), 498 (90), 575 nm (160)) converts to a species with $\lambda_{max} = 444$ nm. Concomitant changes are found in the EPR spectra; the broad X-band (9.3 GHz) EPR spectrum of the high-spin $[Co^{II}(H_2\mathbf{1})_2]^{2-}$ complex ($S = 3/2$) changes to a spectrum with *g* values centered around 2. These changes in spectral properties are consistent with the formation of a $Co–O_2$ adduct,[9] which is proposed to have the formula $[Co(H_2\mathbf{1})_2(O_2)]^{2-}$. This process is partially reversible; bubbling N_2 through a solution of $[Co(H_2\mathbf{1})_2(O_2)]^{2-}$ converts approximately 50% of the sample back to $[Co^{II}(H_2\mathbf{1})_2]^{2-}$ (inset, Scheme 1). The incomplete reversion of $[Co(H_2\mathbf{1})_2(O_2)]^{2-}$ to $[Co^{II}(H_2\mathbf{1})_2]^{2-}$ at room temperature implies that the $Co–O_2$ adduct reacts further to yield new cobalt species with ligands that may be derived from O_2. In fact, after 30 h at room temperature, a reddish-purple complex was isolated with absorbance features at $\lambda_{max}(\varepsilon_M) = 308$ (8500), 435 (4500), 518 (5500), and 1014 nm (370).



Scheme 1. Preparative route for $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$. Inset: X-band (9.3 GHz) EPR spectra measured at 4 K for $[Co^{II}(H_2\mathbf{1})]_2^{2-}$ (– – –), $[Co(H_2\mathbf{1})_2O_2]^{2-}$ (——), and $[Co(H_2\mathbf{1})_2O_2]^{2-} + N_2$ (▲).

The identity of this reddish-purple complex was confirmed as $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ by an X-ray diffraction study. $K_2[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2\cdot 4\,DMA\cdot 0.5\,C_4H_{10}O\cdot 0.25\,H_2O$ crystallized in the orthorhombic space group $P2_12_12_1$, with four independent, but virtually identical, anions in the asymmetric unit (denoted $[Co^{III}H_2\mathbf{1a}\text{–}\mathbf{d}(\mu\text{-}O)]_2^{2-}$). Figure 1 illustrates the molecular structure of $[Co^{III}H_2\mathbf{1a}(\mu\text{-}O)]_2^{2-}$, with selected metrical parameters listed in the legend. Each Co^{III} ion in the $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ unit is ligated by two urea nitrogen and two oxo-bridging oxygen atoms in a distorted square planar arrangement. The planes formed by N8a-Co1a-N11a and N23a-Co2a-N28a are twisted 26.6 and 27.0°, respectively, from the planar $Co^{III}(\mu\text{-}O)_2Co^{III}$ core. Four-coordinate Co^{III} complexes are rare[10] and typically have square-planar coordination geometry. The distortions from planarity in the $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ ion are only exceeded by a Co^{III} complex with a tetraazamacrocyclic tropocoronand ligand, which has a 41° twist angle.[10g]

In $[Co^{III}H_2\mathbf{1a}(O)]_2^{2-}$ the average $Co^{III}–N$ and $Co^{III}–O$ distances are 1.885(3) and 1.817(3) Å. Additional structural values include an average O_{oxo}-Co-O_{oxo} angle of 99.49(8)°, a

