Inorganic Chemistry
Article
pubs.acs.org/IC

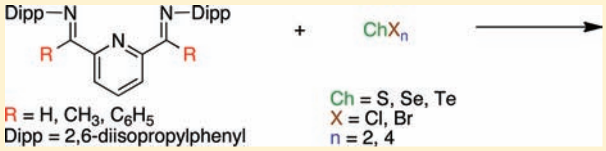
Reactions of Diiminopyridine Ligands with Chalcogen Halides

Caleb D. Martin and Paul J. Ragogna*

Department of Chemistry, The Chemistry Building, The University of Western Ontario, 1151 Richmond Street, London, Ontario, Canada N6A 5B7

Supporting Information

ABSTRACT: The reactions of the chalcogen halides (Ch = S, Se, Te) with a series of diiminopyridine (DIMPY) ligands were explored. It was determined through these studies that varying both the substitution on the α-carbon and the chalcogen halide reagent afforded different products. If methyl groups were present on the α-carbon, reactivity was observed through the eneamine tautomer to yield *N,N′,C*-bound neutral chalcogen complexes. In the cases where H and C_6H_5 groups were in the same position, *N,N′,N″*-chelated chalcogen cations or dications were produced. Many of the reactions resulted in complex mixtures postulated to occur by the release of halogen decomposing the product or, for reactions with the CH_3 substituted ligand, uncontrollable reactivity with the eneamine tautomer. This is the first report of reactions of sulfur and selenium halides with the ubiquitous diiminopyridine ligands and only the second example for a tellurium halide.



■ INTRODUCTION

The use of α-diimine ligands (e.g., diazabutadiene, DAB; diiminopyridine, DIMPY; Figure 1; **1**–**5**) in transition metal chemistry has opened a gateway to a plethora of new discoveries, especially in catalysis.[1] The main group chemistry of these ligands is far less developed.[2−12] The traditional bonding motif for these Schiff bases has typically been via chelation through the nitrogen centers in the multidentate ligands. In virtually all cases, reports detailing the use of the 1,4-diazabutadiene (DAB) ligand with group 13–15 halides produce *N,N′*-bound species regardless of the substitution on the backbone carbon atom.[13−21] For the chalcogens it was determined that, with varying the substitution on the backbone carbon atom within the ligands, different products were obtained.[22−30] Hydrogen atoms, phenyl groups, or an acenaphthene backbone led to the formation of *N,N′*-chelate chalcogen complexes of $TeCl_2$, $TeBr_4$, $SeCl_2$, $SeBr_2$, and Ch^{2+} (Ch = S, Se, Te; Figure 2; **6**–**9**) whereas a methyl group on the α-carbon resulted in N,C-bound heterocycles (**10**–**19**), which was postulated to occur by reaction with the enamine tautomer of the ligand (**4′** and **5′**).[25] The tellurium(IV) halides formed heterocycles featuring an exocyclic imine, whereas when using sulfur and selenium(II) halides exocyclic amines were observed.

Recent discoveries have indicated the DIMPY ligands have the ability to stabilize low oxidation state main group centers (e.g., In(I), As(I), P(I), S(II), Se(II), and Te(II)).[4,8,31−33] Our recent report of the first *N,N′,N″*-DIMPY chalcogen complexes (Ch = S, Se, Te; **20**–**23**), by the facile reaction of a chalcogen bistriflate synthon and ligand **1**, indicated that the tridentate chelate imposed remarkable stability to the dicationic complexes, differing greatly from other chalcogen(II) dications, in particular the very unstable dicationic DAB complexes (**7**).[31] Aside from these systems there has only been one report of a reaction of this class of ligands with the chalcogen halides reported by Cowley et al.[28] The reaction described was $TeCl_4$ using a methyl substituted DIMPY (**2**), which resulted in a *N,N′,C*-bound tellurium complex (**24**), rather than the expected *N,N′,N″*-bound species as observed in the DAB chemistry, once again believed to occur through reaction with the enamine tautomer (**2′**). In this context, we report a synthetic study of the DIMPY ligand with the chalcogen halides varying the substitution at the α-carbon within the ligand, while keeping the groups on the imine nitrogens constant. The difference of a hydrogen versus a methyl or phenyl group greatly influenced the reaction outcome giving either neutral, monocationic, or dicationic chalcogen centers. In some cases uncontrolled halogenation occurred resulting in complex mixtures, indicating that the reactivity of the group 16 halides with the diiminopyridine ligands is not necessarily predictable.

■ EXPERIMENTAL SECTION

All manipulations were performed under an inert atmosphere in a nitrogen filled MBraun Labmaster dp glovebox or using standard Schlenk techniques. Sulfur dichloride, $SeCl_2$, $SeBr_2$, **1**, **2**, and **3** were synthesized according to the literature procedures.[2,33−37] The $SbPh_3Cl_2$ generated from the production of $SeCl_2$ could be easily separated from the desired products in all cases by washing with Et_2O. Selenium tetrabromide, $SeCl_4$, $TeCl_4$, and $TeBr_4$ were purchased from Alfa Aesar and used as received. Dichloromethane, CH_3CN, *n*-pentane, THF, and Et_2O were obtained from Caledon Laboratories and dried using an MBraun Controlled Atmospheres Solvent Purification System. The dried solvents were stored in Strauss flasks under a N_2 atmosphere, or over 4 Å molecular sieves in the glovebox (3 Å for MeCN). Solvents used for ^1H NMR spectroscopy (CD_3CN and $CDCl_3$) were purchased from Sigma-Aldrich, and dried by storing in the glovebox over 3 or 4 Å molecular sieves. Multinuclear NMR data are listed in ppm, relative to Me_4Si (^{13}C and ^1H), coupling constants are in Hertz, and all NMR spectra were recorded on an

Received: October 12, 2011
Published: February 16, 2012

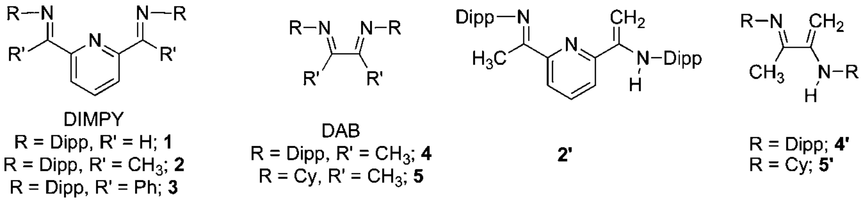


Figure 1. Structures of the diiminopyridine (DIMPY) and diazabutadiene (DAB) ligands and the corresponding enamine tautomers of the methyl substituted derivatives (Dipp = 2,6-diisopropylphenyl; Cy = cyclohexyl).

