Heteroditopic Imino N-Heterocyclic Carbenes and Their Sulfur, Selenium, and Tungsten Tetracarbonyl Derivatives

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New heterditopic imino N-heterocyclic carbenes for use as chelating ligands in homogeneous catalysis are the focus of this contribution. The synthesis of the corresponding imidazolium precursors is accomplished in three steps by alkylation of imidazole with ketoalkyl bromides, imination of the carbonyl functionality with anilines, either by conventional methods or by an aluminum-assisted condensation, and methylation using highly electrophilic methyl triflate. Deprotonation of the imidazolium triflates with potassium hydride gives a different outcome depending on the substitution pattern of the iminomethyl moiety: iminomethyl N-heterocyclic carbenes containing a methylene group between the imino moiety and the N-heterocycle are unstable because of tautomerization to the corresponding methylene-deprotonated ylides. In contrast, iminoisopropyl N-heterocyclic carbenes, where the acidic site of the methylene group is blocked by two methyl groups, are stable in solution, as proven by ^{1}H and ^{13}C NMR spectroscopy. First derivatives of these new [N,C]-ligands include their sulfur and selenium oxidation products (iminoisopropylimidazolin-2-thione and -selenone, respectively) as well as a tungsten tetracarbonyl complex with a six-membered [N,C] chelating moiety. All new products were fully characterized by multinuclear NMR (^{1}H, ^{13}C, ^{77}Se, ^{183}W) and IR spectroscopy, mass spectrometry, as well as by X-ray single crystal structures.

Introduction

The chemistry of N-heterocyclic carbenes (NHCs) and their metal complexes[1] is of great current interest for applications in homogeneous catalysis. The advantages of NHCs as steering ligands of catalytically active transition metal complexes arise from their synthetic, thermodynamic, and technical features. Synthetically, NHC ligands may be designed and more or less easily synthesized in great structural variety, including multidentate and chiral representatives. Thermodynamically, the metal–carbon bond of NHC complexes is stronger than the metal–phosphorus bond of phosphane complexes, which suggests that replacement of phosphanes by NHC ligands will lead to catalysts with improved stability and performance. Technically, NHC complexes are often quite stable towards oxygen and thereby allow catalytic reactions under noninert conditions without catalyst degradation. Up to now, successful applications of NHC catalysts include carbon-carbon cross-coupling reactions, olefin metathesis,[2] hydrosilylation, and CO/ethylene copolymerization.[1] In contrast, the use of NHC-derived catalysts for olefin homopolymerizations[3] have met with rather limited success so far. Established ligand lead structures in late transition metal olefin polymerization catalysis[4] include, inter alia, 1,2-diimines containing bulky peripheral imine donors (type **A**, Scheme 1). We therefore set out to explore new ligand architectures that combine the steric bulk of appropriately substituted imine donors with an electronically favorable NHC moiety.

In earlier work we showed that NHCs with a directly N-bonded imine group of type **B** (Scheme 1) are unstable because of a [1,2] rearrangement of the imidoyl moiety.[5] To avoid this difficulty, we reasoned that an electronically decoupled imine group with a spacer should be compatible with an NHC carbon. Note that type **B** ligands should form five-membered [N,C]-metal chelate rings, whereas type **C** ligands will form six-membered [N,C]-metal chelates due to the C_1 spacer unit. In this contribution we show that such [N,C] ligands are indeed accessible provided that the methylene hydrogens of the C_1 spacer are blocked by two additional methyl groups (type **D**), and we report on their group 6 metal carbonyl complexes and on their thio and seleno derivatives. In a comparable approach, Tilset and coworkers[6] as well as Coleman and coworkers[7] have recently published similar chemistry of type **C** ligands focusing on their monodentate silver and their labile κ^1/κ^2 palladium complexes.

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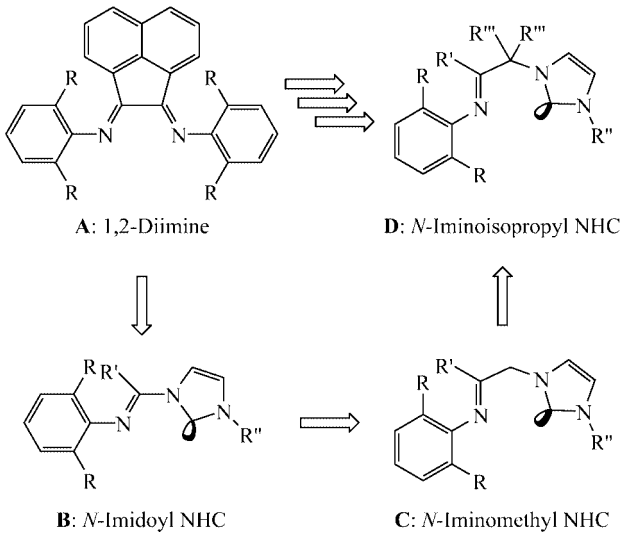


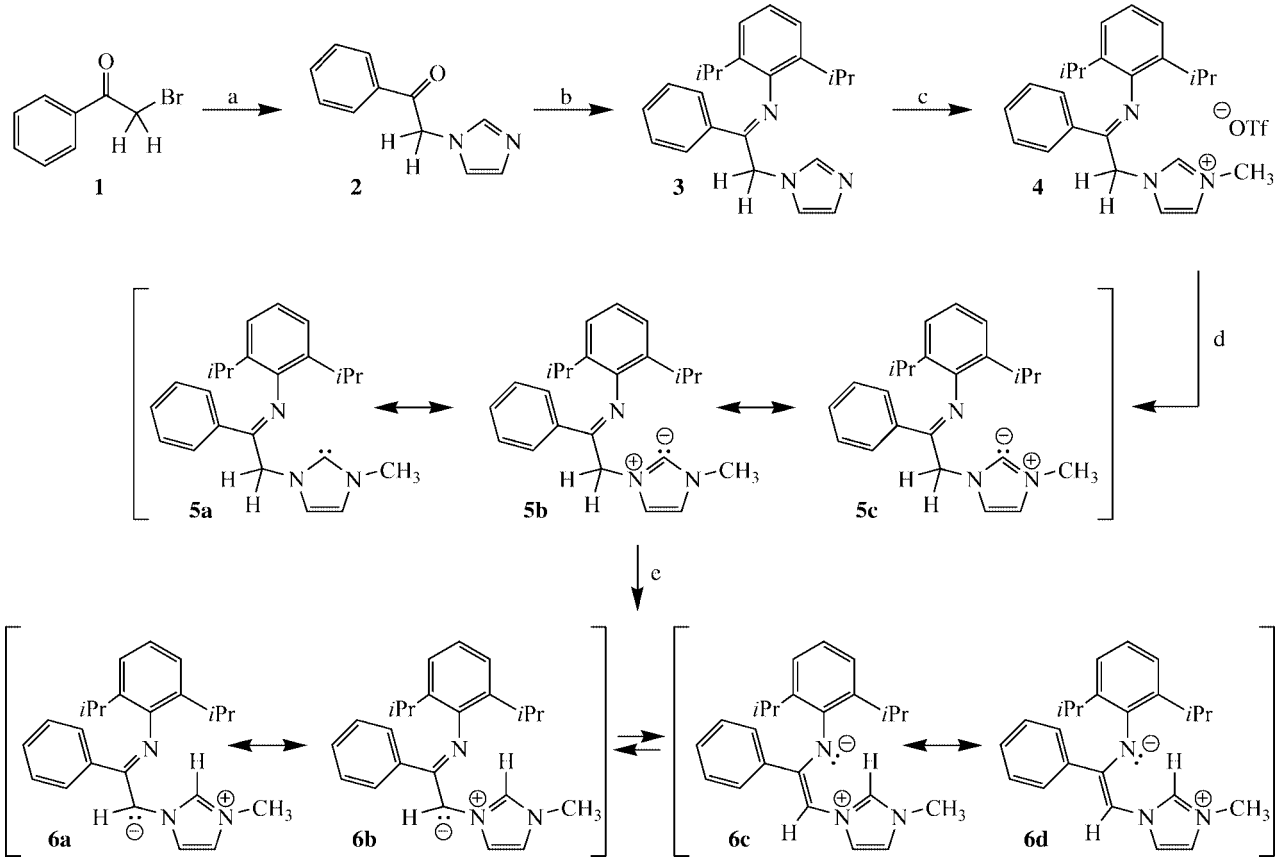
Scheme 1. Design concept for novel [N,C]-ligands.