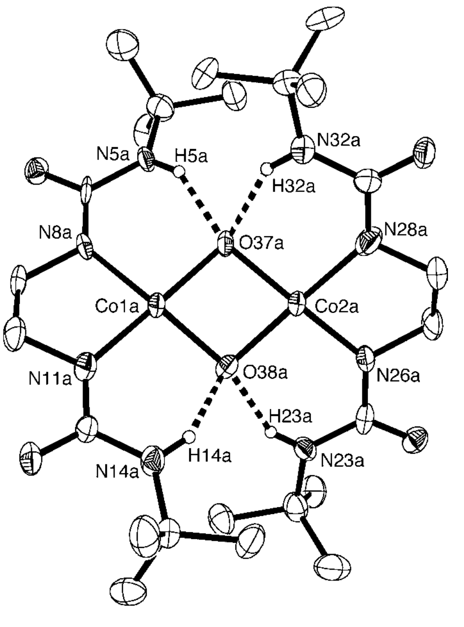


Figure 1. Molecular structure of $[Co^{III}H_2\mathbf{1a}(\mu\text{-}O)]_2^{2-}$. Thermal ellipsoids are drawn at the 50% probability level and only urea hydrogen atoms are shown. Selected bond lengths [Å] and angles [°]: Co1a-O37a 1.799(5), Co1a-O38a 1.821(5), Co1a-N8a 1.890(6), Co1a-N11a 1.899(7), Co2a-O37a 1.814(5), Co2a-O38a 1.832(5), Co2a-N26a 1.849(6), Co2a-N30a 1.903(7), Co1a···Co2a 2.7368(13); O37a-Co1a-O38a 82.5(2), O37a-Co1a-N8a 98.2(2), O38a-Co1a-N8a 161.5(3), O37a-Co1a-N11a 162.9(3), O38a-Co1a-N11a 98.9(3), N8a-Co1a-N11a 85.9(3), O37a-Co2a-O38a 81.8(2), O37a-Co2a-N26a 162.6(3), O38a-Co2a-N26a 99.5(2), O37a-Co2a-N30a 98.2(2), O38a-Co2a-N30a 161.4(3), N26a-Co2a-N30a 86.1(3).

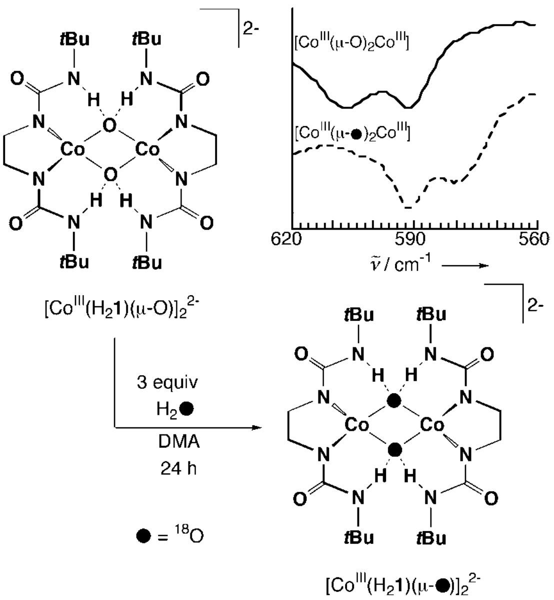
$Co^{III}\cdots Co^{III}$ separation of 2.736(1) Å, and an O···O separation of 2.375(4) Å. These metrical values are comparable to those found in the structures of other late 3d metal complexes containing $\{M(\mu\text{-}O)_2M\}$ rhombs. In particular, the structural parameters of the $\{Co^{III}(\mu\text{-}O)_2Co^{III}\}$ core within the $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ ion nearly match those found in $[Co^{III}Tp^{Me_n}(\mu\text{-}O)]_2$ ($n = 2,3$), the only other structurally characterized cobalt complexes with bis-μ-oxo cores.[3,11] For instance, $[Co^{III}Tp^{Me_3}(\mu\text{-}O)]_2$ (Tp^{Me_3} = hydrotris(3,4,5-trimethyl-1-pyrazolyl)borate), with five-coordinate Co^{III} centers, has a $Co^{III}\cdots Co^{III}$ separation of 2.728(2) Å and an O_{oxo}-Co-O_{oxo} angle of 99.3(2)°.

A unique structural feature of $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ is the network of intramolecular H-bonds that surround the $\{Co^{III}(\mu\text{-}O)_2Co^{III}\}$ rhomb. Each bridging oxo ligand forms two intramolecular H-bonds with the urea α′-NH groups of the $[H_2\mathbf{1}]^{2-}$ ligands. All the $N_{urea}\cdots O_{oxo}$ separations are less than 2.75 Å, which is indicative of the presence of H bonds.[12] Support for this assignment comes from solid-state FTIR results on $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ that show one broad peak for the $\tilde{\nu}$(NH) vibrations at 3184 cm^{-1}. This peak occurs at lower energy and is broader than the comparable signal found in $[Co^{II}(H_2\mathbf{1})_2]^{2-}$ ($\tilde{\nu}$(NH) = 3340 cm^{-1}), which does not contain intramolecular H-bonds.[8,13]

