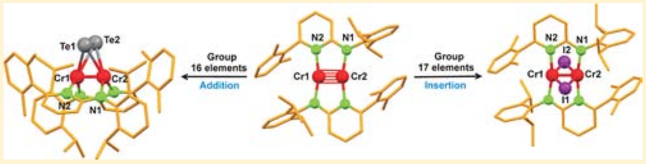
Inorganic Chemistry
Article
pubs.acs.org/IC

Quintuple Bond Reactivity toward Group 16 and 17 Elements: Addition vs Insertion

Emmanuel Sobgwi Tamne, Awal Noor, Sadaf Qayyum, Tobias Bauer, and Rhett Kempe*

Lehrstuhl Anorganische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany

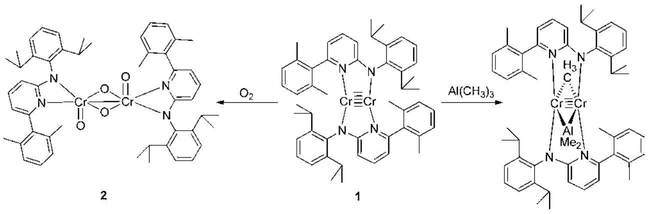
ABSTRACT: The low valent, coordinatively unsaturated, and formally quintuply bonded bimetallic aminopyridinato chromium complex **1** was investigated regarding its reactivity toward group 16 and 17 elements. Reaction of **1** with O_2 yielded a dimeric Cr oxo complex **2**, a compound with a high formal oxidation state carrying both bridging and terminal oxo ligands. Reactions with the higher homologues of the group lead to the formation of dimeric Cr^{II} complexes in which E_2^{2-} ligands were formed [E = S (**3**), Se (**4**), and Te (**5**)]. Here the quintuply bonded dichromium unit formally undergoes an addition reaction. Reaction of **1** with the homo diatomic molecules of the group 17 elements leads to products in which the Cr−Cr quintuple bond is inserted into the corresponding X_2 molecule [X = Cl (**6**), Br (**7**), and I (**8**)]. Complex **1** was also found to insert into the S−S and Se−Se bonds of 1,2-diphenyldisulfane or the corresponding selenium compound (complexes **9** and **10**, respectively). All the compounds have been characterized by NMR and elemental analysis. Additionally, eight of the complexes have been characterized by X-ray analysis. The bimetallic Cr^{II} complexes feature metal−metal distances between 1.8369(18) and 1.918(12) Å.



■ INTRODUCTION

Bond orders are of fundamental interest in chemistry.[1] Looking at the simple hydrocarbons ethane, ethylene, and acetylene we see a drastic increase in reactivity with an increasing bond order. Formally, we store electrons in the C−C linkage and can use them for additional bond formations. Of course, it is not that simple. For the related dinitrogen compounds the triply bonded molecule, rich in electrons too, is stable like a rock and the other two, diazene and hydrazine, are the more reactive. Very high bond orders, namely quintuple and sextuple bonds can be observed between transition metals.[2] Molecules having such high bond orders are known for decades,[3] the transient diatomic molecules M_2 (M = V, Nb, Cr, Mo) being prominent examples.[4] Unfortunately, their instability and highly demanding and partially highly unselective synthesis restricts their use in (for instance) inorganic synthesis, small molecule activation, or catalysis. In 2005, the group of Power reported a breakthrough in this field, the synthesis of the first stable molecule having a quintuple bond.[5] Shortly after and inspired by that compound the groups of Theopold, Tsai, and us reported on N-ligand stabilized dichromium complexes having a quintuple bond.[6] Ultrashort metal−metal bond distances have been observed for these compounds.[1,7] The record is right now at 1.73 Å.[8] Meanwhile, a considerable number of quintuply bonded dichromium complexes have been reported.[9] Furthermore, related dimolybdenum compounds were synthesized.[10] With these stable compounds in hand we are enabled to study their reactivity and by doing so we may understand quintuple bonds chemically. We have previously shown that quintuply bonded complexes can provide from two to eight electrons and observed the carboalumination of a quintuple bond as well as its oxidation with O_2, during which Cr^I has been oxidized to Cr^V (Scheme 1).[11a]

Scheme 1. Carboalumination and Oxidation of a Chromium−Chromium Quintuple Bond



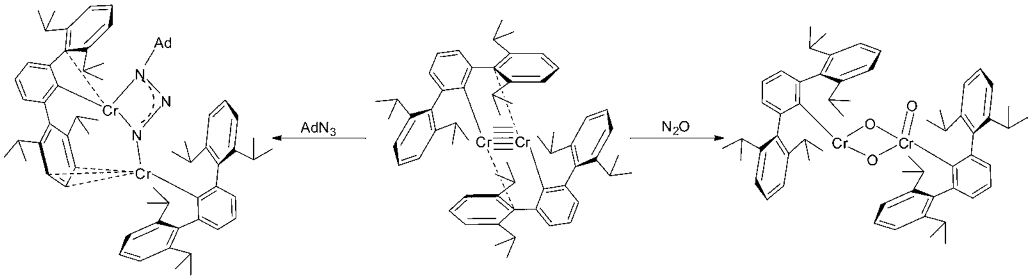
At the same time, Power et al. have shown that the ligand role is crucial in quintuple bond reactivity by observing complete cleavage of the quintuple bond for complexes of the type ArCrCrAr (Ar = substituted terphenyl) if reacted with N_2O and azides (Scheme 2).[12]

Cycloaddition reactions were observed by Theopold et al. and us, when alkynes and dienes were reacted with quintuply bonded dichromium complexes (Scheme 3).[11b,13] While extending our understanding of quintuple bond reactivity we have shown that molecules like phosphorus, yellow arsenic, and AsP_3 can be activated under mild conditions and in a highly selective manner.[11c]

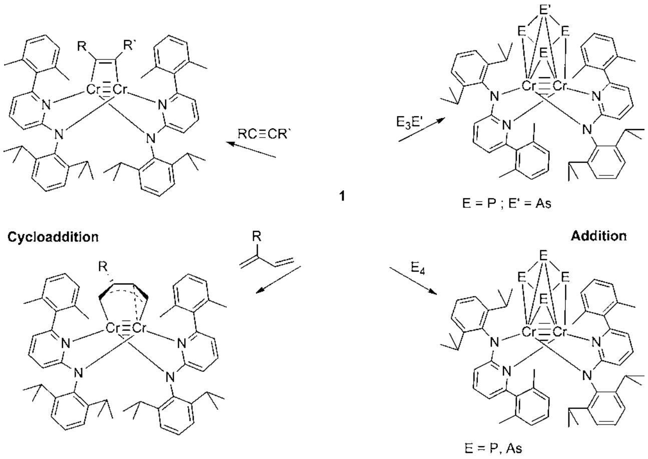
Tsai et al. have shown that amidinate ligands stabilized complexes with a Cr−Cr bond length of 1.7404(8) Å[6e] show weak coordination of tetrahydrofuran (THF) and 2-MeTHF (2-MeTHF = 2-methyltetrahydrofuran) with long Cr−O distances of 2.579(4) and 2.305(7) Å, respectively (Scheme 4).[9] The ligated THF and 2-MeTHF ligands are labile and

Received: September 25, 2012
Published: December 14, 2012

Scheme 2. Cleavage of a Quintuple Bond by N_2O and Admantyl Azide (AdN_3)



Scheme 3. Cycloaddition and Addition Reactions of Quintuply Bonded Cr Complexes



result in comprehensive elongation of the Cr−Cr bond to 1.8115(12) and 1.7636(5) Å, respectively.