Results and Discussion

N-Iminomethyl N-Heterocyclic Carbenes

In general, NHC ligands are generated most easily from their corresponding azolium salts (e.g. imidazolium salts) by deprotonation with suitable strong bases.[1] To get access to imino NHCs of type **C** (Scheme 1), the corresponding iminomethylimidazolium progenitors are therefore obvious synthetic targets. Such compounds may be obtained in a straightforward manner, as outlined in Scheme 2. First, a simple alkylation of imidazole with α-bromoacetophenone (**1**) afforded benzoylmethylimidazole **2** in a reasonable yield of 48%; for simplicity, one additional equivalent of imidazole was used as the base to bind the hydrogen bromide formed during the reaction. Secondly, conventional condensation of the carbonyl moiety of **2** with 2,6-diisopropylaniline with azeotropic removal of water gave iminomethylimidazole **3** as a yellow, air-stable oil. Finally, alkylation by the strongly electrophilic methyl trifluoromethanesulfonate afforded air-sensitive imidazolium triflate **4** in 29% overall yield starting from imidazole. Pertinent key NMR spectroscopic data of **4** include characteristic low-field signals for the imidazolium C(2)-bonded hydrogen [$\delta(^1H)$ = 9.17 ppm] as well as for the imine carbon [$\delta(^{13}C)$ = 161.2 ppm], observation of an imidazolium methyl group [$\delta(^1H)$ = 3.94 ppm, $\delta(^{13}C)$ = 35.8 ppm] and of an acceptor-substituted imidazolium methylene group [$\delta(^1H)$ = 5.85 ppm, $\delta(^{13}C)$ = 64.9 ppm], and detection of diastereotopic methyl groups of the isopropyl substituents [$\delta(^1H)$ = 0.83 and 0.91 ppm, $\delta(^{13}C)$ = 21.7 and 23.5 ppm] due to hindered rotation of the bulky 2,6-diisopropylphenyl substituent.

With the NHC precursor iminomethylimidazolium triflate **4** in hand, we anticipated that formation of the corresponding iminomethyl NHC would be easy to accomplish.

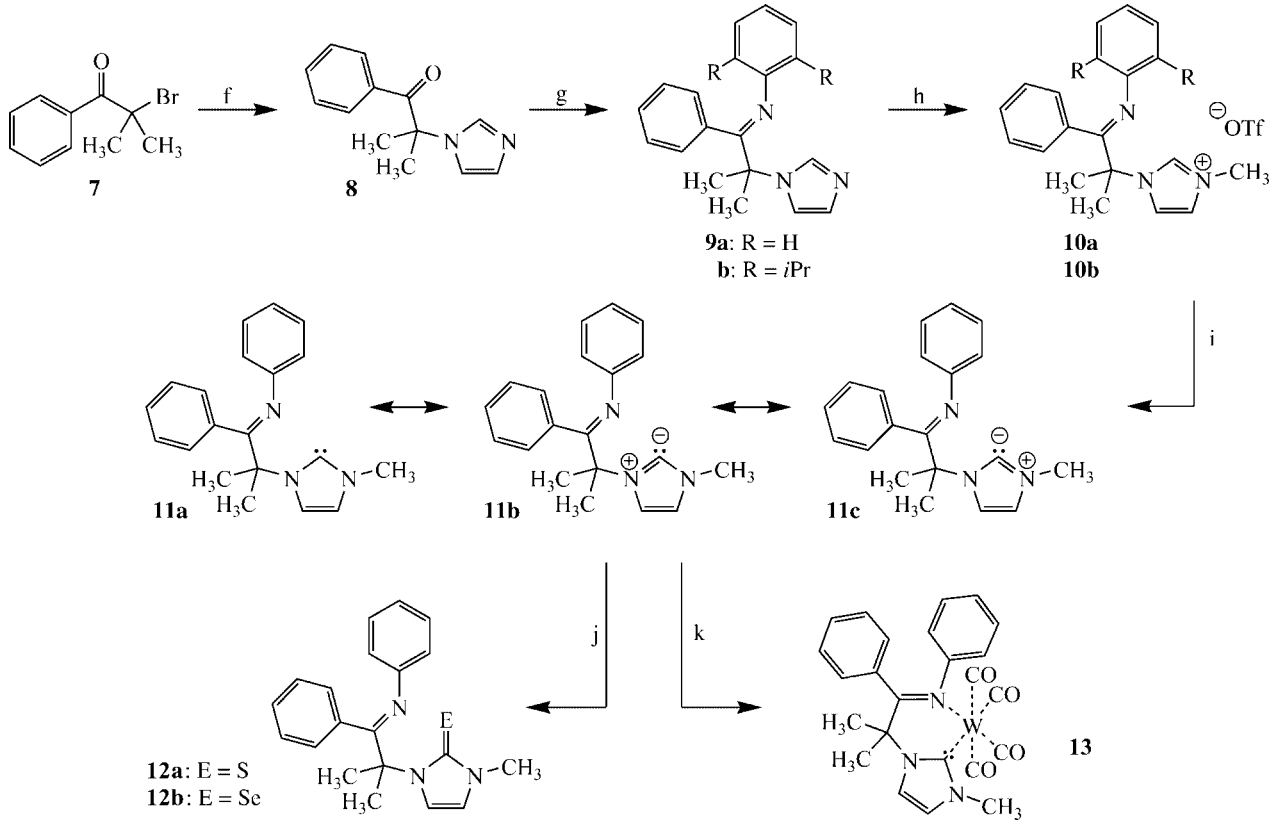


Scheme 2. Synthetic route to *N*-iminomethyl NHC ligands. Conditions: (a) imidazole; (b) 2,6-diisopropylaniline, H^+, reflux; (c) methyl triflate; (d) potassium hydride; (e) tautomerization.

However, this is not the case. Upon reaction of **4** with one equivalent of potassium hydride as proton-abstracting reagent dihydrogen evolution was observed, as expected, and a dark red solution was obtained, presumably containing NHCs **5a**–**c**. Hydrolysis of this solution followed by TLC analysis showed that only the starting material **4** was present, indicating that deprotonation must have occurred without any decomposition, in contrast to earlier work[6] where intractable reaction mixtures were obtained on attempted deprotonation of iminomethylimidazolium salts. Closer inspection of the reactivity of this red solution indicated that no NHC was present, but instead its formal tautomer **6a**,**b** and/or its ylidic enamine **6c**,**d** must have been formed by deprotonation of the methylene group instead of the imidazolium C(2)-hydrogen. The intense red color of this new ylide is obviously due to the spread of charge over six unsaturated atoms, as indicated by formulas **6a**–**d**. In retrospect, this undesired deprotonation at the "wrong" site is not too surprising because similar behavior has been reported for some other imidazolium salts containing acidic methylene groups.[6–8] Based on these results we conclude that the free iminomethyl NHCs **5a**–**c** are unstable or rearrange to their tautomers. However, we note that such carbene ligands have been successfully incorporated into some silver and palladium complexes[6–8] using in situ deprotonation/complexation procedures which avoid the free carbenes as intermediates.