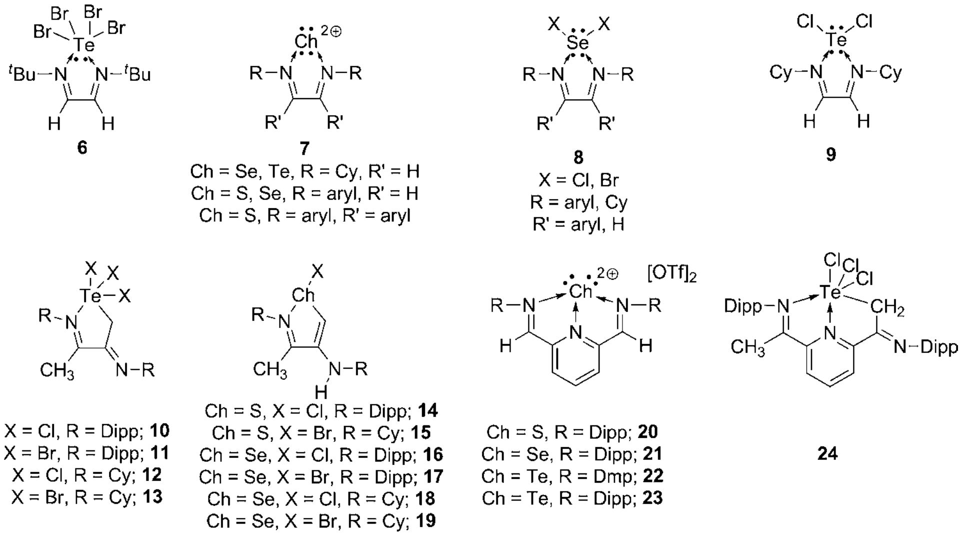


Figure 2. Reaction products of chalcogen halides with DAB and DIMPY ligands (Dmp = 2,6-dimethylphenyl).

INOVA 400 MHz (^{1}H = 399.76 MHz, ^{13}C = 100.52 MHz) spectrometer or INVOVA 600 MHz spectrometer. Single crystal X-ray diffraction data were collected on a Nonius Kappa-CCD area detector or a Bruker Apex II-CCD using Mo Kα radiation (λ = 0.710 73 Å). Crystals were selected under Paratone-N oil, mounted on nylon loops or micromounts, and then immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL.

Samples for FT-Raman spectroscopy were packed in capillary tubes and flame-sealed. Data were collected using a Bruker RFS 100/S spectrometer, with a resolution of 4 cm^{-1}. FT-IR spectra were collected on samples as KBr pellets using a Bruker Tensor 27 spectrometer, with a resolution of 4 cm^{-1}. Decomposition points were recorded in flame-sealed capillary tubes using a Gallenkamp variable heater.

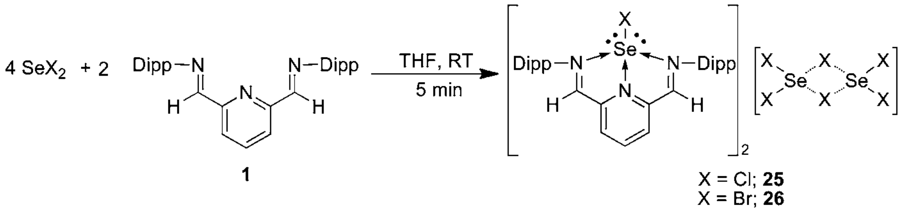
Synthesis of 25. A solution of **1** (0.077 g, 0.170 mmol in 3 mL of THF) was added to a freshly prepared solution of $SeCl_2$ (0.341 mmol in 6 mL of THF) and stirred for 5 min resulting in a red slurry. Normal pentane (6 mL) was added resulting in the formation of more solids. The supernatant was decanted, and the resulting solids were washed with Et_2O (3 × 5 mL). The red powder was dried *in vacuo*. Yield: 0.110 g, 86%. Crystals suitable for X-ray diffraction studies were grown by vapor diffusion of Et_2O into a saturated CH_3CN solution. Decomposition point: 180−182 °C. ^{1}H NMR (CD_3CN, δ) 9.78 (s, 2H, α-C*H*), 9.07 (br, 2H, *m*-H pyridine), 8.96 (br, 1H, *p*-H pyridine), 7.46 (t, 2H, ^3J = 7.6 Hz, *p*-H C_6H_3), 7.37 (d, 4H, ^3J = 7.6 Hz, *m*-H C_6H_3), 2.67 (br, 4H, C*H*(CH_3)$_2$), 1.19 (br, 24H, CH(C*H*$_3$)$_2$). ESI-MS *m*/*z* 567 [M$^+$]. HRMS found (calcd for $C_{33}H_{42}N_3Se_1$): [M$^+$ − HCl] 560.2540 (560.2544).

Synthesis of 26. A solution of **1** (0.115 g, 0.253 mmol in 3 mL of THF) was added to a freshly prepared solution of $SeBr_2$ (0.507 mmol in 6 mL of THF) and stirred for 5 min resulting in a deep red slurry. Normal pentane (6 mL) was added resulting in the formation of more solids. The supernatant was decanted and the red powder was dried *in vacuo*. Yield: 0.196 g, 84%. Crystals suitable for X-ray diffraction studies were grown by vapor diffusion of Et_2O into a saturated CH_3CN solution. Decomposition point: 130−132 °C. ^{1}H NMR (CD_3CN, δ) 9.81 (s, 2H, α-C*H*), 9.09 (d, 2H, ^3J = 7.8 Hz, *m*-H pyridine), 8.99 (t, 1H, ^3J = 7.8 Hz, *p*-H pyridine), 7.47 (t, 2H, ^3J = 7.8 Hz, *p*-H C_6H_3), 7.39 (d, 4H, ^3J = 7.8 Hz, *m*-H C_6H_3), 2.66 (sept, 4H, ^3J = 6.0 Hz, C*H*(CH_3)$_2$), 1.22 (d, 12H, ^3J = 6.0 Hz, CH(C*H*$_3$)$_2$), 1.17 (d, 12H, ^3J = 5.4 Hz, CH(C*H*$_3$)$_2$). ESI-MS *m*/*z* 612 [M$^+$], M = $C_{31}H_{39}N_3SeBr$.