The presence of $NH\cdots O_{oxo}$ bonds in $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ may explain its unusual stability at room temperature. $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ can be prepared, purified, and stored for weeks at room temperature under anhydrous conditions without measurable decomposition. The urea α′-NH groups in $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$, which are strong H-bond donors, help control the secondary coordination sphere around the $\{Co^{III}(\mu\text{-}O)_2Co^{III}\}$ core. The combination of H-bond interactions and a highly anionic ligand field around the Co^{III} ions apparently provides enough stabilization to allow isolation of $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ at room temperature. In contrast, other Co^{III}, Ni^{III}, and Cu^{III} complexes with an $\{M(\mu\text{-}O)_2M\}$ rhomb lack these features, and have limited lifetimes at room temperature. For instance, $[Co^{III}Tp^{Me_3}(\mu\text{-}O)]$ is only stable at or below −50 °C; at higher temperatures it decomposes through pathways that oxidize a methyl group on the Tp^{Me_3} ligands.[3a,e]

Frozen solutions of $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ do not have observable X-band EPR spectra at either 4.2 or 77 K. This finding is consistent with magnetization studies carried out on solid samples of $K_2[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2$ using a SQUID magnetometer in the temperature range of 5 to 250 K and an applied magnetic field of 0.5 T. A computer simulation of the data (Figure S1, Supporting Information) shows a large antiferromagnetic exchange interaction between the Co^{III} ions, with $J = -190(10)$ cm^{-1} for $S_1 = S_2 = 1$ and $g_1 = g_2 = 2.6$.[14] This strong coupling reflects the presence of two efficient exchange pathways furnished by the bis(μ-oxo) ligands.[15]

The oxo ligands in $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ are exchangeable with water. Treating $[Co^{III}H_2\mathbf{1}(\mu\text{-}^{16}O)]_2^{2-}$ with 3 equivalents of $H_2{}^{18}O$ in DMA for 24 h affords the ^{18}O-labeled complex, $[Co^{III}H_2\mathbf{1}(\mu\text{-}^{18}O)]_2^{2-}$ (Scheme 2).[16] FTIR spectroscopy was used to evaluate the incorporation of the $[^{18}O]^{2-}$ ligands into the complex. The FTIR spectrum of $[Co^{III}H_2\mathbf{1}(\mu\text{-}^{16}O)]_2^{2-}$ has a peak at 607 cm^{-1} (inset, Scheme 2), which is tentatively assigned as the $\tilde{\nu}_{asym}(Co^{III}(\mu\text{-}O)_2Co^{III})$ vibration.[17] In $[Co^{III}H_2\mathbf{1}(\mu\text{-}^{18}O)]_2^{2-}$ this peak is shifted to 580 cm^{-1}, which is the expected shift based on a harmonic Co–O oscillator model. $[Co^{III}H_2\mathbf{1}(\mu\text{-}^{18}O)]_2^{2-}$ can also be prepared from $[Co^{II}(H_2\mathbf{1})_2]^{2-}$ and 3 equivalents of $^{18}O_2$ by the procedure outlined in Scheme 1. This result suggests that the source of the oxo ligands in $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ is derived from dioxygen. However, FTIR spectra of the product contain a small peak (less than 20 %) at 607 cm^{-1}, indicating that $[Co^{III}H_2\mathbf{1}(\mu\text{-}^{16}O)]_2^{2-}$ is also present. Because water exchange with the $\{Co^{III}(\mu\text{-}O)_2Co^{III}\}$ core occurs in the same timeframe as dimer formation, we attribute the presence of the ^{16}O complex to oxo exchange of $[Co^{III}H_2\mathbf{1}(\mu\text{-}^{18}O)]_2^{2-}$ with adventitious $H_2{}^{16}O$ in the solvent.



Scheme 2. Reaction of $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ with ^{18}O-labeled water. Inset: FTIR spectra (Nujol) of $[Co^{III}(H_2\mathbf{1})(\mu\text{-}^{16}O)]_2^{2-}$ (——) and $[Co^{III}(H_2\mathbf{1})(\mu\text{-}^{18}O)]_2^{2-}$ (– – –). The peak at approximately 590 cm^{-1} is from DMA.