Complexes stabilized by diamidopyridine ligands undergo two electron oxidation if reacted with AgOTf and thus completely cleave the Cr−Cr bond.[9] Similar cleavage of the quintuple bond has been observed when the diamidopyridine ligand stabilized Cr complexes were reacted with [18] crown-6 ether (Scheme 5).[9]

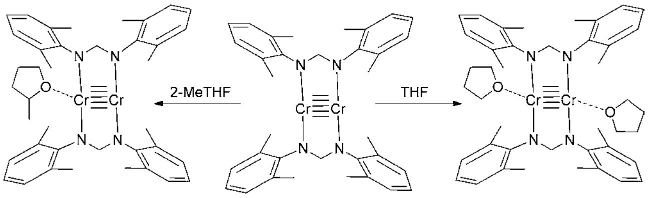
Very recently, Tsai et al. have extended the reactivity studies of quintuply bonded complexes toward Mo and have observed [2+2+2] cycloaddition reactions with alkynes.[14]

Here we report our results involving reactions between a chromium−chromium quintuple bond and chalcogens (S, Se, and Te), halogens, and cleavage of single bonds between chalcogenides (PhSSPh and PhSeSePh).

■ RESULTS AND DISCUSSION

Complex **1** was readily prepared following the published procedure.[11a] Reacting **1** with excess of oxygen afforded **2** as red brown solid in reasonable isolated yield of 72% (Scheme 6).[11a]

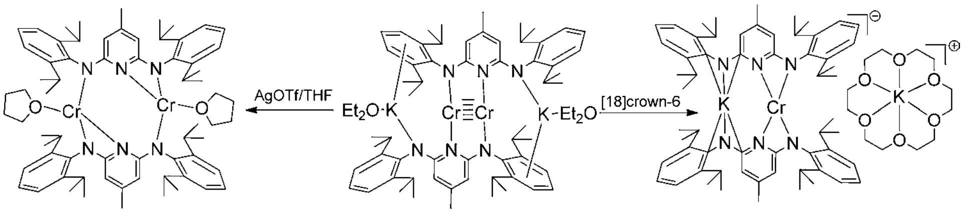
Scheme 4. Weak Coordination of THF and 2-MeTHF to Quintuply Bonded Cr Complexes



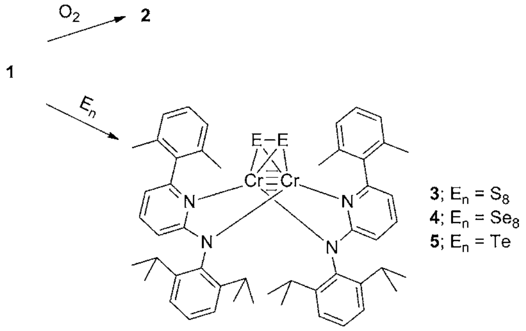
^{1}H NMR shows **2** to be a diamagnetic compound with sharp signals between 0 and 8 ppm. We observe two doublets for the isopropyl groups, two singlets for the CH_3 protons, and two septets for the CH proton of the isopropyl-groups. Crystals suitable for X-ray analysis were grown from hexane solution. The solid state structure shows **2** to be a dimeric Cr(V) oxo complex, in which two oxo ligands are bridging and two oxo ligands coordinate terminally (Figure 1). Chromium oxo complexes of this type are rare[15] and were first reported by Herberhold and co-workers.[16] The bridging Cr−O bond distances of 1.791(2) Å is similar to the respective 1.817(4) Å distance in the Cr(V) complex $[CpCr(O)(\mu\text{-}O)]_2$.[16] The terminal Cr−O bond length of 1.563(2) Å is considerably shorter than the bridging Cr−O distances and indicates a strong double bond character. It is also shorter than the Cr^V complex of Herberhold (1.594(3) Å).[16] The long Cr−Cr distance of 2.5314(10) Å corresponds to a single bond between the two metal centers.

Impressed by the highly selective oxidation of the quintuple bond by O_2 we became interested in exploring the higher homologues of that group. Complex **1** reacts with S_8 at room temperature and with Se_8 and Te at 60 °C in toluene to afford **3**, **4**, and **5**, respectively, in high yields (Scheme 6). Complexes **3**−**5** are diamagnetic and have been characterized by solution NMR spectroscopy and elemental analysis. The ^{1}H NMR spectra of **3**−**5** in C_6D_6 are as expected for diamagnetic complexes, featuring slight shifting for a multitude of sharp resonances between 0 and 8 ppm. We observe four doublets for the non-equivalent isopropyl CH_3 protons, two singlets for the methyl CH_3 protons and two septets for the isopropyl CH protons of the aminopyridinato ligands. Additionally, **3** and **5** have also been characterized by X-ray analysis. The solid state structure shows the oxidation of Cr_2 moiety to give structurally similar bimetallic μ,η^2-disulfide (**3**) and μ,η^2-ditelluride (**5**) complexes (Figure 2). Quintuply bonded diatomic molecules can provide from two to ten electrons if activated with small molecules and can thus show a large disparity in the formal oxidation states of chromium. It can be seen that for dimeric oxo complex **2**, Cr^I has been oxidized to Cr^V and for **3**−**5** to Cr^{II}. In **3** the S−S distance of 2.058(4) Å is shorter than expected for disulfur ligands,[17] but it lies close to other known bimetallic chromium complexes [2.028(2) Å].[18] The averaged Cr−S bond distance, 2.3885(3) Å, is longer than those known for relevant μ,η^2-disulfide bimetallic chromium complexes.[17−20] In comparison to μ,η^2-disulfide ligands, μ,η^2-ditelluride ligands on diatomic transition metals platform are rare and unknown for chromium; thus **5** represents the first example of such Cr complexes. The Te−Te bond distance of 2.6878(8) Å is comparable to a closely known ditellurido vanadium(IV)

Scheme 5. Quintuple Bond Reactivity of Diamidopyridine Stabilized Cr Complexes



Scheme 6. Synthesis of 2−5



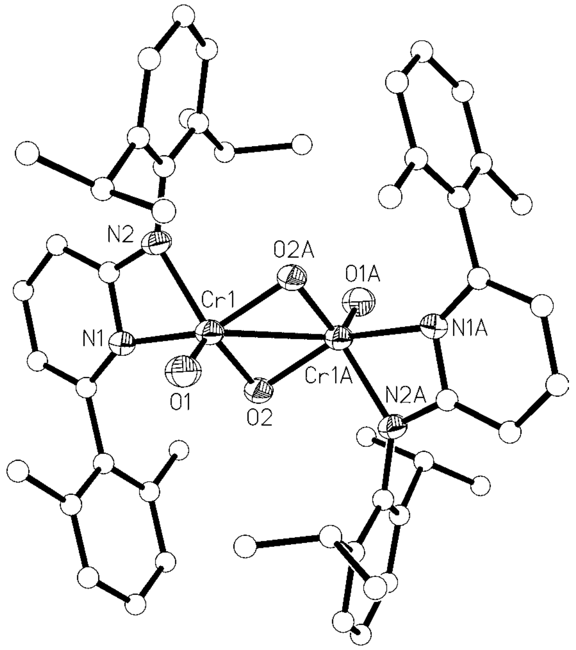


Figure 1. Molecular structure of **2**. ORTEP representation on the 50% probability level for all non-carbon atoms. Hydrogen atoms have been deleted for clarity. Selected bond lengths [Å] and angles [deg]: Cr1−N1 2.053(2), Cr1−N2 1.946(2), O1−Cr1 1.563(2), O2−Cr1 1.791(2), Cr1−Cr1A 2.5314(10); Cr1−Cr1A−O1A 121.69(9), Cr1−Cr1A−O2 45.02(7), N2−Cr1−N1 65.20(10).