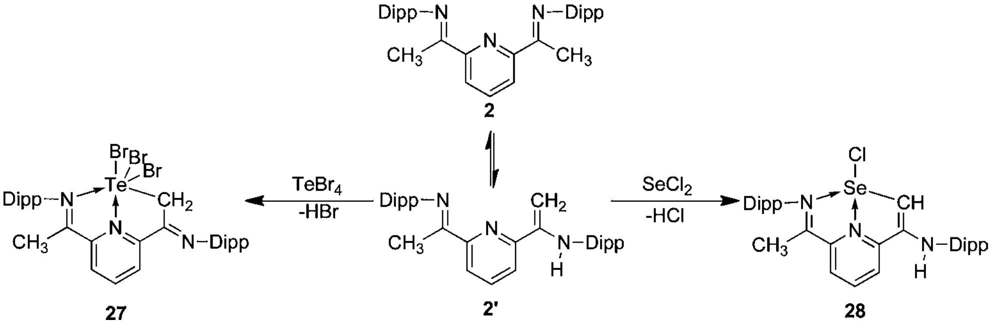
Synthesis of 27. A solution of **2** (0.100 g, 0.208 mmol in 3 mL of THF) was added to a solution of $TeBr_4$ (0.093 g, 0.208 mmol in 3 mL of THF) and stirred for 4 h resulting in an orange solution. The mixture was centrifuged and the solvent removed *in vacuo* from the supernatant producing an orange powder. Yield: 0.109 g, 62%. Crystals for X-ray diffraction studies were grown from vapor diffusion of *n*-pentane into THF. Decomposition point: 171−173 °C. ^{1}H NMR ($CDCl_3$, δ) 8.79 (d, 1H, ^3J = 8.0 Hz, *m*-H pyridine), 8.46 (t, 1H, ^3J = 8.0 Hz, *p*-H pyridine), 8.25 (d, 1H, ^3J = 7.6 Hz, *m*-H pyridine), 7.25−7.17 (m, 6H, *m*, *p*-H C_6H_3), 4.57 (s, 2H, CH_2), 2.97 (sept, 2H, ^3J = 7.2 Hz, C*H*(CH_3)$_2$), 2.79 (sept, 2H, ^3J = 7.2 Hz, C*H*(CH_3)$_2$), 2.37 (s, 3H, C*H*$_3$), 1.27 (overlapping doublets, 12H, CH(C*H*$_3$)$_2$), 1.13 (overlapping doublets, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ) 160.8, 146.2, 142.5, 141.4, 133.8, 133.6, 132.1, 131.6, 129.6, 127.2, 125.1, 28.4, 26.5, 23.4. ^{125}Te{^{1}H} NMR (CD_2Cl_2, δ) 1290.

Synthesis of 28. A solution of **2** (0.164 g, 0.342 mmol in 4 mL THF) was added to a freshly prepared solution of $SeCl_2$ (0.341 mmol in 4 mL of THF) and stirred for 5 min generating a red solution. Normal pentane (8 mL) was added to the mixture resulting in a red precipitate. The supernatant was removed, the solids were washed with Et_2O (5 × 5 mL), and the red solids were dried *in vacuo*. Yield: 0.129 g, 58%. Decomposition point: 188−190 °C. ^{1}H NMR ($CDCl_3$, δ) 8.36−8.23 (m, 2H, *m*, *p*-H pyridine), 8.17 (s, 1H, C*H*), 8.02 (d, 1H, ^3J = 7.2 Hz, *m*-H pyridine), 7.58−7.56 (m, 1H, *p*-H C_6H_3), 7.30−7.16 (m, 5H, *m*, *p*-H C_6H_3), 4.44 (s, 1H, N*H*), 3.11 (sept, 2H, ^3J = 6.8 Hz, C*H*(CH_3)$_2$), 2.69 (sept, 2H, ^3J = 6.8 Hz, C*H*(CH_3)$_2$), 2.37 (s, 3H, C*H*$_3$), 1.22 (d, 18H, ^3J = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.14 (d, 6H, ^3J = 6.8 Hz, CH(C*H*$_3$)$_2$).

Scheme 1. Reaction of Selenium Dihalides with 1 To Produce 25 and 26



Scheme 2. Reactions of $TeBr_4$ and $SeCl_2$ with 2



Synthesis of 29. A solution of **3** (0.150 g, 0.247 mmol in 4 mL of CH_2Cl_2) immediately generating a yellow solution. The solution was stirred for 5 min, *n*-pentane added (9 mL) and the reaction vessel stored at −35 °C overnight resulting in the formation of a large crop of yellow crystals. The supernatant was decanted, and the crystals were dried *in vacuo*. Yield: 95%, 0.166 g. Crystals suitable for X-ray diffraction studies were grown by vapor diffusion of *n*-pentane into a solution of **29** in chloroform. Decomposition point: 124−127 °C. ^1H NMR (CD_3CN, δ) 9.47 (d, 2H, ^3J = 8.4 Hz, *m*-H pyridine), 9.30 (t, 1H, ^3J = 8.4 Hz, *p*-H pyridine), 7.83−7.81 (m, 2H, *p*-H C_6H_5), 7.72−7.68 (m, 8H, *o*, *m*-H C_6H_5), 7.60 (t, 2H, ^3J = 7.8 Hz, *p*-C_6H_3), 7.41 (d, 4H, ^3J = 7.8 Hz, *m*-H C_6H_5), 2.87 (sept, 4H, ^3J = 6.6 Hz, $CH(CH_3)_2$), 1.14 (d, 12H, ^3J = 7.2 Hz, $CH(CH_3)_2$), 0.81 (d, 12H, ^3J = 6.6 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ) 160.8, 146.2, 142.5, 141.4, 133.8, 133.6, 132.1, 131.6, 129.6, 127.2, 125.1, 28.4, 26.5, 23.4. HRMS found (calcd for $C_{43}H_{47}N_3S_1$): [M^+] 637.3484 (637.3475).

