■ Chromium(VI) NHC Complexes

Chromium(VI) Bisimido Dichloro, Bisimido Alkylidene, and Chromium(V) Bisimido Iodo *N*-Heterocyclic Carbene Complexes

Pradeep K. R. Panyam,[a] Laura Stöhr,[a] Dongren Wang,[a] Wolfgang Frey,[b] and Michael R. Buchmeiser*[a,c]

Abstract: Reaction of $CrCl_2(N\text{-}t\text{Bu})_2$ with 1,3-dimethylimidazol-2-ylidene (IMe), 1,3-dimethyl-4,5-dichloroimidazol-2-ylidene (IMeCl₂), 1,3-di(2-propyl)imidazol-2-ylidene (IPr), 1,3-dimesitylimidazol-2-ylidene (IMes) and 1,3-bis(2,6-(2-Pr)₂C₆H₃)imidazol-2-ylidene (IDipp) yields the corresponding *N*-heterocyclic carbene (NHC) adducts $CrCl_2(\text{IMe})(N\text{-}t\text{Bu})_2$ (**1**), $CrCl_2(\text{IMeCl}_2)(N\text{-}t\text{Bu})_2$ (**2**), $CrCl_2(\text{IPr})(N\text{-}t\text{Bu})_2$ (**3**), $CrCl_2(\text{IMes})(N\text{-}t\text{Bu})_2$ (**4**) and $CrCl_2(\text{IDipp})(N\text{-}t\text{Bu})_2$ (**5**). Likewise, reaction of $CrCl_2(N\text{-}2,6\text{-}(2\text{-}Pr)_2C_6H_3)_2$ and $CrCl_2(N\text{-adamantyl})_2$ with IMes yields $CrCl_2(N\text{-}2,6\text{-}(2\text{-}Pr)_2C_6H_3)_2(\text{IMes})$ (**6**) and $CrCl_2(N\text{-adamantyl})_2(\text{IMes})$ (**7**), respectively. Reaction of $CrCl_2(N\text{-}t\text{Bu})_2$ with the bidentate NHCs 1-*R*-3-(1-(2-LiO-C₆H₄))imidazol-2-ylidene yields the corresponding pentacoordinated Cr(VI) complexes $CrCl_2(1\text{-}R\text{-}3\text{-}(1\text{-}(2\text{-}O\text{-}C_6H_4))\text{imidazol-2-ylidene})_2C_6H_3)_2(\text{IMes})$ (R = 2,4,6-(CH₃)₃C₆H₂, **8**), (R = *t*Bu, **9**), (R = 2-phenyl-C₆H₄, **10**). Reaction of the chromium(VI) complex $Cr(N\text{-}2,6\text{-}(2\text{-}Pr)_2C_6H_3)_2(CH_2C(CH_3)_3)_2$ with 1,3-dimethylimidazol-2-ylidene·AgI yields the bimetallic silver adduct of the chromium alkylidene complex (**11**) along with the tetrahedral chromium(V) complex $CrI(N\text{-}2,6\text{-}(2\text{-}Pr)_2C_6H_3)_2(1,3\text{-}dimethylimidazol-2-ylidene})$ (**12**). Compounds **1–4**, **7**, **9–12** were characterized by single-crystal X-ray analysis. Finally, the chromium(VI) bisimido-amido complexes **13–14** bearing the *N*-6-(2-(diethylboryl)phenyl)pyridyl-2-yl-motif are reported.

Introduction

In view of the pivotal role of chromium in catalysis including the worldwide production of polyolefins[1] or in the tri- or tetramerization of ethylene,[1d,2] we devoted our studies to the exploration of chromium(VI) *N*-heterocyclic carbene (NHC) complexes. Notably, incorporation of NHCs as ligands into high oxidation state 3d-metal species proved fruitful, as illustrated by the diverse complexes encompassing 3d metals in higher oxidation states such as V^V, Cr^III, Cr^V, Mn^V, or Fe^V featuring different ancillary ligands including oxo-, imido-, chloro- or nitridemoieties.[3] In continuation of our efforts towards the synthesis of group VI metal alkylidene NHC complexes,[4] we thrived towards the synthesis of chromium(VI) NHC alkylidene complexes. Indeed, chromium has been widely used both in coordination and organometallic chemistry for decades. Similarly, NHCs alongside alkylidenes have also been used for about half a century and turned out to be particularly useful in the case of V, Mo, W, and Ru.[4d,5] However, to the best of our knowledge, till date chromium(VI) NHC complexes have not been reported, which is probably a result of the reducing power of the NHC and also weaker carbon metal bond in the high oxidation metal species. Though chromium is cut below molybdenum and tungsten in terms of the metal-carbene bond strength[6] and ease of synthesis, the synthesis of chromium bisimido dichloro NHC complexes was worth to be investigated.

Here, we report the synthesis and structural characterization of the first examples of chromium(VI) complexes with both monodentate and bidentate NHCs alongside with chromium(VI) alkylidene complexes and chromium(VI) bisimido-amido complexes, bearing the 6-(2-(diethylboryl)phenyl)pyridyl-2-yl- motif.

Results and Discussion

Monodentate Chromium(VI) NHC Complexes

Several novel Cr(VI) NHC complexes (**1–7**) bearing monodentate NHCs based on the chromium bisimido dichloro complexes[7] were synthesized as outlined in Scheme 1. Treatment of a precooled (–34 °C) solution of the precursor in toluene with one equivalent of NHC, either in form of the free carbene or the NHC silver(I) iodide adduct, resulted in the formation of the chromium(VI) NHC complexes **1–7**. All complexes were isolated as red-colored solids but decomposed upon standing in the solid state to brown solids at room temperature. However, they are stable at –34 °C both as solids and even in solution. The ¹H

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European Journal of Inorganic Chemistry

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doi.org/10.1002/ejic.202000550

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NMR spectra of the synthesized complexes showed the protons corresponding to imidazol-2-ylidene confirming the formation of the NHC adduct. The ^{13}C NMR spectra display a characteristic carbene resonance in the range of $183 < \delta < 192$ ppm, confirming the formation of the Cr–carbene bond. We were not able to carry out a full assignment of the ^1H-NMR spectra of the brown solids owing to the mixture of different compounds but we could predict the reduction of one imido to an amido group by the presence of two signals corresponding to an N-tBu and NH-tBu moiety, respectivley. However, our efforts to recrystallize the brown solids were not fruitful and hence any solid conclusion about the molecular structure of the decomposed product (brown solids) could not be established at this point of time.
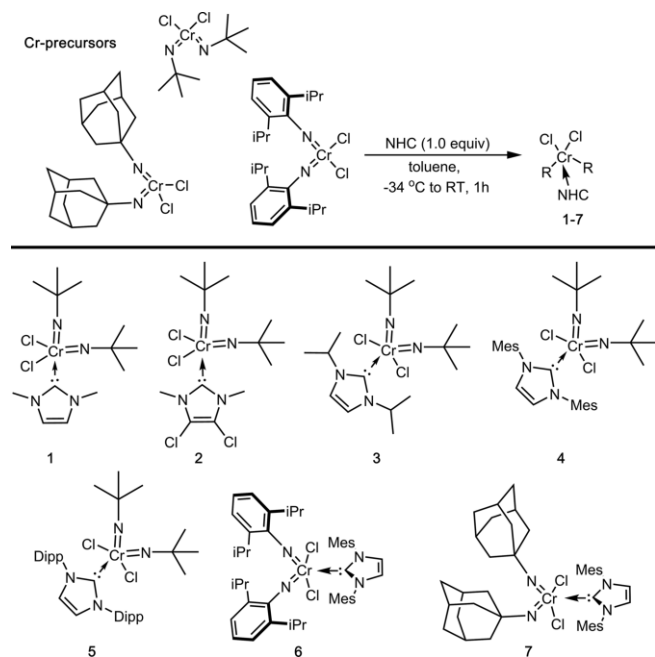
Scheme 1. Synthesis of monodentate chromium(VI) NHC complexes.

The molecular structures of the chromium complexes **1–7** were established by single-crystal X-ray analysis, which also allowed identifying structural similarities. Unlike complexes **1** and **2**, the chromium complexes **3**, **4** and **7** have both chloride ligands *trans* to each another, attributable to the steric influence of the bulky IMes ligand compared to that of its methyl counterpart. The Cr–C bond length slightly increases with increasing size of the NHC from **Cr-1** to **Cr-7**. Crystal suitable for single-crystal X-ray analysis were grown from a mixture of CH_2Cl_2 and pentane at −34 °C.