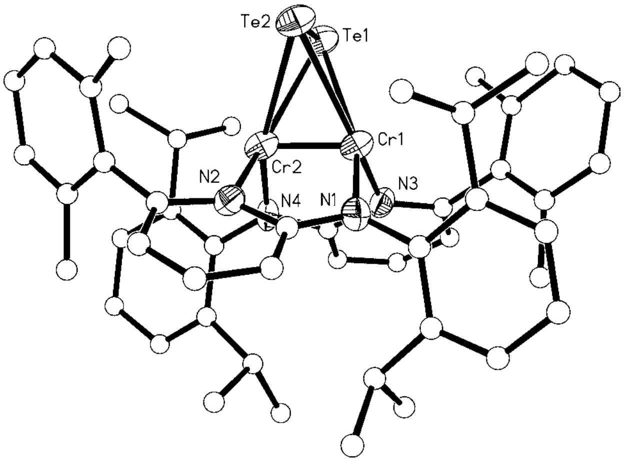


Figure 2. Molecular structure of **5**, ORTEP representation on the 50% probability level for all non-carbon atoms. Hydrogen atoms have been deleted for clarity.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for Complexes 3 and 5[a]

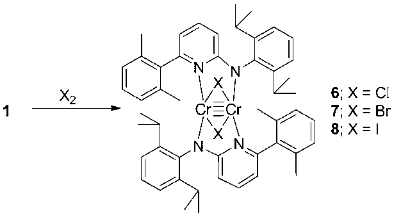
3 (E = S)		5 (E = Te)	
Cr−Cr	1.847(2)	Cr−Cr	1.8369(18)
N_{Am}−Cr	2.004(8)	N_{Am}−Cr	2.030(7)
N_{Py}−Cr	2.004(8)	N_{Py}−Cr	2.030(7)
E−E	2.058(4)	E−E	2.6878(18)
E−Cr	2.388(3)	E−Cr	2.7351(13)
E−E−Cr	64.48(11)	E−E−Cr	60.57(3)
Cr−E−Cr	45.48(7)	Cr−E−Cr	39.24(4)
Cr−Cr−N_{Am}	95.5(2)	Cr−Cr−N_{Am}	95.13(19)
Cr−Cr−N_{Py}	97.4(3)	Cr−Cr−N_{Py}	97.79(19)
N_{Am}−Cr−N_{Py}	104.7(3)	N_{Am}−Cr−N_{Py}	106.2(3)
Cr−Cr−E	67.66(9)	Cr−Cr−E	70.36(6)
E−Cr−E	51.03(10)	E−Cr−E	58.85(3)

[a] $N_{Am} = N_{Amido}$, $N_{Py} = N_{Pyridine}$.

complex [2.6961(5) Å][21] and ditellurido iron complexes [2.700−2.719(4) Å],[22] and are normal for a ditelluride single bond. The Cr−Te distances lie in the range of 2.7231(14) to 2.7511(13) Å. The Cr−Cr bond distances of 1.847(2) Å in **3** and 1.8369(18) Å in **5** lie in the range known for quadruply bonded complexes (Table 1).

Furthermore, we were interested to study the reactivity of **1** toward homo diatomic group 17 molecules, especially in comparison to the activation of sulfur, selenium, and tellurium. Stirring toluene/benzene solution of **1** with the corresponding X_2 molecule yielded complexes **6**−**8** in good yields (**6**: X = Cl; **7**: X = Br; **8**: X = I) (Scheme 7). Compounds **6**−**8** are diamagnetic, and their ^{1}H NMR spectra in solution show a characteristic peak pattern of two doublets for the non-

Scheme 7. Synthesis of 6−8



equivalent CH_3 protons of the isopropyl groups, one singlet for the CH_3 protons, and one septet for the CH proton of the isopropyl groups. A single set of signals was observed for the aromatic protons. Solid state structure analyses show halogen bridged bimetallic Cr^{II} complexes. We observed selective oxidative addition even if an excess of Cl_2, Br_2, or I_2 was used. In similar reactions Power et al. have observed not only complete cleavage of the quintuple bond but also excess of I_2 led to form $[CrI_2(thf)_2]$ species.[23] Structurally characterized chromium complexes with bridging iodides are also rare and only a few examples are known.[24] The halogen-bridged complexes **6**–**8** are structurally similar and feature Cr atoms coordinated to five other atoms thus forming a distorted trigonal bipyramidal geometry (Figure 3). The Cr–Cr distances of 1.918(12) Å for **6**, 1.868(18) Å for **7**, and 1.874(4) Å for **8** are typical for quadruple bonds. The average Cr–X bond length could be classified as Cr–Cl (2.438 Å) < Cr–Br (2.575 Å) < Cr–I (2.758 Å). The short Cr–Cl bond could be due to the more electronegative nature of chlorine than bromine and iodine. This has also an impact on the values of the Cr–X–Cr angles which amount to 46.32(3), 42.54(4), and 39.74(7)° for **6**, **7**, and **8**, respectively. It is also in accordance with the values of the Cr–Cr bond distance which is longest in **6** [1.918(12) Å] (Table 2). The longer Cr–N_{py} distances compared to Cr–N_{am} bond distances show the localization of the anionic function on the amido N-atom which is typical of an amidopyridine mode of coordination of the ligands.[25] Details of the X-ray crystal structure analyses are summarized in Table 2.

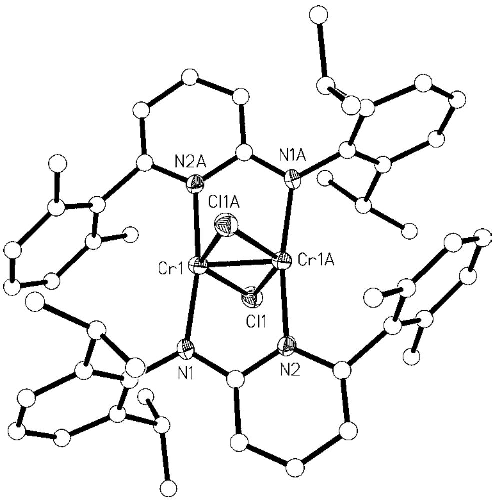
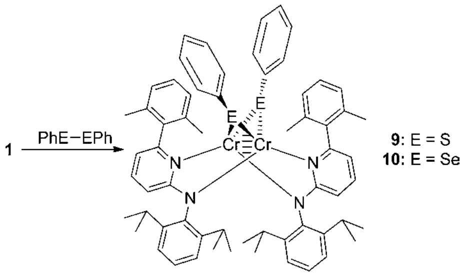


Figure 3. Molecular structure of **6**. ORTEP representation on the 50% probability level for all non-carbon atoms. Hydrogen atoms have been deleted for clarity.