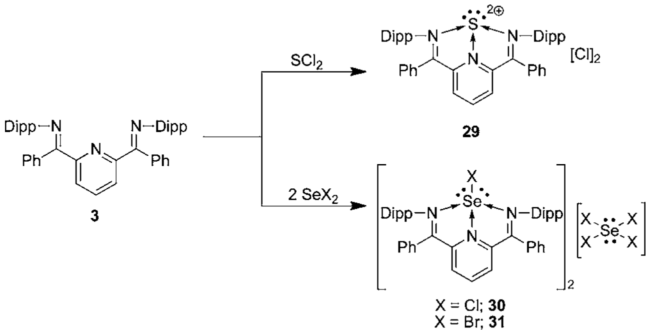
Synthesis of 30. A solution of **3** (0.075 g, 0.124 mmol in 2 mL of THF) was added to a freshly prepared solution of $SeCl_2$ (3.72 mmol in 6 mL of THF) and stirred 5 min generating a red solution. Normal pentane (10 mL) was added to the solution precipitating orange material. The mixture was stored at −35 °C for 30 min and centrifuged. The supernatant was decanted, and the solids were washed with Et_2O (2 × 6 mL). The solids were dried *in vacuo* giving an orange powder. Yield: 0.090 g, 66%. X-ray quality crystals of **30** were obtained by vapor diffusion of *n*-pentane into a saturated CH_2Cl_2 solution. Decomposition point: 174−177 °C. ^1H NMR (CD_3CN, δ) 8.97−8.89 (m, 3H, *m*, *p*-H pyridine), 7.71 (t, 2H, ^3J = 7.2 Hz, *p*-H C_6H_5), 7.63−7.59 (m, 4H, *m*-H C_6H_5), 7.49 (d, 4H, ^3J = 7.2 Hz, *o*-H C_6H_5), 7.41 (t, 2H, ^3J = 8.0 Hz, *p*-H C_6H_3), 7.28 (d, 4H, ^3J = 8.0 Hz, *m*-H C_6H_3), 2.72 (sept, 4H, ^3J = 6.8 Hz, $CH(CH_3)_2$), 1.27 (d, 12H, ^3J = 6.8 Hz, $CH(CH_3)_2$), 0.96 (d, 12H, ^3J = 6.4 Hz, $CH(CH_3)_2$). ESI-MS *m/z* 685 [M^+ − Cl], M = $C_{43}H_{47}N_3SeCl$.

Synthesis of 31. A solution of **3** (0.075 g, 0.124 mmol in 2 mL of THF) was added to a freshly prepared solution of $SeBr_2$ (3.72 mmol in 6 mL of THF) and stirred 5 min resulting in a dark red solution. A red precipitate was generated after adding *n*-pentane (10 mL) to the mixture. The supernatant was removed, and the remaining solids were washed with Et_2O (2 × 6 mL). Yield: 68%, 0.125 g. Decomposition point: 182−184 °C. ^1H NMR (CD_3CN, δ) 9.09−9.03 (m, 3H, *m*, *p*-H pyridine), 7.73 (t, 2H, ^3J = 7.2 Hz, *p*-H C_6H_5), 7.65−7.61 (m, 4H, *m*-H C_6H_5), 7.54 (d, 4H, ^3J = 8.0 Hz, *o*-H C_6H_5), 7.45 (t, 2H, ^3J = 8.0 Hz, *p*-H C_6H_3), 7.31 (d, 4H, ^3J = 8.0 Hz, *m*-H C_6H_3), 2.73 (sept, 4H, ^3J = 6.8 Hz, $CH(CH_3)_2$), 1.24 (d, 12H, ^3J = 6.8 Hz, $CH(CH_3)_2$), 0.94 (d, 12H, ^3J = 6.8 Hz, $CH(CH_3)_2$). HRMS found (calcd for $C_{43}H_{47}N_3Se_1$): [M^+ − HCl] 585.2905 (585.2935).

■ RESULTS AND DISCUSSION

Synthesis. The 1:1 stoichiometric reaction of a selenium dihalide with the hydrogen substituted ligand (**1**) in THF immediately gives orange (X = Cl; **25**) or red (X = Br; **26**) slurries. The products were precipitated from solution by the addition of *n*-pentane to yield fine orange and red powders, respectively. The supernatant was decanted, and the solids were dried *in vacuo*. Redissolving a sample of the powders in CD_3CN

Scheme 3. Reactions of SCl_2 and $SeCl_2$ with 3



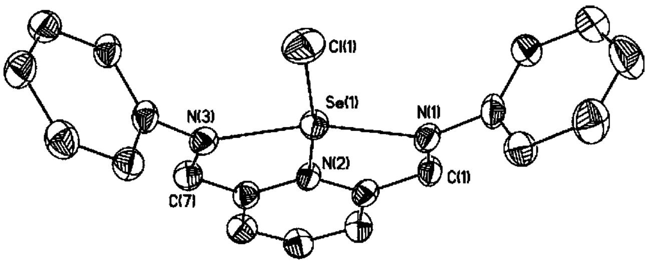


Figure 3. Solid-state structure of the cation in **25**. Ellipsoids are drawn to 50% probability; hydrogen atoms, anion, solvates, and isopropyl groups are omitted for clarity.

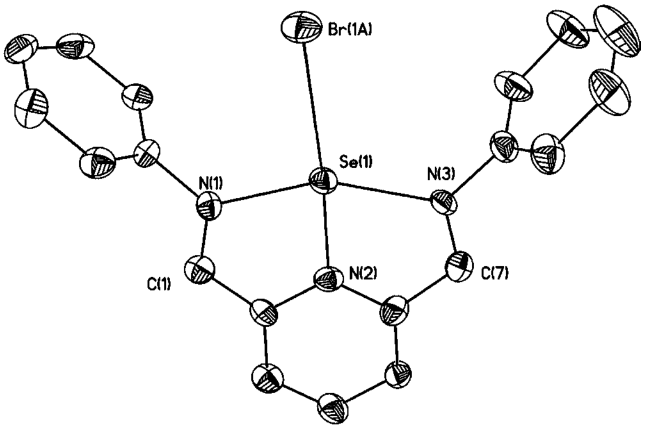


Figure 4. Solid-state structure of the cation in **26**. Ellipsoids are drawn to 50% probability; hydrogen atoms, anion, solvates, and isopropyl groups are omitted for clarity.

and obtaining a ^{1}H NMR spectrum revealed highly pure products with a symmetric ligand framework; virtually identical spectra were obtained for both the $SeCl_2$ and $SeBr_2$ reactions. Downfield shifts were observed for the two protons on the α-carbon atoms with respect to the free ligand but upfield in comparison to the known dicationic complex (X = Cl, **25**, δ_H = 9.78 ppm; X = Br, **26**, δ_H = 9.74 ppm cf. 10.35 ppm).[31,33] Crystals suitable for X-ray diffraction studies were grown by vapor diffusion of Et_2O into saturated CH_3CN solutions and revealed a $[SeX]^+$ monocation sequestered by ligand **1** paired with a $[SeX_3]^-$ anion (dimerizes in the solid state to give $[Se_2X_6]^{2-}$, Scheme 1). This was consistent with a 2:1 stoichiometric reaction between the selenium dihalde and ligand.