Complex **1** (Figure 1) crystallizes in the monoclinic space group $C2/c$ with a = 2379.7(8) pm, b = 970.1(3) pm, c = 2144.1(7) pm, $\alpha = \gamma = 90°$, $\beta = 95.586(2)°$ ($Z = 8$). Complex **1** adopts a distorted square pyramidal geometry ($\tau_5 = 0.44$) around the metal center with the chloride ligands *cis* to each other, attributable to the small IMe-ligand occupying the apex position (Figure 1).

Complex **2** (Figure 2) crystallizes in the monoclinic space group $P2_1/n$ with a = 898.7(5) pm, b = 1151.6(6) pm, c = 2481.9(12) pm, $\alpha = \gamma = 90°$, $\beta = 100.013(2)°$ ($Z = 4$). As in complex **1**, the two chloride ligands are also arranged *cis* to each
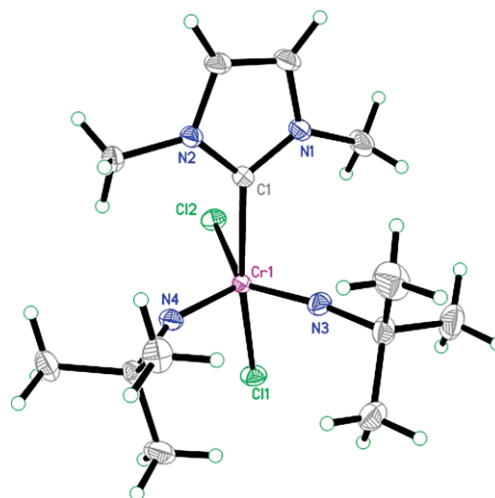

Figure 1. Single crystal X-ray structure of **1**. Relevant bond lengths [pm] and bond angles [°]: Cr1–C1 208.9, Cr1–Cl1 236.7, Cr1–Cl2 237.6, Cr1–N3 163.2, Cr1–N4 164.4; Cl1–Cr1–Cl2 83.81(2), Cl1–Cr1–C1 160.44(4), Cl1–Cr1–N3 92.66(5), Cl1–Cr1–N4 96.09(5), Cl2–Cr1–C1 79.73(4), Cl2–Cr1–N3 133.67(5), Cl2–Cr1–N4 115.84(5), C1–Cr1–N3 91.13(6), C1–Cr1–N4 100.53(6), N3–Cr1–N4 110.47(6). Thermal ellipsoids are set at a 50 % probability level.

other due to the low steric demand of the IMeCl₂-ligand. The geometry at the metal center is distorted square pyramidal ($\tau_5 = 0.405$) with the NHC occupying the apex position. Complex **3** (Figure 3) crystallizes in the monoclinic space group $P2_1/c$ with a = 1481.14(7) pm, b = 1117.8(7) pm, c = 1392.6(6) pm, $\alpha = \gamma = 90°$, $\beta = 96.180(4)°$ ($Z = 4$). The geometry at the metal center is also distorted trigonal bipyramidal ($\tau_5 = 0.52$) with the NHC occupying the apex position.
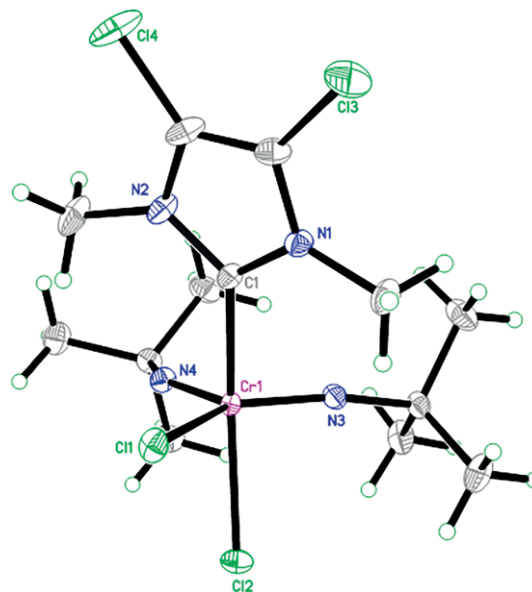
Figure 2. Single crystal X-ray structure of **2**. Relevant bond lengths [pm] and bond angles [°]: Cr1–Cl1 236.6, Cr1–Cl2 234.6, Cr1–C1 208.3, Cr1–N3 163.3, Cr1–N4 164.6; Cl1–Cr1–Cl2 85.04(2), Cl1–Cr1–C1 76.91(3), Cl1–Cr1–N3 134.47(4), Cl1–Cr1–N4 115.04(4), Cl2–Cr1–C1 158.80(4), Cl2–Cr1–N3 89.05(4), Cl2–Cr1–N4 97.92(4), C1–Cr1–N3 95.66(5), C1–Cr1–N4 99.73(5), N3–Cr1–N4 110.49(5). Thermal ellipsoids are set at a 50 % probability level.

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doi.org/10.1002/ejic.202000550

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Figure 3. Single crystal X-ray structure of **3**. Relevant bond lengths [pm] and bond angles [°]: Cr1–C1 211.3, Cr1–Cl1 235.2, Cr1–Cl2 234.5, Cr1–N3 163.3, Cr1–N4 163.4; Cl1–Cr1–Cl2 161.29(4), Cl1–Cr1–C1 81.5(1), Cl1–Cr1–N3 92.1(1), Cl1–Cr1–N4 97.8(1), Cl2–Cr1–C1 80.7(1), Cl2–Cr1–N3 95.0(1), Cl2–Cr1–N4 95.4(1), C1–Cr1–N3 129.9(1), C1–Cr1–N4 117.3(1), N3–Cr1–N4 112.8(2). Thermal ellipsoids are set at a 50 % probability level.

Figure 5. Single crystal X-ray structure of **7**. Relevant bond lengths [pm] and bond angles [°]: Cr1–C1 213.9, Cr1–Cl1 234.5, Cr1–Cl2 233.8, Cr1–N3 163.0, Cr1–N4 164.0; Cl1–Cr1–Cl2 167.1(1), Cl1–Cr1–C1 83.8(2), Cl1–Cr1–N3 95.7(3), Cl1–Cr1–N4 92.9(3), Cl2–Cr1–C1 83.4(2), Cl2–Cr1–N3 91.8(3), Cl2–Cr1–N4 93.0(3), C1–Cr1–N3 120.0(4), C1–Cr1–N4 123.3(4), N3–Cr1–N4 116.7(5). Thermal ellipsoids are set at a 50 % probability level.

Complex **4** (Figure 4) crystallizes in the monoclinic space group $P2_1/c$ with $a = 807.8(7)$ pm, $b = 2231.1(14)$ pm, $c = 1733.2(11)$ pm, $\alpha = \gamma = 90°$, $\beta = 100.752(2)°$ ($Z = 4$). The geometry at the metal center is also distorted trigonal bipyramidal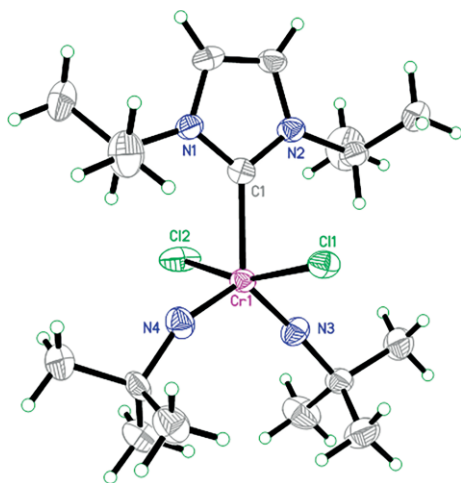 ($\tau_5 = 0.68$) with the NHC occupying the apex position. Complex **7** (Figure 5) crystallized from a saturated solution in CH_2Cl_2 and pentane. It decomposes quickly and the measured data contains two independent Cr complexes in the asymmetric unit with one strongly disordered adamantane moiety. **7** crystallizes in the monoclinic space group $P2_1/c$ with $a = 1001.42(9)$ pm, $b = 2482.6(3)$ pm, $c = 3264.6(3)$ pm, $\alpha = \gamma = 90°$, $\beta = 91.725(7)°$ ($Z = 8$). The geometry at the metal center is distorted trigonal bipyramidal ($\tau_5 = 0.73$) with the NHC occupying the apex position.