The reaction of diphenyldiselenide and diphenyldisulfide with **1** at room temperature in toluene resulted in the formation of complexes **9** and **10**, respectively (Scheme 8).

Scheme 8. Synthesis of 9 and 10



Complexes **9** and **10** show very little solubility in organic solvents once precipitated which excludes detailed characterization by NMR spectroscopy. Crystals of **9** suitable for X-ray analysis were grown from THF-d_8 solution and of **10** from toluene solution. Complexes **9** and **10** are isostructural dinuclear complexes in which the Cr–Cr bond is inserted into the S–S and Se–Se bonds, respectively (Figure 4). The two Cr atoms are joined by two bridging phenylthio or phenylselenato groups. The average Cr–S distance in **9** is 2.44 Å and in **10** the Cr–Se bond distance lies at 2.570 Å. The difference between the Cr–S and Cr–Se bond distances reflects the difference in covalent radii of S and Se (Table 4). The Cr-ligand distances in **9** and **10** are almost identical to each other. The Cr–Cr distances of 1.8486(19) Å (**9**) and 1.8635(16) Å (**10**) fall into the range of "supershort" chromium–chromium quadruple bonds (Cr–Cr 2.0 Å).[26] Details of the X-ray crystal structure analyses are summarized in Table 3.

■ CONCLUSION

In summary, reactivity studies on a quintuply bonded, low valent dichromium complex have been extended to a variety of small inorganic compounds of group 16 and 17 elements. It has

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Complexes 6, 7, and 8[a]

6 (X = Cl)		**7** (X = Br)		**8** (X = I)	
Cr–Cr	1.918(12)	Cr–Cr	1.868(18)	Cr–Cr	1.874(4)
N_{Am}–Cr	2.010(12)	N_{Am}–Cr	1.997(5)	N_{Am}–Cr	2.004(8)
N_{Py}–Cr	2.023(2)	N_{Py}–Cr	2.003(5)	N_{Py}–Cr	2.028(9)
Cr–X	2.438(13)	Cr–X	2.574(12)	Cr–X	2.757(2)
Cr–Cr–X	67.61(3)	Cr–Cr–X	69.73(6)	Cr–Cr–X	69.81(11)
Cr–X–Cr	46.32(5)	Cr–X–Cr	42.54(4)	Cr–X–Cr	39.71(3)
Cr–Cr–N_{Am}	97.91(7)	Cr–Cr–N_{Am}	98.64(14)	Cr–Cr–N_{Am}	97.5(3)
Cr–Cr–N_{Py}	92.55(8)	Cr–Cr–N_{Py}	93.25(14)	Cr–Cr–N_{Py}	94.2(3)
N_{Am}–Cr–N_{Py}	169.54(19)	N_{Am}–Cr–N_{Py}	168.11(19)	N_{Am}–Cr–N_{Py}	168.3(4)
N_{Am}–Cr–X	91.76(7)	N_{Am}–Cr–X	91.22(14)	N_{Am}–Cr–X	93.4(2)
N_{Py}–Cr–X	92.28(7)	N_{Py}–Cr–X	89.22(13)	N_{Py}–Cr–X	90.7(3)
X–Cr–X	133.68(3)	X–Cr–X	142.54(4)	X–Cr–X	140.26(7)

[a] N_{Am} = N_{Amido}, N_{Py} = $N_{Pyridine}$.

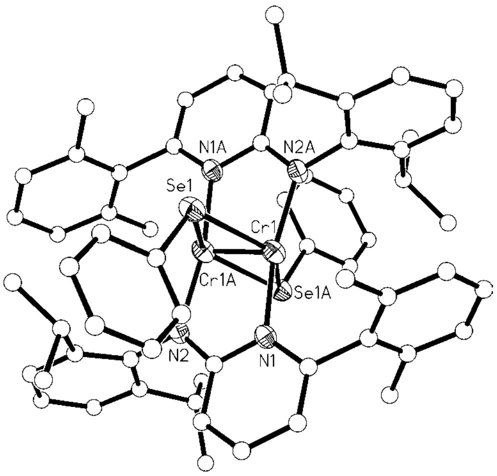


Figure 4. Molecular structure of **10**. ORTEP representation on the 50% probability level for all non-carbon atoms. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for Complexes 9 and 10[a]

9 (E = S)		**10** (E = Se)	
Cr−Cr	1.8486(14)	Cr−Cr	1.8635(16)
N_{Am}−Cr	1.992(5)	N_{Am}−Cr	2.012(5)
N_{Py}−Cr	2.030(5)	N_{Py}−Cr	2.030(5)
E−Cr	2.444(19)	E−Cr	2.5608(10)
Cr−Cr−E	64.54(7)	Cr−Cr−E	69.06(5)
Cr−E−Cr	44.45(5)	Cr−E−Cr	42.53(4)
Cr−Cr−N_{Am}	97.64(14)	Cr−Cr−N_{Am}	98.61(14)
Cr−Cr−N_{Py}	95.09(14)	Cr−Cr−N_{Py}	93.67(12)
N_{Am}−Cr−N_{Py}	167.27(19)	N_{Am}−Cr−N_{Py}	167.72(17)
N_{Am}−Cr−E	86.47(15)	N_{Am}−Cr−E	88.44(14)
N_{Py}−Cr−E	98.28(10)	N_{Py}−Cr−E	96.03(13)
E−Cr−E	135.55(5)	E−Cr−E	137.46(4)

[a] N_{Am} = N_{Amido}, N_{Py} = $N_{Pyridine}$.

been shown that the dichromium platform can provide from two to eight electrons to give dinuclear complexes, in which Cr exists in +II and +V oxidation states. Preferentially, two electrons are donated. For the group 16 elements, O_2 leads to a dimeric Cr^{V} species. Other chalcogens undergo addition reactions in which an E_2^{2-} moiety binds to the Cr^{II}_2-unit (E = S, Se, and Te). For homo diatomic molecules of group 17 insertion of the quintuple bond into the corresponding X−X bond (X = Cl, Br and I) was observed. Complex **1** was also found to cleave the single bonds of dichalcogenides Ph_2S_2 and Ph_2Se_2 forming the corresponding oxidative addition products.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in a N_2 filled glovebox (mBraun 120-G) with a high-capacity recirculator (<0.1 ppm O_2). Solvents were dried by distillation from sodium wire/benzophenone. Complex **1** was prepared according to the published procedure.[11a] Commercial $CrCl_2$, S_8, Se_8, Te, PhSSPh, and PhSeSePh were used as received. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried, and distilled prior to use. NMR spectra were recorded on Bruker 250 MHz, Varian 300 MHz, and Varian 400 MHz spectrometers at ambient temperature. The chemical shifts are reported in ppm relative to the internal TMS. Elemental analyses (CHN) were determined using a Vario EL III instrument. X-ray crystal structure analyses were performed by using a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR97,[27] SHELXL97,[28] and WinGX.[29] Crystallographic details are summarized in Tables 4 and 5. X-ray crystallographic data for compounds **2** (CCDC 713546), **3** (CCDC 901063), **5** (CCDC 901062), **6** (CCDC 901066), **7** (CCDC 901061), **8** (CCDC 901060), **9** (CCDC 901064), and **10** (CCDC 901065) 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.