N-Iminoisopropyl N-Heterocyclic Carbenes

The problems associated with the acidic methylene hydrogens in NHCs of type **C** (Scheme 1) may be overcome by the use of appropriate protecting groups. As the most simple and sterically not too demanding groups we chose two methyl groups for this purpose, selecting NHCs of type **D** as our synthetic targets (Scheme 3). First, imidazole was alkylated with 2-bromo-2-methylpropiophenone (**7**) under reflux for three days in ethanolic solution to affording benzoylisopropylimidazole (**8**) in 61% yield. The longer reaction period and the increased temperature compared to the preparation of **2** reflect the steric shielding imposed by the two additional methyl groups. Besides the spectroscopic data, which are in line with expectations, the identity of **8** was further corroborated by a single crystal structure analysis (Table 2, Figure 1). In the second step, condensation of the carbonyl moiety of **8** with anilines was necessary to introduce the imine functionality. Attempts to perform this conversion under common condensation conditions (proton-catalyzed azeotropic removal of water) failed completely, but applying an aluminum-assisted protocol that was developed by us earlier for difficult substrates[9] worked nicely also in this case, affording iminoisopropylimidazoles **9a** and **9b** in over 75% yield. In the third step, imidazoles **9a** and **9b** were alkylated with methyl triflate to give the



Scheme 3. Synthesis of *N*-iminoisopropyl NHC ligands and their derivatives. Conditions: (f) imidazole, reflux; (g) aniline or 2,6-diisopropylaniline, trimethylaluminum, reflux; (h) methyl triflate; (i) potassium hydride; (j) elemental sulfur or selenium; (k) $(CO)_5W(THF)$, hv.

imidazolium salts **10a** and **10b** in over 40% overall yield starting from imidazole.

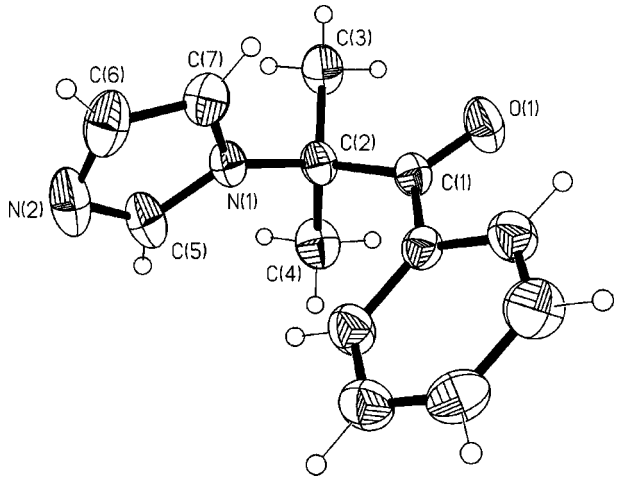


Figure 1. Molecular structure of **8**. Selected bond lengths (pm): C(5)–N(1) 135.24(17), C(5)–N(2) 131.1(2), N(1)–C(7) 137.36(17), N(2)–C(6) 137.4(2), C(6)–C(7) 134.7(2), N(1)–C(2) 147.49(16), C(2)–C(1) 154.95(17), C(1)–O(1) 121.61(15). Selected angles [°]: N(1)–C(5)–N(2) 112.66(13), N(1)–C(2)–C(1) 109.73(9), C(3)–C(2)–C(4) 109.52(11), C(2)–C(1)–O(1) 117.33(11).

Both imidazolium triflates **10a** and **10b** are yellow, slightly air-sensitive powders. Structurally, they differ only in the substitution pattern of the N-bonded aryl group. Because all further chemistry in this contribution was investigated with **10a** as precursor (vide infra), we will discuss only this triflate salt in more detail. Table 1 lists some key NMR spectroscopic data in comparison to its derivatives discussed below. Imidazolium salt **10a** shows a characteristic low-field resonance for the imidazolium C(2)-bonded hydrogen [$\delta(^1H)$ = 8.84 ppm] and an imine carbon signal [$\delta(^{13}C)$ = 171.6 ppm] in the expected range. The two methyl "protecting" groups of the isopropyl moiety are regular, nonshielded alkyl groups [$\delta(^1H)$ = 1.36 ppm, $\delta(^{13}C)$ = 25.7 ppm] as intended, ruling out a deprotonation at this site upon reaction with a strong base. The signals of the imidazolium *N*-methyl group [$\delta(^1H)$ = 3.33 ppm, $\delta(^{13}C)$ = 35.9 ppm] are similar in value to those observed for iminomethylmidazolium salt **4** containing a methylene spacer moiety (vide supra).

Imidazolium triflate **10a** serves as the precursor for the corresponding imino NHC **11a**–**c**. Treatment of **10a** with an equimolar amount of potassium hydride in THF solution caused effervescence due to dihydrogen evolution and the initially yellow solution gradually changed color to orange, which is notably different from the dark-red color of the deprotonation product of **4**. Performing this reaction on a small scale in deuterated THF solution and analyzing the outcome by NMR spectroscopy showed clearly that the desired imino-N-heterocyclic carbene **11a**–**c** had indeed been formed in quantitative yield (Table 1): the ^1H signal of the imidazole-C(2)-bonded hydrogen is absent and the ^{13}C resonance of the imidazole-C(2) carbon is detected at low field [$\delta(^{13}C)$ = 216.3 ppm] in the typical range [$\delta(^{13}C)$ = 205.9 to 231.5 ppm] of imidazolin-2-ylidene carbenes.[1e] All other NMR signals, including the imine carbon resonance [$\delta(^{13}C)$ = 175.0 ppm], are more or less similar to those of the formal conjugate acid **10a**, thus proving that carbene **11a**–**c** exists in solution. Some attempts were undertaken to crystallize NHC **11a**–**c**, but so far no suitable single crystals for an X-ray structure analysis have been obtained.

N-Iminoisopropyl N-Heterocyclic Carbene Derivatives

Having achieved a clean synthesis of the first free imino NHC **11a**–**c**, we explored its chemistry (Scheme 3). Oxidation with elemental sulfur afforded imidazolin-2-thione (**12a**) in 74% yield after workup. Spectroscopically, the sulfur-carbon double bond is clearly evident from the ^{13}C signal at δ = 161.0 ppm (Table 1) and an intense IR absorption ($\nu_{C=S}$ = 1224 cm^{-1}). The carbon resonance of the imine functionality [$\delta(^{13}C)$ = 173.3 ppm] is almost unshifted in comparison to **11a**–**c**, as expected. In addition, the C=N bond manifests itself by a strong IR band ($\nu_{C=N}$ = 1647 cm^{-1}). Further structural proof for **12a** was obtained from a single crystal structure analysis (Table 2, Figure 2); relevant bond lengths and angles are given in the caption.

Carbene **11a**–**c** reacts analogously with elemental selenium to afford the corresponding air-stable imidazolin-2-selenone (**12b**) in 43% isolated yield after workup. As expected, the spectroscopic features of **12b** are quite similar to those of its homologous thione **12a**. Due to the spin-1/2 ^{77}Se isotope further structural proof by ^{77}Se NMR spectroscopy was possible [$\delta(^{13}C)_{C=Se}$ = 153.8 ppm, $^1J(^{13}C\text{-}^{77}Se)$ = 232 Hz; $\delta(^{77}Se)$ = –1182 ppm; $\delta(^{13}C)_{C=N}$ = 172.8 ppm; $\nu_{C=Se}$ = 1222 cm^{-1}; $\nu_{C=N}$ = 1644 cm^{-1}]. These selenium NMR spectroscopic data compare well with those of the few other known imidazolin-2-selenones.[10] In the solid

Table 1. Relevant NMR spectroscopic data for **10a**, **11a**–**c**, **12a**, **12b**, and **13**.