Bidentate O-Chelating Chromium NHC Complexes

In addition to the chromium(VI) NHC complexes with monodentate ligands, we were also interested in the synthesis of complexes with bidentate carbene ligands. We envisioned the chelating effect of the bidentate O-chelating NHC to enhance the stability of the complexes as reported for this class of ligands.[8] Bidentate NHCs with non-chelating N-substituents, i.e. N-tert-butyl, N-2,4,6-trimethylphenyl, and N-2-phenylphenyl) were synthesized according to reported methods.[4b] As depicted in Scheme 2, the imidazolinium salts were deprotonated by employing LiHMDS in toluene for one hour and then added to the chromium precursor $CrCl_2(N\text{-}tBu)_2$ at –34 °C followed by stirring at room temperature for one hour. The corresponding complexes were isolated as red colored solids in 54–71 % yield.
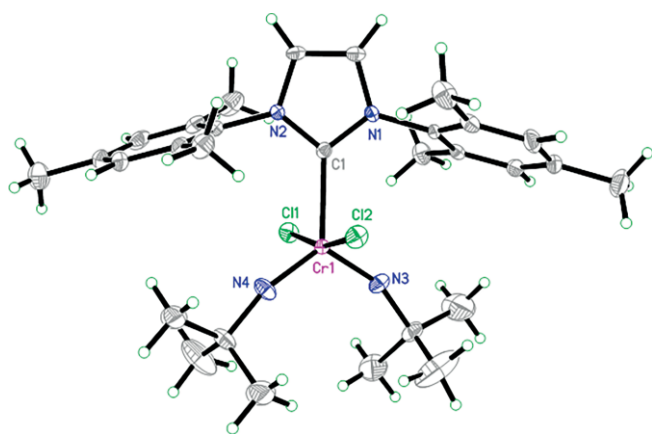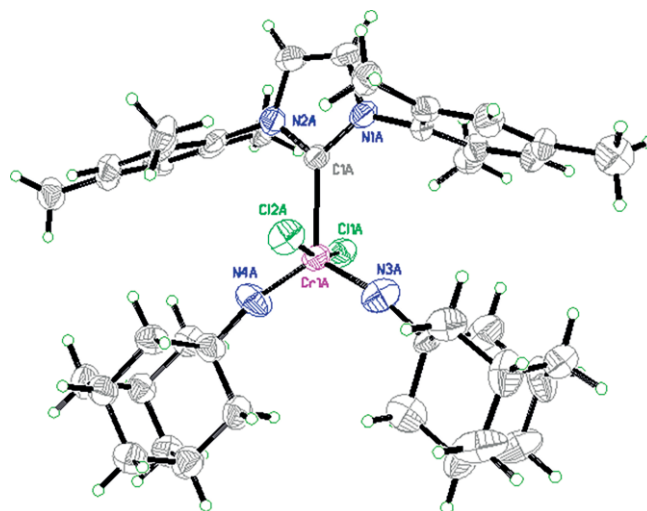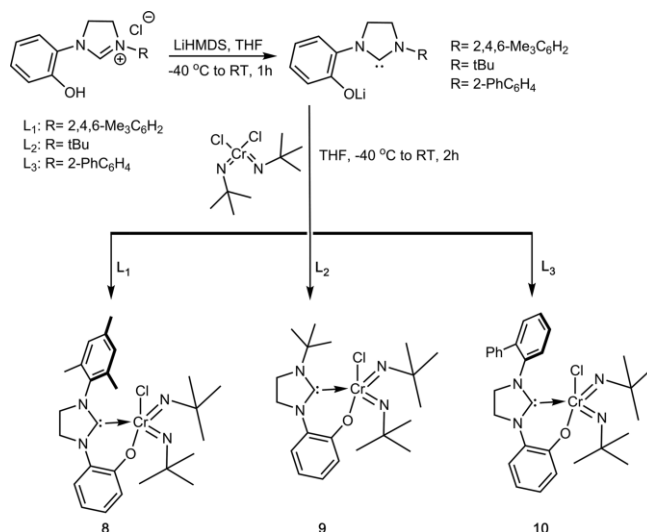

Figure 4. Single crystal X-ray structure of **4**. Relevant bond lengths [pm] and bond angles [°]: Cr1–C1 216.1, Cr1–Cl1 233.4, Cr1–Cl2 233.1, Cr1–N3 163.1, Cr1–N4 163.2; Cl1–Cr1–Cl2 166.46(3), Cl1–Cr1–C1 83.69(6), Cl1–Cr1–N3 92.60(8), Cl1–Cr1–N4 93.82(8), Cl2–Cr1–C1 82.90(6), Cl2–Cr1–N3 95.79(8), Cl2–Cr1–N4 92.46(8), C1–Cr1–N3 120.3(1), C1–Cr1–N4 125.7(1), N3–Cr1–N4 114.0(1). Thermal ellipsoids are set at a 50 % probability level.

Scheme 2. Synthesis of bidentate O-chelating chromium NHC complexes.

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Complexes **8–10** showed resonances for the carbene in the ^{13}C NMR spectra between $190 < \delta < 200$ ppm, confirming the formation of the corresponding Cr-carbene bonds. Generally, the resonances of the Cr-carbene with bidentate NHCs were slightly downfield shifted compared to those of the monodentate NHCs.

Single crystals of **9** and **10** suitable for X-ray diffraction studies were obtained by layering pentane over saturated CH_2Cl_2 solution of the complex. Complex **9** (Figure 6) crystallizes in the orthorhombic space group $P2_1$ with $a = 1049.54(5)$ pm, $b = 1667.47(6)$ pm, $c = 1695.78(8)$ pm, $\alpha = \beta = \gamma = 90°$ ($Z = 4$). The geometry at the metal center is distorted square pyramidal ($\tau_5 = 0.11$) with the NHC occupying the apex position.

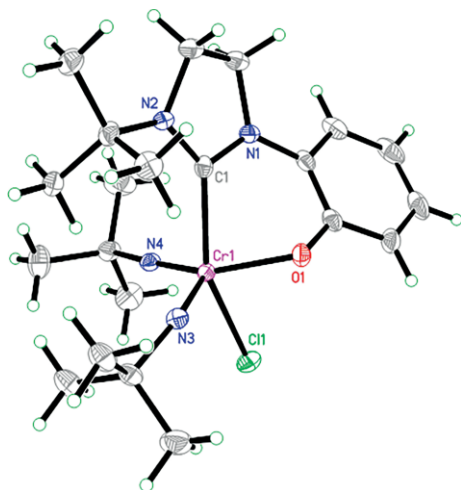Figure 7. Single crystal X-ray structure of **10**. Relevant bond lengths [pm] and bond angles [°]: Cr1–N3 163.6, Cr1–N4 165.4, Cr1–Cl1 236.0, Cr1–O1 195.2, Cr1–C1 207.0; N3–Cr1–N4 111.77(6), N3–Cr1–Cl1 90.92(4), N3–Cr1–O1 136.70(5), N3–Cr1–C1 87.29(6), N4–Cr1–Cl1 99.47(4), N4–Cr1–O1 111.51(5), N4–Cr1–C1 106.68(6), Cl1–Cr1–O1 83.48(3), Cl1–Cr1–C1 152.49(4), O1–Cr1–C1 79.18(5). Thermal ellipsoids are set at a 50 % probability level.

under the same reaction conditions, we could not obtain the expected products, even in trace quantities, employing other NHCs including IMeCl$_2$, IMes or IMesH$_2$. Complexes **11** and **12** are extremely sensitive, both in solution and in the solid state, even under high vacuum. However, a freshly prepared sample of complex **11** was characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of **11** shows a downfield shifted proton at $\delta = 13.5$ ppm ($J = 127.9$ Hz) corresponding to the Cr-alkylidene proton. Notably, the alkylidene proton is significantly upfield shifted compared to the corresponding Cr-THF (15 ppm)[10] and

Figure 6. Single crystal X-ray structure of **9**. Relevant bond lengths [pm] and bond angles [°]: Cr1–N3 164.9, Cr1–N4 163.7, Cr1–Cl1 238.0, Cr1–O1 193.7, Cr1–C1 210.6; N3–Cr1–N4 112.3(1), N3–Cr1–Cl1 96.61(8), N3–Cr1–O1 104.6(1), N3–Cr1–C1 111.8(1), N4–Cr1–Cl1 89.73(8), N4–Cr1–O1 143.0(1), N4–Cr1–C1 89.2(1), Cl1–Cr1–O1 83.70(6), Cl1–Cr1–C1 149.64(8), O1–Cr1–C1 79.1(1). Thermal ellipsoids are set at a 50 % probability level.