Syntheses of the Metal Complexes. *Synthesis of 2.*[11a] O_2 (1 bar) was introduced into a solution of **1** (0.1 g, 0.12 mmol) in hexane (10 mL) at room temperature with continuous stirring. A color change

Table 4. Data of the X-ray Crystal Structure Analyses for Complexes 2, 3, 5, and 6

	2[11a]	**3**	**5**	**6**. 2×C_7H_8
formula	$C_{25}H_{29}CrN_2O_2$	$C_{50}H_{58}Cr_2N_4S_2$	$C_{50}H_{58}Cr_2N_4Te_2$	$C_{64}H_{74}Cl_2Cr_2N_4$
M_r g mol^{-1}	441.50	883.12	1074.23	1074.17
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	*P*2(1)/*c*	$P\bar{1}$	*P*1	$P\bar{1}$
a [Å]	12.6130(10)	10.342(1)	10.3990 (6)	10.584(6)
b [Å]	14.6670(12)	12.5140(14)	11.4990 (7)	11.856(6)
c [Å]	13.6720(12)	18.550(2)	14.5830 (11)	13.473(7)
α [deg]		99.296(9)	107.170 (5)	65.461(4)
β [deg]	116.302(6)	104.196(8)	90.903(5)	88.144(4)
γ [deg]		105.977(8)	107.541(5)	67.808(4)
V [Å^{-3}]	2267.4(3)	2168.9(4)	1578.09(18)	1408.38(13)
crystal size [mm^3]	0.37 × 0.32 × 0.23	0.29 × 0.11 × 0.08	0.26 × 0.13 × 0.11	0.5 × 0.34 × 0.29
$\rho_{calcd.}$ [g.cm^{-3}]	1.293	1.352	1.130	1.266
μ [mm^{-1}] (Mo−Kα)	0.527	0.638	1.278	0.524
T [K]	133(2)	133(2)	133(2)	133(2)
θ range [deg]	1.80−25.79	1.17−25.74	1.47−25.71	1.68−25.63
no. unique refl.	4289	8203	11305	5307
no. of obsd. refl. [$I > 2\sigma(I)$]	3181	2474	6549	3642
no. of parameters	273	524	535	325
wR_2 (all data)	0.1333	0.2318	0.1063	0.1096
R value [$I > 2\sigma(I)$]	0.0528	0.0893	0.0505	0.0443

Table 5. Data of the X-ray Crystal Structure Analyses for Complexes 7, 8, 9, and 10

	7. 2×C_7H_8	8. 2×C_6H_6	9. 2×C_4D_8O	10
formula	$C_{64}H_{74}Cr_2Br_2N_4$	$C_{62}H_{70}Cr_2I_2N_4$	$C_{70}H_{84}Cr_2N_4O_2S_2$	$C_{62}H_{68}Cr_2N_4Se_2$
M_r g mol^{-1}	1163.09	1229.02	1181.55	1131.12
crystal system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	10.474(8)	13.6265(13)	11.5330(8)	11.3100(8)
b [Å]	11.937(9)	13.6621(12)	12.2980(10)	11.4090(9)
c [Å]	13.549(9)	16.0303(13)	12.9370(10)	11.8050(9)
α [deg]	65.290(5)	97.156(7)	102.624(6)	100.458(6)
β [deg]	88.590(6)	97.922(7)	107.411(6)	98.588(6)
γ [deg]	68.247(5)	110.392(7)	110.733(6)	111.989(6)
V [Å^{-3}]	1412.16(18)	2722.3(4)	1525.4(2)	1348.98(18)
crystal size [mm^3]	0.27 × 0.12 × 0.1	0.16 × 0.16 × 0.14	0.29 × 0.24 × 0.07	0.20 × 0.17 × 0.13
$\rho_{\text{calcd.}}$ [g.cm^{-3}]	1.368	1.499	1.286	1.392
μ [mm^{-1}] (Mo−Kα)	1.843	1.576	0.474	1.795
T [K]	133(2)	133(2)	133(2)	133(2)
θ range [deg]	1.67−25.68	1.31−26.17	1.77−24.59	1.81−25.81
no. unique refl.	5328	10275	5105	4518
no. of obsd. refl. [$I > 2\sigma(I)$]	3341	5433	2110	3012
no. of parameters	328	635	367	322
wR_2 (all data)	0.1754	0.1961	0.1672	0.1341
R value [$I > 2\sigma(I)$]	0.0641	0.0609	0.0680	0.0569

from purple to brown was observed within 5 min. The reaction solution was further stirred at ≈300 rpm for 4 h and then filtered using glass fiber filters. The filtrate was kept at −30 °C to afford brown crystals overnight. Yield: 0.079 g (73%). $C_{50}H_{58}Cr_2N_4O_4$ (883.00): calcd. C 68.01, H 6.62, N 6.34; found C 67.71, H 6.88, N 6.10. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.40 (d, 12H, J = 6.8 Hz, $H^{22,23,25,26}$), 1.41 (d, 12H, J = 6.8 Hz, $H^{22,23,25,26}$), 1.80 (s, 6H, $H^{13,14}$), 2.24 (s, 6H, $H^{13,14}$), 2.46 (sept, 2H, J = 6.8 Hz, $H^{21,24}$), 4.76 (sept, 2H, J = 6.8 Hz, $H^{21,24}$), 5.40 (d, 2H, J = 8.4 Hz, H^3), 5.85 (d, 2H, J = 6.8 Hz, H^5), 6.74−7.38 (m, 14H, $H^{4,9,10,11,17,18,19}$) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 19.8 ($C^{13,14}$), 20.2 ($C^{13,14}$), 24.4 ($C^{22,23,25,26}$), 24.7 ($C^{22,23,25,26}$), 25.0 ($C^{22,23,25,26}$), 28.1 ($C^{21,24}$), 28.7 ($C^{21,24}$), 101.0 (C^3), 111.8 (C^5), 123.9 ($C^{9,11}$), 124.3 ($C^{9,11}$), 127.2 (C^{18}), 127.5 ($C^{17,19}$), 136.2 (C^{10}), 136.5 (C^4), 136.7 ($C^{8,12}$), 140.2 (C^7), 142.6 ($C^{8,12}$), 145.3 ($C^{16,20}$), 147.4 (C^{15}), 157.9 (C^6), 173.5 (C^2) ppm (see Figure 5 for the labeling).

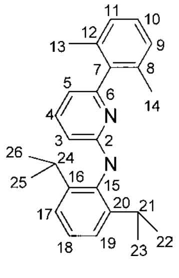


Figure 5. Labeling of the NMR signals.

