Trioxorhenium(VII) Complexes with Imidazolin-2-iminato Ligands

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

The Staudinger reaction of the N-heterocyclic carbenes 1,3-di-tert-butylimidazolin-2-ylidene (1a), 1,3-dimesitylimidazolin-2-ylidene (1b) and 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene (1c) with trimethylsilyl azide in boiling toluene furnishes the corresponding 2-(trimethylsilylimino)imidazolines 2a–c. Treatment of Re2O7 with a twofold excess of these N-silylated imines results in the formation of the imidazolin-2-iminato trioxorhenium(VII) complexes 3a–c and hexamethyldisiloxane, Me3SiOSiMe3. The molecular structures of 2a, 3a and 3b are reported. In addition, the X-ray crystal structure determination of complex 3c·H2O is presented, which has formed by hydrolysis and cleavage of the metal-nitrogen bond in 3c. 3c·H2O consists of 2-aminoimidazolium cations and tetraoxorhenate(VII) anions, which are linked by N–H–O hydrogen bonds.

Key words: Carbenes, Imidazolin-2-ylidenes, Imido Ligands, Imidazolin-2-iminato Complexes, Rhenium

Introduction

Initiated by Hubert Schmidbaur in the mid 1960ies [1, 2], the organometallic chemistry of phosphoraneiminato ligands, R3PN−, has developed into a broad area of research which has produced a large number of structurally diverse main group element and transition metal complexes [3]. Due to their capability to act as 2σ,4π-electron donors, these anionic ligands can be regarded as monodentate analogues to cyclopentadienyls, C5R5, and this relationship has been described as a pseudo-isolobal phenomenon (Fig. 1) [4]. Accordingly, the use of phosphoraneiminato instead of the traditional cyclopentadienyl ancillary ligands could produce complexes of modified and potentially enhanced catalytic activity. This concept was proved successful by the synthesis of extremely active titanium catalysts for olefin polymerization [5].

Another concept, which has been extremely useful for boosting the performance of numerous transition metal catalysts, is based on the striking similarity between electron-rich organophosphanes and nucleophilic carbenes of the imidazolin-2-ylidene type in terms of their ligand properties [6]. In many cases, replacement of phosphane by N-heterocyclic carbene ligands has created transition metal complexes with improved stability and significantly enhanced catalytic activity. Similarly, substitution of the R3P for an imidazolin-2-ylidene moiety in phosphoraneimides gives imidazolin-2-imides of type I, which can be described by the two limiting mesomeric structures IA and IB (Fig. 1). The ability of an imidazolium ring to stabilize a positive charge in a more effective manner than a phosphonium group should increase the negative charge on the nitrogen atom and thus lead to...
the formation of ligands with enhanced basicity and electron donating capacity. However, only a surprisingly small number of publications has been devoted to the preparation of imidazolin-2-iminato transition metal complexes [7], and these reports have been confined to the use of the ligand precursor 2-imino-1,3-dimethylimidazoline [8].

Recently [9], we have presented a novel method for the preparation of imidazolin-2-iminato ligands, which is based on our observation that the stable carbene 1,3-di-tert-butylimidazolin-2-ylidene (1a) undergoes a Staudinger reaction [10] upon treatment with trimethylsilyl azide to furnish the N-silylated 2-iminoimidazoline 2a in a similar way as described for the preparation of silylated phosphoraneimines (Scheme 1) [2, 3c]. With this contribution, we would like to demonstrate that this reaction is indeed generally applicable to different carbenes of the imidazolin-2-ylidene type. In addition, the use of the resulting 2-iminoimidazolines for the preparation of high-valent imidazolin-2-iminato-trioxorhenium(VII) complexes is reported.