Likewise, complex **10** (Figure 7) crystallizes in the monoclinic space group $P2_1/c$ with $a = 1293.69(5)$ pm, $b = 1291.46(5)$ pm, $c = 1853.01(7)$ pm, $\alpha = \gamma = 90°$, $\beta = 95.19(2)°$ ($Z = 4$). The geometry at the metal center is distorted square pyramidal ($\tau_5 = 0.26$) with the NHC occupying the apex position.

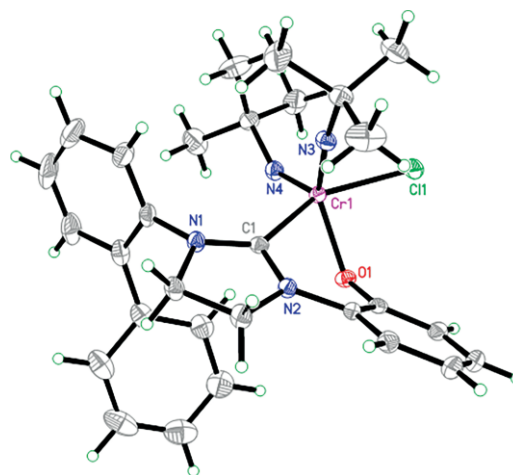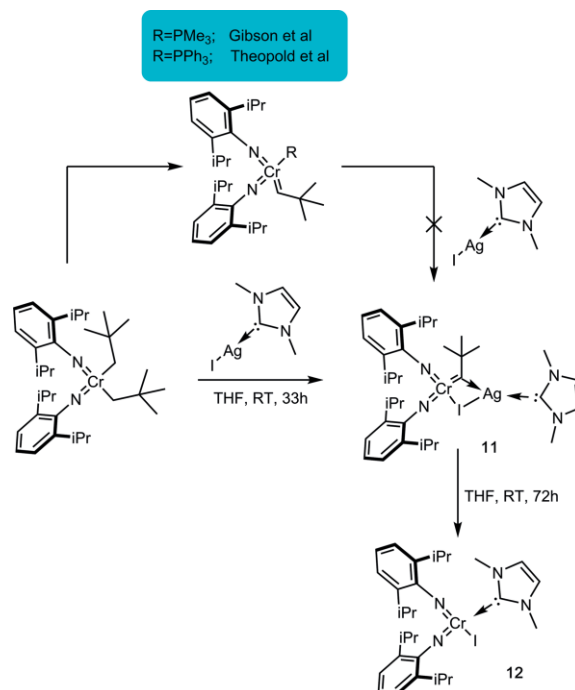## Chromium Alkylidene Complexes

Recently, Theopold and co-workers[6,9] reported on the successful preparation of chromium(VI) alkylidene complexes stabilized by PPh$_3$; results were in line with those reported by Gibson et al.[10]

In view of the most favorable properties of Mo and W imido/oxo alkylidene NHC complexes,[4d,11] we attempted the synthesis of chromium(VI) alkylidene complexes stabilized by NHC ligands (Scheme 3). Interestingly, reaction of the precursor Cr(N-2,6-(2-Pr)$_2$-C$_6$H$_3$)$_2$(CH$_2$C(CH$_3$)$_3$)$_2$[7a,10] with the silver(I) iodide adduct of IMe unexpectedly yielded the bimetallic adduct **11**, which upon prolonged stirring at room temperatures decomposed to yield the tetrahedral chromium(V) complex CrI(N-2,6-(2-Pr)$_2$-C$_6$H$_3$)$_2$(1,3-dimethylimidazol-2-ylidene) (**12**). By contrast,

Scheme 3. Synthesis of chromium(V) bisimido iodo NHC and chromium(VI) bisimido alkylidene NHC complexes.

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Cr-PPh$_3$ (14.5 ppm)[6] complexes. We also performed single-crystal X-ray analysis on both complexes, which unambiguously confirmed their molecular structure. Single crystals of **11** and **12** suitable for single-crystal X-ray analysis were obtained by layering an almost saturated solution of CH$_2$Cl$_2$ with *n*-pentane followed by storage at –40 °C for a week. Complex **11** crystallizes in the monoclinic space group *C*2/*c* with *a* = 3037.53(17) pm, *b* = 1199.04(6) pm, *c* = 2331.63(11) pm, $\alpha = \gamma = 90°$, $\beta = 99.003(3)°$ (*Z* = 8). The geometry at the chromium metal center is distorted tetrahedral (τ_4 = 0.906) with a slightly larger N^3–Cr^1–N^4 angle of 117.5(2)° compared to the metal precursor Cr(*N*-2,6-(2-Pr)$_2$-C$_6$H$_3$)$_2$(CH$_2$C(CH$_3$)$_3$)$_2$ (111.71(8)°). From Figure 8 it is evident that only one neopentyl ligand is attached to chromium and the Cr–C$_6$ bond length is 190.5 pm, which is considerably shorter than the single bond lengths in the precursor Cr(*N*-2,6-(2-Pr)$_2$-C$_6$H$_3$)$_2$(CH$_2$C(CH$_3$)$_3$)$_2$[10] (203.0(2) and 204.2(2) pm) but similar to that of the earlier reported Cr-alkylidene-PPh$_3$ complexes (184.8(5) pm).[6]

Figure 9. Single crystal X-ray structure of 12. Relevant bond lengths [pm] and bond angles [°]: Cr1–I1 260.62, Cr1–C1 205.5, Cr1–N3 166.2, Cr1–N4 166.6; I1–Cr1–C1 102.69(7), I1–Cr1–N3 108.87(7), I1–Cr1–N4 111.59(7), C1–Cr1–N3 107.1(1), C1–Cr1–N4 105.9(1), N3–Cr1–N4 119.2(1). Thermal ellipsoids are set at a 50 % probability level.
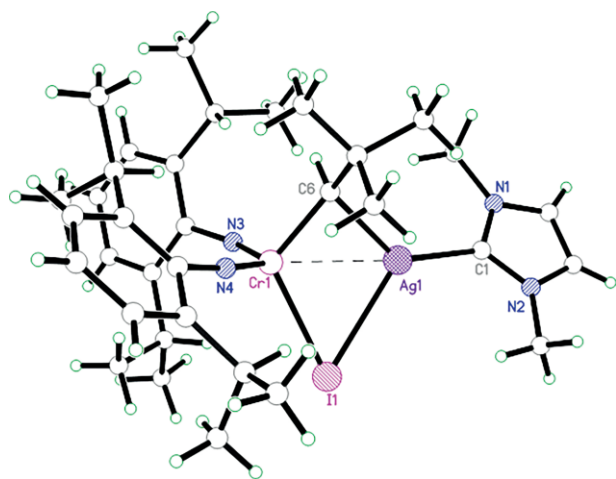

Figure 8. Single crystal X-ray structure of **11**. Relevant bond lengths [pm] and bond angles [°]: Cr1–I1 266.0, Cr1–C6 190.5, Cr1–N3 165.2, Cr1–N4 164.5, Ag1–I1 286.4, Ag1–C6 225.3, Ag1–C1 212.0; N3–Cr1–N4 117.5(2), N3–Cr1–C6 103.5(3), N3–Cr1–I1 109.9(2), N4–Cr1–C6 105.4(3), N4–Cr1–I1 106.4(2), I1–Cr1–C6 114.4(2), Cr1–C6–Ag1 43.2(2), Cr1–I1–Ag1 56.38(2), C6–Ag1–C1 135.3(2), I1–Ag1–C1 127.6(2). Thermal ellipsoids are set at a 50 % probability level.

Likewise, complex **12** (Figure 9) crystallizes in the monoclinic space group *P*2$_1$/*n* with *a* = 1133.50(5) pm, *b* = 1623.64(7) pm, *c* = 1707.94(7) pm, $\alpha = \gamma = 90°$, $\beta = 103.616(2)°$ (*Z* = 4). The geometry at the metal center is also distorted tetrahedral (τ_4 = 0.913).