To our knowledge, $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ is the first complex where definitive evidence exists for the formation of H bonds to a $\{M(\mu\text{-}O)_2M\}$ rhomb. These noncovalent interactions are proposed to aid in extending the thermal stability of $[Co^{III}H_2\mathbf{1}(\mu\text{-}O)]_2^{2-}$ to a temperature more than 70 °C higher than reported for comparable cobalt complexes. Furthermore, $[H_2\mathbf{1}]^{2-}$ species can be readily modified to probe the influences of H bonds on metal ion reactivity; for example, the four-coordinate complex anion $[Co^{II}(\mathbf{2})_2]^{2-}$ has carbamate groups instead of urea groups, and therefore lacks the H-bond donors that are present in $[Co^{II}(H_2\mathbf{1})_2]^{2-}$. Preliminary studies show that the reaction between $[Co^{II}(\mathbf{2})_2]^{2-}$ and O_2 produces species that do not have spectroscopic properties consistent with complexes containing $\{Co^{III}(\mu\text{-}O)_2Co^{III}\}$ cores. Additional studies are planned to probe the formation and stabilization of the $\{M(\mu\text{-}O)_2M\}$ core at room temperature.

Experimental Section

$K_2[CoH_2\mathbf{1}(O)]_2$: A solution of $K_2[Co(H_2\mathbf{1})_2]\cdot 4DMA$[8] (0.705 g, 0.706 mmol) in DMA (10 mL) was purged with a stream of O_2 at room temperature. After 25 min, the bubbling was discontinued and the reaction mixture was allowed to stir for 30 h. Volatiles were removed under reduced pressure and the resulting red-brown solid was dissolved in DMA (5 mL) and crystallized by layering with diethyl ether saturated with O_2. During crystallization a white solid was also obtained, the spectral properties of which matched those of H_4**1**. Analytically pure $K_2[CoH_2$**1**$(O)]_2$ was obtained after three recrystallizations to afford 0.174 g (0.183 mmol, 52 %) of reddish-purple crystals. Elemental analysis (%) calcd for $K_2[CoH_2$**1**$(O)]_2\cdot 2\,DMA\cdot 0.5\,C_4H_{10}O\cdot 0.25\,H_2O$ ($C_{34}H_{71.5}Co_2K_2N_{10}O_{8.75}$): C 42.69, H 7.53, N 14.63; found: C 42.89, H 7.51, N 14.65. FTIR (Nujol): $\tilde{\nu} = 3184$ (NH, b), 1640 (CO, s), 607 cm^{-1} (Co–O, m). ^{1}H NMR (500 MHz, $[D_6]$DMSO, 24 °C): $\delta = 84.1$ (s, 4 H; $-CH_2-$), 74.1 (s, 4 H; $-CH_2-$), 16.4 (s, 4 H; NH), 0.5 ppm (s, 36 H; $C(CH_3)_3$).

X-ray structural analysis for $K_2[Co^{III}H_2$**1**$(\mu\text{-}O)]_2\cdot 4\,DMA\cdot 0.50\,C_4H_{10}O\cdot 0.25\,H_2O$: $0.37 \times 0.23 \times 0.12$ mm, orthorhombic, space group $P2_12_12_1$, $a = 18.8952(10)$, $b = 26.5923(14)$, $c = 46.360(2)$ Å; $V = 23294(2)$ Å^3, $\rho_{calcd} = 1.290$ Mg m^{-3}, $Z = 16$, $2\theta_{max} = 3.30$ to 50.00°; $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $F(000) = 9656$, $T = 100(2)$ K, total reflections = 131 198 collected on a Bruker SMART diffractometer equipped with an APEX CCD area detector, independent reflections = 45 748 ($R_{int} = 0.0539$), observed data = 32 000 ($I > 2\sigma(I)$), restraints(para)$^{-1}$ ratio = 1397(2752)$^{-1}$, absorption correction: SADABS, max(min) transmission, 0.9130(0.7632)$^{-1}$; direct methods, SHELXTL-V5.0; hydrogen atom positions were initially determined by geometry and refined by a riding model and nonhydrogen atoms were refined with anisotropic displacement parameters; full-matrix least-square refinement on F^2; $R1(wR2) = 0.0887$ (0.2413), GOF = 1.088, 3.957, −0.712 e Å^{-3}, residual based on $I > 2\sigma(I)$. The absolute structure was determined by refinement of the Flack parameter.[18] 16 DMA molecules, two diethyl ether molecules, and one water molecule were also present in the asymmetric unit. Five of the DMA molecules were disordered and modeled in two orientations. Restraints on the positional and displacement parameters of the disordered atoms were required for the refinement to converge.