Compound	**10a**	**11a–c**	**12a**	**12b**	**13**
Solvent	[D$_6$]DMSO	[D$_8$]THF	[D$_6$]DMSO	[D$_6$]DMSO	[D$_6$]DMSO
$\delta(^{13}C)$ of imidazole C(2)	149.3 ppm	216.3 ppm	161.0 ppm	153.8 ppm $^1J(^{13}C\text{-}^{77}Se)$ = 232 Hz	192.4 ppm $^1J(^{13}C\text{-}^{183}W)$ = 95 Hz
δ of atom bonded to imidazole C(2)	$\delta(^1H)$ = 8.84 ppm	–	$\delta(^{33}S)$: no data	$\delta(^{77}Se)$ = –1182 ppm	$\delta(^{183}W)$ = –2569 ppm
$\delta(^{13}C)$ of imine carbon	171.6 ppm	175.0 ppm	173.3 ppm	172.8 ppm	184.2 ppm
$\delta(^1H)$ of *N*-CH$_3$	3.33 ppm	3.69 ppm	3.49 ppm	3.59 ppm	3.84 ppm
$\delta(^{13}C)$ of *N*-CH$_3$	35.9 ppm	38.2 ppm	34.5 ppm	36.5 ppm	overlapped by solvent signal
$\delta(^1H)$ of *N*′-C(CH$_3$)$_2$	1.36 ppm	1.83 ppm	1.83 ppm	1.91 ppm	1.80 ppm
$\delta(^{13}C)$ of *N*′-C(CH$_3$)$_2$	25.7 ppm 66.7 ppm	28.4 ppm 64.8 ppm	26.3 ppm 64.6 ppm	26.7 ppm 65.7 ppm	27.6 ppm 64.4 ppm

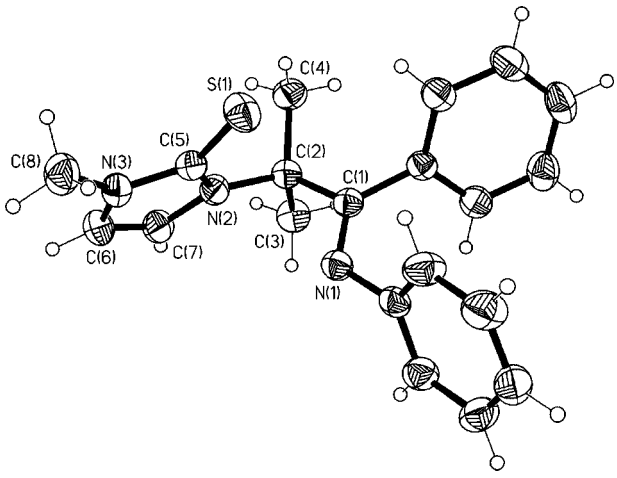


Figure 2. Molecular structure of **12a**. Selected bond lengths (pm): S(1)–C(5) 168.1(2), C(5)–N(2) 137.2(3), C(5)–N(3) 135.8(3), N(2)–C(7) 138.4(3), N(3)–C(6) 137.9(3), C(6)–C(7) 133.4(3), N(3)–C(8) 145.8(3), N(2)–C(2) 148.1(3), C(2)–C(1) 153.5(3), C(1)–N(1) 127.3(3). Selected angles [°]: N(2)–C(5)–N(3) 105.46(17), N(2)–C(2)–C(1) 108.49(16), C(3)–C(2)–C(4) 108.85(18), C(2)–C(1)–N(1) 116.60(18).

state, selenone **12b** (Table 2, Figure 3) is isomorphous with thione **12a**; only some minor differences in bond lengths and angles are observed. Most notable of these is the carbon-selenium bond length [184.0(2) pm] as compared to the shorter C=S bond [168.1(2) pm] of thione **12a**. The rather long C=Se bond length is similar in value to that of an imidazolinselenone published earlier[10] and suggests a reduced bond order due to significant contribution of the zwitterionic C^+-Se^- valence structure.

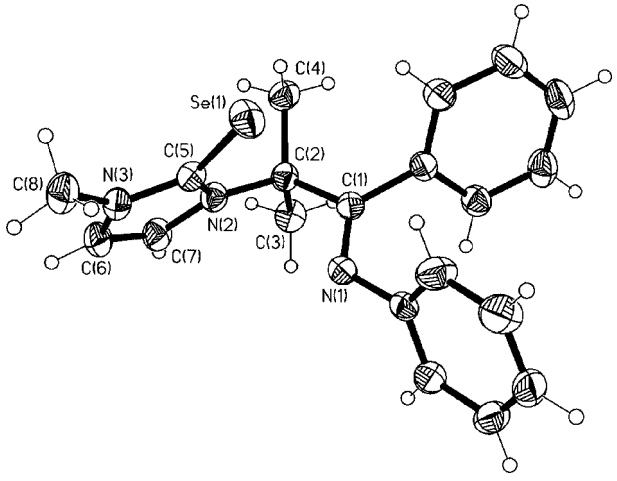


Figure 3. Molecular structure of **12b**. Selected bond lengths (pm): Se(1)–C(5) 184.0(2), C(5)–N(2) 136.7(2), C(5)–N(3) 135.4(3), N(2)–C(7) 138.7(3), N(3)–C(6) 137.5(3), C(6)–C(7) 133.7(3), N(3)–C(8) 146.0(3), N(2)–C(2) 148.2(3), C(2)–C(1) 153.9(3), C(1)–N(1) 127.2(2). Selected angles [°]: N(2)–C(5)–N(3) 105.84(17), N(2)–C(2)–C(1) 108.76(16), C(3)–C(2)–C(4) 108.55(17), C(2)–C(1)–N(1) 116.56(17).

In principal it would be interesting to synthesize the next higher homologue, iminoisopropylimidazolin-2-tellurone, by oxidation of carbene **11a**–**c** with elemental tellurium. However, because of the known sensitivity of such compounds at room temperature and towards sunlight,[11] and because of the obnoxious stench associated with organic tellurium compounds in general, we refrained from attempting this reaction. However, we note that both compounds **12a** and **12b** represent new heteroditopic [N,S]- and [N,Se]-ligands whose coordination chemistry remains unexplored at the moment.

As outlined in the introduction, carbene **11a**–**c** was designed as a member of a new family of heteroditopic [N,C]-imino NHC ligands for application in homogeneous catalysis. Consequently, it was of prime interest to study its coordination chemistry. Reaction with simple metal halides ($PdCl_2$, CuCl, AgCl, $NiCl_2$ etc.) gave, in general, polar products that are obviously [N,C]-bound metal complexes. Full characterization proved quite difficult, however, and the growth of suitable crystals for an unambiguous structural proof by single crystal structure analysis has not yet been possible. In contrast, the reaction with photochemically generated $W(CO)_5$(THF) afforded the air-stable tungsten complex **13**, which was fully characterized in solution by a range of spectroscopic methods as well as in the solid state by single crystal structure analysis. Its ^{13}C NMR spectrum (Table 1) shows the carbene carbon signal at δ = 192.4 ppm, with a one-bond ^{13}C-^{183}W coupling constant of 95 Hz, thereby proving the direct connectivity of the NHC-carbon to the metal center. The imine carbon is shifted to low field [$\delta(^{13}C)$ = 184.2 ppm] in comparison to the free carbene **11a**–**c** [$\delta(^{13}C)$ = 175.0 ppm], thus reflecting the coordination of the imine moiety to the tungsten metal center. The four carbonyl groups are evident from their strong IR absorptions and from three ^{13}C signals with ^{183}W satellites, indicating two magnetically equivalent axial carbonyl groups [$\delta(^{13}C)$ = 205.3 ppm, $^1J_{C,W}$ = 129 Hz] and two different equatorial CO ligands [$\delta(^{13}C)$ = 210.1 ppm, $^1J_{C,W}$ = 146 Hz; $\delta(^{13}C)$ = 218.2 ppm, $^1J_{C,W}$ = 169 Hz] due to the heteroditopic nature of the imino NHC ligand **11a**–**c**. The observation of only one ^{13}C signal for the two axial CO groups indicates rapid interconversion in solution of the two possible boat conformations of the six-membered chelate ring, which is further supported by the two isochronous methyl groups of the isopropyl moiety [$\delta(^{13}C)$ = 27.6 ppm, $\delta(^1H)$ = 1.80 ppm] (Table 1). Several NHC tungsten carbonyl complexes have been reported in the literature,[12] but only for one $(CO)_5$W(NHC) complex[12d] has a direct coupling of the NHC-carbon to the tungsten metal center been reported [$\delta(^{13}C)$ = 176.4 ppm, $^1J_{C,W}$ = 99 Hz];[12d] these data are in good agreement with ours. In addition, we were able to detect for the first time the ^{183}W chemical shift of an NHC-tungsten complex: **13** shows a weak but nevertheless significant ^{183}W signal at δ = –2569 ppm vs. aqueous Na_2WO_4 solution. In general, transition metal NMR spectroscopic data of tungsten metal complexes are very limited due to the unfavorable receptivity of ^{183}W (R^C = 0.0589), and only about 30 organometallic compounds have been investigated by this technique so far. Although the body of ^{183}W chemical shifts is therefore quite small for comparative purposes, the shift of **13** compares well with those of

vinylidene-tungsten complexes $[(dppe)CO]_3W{=}C{=}CHR$] with signals in the range of δ = –2548 to –2596 ppm.[13]