Chromium(VI) Bisimido-Amido-Complexes Bearing the 6-(2-(Diethylboryl)phenyl)pyridyl-2-yl-Motif

We also synthesized Cr^{VI} bisimido-amido complexes containing the 6-(2-(diethylboryl)phenyl)pyridyl-2-yl-group. Indeed, group 4 metal complexes containing the (6(–2-(diethylboryl)phenyl)pyrid-2-yl-amido motif have been demonstrated to be useful pre-catalysts, which upon activation with methylalumoxane (MAO) form highly active catalysts for the homopolymerization of ethylene and styrene,[12] and the copolymerization of ethylene with norborn-2-ene and which, in selected cases, allow for
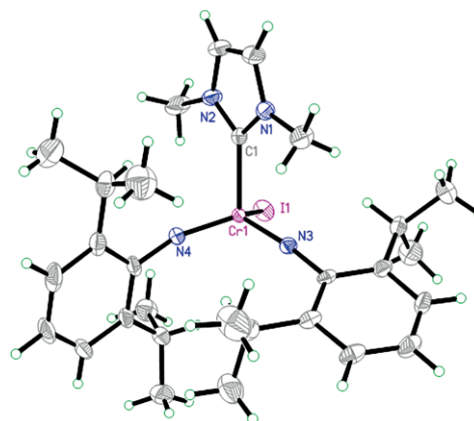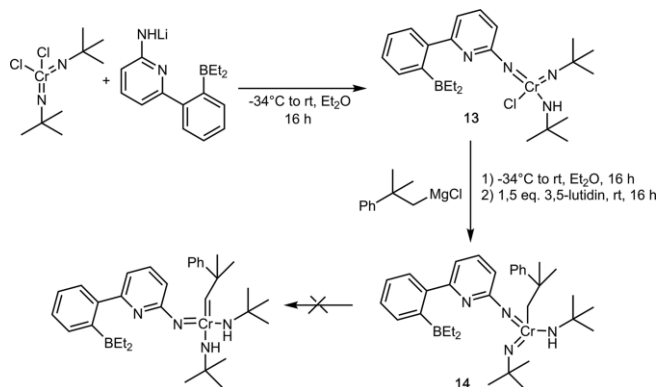
the formation of poly(ethylene)-*co*-poly(norborn-2-ene) with both vinyl insertion and ring opening metathesis polymerization (ROMP) derived structures within the same polymer chain.[12,13] Such polymers can, at least in principle, be further used for the synthesis of functional polyolefins.[14] This (reversible) switch between VIP and ROMP is induced by an α-H$^+$ elimination triggered by the 2-pyridylamido group and is controlled by the dialkylboryl group and concurring aminoborane formation.[13a,13d,15] In view of these most favorable properties, we were interested in the question, whether the corresponding chromium imido and amido complexes would be accessible, too.

Chromium *N*-6(–2-(diethylboryl)phenyl)pyrid-2-yl-imido-*N'*-*tert*-butylimido-*N''*-*tert*-butylamido chloride (**3**) was prepared in 83 % isolated yield via reaction of bis(*N*-*tert*-butylimido) chromium(VI) dichloride (**1**) with 6-(–2-(diethylboryl)phenyl)pyridine-2-amine (**2**, Scheme 4). Subsequent reaction with neophylmagnesium chloride yielded *N*-6-(2-(diethylboryl)phenyl)pyrid-2-yl-imido-*N'*-*tert*-butylimido-*N'*-*tert*-butylamido neophyl chromium (**4**) in 63 % isolated yield. However, all attempts to prepare the corresponding chromium(VI) imido bisamido alkylidene complexes failed.

Scheme 4. Synthesis of chromium(VI) bisimido-amido complexes.

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doi.org/10.1002/ejic.202000550

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Conclusion

We have demonstrated the synthesis of the first examples of high-oxidation state chromium(VI) NHC complexes bearing both mono- and bidentate NHCs in substantial variability in both the imido and NHC ligands. Our efforts towards the synthesis of chromium(VI)-alkylidene NHC complexes were not successful so far as the reaction yields the chromium-silver alkylidene adduct, which further transform to a chromium(V) bisimido iodo NHC complex. In addition, we succeeded in synthesizing chromium(VI) complexes bearing two different imido ligands ((6(–2-(diethylboryl)phenyl)pyrid-2-yl-amido and *tert*-butyl imido) that were so far inaccessible. However, the subsequent α-hydrogen elimination from those complexes to yield the alkylidene complexes did not occur. Further studies on the synthesis of chromium(VI) alkylidene NHC complexes are still underway in our laboratories.

Experimental Section

General

Unless otherwise noted, all reactions were performed under the exclusion of air and moisture by standard Schlenk techniques. Reactions involving metal complexes were performed in a nitrogen-filled glove box (MBraun Labmaster 130). Glassware was stored at 120 °C overnight and cooled in an evacuated antechamber. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 spectrometer at 400 and 100 MHz, respectively. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from residual solvent protons (CDCl$_3$: 7.26 ppm, CD$_2$Cl$_2$ 5.32 ppm) as reference. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, br = broad, m = multiplet), coupling constants (Hz) and integration. High-resolution mass spectra were recorded at the Institute of Organic Chemistry, University of Stuttgart, Germany. CH$_2$Cl$_2$, diethyl ether, toluene and pentane were dried by using an MBraun SPS-800 solvent purification system with alumina drying columns and stored over 4 Å Linde type molecular sieves. THF, benzene and DME were distilled from Na prior to use and stored over 4 Å Linde type molecular sieves and Selexsorb®. Deuterated solvents were filtered through activated alumina and stored over 4 Å Linde type molecular sieves inside the glove box. 1,3-Dimesitylimidazolium tetrafluoroborate,[16] 1,3-diisopropylimidazolium chloride,[17] 1-mesityl-3-(2-hydroxyphenyl)-4,5-dihydroimidazolium tetrafluoroborate,[18] 1-(*tert*-butyl)-3-(2-hydroxyphenyl)-4,5-dihydroimidazolium tetrafluoroborate,[4b] 1-([1,1'-biphenyl-2-yl])-3-(2-hydroxyphenyl)-4,5-dihydroimidazolium chloride,[4b] the silver iodide adduct of 1,3-dimethylimidazol-2-ylidene,[19] 1,3-dimesitylimidazol-2-ylidene,[20] 1,3-diisopropylimidazol-2-ylidene[17] were synthesized according to published procedures. 1,3-Diisopropylimidazolium chloride was additionally washed with boiling acetone, dried by azeotropic distillation with toluene and then dried in vacuo overnight before being transferred into the glove box. The chromium precursors (*N-t*Bu)$_2$CrCl$_2$),[21] Cr(*N*-2,6-diisopropylphenyl)$_2$Cl$_2$,[7a,7d] Cr(*N*Ad)$_2$Cl$_2$[7c] Cr(*N*-2,6-diisopropylphenyl)$_2$(CH$_2$CMe$_3$)$_2$[10] were synthesized using a slightly modified literature procedure.

Deposition Numbers 1996759 (for **1**), 1991460 (for **2**), 1996758 (for **3**), 1996756 (for **4**), 1996757 (for **7**), 2007984 (for **9**), 1996760 (for **10**), 2007983 (for **11**), and 1996761 (for **12**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

CrCl$_2$(IMe)(*N-t*Bu)$_2$ (1): (*N-t*Bu)$_2$CrCl$_2$ (50 mg, 0.189 mmol, 1.0 equiv.) was dissolved in 3 mL of toluene. The dark red solution was cooled to –34 °C, then AgI•1,3-dimethylimidazol-2-ylidene (63 mg, 0.189 mmol, 1.0 equiv.) was added. The resulting reaction mixture was warmed to room temperature, stirred for 2 h and then filtered through Celite. The filtrate was evaporated to dryness under reduced pressure and the residue was washed with pentane (2 × 5 mL) and diethyl ether (1 × 5 mL). A red solid was obtained, which was dried in vacuo. Yield: 37 mg (54 %); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.00 (m, 1H, NHC backbone), 6.87 (s, 1H, NHC backbone), 3.95 (s, 3H, NCH$_3$), 3.89 (s, 3H, NCH$_3$), 1.60 (s, 18H, 2N-*t*Bu). ^{13}C NMR (101 MHz, CD$_2$Cl$_2$) δ = 183.60 (NCN-NHC), 123.13,122.93 (CH=CH-NHC), 79.94 (NCMe$_3$), 30.60 (N*Me*), 29.67 (C*Me*$_3$). Elemental analysis calcd. for C$_{13}$H$_{26}$Cl$_2$CrN$_4$: C 43.22, H 7.25, N 15.51. Found: C 42.82, H 7.39, N 15.12. Orange crystals suitable for X-ray analysis were obtained by layering a saturated solution of complex **1** in CH$_2$Cl$_2$ with diethyl ether and storage at –34 °C for few days.