*Synthesis of **3***. Toluene (5 mL) was added to a mixture of **1** (82 mg, 0.1 mmol) and S (7 mg, 0.2 mmol) at room temperature. The reaction mixture was stirred at ≈300 rpm for 2 h at room temperature as color changed to brown green. Red needles were obtained by cooling a hot toluene solution to room temperature overnight. Yield 0.052 g (58%). $C_{50}H_{58}Cr_2N_4S_2$ (882.29): calcd. C 68.00, H 6.62, N 6.34; found C 67.21, H 6.23, N 6.17. ^{1}H NMR (250 MHz, C_6D_6): δ = 0.31 (d, 6H, J = 6.7 Hz, $H^{22/23/25/26}$), 1.06 (d, 6H, J = 6.7 Hz, $H^{22/23/25/26}$), 1.11 (s, 6H, $H^{13,14}$), 1.14 (d, 6H, J = 6.7 Hz, $H^{22/23/25/26}$), 1.38 (d, 6H, J = 6.7 Hz, $H^{22/23/25/26}$), 2.24 (s, 6H, $H^{13,14}$), 2.84 (sept, 2H, J = 6.7 Hz, $H^{21/24}$), 3.51 (sept, 2H, J = 6.7 Hz, $H^{21/24}$), 5.73 (d, 2H, J = 6.5 Hz, H^3), 6.27 (d, 2H, J = 6.5 Hz, H^5), 6.33 (d, 2H, J = 8.9 Hz, $H^{17/19}$), 6.64−6.79 (m, 5H, $H^{4,9,11/17,19}$), 7.00−7.05 (m, 4H, $H^{10/18}$), 7.19 (m, 2H, $H^{9/11/17/19}$) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 18.9 ($C^{13,14}$), 22.1 ($C^{13,14}$), 23.6 ($C^{\ 22/23/25/26}$), 24.7 ($C^{22/23/25/26}$), 24.9 ($C^{22,23,/25,26}$), 25.4 ($C^{22,23/25,26}$), 27.9 ($C^{21,24}$), 29.6 ($C^{21,24}$), 108.9 (C^3), 109.8 (C^5), 124.0 (C^{10}), 125.7 ($C^{17,19}$), 125.9 ($C^{17,19}$), 127.2 (C^{18}), 127.8 (C^{18}), 128.5 (C^4), 135.5 ($C^{9,11}$), 135.8 ($C^{8,12}$), 137.1 (C^4), 138.5 (C^7), 143.9 ($C^{16,20}$), 144.4 ($C^{16,20}$), 144.9 (C^{15}), 157.8 (C^6), 171.9 (C^2) ppm.

*Synthesis of **4***. Toluene (5 mL) was added to a mixture of **1** (246 mg, 0.3 mmol) and Se (48 mg, 0.6 mmol) at room temperature. The reaction mixture was stirred at ≈300 rpm at 60 °C for 2 h as color changed to brown green. Red needles were obtained by cooling a hot toluene solution to room temperature overnight. Yield 0.180 g (61%) $C_{50}H_{58}Cr_2N_4Se_2$ (978.18): calcd. C 61.47, H 5.98, N 5.73; found C 61.48, H 5.76, N 5.72. ^{1}H NMR (300 MHz, C_6D_6): δ = 0.39 (d, 6H, J = 6.8 Hz, $H^{22/23/25/26}$), 1.03−1.06 (m, 12H, $H^{13,14,22,23,25,26}$), 1.11 (d, 6H, J = 6.8 Hz, $H^{22/23/25/26}$), 1.39 (d, 6H, J = 6.8 Hz, $H^{22/23/25/26}$), 2.18 (s, 6H, $H^{13,14}$), 3.09 (sept, 2H, J = 6.8 Hz, $H^{21/24}$), 3.53 (sept, 2H, J = 6.8 Hz, $H^{21/24}$), 5.74 (d, 2H, J = 6.7 Hz, H^3), 6.27 (d, 2H, J = 6.7 Hz, H^5), 6.32 (d, 2H, J = 9.1 Hz, $H^{17/19}$), 6.64−6.77 (m, 5H, $H^{4,9,11/17,19}$), 7.02−7.05 (m, 2H, $H^{10/18}$), 7.19 (m, 4H, $H^{9/11/17/19}$) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 18.8 ($C^{13,14}$), 22.6 ($C^{13,14}$), 23.7 ($C^{\ 22/23/25/26}$), 24.9 ($C^{22/23/25/26}$), 25.1 ($C^{22,23,/25,26}$), 25.3 ($C^{22,23/25,26}$), 27.9 ($C^{21,24}$), 29.6 ($C^{21,24}$), 109.1 (C^3), 110.0 (C^5), 124.2 (C^{10}), 125.7 ($C^{17,19}$), 126.1 ($C^{17,19}$), 127.1 (C^{18}), 128.5 (C^4), 134.0 (C^{10}), 135.5 ($C^{9,11}$), 135.2 ($C^{8,12}$), 135.7 ($C^{8,12}$), 137.3 (C^4), 138.6 (C^7), 144.3 ($C^{16,20}$), 144.4 ($C^{16,20}$), 145.2 (C^{15}), 157.8 (C^6), 172.6 (C^2) ppm.

*Synthesis of **5***. Toluene (5 mL) was added to a mixture of **1** (41 mg, 0.05 mmol) and Te (25 mg, 0.2 mmol) at room temperature, and the reaction mixture was then heated at 60 °C and stirred at ≈300 rpm for 3 h as color changed to brown green. The solution was filtered using glass fiber filters, and the volume of the filtrate was reduced to about 1 mL to afford red crystals overnight at low temperature. Yield 0.025 g (47%). $C_{50}H_{58}Cr_2N_4Te_2\cdot C_7H_8$ (1074.21): calcd: C 58.70, H 5.70, N 4.80; found C 58.46, H 6.09, N 5.35. ^{1}H NMR (250 MHz, C_6D_6): δ = 0.49 (d, 6H, J = 6.7 Hz, $H^{22/23/25/26}$), 0.96 (s, 6H, $H^{13,14}$), 1.01−1.06 (m, 12H, $H^{22/23/25/26}$), 1.42 (d, 6H, J = 6.7 Hz, $H^{22/23/25/26}$), 2.11 (s, 12H, $H^{13,14}$), 3.47 (sept, 2H, J = 6.7 Hz, $H^{21/24}$), 3.59 (sept, 2H, J = 6.7 Hz, $H^{21/24}$), 5.79 (d, 2H, J = 4.9 Hz, H^3), 6.25 (d, 2H, J = 6.5 Hz, H^5), 6.33 (d, 2H, J = 8.9 Hz, $H^{17/19}$), 6.66−6.77 (m, 5H, $H^{4/10}$), 7.03−7.18 (m, 6H, $H^{10/18,9/11/17/19}$) ppm.

*Synthesis of **6***. Cl_2 (ca. 0.2 bar) was introduced into a solution of **1** (0.4 g, 0.48 mmol) in toluene (10 mL) at room temperature with continuous stirring. A color change from purple to red-brown was observed within 10 min. The mixture was stirred at ≈300 rpm under Cl_2 atmosphere overnight after which some dark precipitate had formed. Then the solution was filtered using glass fiber filters, and the filtrate was kept at −30 °C to afford brown crystals. Yield 0.032g (33%). $C_{50}H_{58}Cr_2N_4Cl_2 \cdot C_7H_8$ (980.3): calcd. C 69.71, H 6.77, N 5.71; found C 69.95, H 6.81, N 5.26. ^1H NMR (400 MHz, C_6D_6, 298 K): δ = 1.09 (d, 12H, J = 7.5 Hz, $H^{22/23/25/26}$), 1.40 (d, 12H, J = 7.5 Hz, $H^{22/23/25/26}$), 2.80 (s, 6H, $H^{13/14}$), 4.71 (sept, 2H, J = 7.5 Hz, $H^{21/24}$), 5.20 (d, 2H, J = 7.5 Hz, H^3), 6.17 (d, 2H, J = 5.2 Hz, H^5), 6.38 (t, 2H, J = 5.2 Hz, H^4), 6.98−7.37 (m, 12H, $H^{9/10/11,17/18/19}$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 20.5 ($C^{13/14}$), 23.8 ($C^{22/23/25/26}$), 28.7 ($C^{21/24}$), 103.7 (C^3), 114.5 (C^5), 124.2 ($C^{9/11}$), 125.6 ($C^{17/19}$), 127.7 (C^{18}), 128.0 (C^{10}), 134.1 ($C^{8/12}$), 135.9 ($C^{8/12}$), 137.9 (C^4), 142.0 (C^7), 148.1 ($C^{16/20}$), 154.3 (C^{15}), 159.5(C^6), 160.0 (C^2) ppm.