In the solid state (Figure 4, Table 2), complex **13** shows the expected κ^2-coordination of the [N,C]-ligand in a boat conformation, with tungsten and the isopropylmethyl group occupying the apical sites. Pertinent bond lengths and angles are given in the caption of Figure 4. Due to geometrical constraints of the six-membered chelate ring, the coordination angle at the formally octahedral tungsten center is only 78.0° as compared to the idealized normal angle. In addition, due to the steric requirements of the [N,C]-ligand, the tungsten center shows a slightly distorted octahedron, indicated by an "umbrella-like" back-bending of the four carbonyl ligands. The W–N [226.5(8) pm] and W–C [221.8(9) pm] bond lengths of the tungsten-coordinated imino NHC ligand are in the normal range of other tungsten-imino and tungsten-NHC complexes.[12] As a consequence of the boat conformation of the [N,C] six-membered chelate the two axial carbonyl groups at the tungsten center are inequivalent. However, this is just a solid-state effect; in solution, a rapid ring flip process occurs as indicated by the simplicity of the NMR spectra discussed above. Overall the X-ray structure of **13** shows the desired heteroditopic imino NHC chelate metal structure and indicates that steric tuning will easily be possible in the future by altering the substitution pattern of the N-bonded aryl moiety.

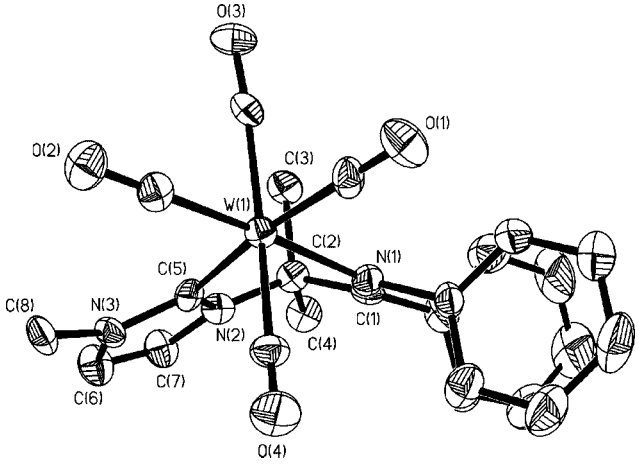


Figure 4. Molecular structure of **13**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (pm): W(1)–C(5) 221.8(9), W(1)–N(1) 226.5(8), W(1)–C(01) 196.5(11), W(1)–C(02) 194.3(11), W(1)–C(03) 201.3(12), W(1)–C(04) 204.5(11), C(01)–O(1) 116.3(13), C(02)–O(2) 119.0(13), C(03)–(O3) 115.0(13), C(04)–O(4) 112.3(13), C(5)–N(2) 137.5(13), C(5)–N(3) 136.1(13), N(2)–C(7) 137.4(13), N(3)–C(6) 138.1(14), C(6)–C(7) 131.2(17), N(3)–C(8) 147.8(14), N(2)–C(2) 147.9(14), C(2)–C(1) 153.6(14), C(1)–N(1) 129.8(12). Selected angles [°]: N(1)–W(1)–C(5) 78.0(3), C(01)–W(1)–C(02) 88.3(4), C(03)–W(1)–C(04) 166.0(4), N(2)–C(5)–N(3) 102.7(8), N(2)–C(2)–C(1) 111.3(8), C(3)–C(2)–C(4) 106.8(9), C(2)–C(1)–N(1) 120.7(9).

Conclusions

New heteroditopic ligands combining the advantageous properties of N-heterocyclic carbenes and imine donors with *N*-aryl groups have been investigated. Such imino NHC systems can be prepared by alkylation of imidazole with a ketoalkyl bromide, condensation of the carbonyl group with anilines, alkylation of the iminoalkylimidazole with methyl trifluoromethanesulfonate, and deprotonation of the *N*-iminoalkyl-*N*′-methylimidazolium triflate with potassium hydride. For a successful generation of the imino NHC it is necessary to block the methylene group between the heterocycle and the imine group by two methyl substituents, otherwise deprotonation at this undesired "wrong" site occurs and an ylidic non-NHC product is observed. Spectroscopically, the imino NHC ligand is characterized by a typical low-field ^{13}C chemical shift of the NHC-carbene carbon together with an imine carbon signal. The chemical reactivity of the imino NHC comprises oxidation by elemental sulfur and selenium to afford the corresponding imidazolin-2-thione and selenone, which were fully characterized by solid state structures and multinuclear NMR spectroscopy, including ^{77}Se spectroscopy. A first transition metal complex of the imino NHC ligand was obtained by treatment with tungsten hexacarbonyl; the resulting [N,C] $W(CO)_4$ complex shows the anticipated six-membered metal [N,C] chelate in solution and in the solid state, as proven by an X-ray structure and by multinuclear NMR spectroscopy, including ^{183}W spectroscopy.

Experimental Section

General: Commercially available starting materials were used as obtained. Solvents were dried, deoxygenated, and saturated with argon according to standard procedures in organometallic chemistry. Reactions of air-sensitive materials were performed in Schlenk glassware under an atmosphere of argon using techniques common in organometallic chemistry.

Imidazole 2 (CA registry no. 24155-34-8): A round-bottomed flask was charged with imidazole (4.3 g, 62.8 mmol), α-bromoacetophenone (**1**; 5 g, 25.1 mmol), and 100 mL of THF. The yellow solution was stirred overnight at ambient temperature to give a yellow suspension of the product with precipitated imidazolium bromide. Aqueous workup and recrystallization from methanol/diethyl ether yielded pure, yellow **2** (2.24 g, 12 mmol, 48%). M.p.: 117–119 °C. IR (KBr): $\tilde{\nu}$ = 2965 cm^{-1} (w), 2919 (w), 1696 (vs), 1597 (s), 1503 (s), 1451 (s), 1360 (s), 1344 (m), 1288 (m), 1227 (vs), 1107 (s), 1074 (s), 1038 (s), 984 (s), 906 (s), 816 (s), 762 (s), 746 (vs), 692 (vs). ^1H NMR (300 MHz, CD_2Cl_2): δ = 5.43 (s, 2 H, CH_2), 6.94–7.99 (m, 8 H, C_6H_5, $C_3H_3N_2$) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): δ = 52.9 (CH_2), 120.7, 128.2, 129.3, 134.6, and 138.5 (C_6H_5, $C_3H_3N_2$), 192.4 (C=O) ppm.

Imidazole 3: A Dean–Stark apparatus was charged with **2** (940 mg, 5.05 mmol), 2,6-diisopropylaniline (2.80 mL, 15.1 mmol), *p*-toluenesulfonic acid monohydrate (2.9 g, 15.1 mmol), and 100 mL of toluene. The mixture was refluxed for 3 d, followed by aqueous workup. Chromatography on alumina with diethyl ether/*n*-hexane (v/v = 1:1) as eluent removed the excess of aniline, and elution with methanol yielded pure **3** (1.07 g, 3.1 mmol, 61.4%) as a yellow oil. MS (EI): *m*/*z* = 345.3 $[M]^+$. ^1H NMR (300 MHz, CD_2Cl_2): δ = 0.87–1.23 (m, 12 H, CH_3), 2.67 (m, 2 H, CH), 4.90 (s, 2 H, CH_2), 6.64–7.88 (m, 11 H, C_6H_5, C_6H_3, $C_3H_3N_2$) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): δ = 22.1, 23.7, and 28.8 [$CH(CH_3)_2$], 44.7 (CH_2), 119.4, 120.2, 123.2, 123.5, 124.2, 124.7, 127.6, 128.7, 129.1, 129.7, 130.2, 131.3, 135.7, 136.1, 136.9, 137.8, 138.2, and 145.1

(C_6H_5, C_6H_3, $C_3H_3N_2$), 162.2, 162.9 (C=N) ppm. $C_{23}H_{27}N_3$ (345.48): calcd. C 79.96, H 7.88, N 12.16; found C 80.11, H 7.86, N 12.13.