Upon removing the solvent *in vacuo* from the reaction supernatant, the mass of the solids obtained corresponded to half of the ligand used. Redissolving the powder in $CDCl_3$ and obtaining a ^{1}H NMR spectrum indicated only the presence of unreacted ligand. Given the 1:1 stoichiometric reaction only resulted in ~45% yield and a ratio of one ligand to two SeX_2 moieties incorporated in the product, the stoichiometry of SeX_2 was increased to two, where the yields then improved to over 85%. This demonstrates that regardless of the stiochiometry only **25** and **26** were produced. This reactivity was different from the SeX_2 DAB complexes (**7**; Figure 2), which do not displace a halide.[26] The rationalization is that having the additional donor on the DIMPY ligand requires a halide to vacate a coordination site to form the preferential square planar bonding arrangement about selenium.

Stirring a CH_2Cl_2 solution of **1** with solution of SCl_2 in CH_2Cl_2 resulted in no reaction as indicated by ^{1}H NMR spectroscopy. Reactions of the same ligand with the chalcogen tetrahalides $SeCl_4$, $SeBr_4$, $TeBr_4$, $TeCl_4$ resulted in complex mixtures, which were not further investigated. It has been established in related work that the chalcogen halides are susceptible to releasing X_2 in the presence of strong Lewis bases, subsequently degrading what is present in solution, which includes the ligand.[38−40]

The reactions of the chalcogen halides with the methyl-substituted ligand (**2**) were also examined. Literature precedent indicated that $TeCl_4$ reacts with **2** in THF to produce the *N,N′,C*-bound complex (**24**) by reacting with the enamine tautomer (**2′**) and ultimately eliminating HCl.[8] Stirring $TeBr_4$ with **2** in THF produced an orange solution with an orange suspension over 4 h (Scheme 2). Filtering the solids and removing the solvent from the supernatant gave an orange powder, which was washed with Et_2O. Redissolving a sample of the powder in $CDCl_3$ and obtaining an ^{1}H NMR spectrum revealed a single product with a break in symmetry of the ligand framework with two separate isopropyl resonances. It was also apparent that one methyl group on the α-carbon was absent indicating that the *N,N,C*-bound $TeBr_3$ unit, analogous to the $TeCl_3$ complex observed by Cowley et al., was likely the isolated product.[28] A signal at δ_H = 4.57 ppm integrating to 2 was consistent with a methylene resonance, and a peak at δ_H = 2.37 ppm integrating to 3 accounts for the methyl group, both of which are shifted downfield with respect to the free ligand (δ = 2.28 ppm).[37] The FT-IR spectrum lacked an N−H stretch, consistent with the formation of an exocyclic imine. Crystals for X-ray diffraction studies were grown from vapor diffusion of *n*-pentane into THF confirming the identity of **27**, the DIMPY analogue of the $TeBr_3$ DAB complexes **11** and **13** (Figure 2).

The reaction of $SeCl_2$ with **2** in THF produced a dark red solution. Normal pentane was added to precipitate the product, and the solids were washed with Et_2O. A red powder was obtained after drying *in vacuo*. The ^{1}H NMR spectrum of the redissolved solids in $CDCl_3$ displayed a break in symmetry once again, in addition to a reduction of the integration of the methyl group to 3, consistent with binding of the ligand through one of

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the *N,N′,N″*-DIMPY Complexes 25, 26, 29, 30 and the Previously Reported Complexes 20−22

	25	**26**	**29**	**30**	**20**[31]	**21**[31]	**22**[31]
				Bond Lengths			
Ch(1)−N(1)	2.209(4)	2.087(9)	1.883(4)	2.077(4)	1.9068(17)	2.025(2)	2.243(4)
Ch(1)−N(3/1A^a)	2.056(4)	2.138(9)	1.923(4)	2.103(4)	1.9068(17)^a	2.025(2)^a	2.241(4)
Ch(1)−N(2)	1.932(4)	1.932(9)	1.727(4)	1.946(5)	1.719(3)	1.872(3)	2.098(3)
C(1)−N(1/1A^a)	1.276(6)	1.276(15)	1.295(6)	1.275(7)	1.280(3)	1.275(3)	1.284(6)
C(7/1A^a)−N(3/1A^a)	1.298(6)	1.290(15)	1.279(5)	1.286(7)	1.280(3)^a	1.275(3)^a	1.284(7)
Ch(1)−X(1)	2.6499(14)	2.845(2)		2.6948(18)			
				Bond Angles			
N(1)−Ch(1)−N(2)	76.00(16)	78.0(4)	82.37(18)	78.03(19)	82.39(6)	78.79(6)	72.77(15)
N(2)−Ch(1)−N(3/1A^a)	78.56(15)	76.8(4)	82.68(17)	76.85(18)	82.39(6)^a	78.79(6)^a	73.35(16)
N(1)−Ch(1)−X(1)	111.23(11)	92.4(3)		97.93(14)			
N(3/1A^a)−Ch(1)−X(1)	94.17(11)	109.7(3)		106.94(14)			

[a] The dications in **20** and **21** lie on a site of symmetry with N(1) and N(3) being symmetry related.

Table 2. X-ray Details for **25**, **26**, **27**, **29**, and **30**

	25	**26**	**27**	**29**	**30**
empirical formula	$C_{37}H_{45}F_6Cl_4N_6Se_2$	$C_{37}H_{39}F_6Br_4N_3Se_2$	$C_{37}H_{42}Br_3N_3OTe$	$C_{45}H_{49}Cl_8N_3S$	$C_{86}H_{94}Cl_6N_6Se_3$
fw (g/mol)	873.51	1045.30	912.07	947.53	1661.25
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	11.413(2)	11.950(2)	10.592(2)	12.5843(19)	12.7211
b (Å)	14.310(3)	14.476(3)	14.103(3)	13.324(2)	20.3795
c (Å)	26.554(7)	26.043(8)	26.737(7)	16.054(2)	17.9128
α (deg)	90	90	90	71.556(3)	90
β (deg)	101.87(3)	103.39(3)	104.43(3)	72.774(3)	95.894
γ (deg)	90	90	90	80.973(4)	90
V (Å^3)	4225.6(16)	4382.7(18)	3867.9(15)	2433.1(6)	4619.3(8)
Z	4	4	4	2	2
D_c (mg m^{-3})	1.373	1.584	1.566	1.293	1.194
radiation, λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
temp (K)	150(2)	150(2)	150(2)	150(2)	150(2)
R1^a [$I > 2\sigma I$]	0.0604	0.0924	0.0438	0.0775	0.0652
wR2^a (F^2)	0.1822	0.2812	0.1337	0.2031	0.1768
GOF^a (S)	0.965	1.227	1.055	1.045	0.949