Results and Discussion

Synthesis of N-silylated 2-iminoimidazolines

The reaction of the imidazolin-2-ylidenes 1a–c with trimethylsilyl azide in boiling toluene for 72 h furnishes the 2-(trimethylsilylimino)imidazolines 2a–c in excellent yield (Scheme 1). Recrystallization from hexane affords 2a and 2b as colourless crystals. 2c is isolated as a brownish oil, which can be purified by bulb-to-bulb distillation. The conversion of the carbenes 1,3-di-tert-butylimidazolin-2-ylidene (1a) and 1,3-dimesitylimidazolin-2-ylidene (1b) can be easily followed by 1H NMR spectroscopy as pronounced high-field shifts of −0.74 (1a) and −0.72 ppm (1b) are observed for the resonances of the NCH hydrogen atoms upon formation of the imines 2a and 2b. For the conversion of 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene (1c) into the corresponding imine 2c on the other hand, a marked low-field shift of the septet CH resonance from 3.95 ppm to 4.61 ppm is indicative of product formation. According to their 1H and 13C NMR spectra, the imines 2 exhibit pseudo-C2v symmetry in solution implying that rotation around the N1–C1 axis is fast on the NMR time scale.

Crystals of 2a were subjected to an X-ray diffraction analysis, and the molecular structure of 2a is shown in Fig. 2 [9, 11]. The exocyclic C1–N1 bond distance of 1.275(3) Å is shorter than the corresponding distance in 2-imino-1,3-dimethylimidazoline [1.296(2) Å] [8] despite the steric bulk of the tert-butyl and trimethylsilyl substituents. The C1–N1–Si angle of 169.3(2)° in 2a is close to linearity and thereby significantly larger than the corresponding P–N–Si angles in silylated iminophosphoranes such as Ph3PNSiMe3 [140.2(2)°] [12], (C6H11)3PNSiMe3 [149.8(2)°] [13] and (Me2N)3PNSiMe3 [160.0(2)°] [14]. This observation follows the accepted electron donor trend [15], which is expected to increase in the order PPh3 < P(C6H11)3 < P(NMe2)3 < 1. For a more detailed structural comparison, however, not only the electronic influence of the carbene and phosphane substituents but also their steric bulk as well as molecule packing forces must be taken into account (vide infra).

Scheme 1.
Synthesis of imidazolin-2-iminatotrioxorhenium(VII) complexes

In a similar fashion as described by M. Schmidt and H. Schmidbaur [16] for the synthesis of [Me₃SiOReO₃] from Re₂O₇ and Me₃SiOSiMe₃ and as described by H. W. Roessler [17] and K. Dehnicke [18] for the syntheses of phosphoraneiminato rhenium complexes, [(R₃PN)ReO₃] (R = Ph, Et), from R₃PNSiMe₃, treatment of rhenium(VII) oxide with a twofold excess of the silylated 2-iminoimidazolines 2 in THF leads to the clean formation of the imidazolin-2-iminato complexes 3a–c, which can be isolated as yellow-orange crystals in good yield (Scheme 1). Desilylation of 2a and 2b and formation of 3a and 3b results in a pronounced down-field shift (Δδ ≈ +1.40 ppm) of the resonances observed for the NHC hydrogen atoms indicating a strong electron release towards the metal atom. To assess the electron donating ability of the imidazolin-2-iminato ligands, the IR spectra of 3a–c were measured in Nujol, and these results are summarized in Table 1. As expected for local C₃ᵥ symmetry at the metal atom, each complex exhibits two IR absorptions, which can be assigned to the symmetric and asymmetric Re–O stretching vibrations, respectively [19]. Comparison with the stretching frequencies reported for [(R₃PN)ReO₃] (R = Ph, Et) [18] (Table 1) reveals that the N,N'-diaryl/imidazolin-2-iminato ligands in 3a and 3c are stronger electron donors or, in other words, exhibit a stronger π-electron release capability than the phosphoraneimides R₃PN⁻ (R = Ph, Et), which results in a more pronounced weakening of the Re–O bonds and the observation of lower wavenumbers. In contrast, the N,N'-dialkylimidazolin-2-iminato ligand in 3b appears to have similar or even poorer donor properties than the triethyl derivative Et₃PN⁻, but it can still be regarded as a slightly better electron donor than the triphenyl derivative Ph₃PN⁻. It should also be noted that the corresponding Re–O absorptions of related cyclopentadienyl complexes [(η-C₅R₅)ReO₃] (R = H, Me) are observed at significantly lower wavenumbers (νs = 925 – 915 cm⁻¹, νas = 985 – 880 cm⁻¹) [19].