Imidazolium Triflate 4: A Schlenk tube was charged with **3** (392 mg, 1.13 mmol) and dry dichloromethane (40 mL). The solution was cooled to –80 °C and methyl trifluoromethanesulfonate (124 μL, 1.13 mmol) was added from a syringe. After 90 min stirring at –80 °C, the cooling bath was removed and the mixture was stirred for a further 90 min. Workup: all volatile materials were removed on a vacuum line, the solid yellow residue was washed with two portions of dry diethyl ether, and dried in vacuo to afford 570 mg of **4** as a yellow, air-sensitive powder in 99% yield. MS (FAB): *m*/*z* = M of cation not observed due to hydrolysis. ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ = 0.83 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, $CH(CH_3)_2$], 0.91 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, $CH(CH_3)_2$], 2.65 [m, 2 H, $2\times CH(CH_3)_2$], 3.94 (s, 3 H, CH_3), 5.85 (s, 2 H, CH_2), 6.95–7.82 (m, 10 H, C_6H_5, C_6H_3, $C_3H_3N_2$), 9.17 (s, 1 H, $C_3H_3N_2$) ppm. ^{13}C NMR [75.432 MHz, $(CD_3)_2SO$]: δ = 21.7, 23.5, and 27.4 [$CH(CH_3)_2$], 35.8 (N-CH_3), 64.9 (CH_2), 118.6, 122.6, 122.8, 123.2, 123.8, 124.1, 127.2, 128.5, 128.8, 130.4, 133.6, 134.8, 137.8, and 144.0 (C_6H_5, C_6H_3, $C_3H_3N_2$), 161.2 (C=N) ppm. The weak ^{13}C signals for the triflate anion [δ = 121 ppm, q, $^1J(^{13}C\text{-}^{19}F)$ = 322 Hz] were not observed due to insufficient concentration and/or too short an acquisition period. $C_{25}H_{30}F_3N_3O_3S$ (509.59): calcd. C 58.92, H 5.93, N 8.25; found C 58.69, H 5.95, N 8.22.

Imidazole 8: A round-bottomed flask was charged with imidazole (3.40 g, 49.9 mmol), 2-bromo-2-methylpropiophenone (**7**; 4 mL, 23.8 mmol), and 40 mL of ethanol. The yellow solution was refluxed for 3 d. Aqueous workup yielded a yellow oil which crystallized in the freezer. Recrystallization from dichloromethane/*n*-hexane (1:2) afforded pure, colorless **8** (3.11 g, 14.5 mmol, 61%). MS (EI): *m*/*z* = 214.1 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 3145 cm^{-1} (w), 3000(w), 1672(vs), 1599(m), 1576(w), 1493(m), 1470(m), 1451(m), 1393(w), 1375(m), 1339(w), 1285(w), 1261(s), 1240(vs), 1177(s), 1167(s), 1153(m), 1082(s), 1013(s), 976(s), 906(s), 893(s), 820(s), 750(s). ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ = 1.80 (s, 6 H, CH_3), 6.94–7.87 (m, 8 H, C_6H_5, $C_3H_3N_2$) ppm. ^{13}C NMR [75.432 MHz, $(CD_3)_2SO$]: δ = 26.6 and 64.7 [$C(CH_3)_2$], 118.1, 128.0, 128.5, 129.1, 132.6, 134.8, and 135.6 (C_6H_5, $C_3H_3N_2$), 199.3 (C=O) ppm. $C_{13}H_{14}N_2O$ (214.26): calcd. C 72.87, H 6.59, N 13.07; found C 72.95, H 6.57, N 13.03.

Imidazole 9a: A Schlenk tube was charged with aniline (524 μL, 5.75 mmol), 40 mL of toluene, and 2.87 mL of a 2.0 M toluene solution of trimethylaluminum (5.75 mmol). The stirred solution was heated to 80 °C. After 90 min methane evolution was complete and the solution was cooled to ambient temperature. Under protection from air, imidazole **8** (560 mg, 2.61 mmol) was added in one portion. The mixture was stirred overnight at ambient temperature and then heated to 80 °C for a further three hours to afford a bright-yellow solution. Workup: the solution was cooled to 0 °C, the mixture was carefully hydrolyzed with crushed ice, the organic product was extracted with three portions of dichloromethane, the combined organic layers were washed with three portions of a 5% aqueous NaOH solution, the dichloromethane solution was washed with two portions of water, the organic phase was dried with Na_2SO_4, and all volatile materials were removed in vacuo on a rotary evaporator to afford the crude product together with aniline. Chromatography on alumina with diethyl ether/*n*-hexane (v/v, 1:1) as eluent followed by methanol afforded 651 mg of pure **9a** in 86% yield as a yellow oil. MS (FAB): *m*/*z* = 290.2 $[M + H]^+$. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.85 (s, 6 H, CH_3), 6.39–7.53 (m, 13 H, C_6H_5, $C_3H_3N_2$) ppm. ^{13}C NMR (75.432 MHz, CD_2Cl_2): δ = 26.7 and 63.1 [$C(CH_3)_2$], 117, 8, 120.2, 123.6, 127.8, 128.1, 128.5, 128.7, 129.6, 134.6, 135.6, and 150.3 (C_6H_5, $C_3H_3N_2$), 173.0 (C=N) ppm. $C_{19}H_{19}N_3$ (289.37): calcd. C 78.86, H 6.62, N 14.52; found C 78.99, H 6.59, N 14.48.

Imidazole 9b: A Schlenk tube was charged with 2,6-diisopropylaniline (2.96 mL, 15.7 mmol), 40 mL of toluene, and 7.84 mL of a 2.0 M toluene solution of trimethylaluminum (15.7 mmol). The stirred solution was heated to 80 °C. After 90 min methane evolution was complete and the solution was cooled to ambient temperature. Under protection from air, imidazole **8** (1.12 g, 5.23 mmol) was added in one portion. The mixture was stirred overnight at ambient temperature and heated to 80 °C for a further three hours to afford a bright-yellow solution. Workup as described above for **9a** afforded 1.46 g of pure **9b** in 75% yield as a yellow oil. MS (EI): *m*/*z* = 373.3 $[M]^+$. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.06 [d, $^3J_{H,H}$ = 6.94 Hz, 6 H, $CH(CH_3)_2$], 1.14 [d, $^3J_{H,H}$ = 6.61 Hz, 6 H, $CH(CH_3)_2$], 2.74 [m, 2 H, $2\times CH(CH_3)_2$], 6.38–7.49 (m, 11 H, C_6H_5, C_6H_3, $C_3H_3N_2$) ppm. ^{13}C NMR (75.432 MHz, $CDCl_3$): δ = 21.3, 23.9, and 28.7 [$CH(CH_3)_2$], 27.3 and 63.4 [$C(CH_3)_2$], 117.8, 122.7, 126.4, 127.6, 128.0, 128.8, 129.5, 134.7, 135.5, 136.9, and 145.0 (C_6H_5, C_6H_3, $C_3H_3N_2$), 170.4 (C=N) ppm. $C_{25}H_{31}N_3$ (373.53): calcd. C 80.39, H 8.37, N 11.25; found C 80.52, H 8.34, N 11.20.