CrCl$_2$(IMeCl$_2$)(*N-t*Bu)$_2$ (2): (*N-t*Bu)$_2$CrCl$_2$ (50 mg, 0.189 mmol, 1.0 equiv.) was dissolved in 3 mL of toluene. The dark red solution was cooled to –34 °C; then, AgI•4,5-dichloro-1,3-dimethylimidazol-2-ylidene (75.5 mg, 0.189 mmol, 1.0 equiv.) was added. The reaction mixture was warmed to room temperature, stirred for 2 h; then, filtered through Celite. The filtrate was concentrated under reduced pressure and the residue was washed with pentane (2 × 5 mL) and diethyl ether (1 × 5 mL) yielding a red solid, which was dried in vacuo. Yield: 48 mg (59 %); ^{1}H NMR (400 MHz, C$_6$D$_6$) δ = 3.56 (s, 6H, 2N*Me*$_2$), 1.52 (s, 18H, 2N^t*Bu*); ^{13}C NMR (101 MHz, C$_6$D$_6$) δ = 191.98 (NCN-NHC), 116.16 (CH=CH-NHC), 79.10 (NCMe$_3$), 36.22 (N*Me*), 29.57 (C*Me*$_3$). Elemental analysis calcd. for C$_{13}$H$_{24}$Cl$_4$CrN$_4$: C 36.30, H 5.62, N 13.02. Found: C 36.28, H 5.65, N 12.93. Dark red colored crystals were obtained from a mixture of CH$_2$Cl$_2$ and pentane at –34 °C for few days.

CrCl$_2$(IPr)(*N-t*Bu)$_2$ (3): (*Nt*Bu)$_2$CrCl$_2$ (50 mg, 0.189 mmol, 1.0 equiv.) was dissolved in 3 mL of toluene giving a dark red solution and the solution was cooled to –34 °C. To the chilled solution, 1,3-diisopropylimidazol-2-ylidene (28.8 mg, 0.189 mmol, 1.0 equiv.) was added, the reaction mixture was warmed to room temperature, stirred for 2 h and then filtered through Celite. The filtrate was evaporated to dryness under reduced pressure and the residue was washed with pentane (2 × 5 mL) and diethyl ether (1 × 5 mL). A pale red solid was obtained, which was dried in vacuo. Yield: 53 mg (67 %); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 6.46 (s, 2H, NHC backbone), 5.61–5.51 (sept, 2H, NCHMe$_2$), 1.65 (s, 18H, 2N-*t*Bu), 1.40 (d, J = 8 Hz, 12H, NCHMe$_2$). ^{13}C NMR (101 MHz, C$_6$D$_6$) δ = 190.05 (NCN-NHC), 115.63 (CH=CH-NHC), 79.58 (NCMe$_3$), 30.48 (N*Me*), 29.55 (NC*Me*$_3$), 22.94 (NC*Me*$_2$). Elemental analysis calcd. for C$_{17}$H$_{34}$Cl$_2$CrN$_4$: C 48.92, H 8.21, N 13.42. Found: C 48.86, H 8.17, N 13.31. Orange crystals suitable for X-ray analysis were obtained by the layering the saturated solution of complex **3** in CH$_2$Cl$_2$ with pentane and storage at –34 °C for few days.

CrCl$_2$(IMes)(*N-t*Bu)$_2$ (4): Cr(*N-t*Bu)$_2$Cl$_2$ (50 mg, 0.189 mmol, 1.0 equiv.) was dissolved in 3 mL of toluene and the solution was cooled to –34 °C. Next, IMes (57.5 mg, 0.189 mmol, 1.0 equiv.) was dissolved in toluene and the solution was cooled to –34 °C. Both solutions were combined, the resulting mixture was stirred at room temperature for 2 h and then filtered through Celite. The filtrate was concentrated under reduced pressure and repeatedly washed with pentane (2 × 5 mL) and diethyl ether (2 × 5 mL) to obtain an orange colored solid. Yield: 77 mg (72 %); ^{1}H NMR (400 MHz, CDCl$_3$)

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δ = 7.26 (s, 2H, C*H*=C*H*-NHC), 7.17 (m, 4H, *m*-Ar-Mes), 2.58 (s, 12H, *Me*-Mes), 2.52 (s, 6H, *Me*-Mes), 1.36 (s, 18H, 2N-*tBu*); **13C NMR** (101 MHz, CDCl$_3$) δ = 191.49 (NCN-NHC), 138.50 (Ar), 136.94 (Ar), 136.66 (Ar), 128.84 (Ar), 122.22 (CH=CH-NHC), 79.22 (NCMe$_3$), 29.07 (C*Me*$_3$), 20.95 (*p*-Me-Mes), 19.33 (*o*-Me-Mes). Elemental analysis calcd. for C$_{29}$H$_{42}$Cl$_2$CrN$_4$: C 61.15, H 7.43, N 9.84. Found: C 61.12, H 7.44, N 9.80. Red colored crystals were obtained from a mixture of CH$_2$Cl$_2$, pentane and few drops of toluene at –34 °C for few days.

CrCl$_2$(IDipp)(N-tBu)$_2$ (5): Cr(N*t*Bu)$_2$Cl$_2$ (50 mg, 0.189 mmol, 1.0 equiv.) was dissolved in 3 mL of toluene and the solution was cooled to –34 °C. Next, Dipp (73.5 mg, 0.189 mmol, 1.0 equiv.) was dissolved in toluene and cooled to –34 °C. Both solutions were combined; the resulting mixture was stirred at room temperature for 2 h and filtered through Celite. The filtrate was then concentrated under reduced pressure and repeatedly washed with pentane (2 × 5 mL) and diethyl ether (2 × 5 mL) to obtain a pink colored solid. Yield: 58 mg (47 %); **1H NMR** (400 MHz, CDCl$_3$) δ = 7.40–7.36 (m, 2H, Ar), 7.27 (s, 2H, C*H*=C*H*-NHC), 7.25 (m, 2H, Ar), 7.07 (s, 2H, Ar), 3.35–3.25 (sept, 4H, 4C*H*Me$_2$), 1.37–1.36 (d, *J* = 6.56 Hz, 12H, CH*Me*$_2$), 1.09–1.07 (d, *J* = 6.92Hz, 12H, CH*Me*$_2$), 1.02 (s, 18H, 2N*tBu*); **13C NMR**(101 MHz, CDCl$_3$) δ = 192.29 (NCN-NHC), 147.56 (Ar), 136.57 (Ar), 129.78 (Ar), 123.69 (Ar), 123.24 (Ar), 78.59 (NCMe$_3$), 29.31 (C*Me*$_3$), 28.62(*C*HMe$_2$), 26.55 (CH*Me*$_2$), 22.82 (CH*Me*$_2$). Elemental analysis calcd. for C$_{35}$H$_{54}$Cl$_2$CrN$_4$: C 64.30, H 8.33, N 8.57. Found: C 64.13, H 8.41, N 8.47.

CrCl$_2$(N-2,6-(2-Pr)$_2$C$_6$H$_3$)$_2$(IMes) (6): Cr(N-2,6-diisopropylphenyl)$_2$Cl$_2$ (50 mg, 0.106 mmol, 1.0 equiv.) was dissolved in 3 mL of toluene and the solution was cooled to –34 °C. IMes (32.2 mg, 0.106 mmol, 1.0 equiv.) was also dissolved in toluene and cooled to –34 °C. Both solutions were combined, the resulting reaction mixture was stirred at room temperature for 2 h and then filtered through Celite. The filtrate was then evaporated to dryness under reduced pressure and washed repeatedly with pentane (2 × 5 mL) and diethyl ether (2 × 5 mL) to obtain a black colored solid. Yield: 36 mg (44 %); **1H NMR** (400 MHz, C$_6$D$_6$) δ = 6.87–6.85 (m, 4H, Ar), 6.79–6.75 (m, 2H, Ar), 6.70–6.69 (m, 4H, Ar), 6.16 (s, 2H, C*H*=C*H*-NHC), 3.73–3.67 (sept, 4H, 4C*H*Me$_2$), 2.54 (s, 12H, *Me*-Mes), 1.96 (s, 6H, *Me*-Mes), 1.12(d, *J* = 4Hz, 24H, 4CH*Me*$_2$). **13C NMR** (101 MHz, CD$_2$Cl$_2$) δ = 192.61 (NCN-NHC), 160.70 (Ar), 147.41, 138.16, 137.44, 136.42, 134.35, 130.23, 129.78, 129.01, 123.18, 122.83, 28.05, 24.94, 20.66, 18.92, 18.89. Elemental analysis calcd. for C$_{45}$H$_{58}$Cl$_2$CrN$_4$: C 69.48; H 7.52, N 7.20. Found: C 69.50; H 7.67; N 7.16.