Recrystallization of 3a and 3b from acetonitrile afforded single crystals suitable for structure determination by X-ray diffraction; the molecular structures of 3a and 3b are shown in Fig. 3 and 4, respectively. In both complexes, the angles about the rhenium atom are in agreement with a slightly distorted tetrahedral environment with local C₃ᵥ symmetry at the metal atom. The Re–O bond lengths in 3a [1.698(5) – 1.733(6) Å] and 3b [1.700(5) – 1.715(4) Å] fall in the expected ranges and are in good agreement with those observed in [(Ph₃PN)ReO₃] [1.691(7) – 1.710(8) Å] and [(Et₃PN)ReO₃] [1.701(4) – 1.714(3) Å] [18] as well as with those found for the analogous cyclopentadienyl complex [(η-C₅H₅)ReO₃] [1.693(4) – 1.711(4) Å] [20]. Surprisingly, both structures differ significantly with respect to the coordination and orientation of the imidazolin-2-iminato ligands. Whereas an almost linear Re–N₁–C₁ arrangement is observed for the di-tert-butylimidazolin-2-iminato ligand and in 3a [172.0(5) and 172.0(6)° for two crystallographically independent molecules], its dimesityl substituted counterpart in 3b exhibits a considerably smaller Re–N₁–C₁ angle of 150.1(4)°. Thereby, the imidazolin-2-iminato ligand bends away from the O1 oxygen atom and adopts a staggered conformation, in which the plane containing the imidazoline ring, N1 and Re is bisecting the O2–Re–O3 plane (Fig. 4). As expected, the considerably stronger bending of the ligand in 3b produces a longer Re–N₁ distance in comparison with 3a [1.805(4) Å versus 1.792(6) and 1.747(7) Å]; a clear trend, however, can not be derived due to the observation of two distinctly different Re–N₁ distances for the two independent molecules in 3a. With 1.793(7) and 1.786(4) Å, the Re–N bond lengths in [(R₃PN)ReO₃] (R = Ph, Et) fall in the same range, whereas the values of the corresponding Re–N–P angles [162.0(5) and 160.6(2)°] are intermediate between those found for 3a and 3b. The strong variation of the Re–N–C and Re–N–P angles, respectively, is not surprising in view of quantum chemical calculations, which reveal that the potential energy surface of the model complex [(H₃PN)ReO₃] is extremely shallow with respect to the Re–N–P angle [4]. Therefore, this geometric parameter is highly responsive to structural changes of the ligand substitution pattern and should also be easily affected by molecule packing forces.

Table 1. Re–O stretching frequencies (cm⁻¹) for L-ReO₃ complexes (L = imidazolin-2-imide or phosphoraneimide).a

<table>
<thead>
<tr>
<th>Compound</th>
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<tr>
<td>νs (Å1)</td>
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<tr>
<td>νas (ÅE)</td>
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<td>3a</td>
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<td>3b</td>
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a In Nujol; b taken from reference [18].
Fig. 3. ORTEP drawing of 3a (molecule A) with displacement ellipsoids drawn at 50% probability. Molecules A and B differ in the orientation of the ReO₃ moiety with respect to the imidazole ring. Selected bond lengths [Å] and bond angles [°]: Re−O1 1.718(5) [1.698(5)], Re−O2 1.705(4) [1.703(5)], Re−O3 1.733(6) [1.727(6)], Re−N1 1.792(6) [1.747(7)], N1−C1 1.315(8) [1.348(10)], C1−N2 1.348(9) [1.382(8)], C1−N3 1.394(10) [1.378(10)], C2−C3 1.339(6); N1−N2 1.805(4), N1−N3 1.353(6), N2−C1 172.0(5) [172.0(6)], N3−C1 150.1(4), N1−Re−O1 108.0(2), N1−Re−O2 107.9(2), N1−Re−O3 109.0(3) [109.5(3)], O1−Re−O2 110.0(2) [108.8(2)], O1−Re−O3 109.0(3) [109.5(3)], O2−Re−O3 109.1(3) [109.2(3)].