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[15] Strong antiferromagnetic coupling has also been observed in a complex containing an $\{Fe^{III}(\mu\text{-}O)_2Fe^{III}\}$ rhomb.[4b]

[16] $K_2[Co(H_2\mathbf{1})_2]$ (0.021 mmol, 0.020 g) was treated with 1.1 µL (0.063 mmol) of $H_2{}^{18}O$ in DMA (5 mL)for 24 h. A small amount (less than 10%) of free ligand was also found in the FTIR spectrum, which did not hinder detection of the changes in $\tilde{\nu}_{asym}(\{Co^{III}(\mu\text{-}O)_2Co^{III}\})$.

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Ir-Catalyzed C-C Bond Formation

Iridium-Catalyzed Mizoroki–Heck-Type Reaction of Organosilicon Reagents

*Tooru Koike, Xiaoli Du, Tomoyuki Sanada, Yasuaki Danda, and Atsunori Mori**

Iridium-catalyzed C–C bond-forming reactions have recently attracted much attention.[1] However, the reaction with main group organometallic reagents containing elements such as boron, tin, and silicon has not been demonstrated so far. Although carbon–carbon bond formation with such main group reagents with an α,β-unsaturated carbonyl compound has been reported recently to undergo a Mizoroki–Heck-type or conjugate addition reaction with palladium,[2] rhodium,[3] and ruthenium[4] catalysts, the specific nature of the metal catalysts largely influences the reaction mechanism as well as the reaction course. Herein, we report that an iridium catalyst effects the Mizoroki–Heck-type addition/elimination reaction of α,β-unsaturated carbonyl compounds with several organosilicon reagents, and constitutes the first C–C bond formation with a main group reagent.[5]

The reaction of $PhSi(OMe)_3$ (**1**) with butyl acrylate (**2a**) in the presence of 5 mol% of $[\{IrCl(cod)\}_2]$ (cod = 1,5-cyclooctadiene) and tetrabutylammonium fluoride (TBAF) in toluene/H_2O (6/1) at 120 °C for 24 h afforded the addition/elimination product **3a** in 71% yield while the conjugate addition product **4a** was not obtained at all. This result sharply contrasts that of the related reaction with the rhodium catalyst $[\{RhCl(cod)\}_2]$ at 60 °C in THF/H_2O (6/1), which affords the conjugate adduct **4a** as the major product with high selectivity, **3a**/**4a** = 3/97 (Scheme 1).[6] In contrast to the combination of silicon reagent **1** and TBAF under anhydrous conditions, which is highly effective for the palladium-catalyzed cross-coupling reaction with organic halides,[7] the rhodium- or iridium-catalyzed reaction of this combination with **2a** proceeded only very slightly without the addition of water.

Table 1 summarizes the iridium-catalyzed Mizoroki–Heck-type addition/elimination reactions of several organosilicon reagents with α,β-unsaturated carbonyl compounds. Both iridium chloride and methoxide exhibited similar reactivities in the reactions with TBAF. The reaction also proceeded in THF/H_2O at lower temperature (70 °C), although a small amount of conjugate addition product was formed (70/5). Several aryl silanes bearing a substituent on the aromatic ring also effected the reaction. Although the reaction of an *ortho*-substituted aryl silane was found to be slightly slower, the Mizoroki–Heck-type product was selectively obtained over the 1,4-addition product. Alkenylsilanes, which were prepared by hydrosilylation of alkynes, could also effect the reaction to afford a diene in 67% yield.

Aryl silanediols (**7**–**9**) were also found to participate in the addition/elimination reaction. By contrast to alkoxysilanes, silanediols effected the reactions without addition of TBAF and water. However, no reaction occurred when $[\{IrCl(cod)\}_2]$ was used as the catalyst. Only $[\{Ir(OMe)(cod)\}_2]$ was found to be an effective catalyst. Worthy of note is that the reaction with silanediols can be a halogen-free process, which is in contrast to the palladium-catalyzed Mizoroki–Heck reaction with aryl halides. Reactions of other main group reagents such as those derived from boron and tin were found to proceed in a similar manner. Methyl vinyl ketone (**2b**) also underwent reaction to give **3b** in good yields.

In contrast to our recent report on rhodium catalysts in which addition/elimination versus conjugate addition of esters was controlled by the addition of water, while ketones underwent conjugate addition with or without water,[3e] the iridium-catalyzed reaction predominantly proceeded through

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[*] Prof. Dr. A. Mori, T. Koike, X. Du, T. Sanada, Y. Danda
Chemical Resources Laboratory
Tokyo Institute of Technology
4259 Nagatsuta, Yokohama 226–8503 (Japan)
Fax: (+81) 45–924–5224
E-mail: amori@res.titech.ac.jp