[a] $R1(F[I > 2(I)]) = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2(F^2 \text{ [all data]}) = [w(F_o^2 - F_c^2)^2]^{1/2}$; $S(\text{all data}) = [w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

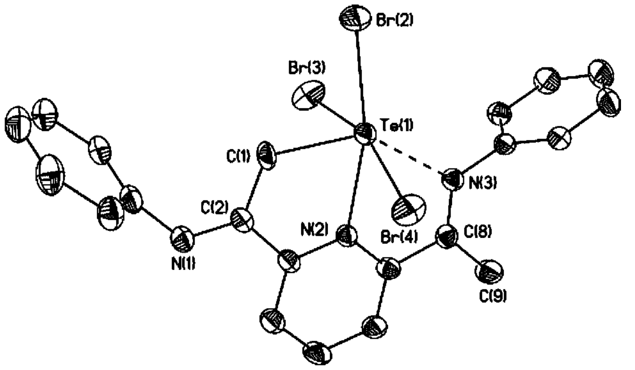


Figure 5. Solid-state structure of **27**. Ellipsoids are drawn to 50% probability; hydrogen atoms, solvate, and isopropyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): Te(1)−C(1) 2.133(4), Te(1)−N(2) 2.359(3), Te(1)−Br(2) 2.6323(7), Te(1)−Br(3) 2.6562(8), Te(1)−Br(4) 2.6774(7), Te(1)−N(3) 2.793(3), N(3)−C(8) 1.269(5), N(1)−C(2) 1.268(5), C(2)−C(1) 1.507(6). C1−Te1−N2 77.84(14), C(1)−Te(1)−Br(2) 86.40(12), N(2)−Te(1)−Br(2) 164.07(8), C(1)−Te(1)−Br(3) 84.59(14), N(2)−Te(1)−Br(3) 83.56(9), Br(2)−Te(1)−Br(3) 97.42(2), C(1)−Te(1)−Br(4) 85.25(14), N(2)−Te(1)−Br(4) 82.36(9), Br(2)−Te(1)−Br(4) 94.12(2), Br(3)−Te(1)−Br(4) 164.10(2).

the methyl carbon atoms. A new peak with respect to the free ligand was observed at 8.16 ppm consistent with a single C−H integrating to 1 rather than the CH_2 group observed for **27**. Obtaining an FT-IR spectrum of the powder displayed a diagnostic N−H stretch (broad peak at 3425 cm^{-1}) supporting the presence of an exocyclic amino group corresponding to the singlet integrating to 1 at 4.44 ppm in the ^{1}H NMR spectrum. Although crystals of suitable quality for X-ray diffraction studies could not be grown, the identity of the compound could be assigned as the SeCl complex **28** bound to one of the carbon atoms of the ligand based on the data and analogy to the DAB chemistry.[25] As with the DAB chemistry, Te forms a complex with an exocyclic imine (**10**−**13**; Figure 2) whereas Se produces an exocyclic amine (**16**−**19**).

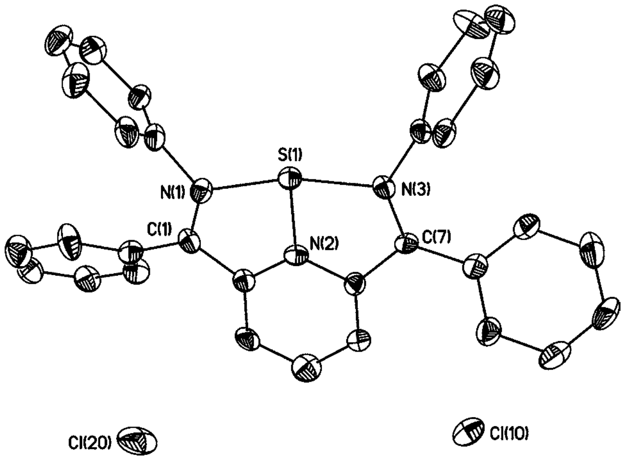


Figure 6. Solid-state structure of **29**. Ellipsoids are drawn to 50% probability; hydrogen atoms, solvate, and isopropyl groups are omitted for clarity.

In examing the reactivity of the other chalcogen halides with **2**, reactions with $SeCl_4$, $SeBr_4$, $SeBr_2$, and SCl_2 all produced complex mixtures, likely resulting from the release of X_2 giving uncontrollable side reactions.

In order to examine the effect of an aryl group at the α-carbon, the reaction of SCl_2 with **3** in CH_2Cl_2 was carried out, resulting in the generation of an orange solution (Scheme 3). Adding *n*-pentane to the solution and storing the reaction vial at −35 °C produced a large crop of yellow crystals. Obtaining a ^{1}H NMR spectrum of the dried crystals redissolved in $CDCl_3$ displayed a single symmetric product. The protons on the 3 and 5 positions on the pyridine group were shifted downfield with respect to free ligand (δ_H = 9.43 cf. δ_H = 7.53 ppm).[2] Obtaining a solid-state structure from crystals grown by vapor diffusion of *n*-pentane into chloroform revealed a *N,N′,N″*-bound sulfur(II) dication with two chloride counteranions (**29**), reminiscent of the reaction of **1** with "S(OTf)$_2$" (**20**; Figure 2).[31] This was surprising as the aryl substituted DAB ligands did not react at all with SCl_2 in the absence of TMSOTf, confirming the higher

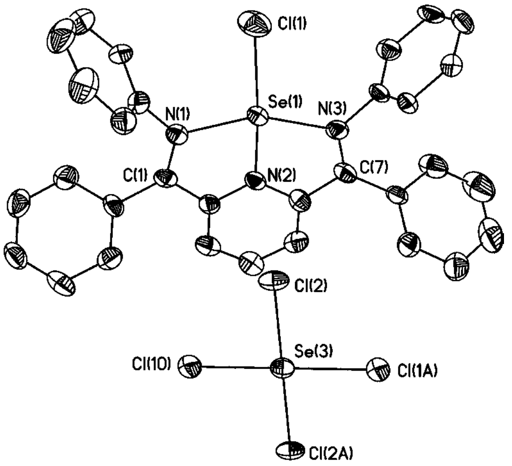


Figure 7. Solid-state structure of **30**. Ellipsoids are drawn to 50% probability; hydrogen atoms, solvate, and isopropyl groups are omitted for clarity.