CrCl$_2$(N-adamantyl)$_2$(IMes) (7): Cr(NAd)$_2$Cl$_2$ (50 mg, 0.119 mmol, 1.0 equiv.) was dissolved in 3 mL of toluene and the solution was cooled to –34 °C. IMes (36.1 mg, 0.119 mmol, 1.0 equiv.) was also dissolved in toluene and the solution was cooled to –34 °C. The IMes solution was then added dropwise to the one of Cr(NAd)$_2$Cl$_2$, the resulting reaction mixture was stirred at room temperature for 3 h and then filtered through Celite. The filtrate was then evaporated to dryness under reduced pressure and repeatedly washed with pentane (2 × 5 mL) and diethyl ether (2 × 5 mL) to obtain a black colored solid. Yield: 51 mg (61 %); **1H NMR** (400 MHz, CD$_2$Cl$_2$) δ = 7.07 (s, 2H, C*H*=C*H*-NHC), 6.95 (m, 4H, Ar), 2.32 (s, 12H, *Me*-Mes), 2.30 (s, 6H, *Me*-Mes), 2.20 (m, 4H, Ad), 1.98–1.96 (m, 6H, Ad), 1.72–1.66 (m, 12H, Ad), 1.55–1.52 (m, 8H, Ad). The recording of 13C NMR spectra was impossible as the complex decomposes immediately in the solution. Despite numerous efforts, inconsistent elemental analysis data were obtained. Nonetheless, the molecular structure was established by single crystal analysis. Red colored crystals were obtained from a mixture of CH$_2$Cl$_2$ and pentane at –34 °C for few days. The crystals quickly decomposed at room temperature.

CrCl$_2$(1-Mes-3-(1-(2-O-C$_6$H$_4$))imidazol-2-ylidene)$_2$C$_6$H$_3$)$_2$(IMes) (8): To a chilled (–34 °C) suspension of 1-mesityl-3-(2-hydroxy-phenyl)-4,5-dihydro-1*H*-imidazolium chloride (**L$_1$**, 59.7 mg, 0.188 mmol, 1.0 equiv.) in 1 mL of toluene was added a chilled solution of LiHMDS (63 mg, 0.376 mmol, 2.0 equiv.) in 1 mL of toluene. The resulting mixture was stirred at room temperature for 1 h, then filtered through Celite and cooled to –34 °C. This solution was then added dropwise to a chilled solution of Cr(N-*tBu*)$_2$Cl$_2$ (50 mg, 0.188 mmol, 1.0 equiv.) in 1 mL of toluene. The resulting mixture was stirred at room temperature for 2 h and then filtered through celite. The filtrate was evaporated to dryness under reduced pressure and then washed repeatedly washed with pentane (2 × 5 mL) and diethyl ether (2 × 5 mL) to obtain A pink colored solid. Yield: 60 mg (61 %). **1H NMR** (400 MHz, CDCl$_3$) δ = 7.14–7.12 (dd, *J* = 1.4, 8.08Hz, 1H, Ar), 7.09–7.05 (m, 1H, Ar), 6.95–6.94 (m, 2H,Ar), 6.89–6.86 (dd, *J* = 1.42, 7.76Hz, 1H, Ar), 6.73–6.69 (td, 1H, Ar), 5.30 (0.5 CH$_2$Cl$_2$) 4.28–4.23 (t, *J* = 9.96Hz, 2H, CH$_2$-NHC), 3.93–3.88 (t, *J* = 9.94Hz, 2H, CH$_2$-NHC), 2.39 (s, 6H, 2CH$_3$-Ar), 2.28 (s, 3H,CH$_3$-Ar), 1.12 (s, 18H, 2N-*tBu*). **13C NMR** (101 MHz, CD$_2$Cl$_2$) δ = 202.5 (NCN-NHC), 157.4, 139.0, 136.4, 136.2, 132.3, 130.1, 125.7, 119.4, 116.5, 116.5, 78.8, 67.8, 49.1, 29.8, 25.6, 20.61, 20.59, 18.24, 18.22. All bidentate complexes crystallized with trapped solvents, which were difficult to remove even under high vacuum (0.001 mbar). 1H NMR indicated the trapping of substoichiometric quantities (0.5 mol) of CH$_2$Cl$_2$ along with **8**. Elemental analysis calcd. for C$_{26}$H$_{37}$ClCrN$_4$O·0.5CH$_2$Cl$_2$: C 57.71, H 6.95, N 10.16. Found: C 57.81, H 6.931, N 10.25.

CrCl$_2$(1-tBu-3-(1-(2-O-C$_6$H$_4$))imidazol-2-ylidene)$_2$C$_6$H$_3$)$_2$(IMes) (9): To a chilled (–34 °C) suspension of 1-(tert-butyl)-3-(2-hydroxy-phenyl)-4,5-dihydro-1*H*-imidazolium chloride (**L$_2$**, 47.9 mg, 0.188 mmol, 1.0 equiv.) in 1 mL of toluene was added a chilled solution of LiHMDS (63 mg, 0.376 mmol, 2.0 equiv.) in 1 mL of toluene. The resulting mixture was stirred at room temperature for 1 h, then filtered through celite and stored in the freezer at –34 °C. The free carbene was then added dropwise to the chilled solution of Cr(N-*tBu*)$_2$Cl$_2$ (50 mg, 0.188 mmol, 1.0 equiv.) in 1 mL of toluene, the resulting mixture was stirred at room temperature for 2 h and then filtered through Celite. The filtrate was evaporated to dryness under reduced pressure and washed repeatedly with pentane (2 × 5 mL) and diethyl ether (2 × 5 mL) to obtain a pale red colored solid. Yield: 62 mg (71 %). **1H NMR** (400 MHz, CDCl$_3$) δ = 6.98–6.96 (t, *J* = 4, 8Hz, 1H, Ar), 6.84 (t, *J* = 8Hz, 1H, Ar), 6.79 (t, *J* = 8Hz, 1H, Ar), 6.70–6.66 (t, *J* = 8Hz, 1H, Ar), 4.00–3.91 (m, 4H, CH$_2$-CH$_2$-NHC), 1.59 (s, 9H, NC*Me*$_3$), 1.41 (s, 18H, N-*tBu*). The molecule crystallizes from diethyl ether with one molecule of diethyl ether trapped that cannot be removed even under high vacuum. Elemental analysis calcd. for C$_{21}$H$_{35}$ClCrN$_4$O. C$_4$H$_{10}$O: C 57.62, H 8.70, N 10.75. Found: C 57.22, H 8.635, N 10.40. The molecular structure was confirmed by single-crystal X-ray analysis. Dark red colored crystals suitable for single-crystal X-ray analysis were obtained from a solution of CH$_2$Cl$_2$ and pentane with a few drops of diethyl ether at –34 °C.