Fig. 4. ORTEP drawing of 3b with displacement ellipsoids drawn at 50% probability. Selected bond lengths [Å] and bond angles [°]: Re−O1 1.700(5), Re−O2 1.715(4), Re−O3 1.712(5), Re−N1 1.805(4), N1−C1 1.309(7), C1−N2 1.358(7), C1−N3 1.335(6), N2−C2 1.396(7), N3−C3 1.396(7), C2−C3 1.341(13); N1−C1 106.9(4), Re−N1−C1 150.1(4), N1−Re−O1 108.0(2), N1−Re−O2 112.9(2), N1−Re−O3 111.1(2), O1−Re−O2 107.9(2), O1−Re−O3 108.8(2), O2−Re−O3 108.0(3).

The structural characterization of 3c would have allowed to further investigate the impact of such changes on the structural properties of imidazolin-2-iminato complexes. Unfortunately, several attempts to obtain single crystals of 3c have repeatedly lead to the isolation of a crystalline hydrolysis product, in which the metal-nitrogen bond in 3c is cleaved with one water molecule to give the corresponding 2-aminoimidazolium tetraoxorhenenate(VII) 3c · H₂O (Scheme 1). In the solid state, 3c · H₂O forms an extended structure, in which the amino group of each imidazolium cation is involved in N−H−O hydrogen bonding to two perrenate anions. As each ReO₄ anion is also linking two counterions via an NH−O−Re−O−HN arrangement, a polymeric zigzag chain is formed, a part of which is shown in Fig. 5. All structural parameters fall in the expected ranges and are in good agreement with the values obtained by X-ray structure determination of other salts containing either 2-aminoimidazolium [7b, 21] or tetraoxorhenenate(VII) ions involved in hydrogen bonding [22].

Conclusion

With this contribution, we have demonstrated that the Staudinger reaction between various stable carbenes of the imidazolin-2-yldene type and trimethylsilyl azide gives access to N-silylated 2-iminimidazolines, which can be used directly for the preparation of imidazolin-2-iminato transition metal complexes from metal halides or oxides with cleavage of the N−Si bond and concomitant formation of trimethylsilyl halides or hexamethyldisiloxane, respectively. These imidazolin-2-imides represent a suitable addition to well-established phosphoraneimides and are a novel class of promising ancillary ligands for the design and preparation of homogeneous catalysts. The trioxorhenium(VII) complexes presented here are structurally remarkably different indicating that the electronic and steric features of these ligands as well as the properties of the resulting transition metal complexes can be easily varied. As trioxorhenium(VII) complexes of the general type [LReO₃] are particularly useful for applications in homogeneous oxidation catalysis [19], the reactivity and catalytic activity of the corresponding imidazolin-2-iminato complexes 3 will be further investigated.

Experimental Section

All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. All solvents were purified by standard methods and distilled prior to use.
The imidazolin-2-ylidene 1a [23], 1b [24], and 1c [25] were prepared according to published procedures. Trimethylsilyl azide was received from Aldrich and dried over molecular sieve (4 Å).