reactivity of DIMPY ligands in comparison to their DAB counterparts.[29,30]

The 1:2 stoichiometric reactions of **3** with SeX_2 in THF produced brown (X = Br) and red (X = Cl) solutions. Adding *n*-pentane to the mixture resulted in the precipitation of orange (X = Cl; **30**) and brown (X = Br; **31**) powders. Redissolving a sample of the powders in $CDCl_3$ and obtaining a ^1H NMR spectrum revealed a new product; the most diagnostic features were the downfield shifts of the pyridine protons. X-ray quality crystals of **30** were obtained by vapor diffusion of *n*-pentane into a saturated CH_2Cl_2 solution indicating the identity as two $SeCl^+$ monocations paired with with a $SeCl_4^{2-}$ dianion. A virtually identical proton NMR spectrum was obtained from the $SeBr_2$ reaction, supporting that the reaction product is the analogous $SeBr^+$ cation **31**, although the exact nature of the anion is not certain. Unfortunately, repeated attempts at crystallization were unsuccessful, so a solid-state structure was not obtained.

Further evidence that complexation of ligand **3** has occurred are sharp resonances in the proton NMR spectra. The free ligand undergoes restricted rotation on the NMR time scale due to the presence of the bulky phenyl groups that results in severe broadening of all signals except at elevated temperatures (115 °C in DMSO-d_6).[2] However, the complexes formed with SeX_2 and SCl_2 do not display hindered dynamics at ambient temperature on the NMR time scale. This phenomenon has also been observed in other complexes with phenyl substituted DIMPY ligands.[2−4] The corresponding reactions of $SeCl_4$, $SeBr_4$, $TeCl_4$, and $TeBr_4$ all resulted in complex mixtures or decomposition likely due to the concomitant release of dihalogen.

X-ray Crystallography. The solid-state structures of **25** and **26** both revealed a selenium halide monocation sequestered in the DIMPY chelate (Figures 3 and 4; see Table 1 for selected bond lengths and angles and Table 2 for X-ray details). The cationic selenium center is in a distorted square planar geometry consistent with an AX_4E_2 electron pair configuration. The Se−N bond lengths are slightly longer than the dicationic analogues which can be accounted for by the lesser degree of attraction from the ligand to the monocationic center as well as the presence of the halide *trans* to the pyridine nitrogen. The anion is a $Se_2X_6^{2-}$ dianion (SeX_3^- dimer) shared over two asymmetric units. The selenium halide bonds within the cations are long [X = Cl, 2.6498(14) Å; X = Br, 2.845(2) Å], which is attributed to the strong donation of the pyridine nitrogen *trans* to the halide. The imine within the ligand framework is retained [C−N = 1.276(6)−1.298(6) Å].

Upon examination of the solid-state structure of **2TeBr**, the tellurium center is best described as a distorted octahedron with a stereochemically inactive lone pair (Figure 5). The electronic configuration is viewed as AX_6 with a distant nitrogen contact. The Te−Br bond lengths are similar to the CH_3DAB reaction products [range 2.6323(7)−2.6774(7) Å, cf. 2.634(1)−2.680(1) Å]. The N−Te bond distance for the pyridine nitrogen is markedly shorter than that of the imine [2.359(3) Å, cf. 2.793(3) Å] which retains its N−C double bond [1.268(5) Å], and the exocyclic carbon−nitrogen bond is also characteristic of an imine moiety [1.269(5) Å]. The carbon−tellurium bond of 2.133(4) Å is consistent with a typical Te−C single bond.[28]

The structure of the dicationic center in **29** is isostructural to **20** (Figure 2) as both are T-shaped consistent with an AX_3E_2 electron pair configuration (Figure 6). The S−N bond lengths are almost identical [av S−N_{imine} 1.903 Å, cf. 1.9068(17) Å; S−$N_{pyridine}$ 1.727(4) Å, cf. 1.719(3) Å].[31] There are no detectable S···Cl contacts between the cation and chloride anions within the sum of the van der Waals radii (3.25 Å) indicative of a dicationic species.[41] On the basis of the similarities between **29** and **20**, it is reasonable to believe a complex with **1** and SCl_2 should be stable, but the observations indicate that **3** is more reactive than **1** toward SCl_2.

The solid-state structure of **30** reveals a $SeCl^+$ monocation as observed in **25**, and the bond lengths within the cation are similar (Figure 7). The main difference in **30** lies with the counteranion which is a $SeCl_4^{2-}$ dianion, a rare counteranion with only two other solid-state structures reported in the CSD.[42,43]

CONCLUSION

By the reactions of chalcogen halides with diiminopyridine ligands featuring H, Ph, or CH_3 substitution on the α-carbon, new sulfur, selenium, and tellurium complexes were isolated. The methyl DIMPY derivative (**2**) reacted through a methyl group to give *N,N′,C*-bound complexes with an exocyclic imine (Ch = Te) or an exocyclic amine moiety (Ch = Se). The reaction is believed to go through the enamine tautomer and expel hydrohalide in the process similar to the related DAB chemistry. The hydrogen DIMPY ligand (**1**) reacted with the selenium dihalides in a 1:2 stoichiometry to afford the *N,N′,N″*-chelated SeX^+ monocationic complexes differing from the neutral DAB SeX_2 complexes. The phenyl substituted DIMPY (**3**) proved to be more reactive than the H substituted derivative to produce a dicationic sulfur complex with two chloride counteranions. In the case of selenium, a four coordinate monocationic complex with a SeX_4^{2-} anion was isolated. Selenium binds weakly to a halide in contrast to sulfur as it can accommodate higher coordination numbers making a square planar geometry. In many cases with chalcogen halide starting materials in the +4 oxidation state undesireable halogenation occurred.

ASSOCIATED CONTENT

Supporting Information

^1H NMR spectra as well as FT-IR and FT-Raman data for all of the reported compounds. Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pragogna@uwo.ca. Phone: 1-519-661-2111 ext 87048. Fax: 1-519-661-3022

■ ACKNOWLEDGMENTS

The authors are very grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canada Foundation for Innovation, Ontario Ministry of Research and Innovation, and The University of Western Ontario for generous financial support. We acknowledge P. Break for inspiration.

■ REFERENCES

(1) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745−1776.

(2) Jurca, T.; Dawson, K.; Mallov, I.; Burchell, T.; Yap, G. P. A; Richeson, D. S. *Dalton Trans.* **2010**, *39*, 1266−1272.