*Synthesis of **7**.* Br_2 (7 μL, 0.1 mmol) was added to a solution of **1** (82 mg, 0.1 mmol) in toluene (10 mL) at room temperature with continuous stirring at ≈300 rpm. A color change from purple to brown was observed. The reaction solution was filtered using glass fiber filters, and the filtrate was kept at −30 °C to afford brown crystals. Yield 0.052g (48%). $C_{50}H_{58}Cr_2N_4Br_2 \cdot C_7H_8$ (1070.7): calcd. C 63.92, H 6.21, N 5.23; found C 64.17, H 5.39, N 5.35. ^1H NMR (400 MHz, C_6D_6, 298 K): δ = 1.10 (d, 12H, J = 6.5 Hz $H^{22/23/25/26}$), 1.32 (d, 12H, J = 6.5 Hz, $H^{22/23/25/26}$), 2.38 (s, 6H, $H^{13/14}$), 5.37 (sept, 2H, J = 6.8 Hz, $H^{21/24}$), 5.52 (d, 2H, J = 6.8 Hz, H^3), 6.15 (d, 2H, J = 6.5 Hz, H^5), 6.28 (t, 2H, J = 6.5 Hz, H^4), 6.49 (m, 6H, $H^{17/18/19}$), 6.96−7.36 (m, 12H, $H^{9/10/11}$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 19.8 ($C^{13/14}$), 20.5 ($C^{13/14}$), 23.7 ($C^{22/23/25/26}$), 24.6 ($C^{22/23/25/26}$), 25.7 ($C^{22/23/25/26}$), 28.7 ($C^{21/24}$), 103.7 (C^3), 114.6 (C^5), 124.2 ($C^{9/11}$), 124.9 ($C^{17/19}$), 125.6 (C^{18}), 127.7 (C^{10}), 130.1 ($C^{8/12}$), 135.8 ($C^{8/12}$), 137.2 (C^4), 137.9 (C^7), 142.2 ($C^{16/20}$), 148.0 (C^{15}), 148.7 (C^6), 160.4 (C^2) ppm.

*Synthesis of **8**.* I_2 (6 mg, 0.025 mmol) was added to a solution of **1** (21 mg, 0.025 mmol) in C_6D_6 (0.5 mL) at room temperature and was shaken briefly. A color change from purple to brown was observed. Standing of the solution at room temperature afforded red crystals. $C_{50}H_{58}Cr_2N_4I_2$ (1072.16): Calc. C 55.98, H 5.45, N 5.22; found. C 55.99, H 5.88, N 4.78. ^1H NMR (400 MHz, C_6D_6): δ = 1.14 (br d, 12H, $H^{22,23,25,26}$), 1.24 (br d, 12H, $H^{22,23,25,26}$), 2.19 (s, 6H, $H^{13,14}$), 3.97 (br sept, 2H, $H^{21,24}$), 5.74 (d, 2H, J = 6.8 Hz, H^3), 6.15 (d, 2H, J = 6.5 Hz, H^5), 6.28 (t, 2H, J = 6.5 Hz, H^4), 6.49 (m, 6H, $H^{17,18,19}$), 6.96−7.36 (m, 12H, $H^{9,10,11}$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 19.8 ($C^{13,14}$), 20.5 ($C^{13,14}$), 23.7 ($C^{22,23,25,26}$), 24.6 ($C^{22,23,25,26}$), 25.7 ($C^{22,23,25,26}$), 28.7 ($C^{21,24}$), 103.7 (C^3), 108.1 (C^5), 124.2 ($C^{9,11}$), 124.9 ($C^{17,19}$), 125.6 (C^{18}), 127.7 (C^{10}), 134.7 ($C^{8,12}$), 135.8 ($C^{8,12}$), 137.2 (C^4), 140.2 (C^7), 142.2 ($C^{16,20}$), 148.0 (C^{15}), 148.7 (C^6), 160.0 (C^2) ppm.

*Synthesis of **9**.* Toluene (20 mL) was added to a mixture of **1** (82 mg, 0.1 mmol) and Ph_2SSPh_2 (22 mg, 0.1 mmol) at room temperature, and the resulting green reaction mixture was stirred at ≈300 rpm at room temperature for 6 h. Standing of the solution at room temperature afforded red crystalline material over 48 h. Yield 0.072 g (69%). $C_{62}H_{68}Cr_2N_4S_2$ (1037.36): calcd. C 71.79, H 6.61, N 5.40; found C 71.94, H 6.60, N 5.54. ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 0.87 (br d, 12H, $H^{22/23/25/26}$), 0.96 (br d, 12H, $H^{22/23/25/26}$), 2.19 (s, 12H, $H^{13/14}$), 3.80 (br sept, 4H, $H^{21/24}$), 5.95 (d, 2H, J = 6.3 Hz, H^3), 6.42 (br t, 2H, H^4), 6.49 (d, 2H, J = 8.5 Hz, H^5), 6.90−7.41 (m, 16H, $H^{9/10/11,17/18/19/Ph}$) ppm.

*Synthesis of **10**.* Toluene (20 mL) was added to a mixture of **1** (82 mg, 0.1 mmol) and $Ph_2SeSePh_2$ (32 mg, 0.1 mmol) at room temperature, and the resulting green reaction mixture was stirred at ≈300 rpm at room temperature for 6 h. Standing of the solution at room temperature afforded red crystalline material overnight. Yield 0.083 g (73%). $C_{62}H_{68}Cr_2N_4Se_2$ (1131.14): calcd. C 65.83, H 6.06, N 4.95; found C 64.65, H 5.90, N 4.77. ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 0.47 (m, 12H, $H^{22/23/25/26}$), 1.35 (br d, 6H, $H^{22/23/25/26}$), 1.42 (br d, 6H, $H^{22/23/25/26}$), 1.96 (s, 6H, $H^{13/14}$), 2.40 (s, 6H, $H^{13/14}$), 2.96 (sept, 2H, J = 7.5 Hz, $H^{21/24}$), 4.71 (sept, 2H, J = 7.5 Hz, $H^{21/24}$), 5.95 (d, 2H, J = 7.5 Hz, H^3), 6.42 (t, 2H, J = 6.9 Hz, H^4), 6.52 (d, 2H, J = 8.7 Hz, H^5), 6.65−7.05 (m, 16H, $H^{9/10/11,17/18/19/Ph}$) ppm.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Kempe@uni-bayreuth.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the Deutsche Forschungsgemeinschaft (DFG KE 756/20-1) is gratefully acknowledged. E.S.T. thanks the Deutscher Akademischer Austausch Dienst (DAAD) for a Ph.D. scholarship.