**General procedure for the preparation of 2-(trimethylsilyl-imino)imidazolines (2)**

A solution of the imidazolin-2-ylidine 1 (10 mmol) in toluene (20 ml) was treated dropwise with trimethylsilyl azide (24 mmol) at ambient temperature, and the resulting reaction mixture was subsequently heated in boiling toluene for 72 h. Filtration and evaporation of the solvent afforded the imines as yellowish solids (2a and 2b) or as a brownish oil (2c), respectively, which can be purified by bulb-to-bulb distillation at 180 °C/9 mbar.

**2a:** Yield: 88%. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 6.03$ (s, 2 H, NCH$_3$), 1.36 (s, 18 H, CH$_3$Si), 0.52 (s, 9 H, SiCH$_3$). – $^{13}$C $^1$H NMR (100.52 MHz, CD$_2$Cl$_2$): $\delta = 139.7$ (NCN), 107.5 (NCH$_3$), 54.2 (NCCH$_3$), 28.1 (CH$_3$Si). – C$_{14}$H$_{33}$N$_3$Si (267.68): calcd. C 62.86, H 10.93, N 15.71; found C 62.55, H 11.10, N 15.34.

**2b:** Yield: 80%. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 6.78$ (s, 4 H, m-CH$_3$), 5.76 (s, 2 H, NCH$_3$), 2.21 (s, 12 H, o-CH$_3$). 2.10 (s, 6 H, p-CH$_3$), 0.09 (s, 9 H, SiCH$_3$). – $^{13}$C $^1$H NMR (100.52 MHz, CD$_2$Cl$_2$): $\delta = 140.7$ (NCN), 137.6 ($\delta$-isop-C), 136.9 ($\omega$-CMe), 134.5 ($p$-CMe), 128.9 (m-CH$_3$), 112.1 (NCH$_3$), 20.8 (p-CH$_3$), 18.0 (o-CH$_3$), 3.1 (SiCH$_3$). – C$_{24}$H$_{39}$N$_3$Si (391.63): calcd. C 73.61, H 8.49, N 15.70; found C 72.55, H 8.16, N 10.58.

**2c:** Yield: 92%. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 4.59$ (sept, 2 H, NCH$_3$Me), 1.71 (s, 6 H, NCCCH$_3$), 1.18 (d, 12 H, CHCH$_3$), 0.44 (s, 9 H, SiCH$_3$). – $^{13}$C $^1$H NMR (100.52 MHz, CD$_2$Cl$_2$): $\delta = 144.4$ (NCN), 113.9 (NCMe), 45.0 (NCH$_3$), 21.3 (NCHCH$_3$), 10.0 (NCH$_3$). – C$_{14}$H$_{27}$N$_3$Si (267.48): calcd. C 62.86, H 10.93, N 15.71; found C 62.55, H 11.10, N 15.34.

**General procedure for the preparation of imidazolin-2-iminatrioxorhenium(VII) complexes (3)**

The imine 2 (0.5 mmol) and Re$_2$O$_7$ (0.25 mmol) were dissolved in THF (15 ml), and the resulting reaction mixture was stirred at ambient temperature for 24 h. The resulting precipitate was isolated by filtration, washed with THF and dried in vacuo. The rhenium complexes were obtained as crystalline yellow (3a and 3b) or orange solids (3c), respectively.

**3a:** Yield: 78%. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta = 7.40$ (s, 2 H, NCH$_3$), 1.54 (s, 18 H, CH$_3$Si), $^{13}$C $^1$H NMR (100.52 MHz, DMSO-d$_6$): $\delta = 125.6$ (NCN), 114.6 (NCH$_3$), 59.1 (NCH$_3$), 28.4 (CCH$_3$). – IR (Nujol): $\nu = 928, 907$ (Re-O) cm$^{-1}$. – C$_{14}$H$_{27}$N$_3$O$_3$Re (428.50): calcd. C 30.83, H 4.70, N 9.81; found C 30.82, H 4.34, N 9.73.