Imidazolium Triflate 10a: A Schlenk tube was charged with **9a** (650 mg, 2.25 mmol) and dry dichloromethane (40 mL). The solution was cooled to –80 °C and methyl trifluoromethanesulfonate (246 μL, 2.25 mmol) was added with a syringe. After 90 min stirring at –80 °C, the cooling bath was removed and the mixture was stirred for a further 90 min. Workup: all volatile materials were removed on a vacuum line, the solid yellow residue was washed with two portions of dry diethyl ether, and dried in vacuo to afford 920 mg of **10a** as a yellow, slightly air-sensitive powder in 90% yield. MS (FAB): *m*/*z* = 304.1 $[M]^+$ of cation. ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ = 1.36 (s, 6 H, CH_3), 3.33 (s, 3 H, CH_3), 6.03–7.54 (m, 12 H, C_6H_5, $C_3H_3N_2$), 8.84 (s, 1 H, $C_3H_3N_2$) ppm. ^{13}C NMR [75.432 MHz, $(CD_3)_2SO$]: δ = 25.7 and 66.7 [$C(CH_3)_2$], 35.8 (N-CH_3), 119.4, 121.6, 121.8, 123.3, 123.6, 123.8, 127.8, 127.9, 128.3, 128.5, 128.6, 128.8, 133.4, 136.5, and 149.3 (C_6H_5, $C_3H_3N_2$), 171.6 (C=N), 120.7 (q, $^1J_{C,F}$ = 322 Hz, CF_3 of triflate) ppm. $C_{21}H_{22}F_3N_3O_3S$ (453.48): calcd. C 55.62, H 4.89, N 9.27; found C 55.34, H 4.91, N 9.24.

Imidazolium Triflate 10b: A Schlenk tube was charged with **9b** (1.47 g, 3.94 mmol) and dry dichloromethane (40 mL). The solution was cooled to –80 °C and methyl trifluoromethanesulfonate (432 μL, 3.94 mmol) was added with a syringe. After 90 min stirring at –80 °C, the cooling bath was removed and the mixture was stirred for a further 90 min. Workup: all volatile materials were removed on a vacuum line, the solid yellow residue was washed with two portions of dry diethyl ether, and dried in vacuo to afford 2.00 g of **10b** as a yellow, slightly air-sensitive powder in 95% yield. MS (FAB): *m*/*z* = 388.4 $[M]^+$ of cation. ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ = 0.91 [d, $^3J_{H,H}$ = 6.61 Hz, 6 H, $CH(CH_3)_2$], 1.05 [d, $^3J_{H,H}$ = 6.93 Hz, 6 H, $CH(CH_3)_2$], 2.00 [s, 6 H, $C(CH_3)_2$], 2.65 [m, 2 H, $2\times CH(CH_3)_2$], 3.87 (s, 3 H, CH_3), 6.82–8.10 (m, 10 H, C_6H_5, C_6H_3, $C_3H_3N_2$), 8.94 (s, 1 H, $C_3H_3N_2$) ppm. ^{13}C NMR [75.432 MHz, $(CD_3)_2SO$]: δ = 21.2, 23.6, and 27.7 [$CH(CH_3)_2$], 26.1 and 66.9 [$C(CH_3)_2$], 35.8 (N-CH_3), 121.7, 122.2, 123.4, 123.8, 126.1, 126.8, 127.3, 127.5, 128.0, 129.1, 133.6, 134.6, 136.8, 143.7, and 143.8 (C_6H_5, C_6H_3, $C_3H_3N_2$), 170.5 (C=N), 120,7 (q, $^1J_{C,F}$ = 322 Hz, CF_3 of triflate) ppm. $C_{27}H_{34}F_3N_3O_3S$ (537.64): calcd. C 60.32, H 6.37, N 7.82; found C 60.04, H 6.40, N 7.78.

Imino N-Heterocyclic Carbene 11a–c: A small Schlenk tube was charged with imidazolium triflate **10a** (50 mg, 0.110 mmol) dis-

solved in 1 mL of dry, deuterated THF. Under protection from air, potassium hydride (4.4 mg, 0.110 mmol) was added in one portion. The mixture was stirred at ambient temperature for 2 h. Dihydrogen evolution was observed and a white precipitate of potassium triflate formed during this period. The orange suspension was transferred under an atmosphere of argon to an NMR tube and analyzed spectroscopically: ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 1.83 (s, 6 H, CH_3), 3.69 (s, 3 H, CH_3), 6.55–7.12 (m, 12 H, C_6H_5, $C_3H_2N_2$) ppm. ^{13}C NMR (75.432 MHz, [D$_8$]THF): δ = 28.4 and 64.8 [$C(CH_3)_2$], 38.2 (N-CH_3), 118.1, 120.7, 121.0, 123.3, 127.8, 128.2, 128.7, 129.4, 136.7, and 151.9 (C_6H_5, $C_3H_2N_2$), 175.0 (C=N), 216.3 (carbene C) ppm.

Imidazolin-2-thione 12a: A Schlenk tube was charged with imidazolium triflate **10a** (165 mg, 0.364 mmol), 40 mL of THF, and potassium hydride (15 mg, 0.364 mmol). The mixture was stirred for 2 h at ambient temperature. Dihydrogen evolution occurred during this period and the mixture gradually changed in color from yellow to orange. Elemental sulfur (93 mg, 0.364 mmol) was added to the stirred mixture and the reaction was allowed to proceed overnight at ambient temperature. Chromatography on alumina with diethyl ether/*n*-hexane (v/v, 1:1) and methanol as eluents afforded air-stable, yellow **12a** (90 mg, 0.268 mmol, 74%). MS (FAB): *m*/*z* = 335.0 [M]$^+$. IR (KBr): $\tilde{\nu}$ = 3140 cm^{-1} (w), 3071 (w), 2979 (w), 2928 (w), 1647 (vs) ($\nu_{C=N}$), 1591 (s), 1478 (s), 1453 (s), 1403 (s), 1386 (vs), 1362 (s), 1292 (m), 1265 (m), 1224 (vs) ($\nu_{C=S}$), 1149 (m), 989 (m), 778 (s), 704 (s), 697 (vs), 670 (vs). ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ = 1.83 (s, 6 H, CH_3), 3.49 (s, 3 H, CH_3), 6.62–7.37 (m, 12 H, C_6H_5, $C_3H_2N_2$) ppm. ^{13}C NMR [75.432 MHz, $(CD_3)_2SO$]: δ = 26.3 and 64.6 [$C(CH_3)_2$], 34.5 (CH_3), 115.6, 117.9, 119.6, 122.4, 127.5, 128.0, 128.1, 128.6, 135.6, and 150.9 (C_6H_5, $C_3H_2N_2$), 161.0 (C=S), 173.3 (C=N) ppm. $C_{20}H_{21}N_3S$ (335.47): calcd. C 71.61, H 6.31, N 12.53; found C 71.34, H 6.33, N 12.48.

Imidazolin-2-selenone 12b: A Schlenk tube was charged with imidazolium triflate **10a** (220 mg, 0.485 mmol), 40 mL of THF, and potassium hydride (20 mg, 0.485 mmol). The mixture was stirred for 2 h at ambient temperature. Dihydrogen evolution occurred during this period and the mixture gradually changed in color from yellow to orange. Elemental selenium (40 mg, 0.507 mmol) was added to the stirred mixture and the reaction was allowed to proceed overnight at ambient temperature. Chromatography on alumina with diethyl ether/*n*-hexane (v/v, 1:1) and methanol as eluents afforded air-stable, yellow **12b** (80 mg, 0.209 mmol, 43%). MS (FAB): *m*/*z* = 383.1 [M]$^+$. IR (KBr): $\tilde{\nu}$ = 3141 cm^{-1} (w), 3072 (w), 2979 (w), 1644 (vs) ($\nu_{C=N}$), 1591 (s), 1478 (s), 1452 (vs), 1377 (vs), 1296 (s), 1222 (vs) ($\nu_{C=Se}$), 1131 (s), 938 (m), 778 (s), 733 (m), 697 (vs). ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ = 1.91 (s, 6 H, CH_3), 3.59 (s, 3 H, CH_3), 6.70–7.48 (m, 12 H, C_6H_5, $C_3H_2N_2$) ppm. ^{13}C NMR [75.432 MHz, $(CD_3)_2SO$]: δ = 26.7 and 65.7 [$C(CH_3)_2$], 36.5 (CH_3), 118.2, 119.6, 119.8, 122.3, 127.4, 127.9, 128.8, 135.5, and 150.8 (C_6H_5, $C_3H_2N_2$), 153.8 ($^1J_{C,Se}$ = 232 Hz, C=Se), 172.8 (C=N) ppm. ^{77}Se NMR (57.203 MHz, $(CD_3)_2SO$, vs. H_2SeO_3): δ = –1182 (C=Se) ppm. $C_{20}H_{21}N_3Se$ (382.36): calcd. C 62.82, H 5.54, N 10.99; found C 62.62, H 5.56, N 10.95.