■ REFERENCES

(1) (a) Wagner, F.; Noor, A.; Kempe, R. *Nat. Chem* **2009**, *1*, 529−536. (b) Cotton, F. A.; Murillo, L. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 3rd ed.; Springer: Berlin, Germany, 2005.

(2) Roos, B. O.; Borin, A. C.; Gagliardi, L. *Angew. Chem.* **2007**, *119*, 1491−1494; *Angew. Chem., Int. Ed.* **2007**, *46*, 1469−1472.

(3) Morse, M. D. *Chem. Rev.* **1986**, *86*, 1049−1109.

(4) (a) Efremov, Y. M.; Samoilova, A. N.; Gurvich, L. V. *Opt. Spektrosc.* **1974**, *36*, 654−657. (b) Künding, E. P.; Moskovits, M.; Ozin, G. A. *Nature* **1975**, *254*, 503−504. (c) Klotzbücher, W.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 984−987. (d) Bondybey, V. E.; English, J. H. *Chem. Phys. Lett.* **1983**, *94*, 443−447.

(5) Nguyen, T.; Sutton, A. D.; Brynda, M.; Fettinger, J. C.; Long, G. J.; Power, P. P. *Science* **2005**, *310*, 844−847.

(6) (a) Kreisel, K. A.; Yap, G. P. A.; Dmitrenko, O.; Landis, C. R.; Theopold, K. H. *J. Am. Chem. Soc.* **2007**, *129*, 14162−14163. (b) Wolf, R.; Ni, C.; Nguyen, T.; Brynda, M.; Long, G. J.; Sutton, A. D.; Fischer, R. C.; Fettinger, J. C.; Hellman, M.; Pu, L.; Power, P. P. *Inorg. Chem.* **2007**, *46*, 11277−11290. (c) Noor, A.; Wagner, F. R.; Kempe, R. *Angew. Chem.* **2008**, *120*, 7356−7359;(d) *Angew. Chem., Int. Ed.* **2008**, *47*, 7246−7249. (e) Tsai, Y.-C.; Hsu, C.-W.; Yu, J.-S. K.; Lee, G.-H.; Wang, Y.; Kuo, T.-S. *Angew. Chem.* **2008**, *120*, 7360−7363;(f) *Angew. Chem., Int. Ed.* **2008**, *47*, 7250−7253. (g) Hsu, C.-W.; Yu, J.-S. K.; Yen, C.-H.; Lee, G.-H.; Wang, Y.; Tsai, Y.-C. *Angew. Chem.* **2008**, *120*, 10081−10084;(h) *Angew. Chem., Int. Ed.* **2008**, *47*, 9933−9936.

(7) Noor, A.; Kempe, R. *Chem. Rec.* **2010**, *10*, 413−416.

(8) Noor, A.; Glatz, G.; Müller, R.; Kaupp, M.; Demeshko, S.; Kempe, R. *Z. Anorg. Allg. Chem.* **2009**, *635*, 1149−1152.

(9) Huang, Y.−L.; Lu, D.-Y.; Yu, H.-C.; Yu, J.-S. K.; Hsu, C.-W.; Kuo, T.-S.; Lee, G.-H.; Wang, Y.; Tsai, Y.-C. *Angew. Chem.* **2012**, *124*, 7901−7905; *Angew. Chem., Int. Ed.* **2012**, *51*, 7781−7785.

(10) (a) Tsai, Y.-C.; Chen, H.-Z.; Chang, C.-C.; Yu, J.-S. K.; Lee, G.-H.; Wang, Y.; Kuo, T.-S. *J. Am. Chem. Soc.* **2009**, *131*, 12534−12535. (b) Liu, S.-C.; Ke, W.-L.; Yu, J.-S. K.; Kuo, T.-S.; Tsai, Y.-C. *Angew. Chem.* **2012**, *124*, 6500−6503; *Angew. Chem., Int. Ed.* **2012**, *51*, 6394−6397.

(11) (a) Noor, A.; Glatz, G.; Müller, R.; Kaupp, M.; Demeshko, S.; Kempe, R. *Nat. Chem.* **2009**, *1*, 322−325. (b) Noor, A.; Tamne, E. S.; Qayyum, S.; Bauer, T.; Kempe, R. *Chem.—Eur. J.* **2011**, *17*, 6900−6903. (c) Schwarzmaier, C.; Noor, A.; Glatz, G.; Zabel, M.; Timoshkin, A. Y.; Cossairt, B. M.; Cummins, C. C.; Kempe, R.; Scheer, M. *Angew. Chem.* **2011**, *123*, 7421−7424. (d) *Angew. Chem., Int. Ed.* **2011**, *50*, 7283−7286.

(12) Ni, C.; Ellis, B. D.; Long, G. J.; Power, P. P. *Chem. Commun.* **2009**, 2332−2334.

(13) Shen, J.; Yap, G. P. A.; Werner, J.-P.; Theopold, K. H. *Chem. Commun.* **2011**, *47*, 12191−12193.

(14) Chen, H.-Z.; Liu, S.-C.; Yen, C.-H.; Yu, J.-S. K.; Shieh, Y.-J.; Kuo, T.-S.; Tsai, Y.-C. *Angew. Chem.* **2012**, *51* (41), 10342−10346; *Angew. Chem., Int. Ed.* **2012**, *51* (41), 10342−10346.

(15) (a) Nishino, H.; Kochi, J. K. *Inorg. Chim. Acta* **1990**, *174*, 93−102. (b) Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *Polyhedron* **1996**, *15*, 873−879.

(16) Herberhold, M.; Kremnitz, W.; Razavi, A.; Schollhorn, H.; Thewalt, U. *Angew. Chem.* **1985**, *97*, 603−604; *Angew. Chem., Int. Ed.* **1985**, *24*, 601−602.

(17) Muller, A.; Jaegermann, W. *Inorg. Chem.* **1979**, *18*, 2631−2632.

(18) Goh, L. Y.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1986**, 1474−1476.

(19) Brunner, H.; Pfauntsch, J.; Wachter, J.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1989**, *359*, 179−188.

(20) Brunner, H.; Wachter, J.; Guggolz, E.; Ziegler, M. L. *J. Am. Chem. Soc.* **1982**, *104*, 1765−1766.

(21) Preuss, F.; Billen, M.; Tabellion, F.; Wolmershäuser, G. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2446−2448.

(22) Bachman, R. E.; Whitmire, K. H. *J. Organomet. Chem.* **1994**, *479*, 31−35.

(23) Ni, C.; Power, P. P. *Struct. Bonding (Berlin, Germany)* **2010**, *136*, 59−112 ; Metal-Metal Bonding Issue.

(24) (a) Handy, L. B.; Ruff, J. K.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7327−7337. (b) Morse, D. B.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1990**, *112*, 1860−1864. (c) Burin, M. E.; Smirnova, M. V.; Fukin, G. K.; Baranov, E. V.; Bochkarev, M. N. *Eur. J. Inorg. Chem.* **2006**, 351−356.

(25) Deeken, S.; Motz, G.; Kempe, R. *Z. Anorg. Allg. Chem.* **2007**, *633*, 320−325.

(26) Cotton, F. A. *Multiple Bonds Between Metal Atoms*; Wiley, New York, 1982.

(27) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

(28) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112−122.

(29) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.