(3) Jurca, T.; Korobkov, I.; Yap, G. P. A.; Gorelsky, S. I.; Richeson, D. S. *Inorg. Chem.* **2010**, *49*, 10635−10641.

(4) Jurca, T.; Lummiss, J.; Burchell, T. J.; Gorelsky, S. I.; Richeson, D. S. *J. Am. Chem. Soc.* **2009**, *131*, 4608−4609.

(5) Baker, R. J.; Jones, C.; Kloth, M.; Mills, D. P. *New J. Chem.* **2004**, *28*, 207−213.

(6) Knijnenburg, Q.; Smits, J. M. M.; Budzelaar, P. H. M. *Organometallics* **2006**, *25*, 1036−1046.

(7) Scott, J.; Gambarotta, S.; Korobkov, I.; Knijnenburg, Q.; de Bruin, B.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2005**, *127*, 17204−17206.

(8) Reeske, G.; Cowley, A. H. *Chem. Commun.* **2006**, 1784−1786.

(9) Pedrido, R.; Romero, M. J.; Bermejo, M. R.; González-Noya, A. M.; Maneiro, M.; Rodríguez, M. J.; Zaragoza, G. *Dalton Trans.* **2006**, 5304−5314.

(10) Casas, J. S.; Castellano, E. E.; Ellena, J.; García-Tasende, M. S.; Sánchez, A.; Sordo, J.; Vázquez-López, E. M.; Vidarte, M. J. *Z. Anorg. Allg. Chem.* **2003**, *629*, 261−267.

(11) Reger, D. L.; Wright, R. D.; Smith, M. D.; Rheingold, A. L.; Kassel, S.; Concolino, T.; Rhagitan, B. *Polyhedron* **2002**, *21*, 1795−1807.

(12) Nomiya, K.; Sekino, K.; Ishikawa, M.; Honda, A.; Yokoyama, M.; Kasuga, N. C.; Yokoyama, H.; Nakano, S.; Onodera, K. *J. Inorg. Biochem.* **2004**, *98*, 601−615.

(13) Jenkins, H. A.; Dumaresque, C. L.; Vidovic, D.; Clyburne, J. A. C. *Can. J. Chem.* **2002**, *80*, 1398−1403.

(14) Hill, N. J.; Vasudevan, K.; Cowley, A. H. *Jordan J. Chem.* **2008**, *1*, 47−54.

(15) Weber, L.; Rausc, A.; Wartig, H. B.; Stammler, H.-G.; Neumann, B. *Eur. J. Inorg. Chem.* **2002**, 2438−2446.

(16) Dube, J. W.; Farrar, G. J.; Norton, E. L.; Szekely, K. L. S.; Cooper, B. F. T.; MacDonald, C. L. B. *Organometallics* **2009**, *28*, 4377−4384.

(17) Reeske, G.; Hoberg, C. R.; Hill, N. J.; Cowley, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 2800−2801.

(18) Reeske, G.; Hoberg, C. R.; Cowley, A. H. *Inorg. Chem.* **2007**, *46*, 1426−1430.

(19) Ellis, B. D.; Macdonald, C. L. B. *Inorg. Chim. Acta* **2007**, *360*, 329−344.

(20) Mair, F. S.; Manning, R.; Pritchard, R. G.; Warren, J. E. *Chem. Commun.* **2001**, 1136−1137.

(21) Hinchliffe, A.; Mair, F. S.; McInnes, E. J. L.; Pritchard, R. G.; Warren, J. E. *Dalton Trans.* **2008**, 222−233.

(22) Dutton, J. L.; Tindale, J. J.; Jennings, M. C.; Ragogna, P. J. *Chem. Commun.* **2006**, 2474−2476.

(23) Dutton, J. L.; Tuononen, H. M.; Jennings, M. C.; Ragogna, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 12624−12625.

(24) Dutton, J. L.; Sutrisno, A.; Schurko, R. W.; Ragogna, P. J. *Dalton Trans.* **2008**, 3470−3477.

(25) Dutton, J. L.; Martin, C. D.; Sgro, M. J.; Jones, N. D.; Ragogna, P. J. *Inorg. Chem.* **2009**, *48*, 3239−3247.

(26) Dutton, J. L.; Farrar, G. J.; Sgro, M. J.; Battista, T. L.; Ragogna, P. J. *Chem.—Eur. J.* **2009**, *15*, 10263−10271.

(27) Dutton, J. L.; Battista, T. L.; Sgro, M. J.; Ragogna, P. J. *Chem. Commun.* **2010**, *46*, 1041−1043.

(28) Reeske, G.; Cowley, A. H. *Chem. Commun.* **2006**, 4856−4858.

(29) Martin, C. D.; Ragogna, P. J. *Inorg. Chem.* **2010**, *49*, 4324−4330.

(30) Martin, C. D.; Jennings, M. C.; Ferguson, M. J.; Ragogna, P. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2210−2213.

(31) Martin, C. D.; Le, C. M.; Ragogna, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 15126−15127.

(32) Martin, C. D.; Ragogna, P. J. *Dalton Trans.* **2011**1197611980.

(33) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Strmberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728−8740.

(34) Steudel, R.; Jensen, D.; Plinke, B. *Z. Naturforsch.* **1987**, *42b*, 163−168.

(35) Del Bel Belluz, P.; Cordes, A. W.; Kristof, E. M.; Kristof, P. V.; Liblong, S. W.; Oakley, R. T. *J. Am. Chem. Soc.* **1989**, *111*, 9276−9278.

(36) Milne, J. *Polyhedron* **1985**, *4*, 65−68.

(37) Kleigrewe, N.; Steffen, W.; Blömker, T.; Kehr, G.; Fröhlich, R.; Wibbeling, B.; Erker, G.; Wasilke, J.-C.; Wu, G.; Bazan, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 13955−13968.

(38) Gushwa, A. F.; Richards, A. F. *Eur. J. Inorg. Chem.* **2008**, 728−736.

(39) Gushwa, A. F.; Karlin, J. G.; Fleischer, R. A.; Richards, A. F. *J. Organomet. Chem.* **2006**, *691*, 5069−5073.

(40) Dutton, J. L.; Tabeshi, R.; Jennings, M. C.; Lough, A.; Ragogna, P. J. *Inorg. Chem.* **2007**, *46*, 8594−8602.

(41) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

(42) Krebs, B.; Luhrs, E.; Willmer, R.; Ahlers, F. P. *Z. Anorg. Allg. Chem.* **1991**, *592*, 17−34.

(43) Neumuller, B.; Lau, C.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1847−1853.