CrCl$_2$(1–2-phenyl-C$_6$H$_4$-3-(1-(2-O-C$_6$H$_4$))imidazol-2-ylidene)$_2$C$_6$H$_3$)$_2$(IMes) (10): To a chilled (–34 °C) suspension of 1-(2-phenyl-C$_6$H$_4$)-3-(2-hydroxyphenyl)-4,5-dihydro-1H-imidazolium chloride (**L$_3$**, 66 mg, 0.188 mmol, 1.0 equiv.) in 1 mL of toluene was added to a chilled solution of LiHMDS (63 mg, 0.376 mmol, 2.0 equiv.) in 1 mL of toluene at –34 °C. The resulting mixture was stirred for 1 h at room temperature, then filtered through Celite and stored at –34 °C. The free carbene was then added dropwise to a chilled solution of Cr(N-*tBu*)$_2$Cl$_2$ (50 mg, 0.188 mmol, 1.0 equiv.) in 2 mL of toluene and the resulting mixture was stirred at room temperature for 2 h, then filtered through celite. The filtrate was evaporated to dryness under reduced pressure and washed repeatedly

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doi.org/10.1002/ejic.202000550

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washed with pentane (2 × 5 mL) and diethyl ether (2 × 5 mL) to obtain a dark red colored solid. Yield: 57 mg (54 %). One molecule of toluene co-crystallized along with the complex. **¹H NMR** (400 MHz, CD₂Cl₂) δ = 7.71–7.69 (m, 2H, Ar), 7.53–7.45 (6H, Ar), 7.40–7.36 (m, 1H, Ar), 7.24–7.22 (m, 2H, Ar), 7.18–7.16 (m, 3H, Ar), 7.04–7.02 (m, 1H, Ar), 6.95–6.93 (dd, J = 8Hz, 1H, Ar), 6.87–6.84 (dd, J = 4, 8Hz, 1H, Ar), 6.71–6.66 (m, 1H, Ar), 4.24–4.16 (m, 1H, CH₂-CH₂-NHC), 3.74–3.67 (m, 1H, CH₂-CH₂-NHC), 3.63–3.56 (m, 1H, CH₂-CH₂-NHC), 3.46–3.38 (m, 1H, CH₂-CH₂-NHC), 2.34 (s, 3H, Ar-CH₃ from toluene), 1.31 (s, 9H, N-tBu), 1.04 (s, 9H, N-tBu); **¹³C NMR** (101 MHz, CD₂Cl₂) δ = 201.9 (NCN-NHC), 157.3, 139.7, 139.1, 138.0, 137.7, 131.7, 131.3, 130.3, 129.5, 129.0, 128.92, 128.90, 128.2, 125.8, 125.2, 119.3, 116.5, 116.4, 79.7(NCMe₃), 78.4(NCMe₃), 49.3(CH₂-CH₂-NHC), 30.1(NCMe₃), 29.4 (NCMe₃). One molecule of CH₂Cl₂ is trapped in the crystal as confirmed by single-crystal X-ray analysis, which cannot be removed even under high vacuum (0.001 mbar). Red colored crystals were obtained by the layering of pentane to a saturated solution of complex **10** in CH₂Cl₂ and storage at –34 °C. Elemental analysis calcd. for C₂₉H₃₅ClCrN₄O•□ CH₂Cl₂: C 57.38, H 5.94, N 8.92. Found: C 57.36, 5.88, 8.81.

Complex 11: Cr(N-2,6-diisopropylphenyl)₂(CH₂CMe₃)₂ (50 mg, 0.0918 mmol,1 equiv.) was dissolved in 1 mL of THF and cooled to –34 °C. Next, solid AgI•1,3-dimethylimidazol-2-ylidene (30.3 mg, 0.0918 mmol, 1 equiv.) was added. The reaction mixture was stirred at room temperature for 33 h and then evaporated to dryness under reduced pressure. The residue was then dissolved in 5 mL of pentane and filtered through a short pad of Celite. All volatiles were removed in vacuo. Analytically pure **11** was obtained via crystallization from pentane at –34 °C. Yield: 17 mg (33 %). **¹H NMR** (400 MHz, [D₈]THF) δ = 13.01 (s,1H, Cr=CH), 7.11 (s, 2H, NHC backbone), 6.87 (m, 3H, Ar), 6.81 (m, 3H, Ar), 3.99–3.93 (m, 2H, CH(CH₃)₂), 3.72 (s, 6H, 2N(CH₃)), 3.70–3.66 (m, 2H, CH(CH₃)₂), 1.16 (br, 9H, tBu), 1.15–1.11 (m, 12H, 2CHMe₂), 0.95–0.93 (d, J = 8Hz, 6H, CHMe₂), 0.70- 0.69 (d, J = 4Hz, 6H, CHMe₂). ¹³C NMR analysis and elemental analysis were impossible due to the extreme sensitivity of the complex in solution and also in the solid state. Crystals suitable for single-crystal X-ray analysis were grown from a mixture of CH₂Cl₂ and pentane at –34 °C over a course of few days.

Chromium N-6(–2-(diethylboryl)phenyl)pyrid-2-yl-imido-N′-tert-butylimido-N′′-tert-butylamido chloride (13): To a solution of 6(–2-(diethylboryl)phenyl)pyridine-2-amine (0.50 g, 2.10 mmol) in diethyl ether (12 mL) was added n-butyllithium (1.31 mL, 1.6 m in hexane, 2.10 mmol, 1.0 equiv.) at –37 °C. The solution was stirred at room temperature for three hours, then the precipitated solid was filtered off, washed with cold pentane and dried in vacuo. The lithium salt (0.52 g, 1.80 mmol, 1 equiv.) was dissolved in diethyl ether (10 mL) and added at –34 °C to a solution of bis(N-tert-butylimido) chromium(VI) dichloride (1, 0.42 g, 1.80 mmol, 1 equiv.) in diethyl ether (10 mL). After stirring for one hour, triethylamine (0.25 mL, 1.80 mmol, 1 equiv.) was added. The purple solution was stirred overnight at room temperature. The solvent was removed, and the crude product was extracted with pentane, LiCl was filtered off. Pure product was obtained by recrystallization from cold pentane. Yield: 0.77 g (1.49 mmol, 83 %). **¹H-NMR** (C₆D₆): δ = 11.18 (s, 1H, NH) 7.77 (m, 1H, Ar-H), 7.59 (m, 2H, Ar-H), 7.40 (m, 1H, Ar-H), 7.22 (m, 1H, Ar-H), 7.05 (t, 1H, J = 8 Hz, Ar-H), 6.84 (m, 1H, Ar-H), 1.42–1.38 (m, 2H, CH₂), 1.21 (s, 18H, CCH₃), 1.18–1.12 (m, 2H, CH₂), 0.71 (t, 6H, CH₃). **¹³C-NMR** (C₆D₆): δ = 163.6, 155.9, 140.2, 137.3, 130.4; 129.4, 125.7; 121.7, 116.0, 111.2, 80.4, 33.7, 31.1, 30.0, 15.6, 10.4, 1.4. Elemental analysis: calculated for C₂₃H₃₆BClCrN₄: C 59.18, H 7.77, N 12.00, found: C 59.01, H 8.03, N 11.88.

N-6(–2-(Diethylboryl)phenyl)pyrid-2-yl-imido-N′-tert-butylimido-N′′-tert-butylamido neophyl chromium (14): 2-Methyl-2-phenylpropylmagnesium chloride (0.57 mL, 0.5 m, 0.3 mmol, 1 equiv.) was added dropwise to a solution of chromium N-6(–2-(diethylboryl)phenyl)pyrid-2-yl-imido-N′-tert-butylimido-N′′-tert-butylamido chloride (0.15 g, 0.3 mmol, 1 equiv.) in diethyl ether (10 mL) at –34 °C. The orange solution was stirred at room temperature overnight. Then the solvent was removed under reduced pressure and the crude product was extracted with pentane. At –34 °C, 3,5-lutidine (0.05 mg, 0.4 mmol, 1.5 equiv.) was added and the solution was stirred at room temperature overnight. The precipitated solid was filtered off and the product recrystallized from pentane. Yield: 0.11 g (0.02 mmol, 63.1 %). **¹H-NMR** (C₆D₆): δ = 10.05 (s, 1H, NH), 7.84–7.80 (m, 1H, Ar-H), 7.64–7.62 (d, 2H, Ar-H), 7.45–7.39 (m, 3H, Ar-H), 7.26–7.20 (m, 3H, Ar-H), 7.08–7.04 (m, 3H, J = 7.9 Hz, Ar-H), 6.86 (dd, 1H, J = 7.5 Hz, Ar-H), 3.14 (s, 2H, CrCH₂), 1.54 (s, 18H, CCH₃), 1.40–1.25 (m, 4H, BCH₂), 1.21 (t, 6H, CH₃). **¹³C-NMR** (C₆D₆): δ = 162.5, 156.1, 152.1, 139.8, 139.5, 138.0, 132.0, 130.2, 130.1, 126.1, 125.7, 125.5, 121.3, 112.8, 108.1, 77.9, 74.7, 41.2, 32.9, 31.6, 15.6, 14.2, 10.5, 1.4. Elemental analysis calculated for C₃₃H₄₉BCrN₄: C 70.20, H 8.75, N 9.92, found: C 69.85, H 9.04, N 9.64.

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