Tungsten Complex 13: A Schlenk tube was charged with imidazolium triflate **10a** (768 mg, 1.69 mmol), 50 mL of THF, and potassium hydride (86 mg, 1.69 mmol). The mixture was stirred for 2 h at ambient temperature. Dihydrogen evolution occurred during this period and the mixture gradually changed in color from yellow to orange. Tungsten hexacarbonyl (596 mg, 1.69 mmol) was added to

Table 2. Crystallographic data for **8**, **12a**, **12b**, and **13**.

Compound	**8**	**12a**	**12b**	**13**
Molecular formula	$C_{13}H_{14}N_2O$	$C_{20}H_2N_3S$	$C_{20}H_{21}N_3Se$	$C_{24}H_{21}N_3O_4W$
Molecular mass	214.26	335.46	382.36	599.29
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	*P*1 (no. 2)	*C*2/*c* (no. 15)	*C*2/*c* (no. 15)	*P*1 (No. 2)
a [pm]	626.64(3)	3330.04(5)	3344.67(2)	856.58(2)
b [pm]	792.77(4)	673.30(2)	680.17(4)	1363.90(5)
c [pm]	1238.73(6)	1626.7(2)	1622.54(5)	2014.61(7)
α [°]	97.332(2)	90	90	82.654(2)
β [°]	91.089(2)	101.313(6)	101.519(2)	79.147(2)
γ [°]	112.391(3)	90	90	89.959(2)
Z	2	8	8	4
V [nm^3]	0.56279(5)	3.5764(5)	3.6168(2)	2.29187(13)
ρ_{calcd} [Mg m^{-3}]	1.264	1.246	1.404	1.737
Temp. [K]	233(2)	233(2)	233(2)	233(2)
Absorption coeff. [mm^{-1}]	0.082	0.187	2.082	5.075
F_{000}	228	1424	1568	1168
Color, habit	colorless prism	colorless plate	colorless plate	yellow plate
Crystal size	0.4 × 0.2 × 0.15 mm	0.4 × 0.2 × 0.05 mm	0.35 × 0.15 × 0.07 mm	0.25 × 0.11 × 0.04 mm
θ range for data collection	1.66° to 24.00°	2.49° to 22.50°	2.49° to 25.00°	1.51° to 23.00°
Index ranges	$0 \le h \le 7$	$0 \le h \le 35$	$0 \le h \le 39$	$-9 \le h \le 0$
	$-9 \le k \le 8$	$-7 \le k \le 7$	$-8 \le k \le 8$	$-14 \le k \le 14$
	$-14 \le l \le 14$	$-17 \le l \le 16$	$-19 \le l \le 18$	$-22 \le l \le 21$
Reflections collected	2780	7515	10789	10971
Independent reflections	1754 (R_{int} = 0.0143)	2333 (R_{int} = 0.0293)	3180 (R_{int} = 0.0286)	6341 (R_{int} = 0.0370)
Reflections with $I > 2\sigma(I)$	1593	1909	2698	5407
Absorption correction	none	none	none	none
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	1754/0/146	2333/0/219	3180/0/219	6341/0/581
Goodness-of-fit on F^2	1.065	1.028	1.040	1.025
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0341	R_1 = 0.0385	R_1 = 0.0274	R_1 = 0.0542
	wR_2 = 0.0874	wR_2 = 0.0957	wR_2 = 0.0640	wR_2 = 0.1352
R indices (all data)	R_1 = 0.0379	R_1 = 0.0518	R_1 = 0.0365	R_1 = 0.0630
	wR_2 = 0.0899	wR_2 = 0.1017	wR_2 = 0.0671	wR_2 = 0.1405
Extinction coefficient	0.171(18)	0.0017(3)	0.00029(11)	0.0043(10)
Largest diff. peak and hole	176 and –149 e nm^{-3}	168 and –200 e nm^{-3}	191 and –301 e nm^{-3}	6779 and –1654 e nm^{-3}

the mixture and the reaction was stirred overnight at room temperature followed by irradiation at 0 °C with a 150 W high pressure mercury lamp for the period of 3 h. Chromatography on alumina with diethyl ether/*n*-hexane (v/v, 1:1) and methanol as eluents afforded air-stable, yellow **13** (253 mg, 0.422 mmol, 25%). M.p. 169 °C. MS (FAB): m/z = 600.9 $[M]^+$. IR (KBr): $\tilde{\nu}$ = 3206 cm^{-1} (w), 3057(w), 1990(vs), 1865 (vs), 1854 (vs), 1819 (vs), 1576 (m), 1466 (m), 1440 (s), 1390 (m), 1360 (s), 1287 (m), 1216 (s), 1125 (m), 1077 (m), 990 (m), 719 (s), 704 (s), 694 (s), 683 (s). ^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ = 1.80 (s, 6 H, CH_3), 3.84 (s, 3 H, CH_3), 6.69–7.19 (m, 10 H, C_6H_5), 7.54 (d, ^3J = 1.6 Hz, 1 H, $C_3H_2N_2$), 7.67 (d, ^3J = 1.6 Hz, 1 H, $C_3H_2N_2$) ppm. ^{13}C NMR [75.432 MHz, $(CD_3)_2SO$]: δ = 27.6 and 64.4 [$C(CH_3)_2$], 119.6, 121.2, 122.7, 124.3, 127.1, 127.4, 127.7, 128.1, 136.1, and 155.5 (C_6H_5, $C_3H_2N_2$), 184.2 (C=N), 192.4 ($^1J_{C,W}$ = 95 Hz, carbene C), 205.3 [$^1J_{C,W}$ = 129 Hz, $W(CO)_{axial}$], 210.1 [$^1J_{C,W}$ = 146 Hz, $W(CO)_{equatorial}$], 218.2 [$^1J_{C,W}$ = 169 Hz, $W(CO)_{equatorial}$] ppm. ^{183}W NMR [12.483 MHz, $(CD_3)_2SO$, vs. saturated aqueous Na_2WO_4]: δ = –2569 [$W(CO)_4$] ppm. $C_{24}H_{21}N_3O_4W$ (599.28): calcd. C 48.10, H 3.53, N 7.01; found C 47.97, H 3.52, N 6.97.

Crystallography: Crystallographic data for **8**, **12a**, **12b**, and **13** are given in Table 2. The data collection was performed on a Nonius Kappa-CCD equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and a nominal crystal-to-area-detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK.[14] Several scans in φ and ω direction were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces an empirical absorption correction. The structures were solved by direct methods (SHELXS-86) and refined against F^2 (SHELX-97).[15] Hydrogen atoms at carbon atoms were added geometrically and refined using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

The structure determination of **13** was complicated by two crystallographic characteristics. First, several crystals were examined and showed systematic twinning. The best crystal was measured and the 20 worst overlying reflections were omitted in the refinement. Second, the correct determination of the space group because of a possible transformation to bravais lattice higher in symmetry. In the triclinic space group were two identical molecules, which can be transferred into each other by refinement in the monoclinic space group *C*2/*c*. Nevertheless, the space group *C*2/*c* was excluded because the R_{int} value of 0.176 for 8154 symmetry-equivalent reflections is much higher than the R_{int} value of 0.038 for 4919 reflections in the triclinic space group. In addition, the conventional R_1 value of 0.0750 is also higher (0.0542). The unit cell constants of the transformed C-centered lattice are 3958.4, 856.6, 136.39 pm and 90.04, 97.48, 91.42°. The deviation of the angle γ from over 1° to the correct 90° angle is also too high for this monoclinic space group.

CCDC-252740 (for **8**), -252741 (for **12a**), -252742 (for **12b**), and -252743 (for **13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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