**3b:** Yield: 85%. $^1$H NMR (270 MHz, CD$_2$CN): $\delta = 7.16$ (s, 2 H, NCH$_3$), 7.10 (s, 4 H, m-CH$_3$), 2.35 (s, 6 H, $p$-CH$_3$), 2.11 (s, 12 H, o-CH$_3$). – $^{13}$C $^1$H NMR (100.52 MHz, CD$_2$CN): $\delta = 140.8$ (isop-C), 136.0 ($\omega$-CMe), 135.2 (NCN), 129.4 (m-CH$_3$), 119.9 (p-CMe), 118.6 (NCH$_3$), 20.2 ($p$-CMe), 16.7 (o-CH$_3$). – IR (Nujol): $\nu = 949, 917$ (Re-O) cm$^{-1}$. – C$_{21}$H$_{33}$N$_3$O$_3$Re (552.64): calcd. C 45.64, H 4.38, N 7.60; found C 44.79, H 3.87, N 7.14.

**3c:** Yield 78%. $^1$H NMR (270 MHz, CD$_2$Cl$_2$): $\delta = 4.07$ (sept, 2 H, NCHMe$_2$), 1.21 (s, 6 H, NCCCH$_3$), 1.03 (d, 12 H, CHCH$_3$). – $^{13}$C $^1$H NMR (100.52 MHz, CD$_2$Cl$_2$): $\delta = 119.3$ (NCMe), 48.4 (NCH$_3$), 20.5 (NCHCH$_3$), 8.6 (NCCH$_3$); the NCN resonance could not be detected. – IR (Nujol): $\nu = 929, 903$ (Re-O) cm$^{-1}$. – C$_{14}$H$_{27}$N$_3$O$_3$Re (428.50): calcd. C 30.83, H 4.70, N 9.81; found C 29.84, H 4.82, N 9.24.
Single crystal X-ray structure determination of compounds 3a, 3b, and 3c · H2O

3a (3b, 3c · H2O): Crystal data and details of the structure determination are presented in Table 2. Suitable single crystals for the X-ray diffraction study were grown from CH3CN (CH3CN, CH3CN). A clear yellow fragment (yellow plate, colorless prism) was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR951) and graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 2930 (1985, 2907) reflections. Data collection was performed at 123 (123, 293) K (OXFORD CRYOSYSTEMS) within a θ-range of 1.13° < θ < 25.37° (2.31° < θ < 25.43°, 2.03° < θ < 25.33°). Measured each with nine data sets in rotation scan mode with Δφ/Δω = 1.0° (1.0°, 2.0°). A total number of 61483 (20674, 37653) intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects. After merging [Rint = 0.078 (0.070, 0.046)] a sum of 4946 (3801, 2776) (all data) and 4750 (3628, 2595) [I > 2σ(I)] respectively, remained and all data were used. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. For 3a and 3b, all hydrogen atom positions were calculated in ideal positions (riding model). For 3c · H2O, all hydrogen atom positions were found in the difference map calculated from the model containing all non-hydrogen atoms, and the hydrogen positions were refined with individual isotropic displacement parameters. Full-matrix least-squares refinements with 338 (259, 261) parameters were carried out by minimizing Σw(Fo − Fe)2 with the SHELXL-97 weighting scheme and stopped at shift/error < 0.001. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.

All calculations were performed on an Intel Pentium II PC, with the STRUX-V system, including the programs PLATON, SIR92, and SHELXL-97 [26]. 3a: As shown by Flack’s parameter the crystal is twinned. [TWIN / BASF = 0.453(11)]. The asymmetric unit cell contains two crystallographically independent molecules A and B, which differ in the orientation of the ReO₃ moiety with respect to the imidazolin ring. 3b: The correct enantiomer is proved by Flack’s parameter ε = −0.004(11). 3c · H2O: Small extinction effects were corrected with the SHELXL-97 procedure [ε = 0.00130(9)].
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[11] The molecular structure of 2a has been previously communicated (CCDC-229688) [9]. See http://www.rsc.org/suppdata/cc/b4/b401041h/ for crystallographic data in .cif or other electronic format.


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