Structural and Solution Calorimetric Studies of Sulfur Binding to Nucleophilic Carbenes

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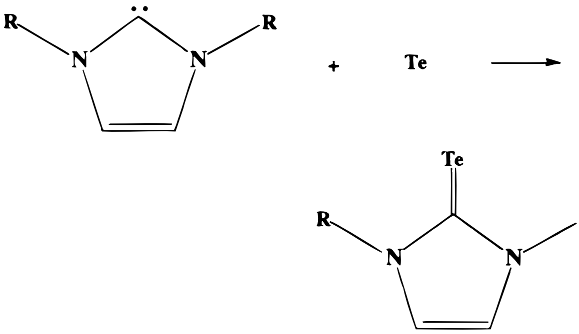
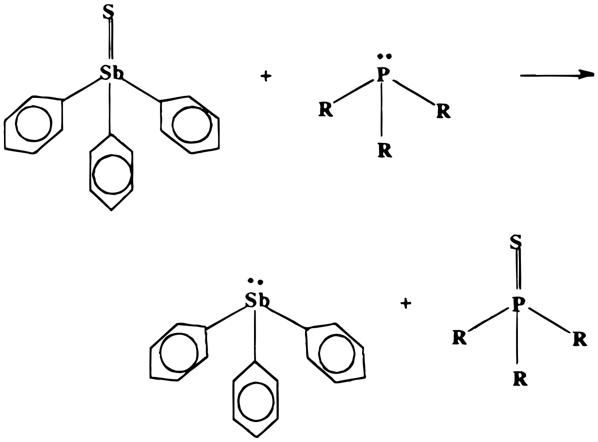
Introduction

The recent synthesis by Arduengo and co-workers[1] of isolable carbenes has led to detailed investigation of their reaction chemistry as well as utilization as ligands in metal complexes of potential utility in homogeneous catalysis.[2] Reaction of cyclic carbene ligands with tellurium forming the tellurone complexes shown in eq 1 have recently been reported.[3]



(1)

As part of an overall program aimed at determining enthalpies of sulfur atom transfer for main group[4] and transition metal complexes,[5] we have recently reported enthalpies of formation of $R_3P{=}S$ complexes from tertiary phosphines utilizing elemental sulfur and sulfur transfer reagents[6] such as shown in eq 2.



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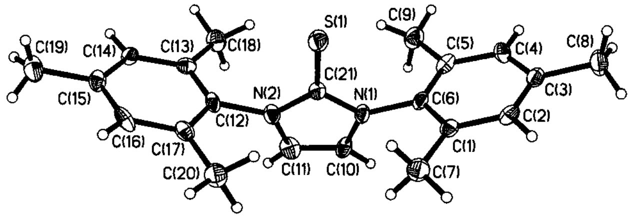

Figure 1. ORTEP diagram for **2**.

The goal of this work was to determine the enthalpies of sulfurization of Arduengo carbene ligands and compare them to enthalpies of binding of these ligands to metals.[7]

Experimental Section

General Considerations. All manipulations involving carbene compounds were performed under an inert atmosphere of argon or nitrogen using standard high-vacuum or Schlenk tube techniques or in an MBraun or a Vacuum/Atmospheres glovebox containing less than 1 ppm of oxygen and water. Toluene, benzene, and deuteriobenzene were dried and distilled from Na/benzophenone under argon. Carbene ligands were synthesized according to the literature.[1] NMR spectra were recorded on a Varian VXR 400 spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80). Enthalpies of reactions with $Ph_3As{=}S$ and $Ph_3Sb{=}S$ were established in a fashion strictly analogous to that of work described earlier.[4] For all reactions, at least one measurement was performed in C_6D_6 and reaction products were analyzed by NMR spectroscopy to confirm complete and quantitative reactions. NMR data were in agreement with literature reports.[1,4]

Structure Determinations of IMes═S (2) and IAd═S (4). Colorless crystals of **2** and **4** were both obtained by slow evaporation of C_6D_6 from samples stored in NMR tubes in a glovebox. A single crystal of each was placed in a capillary tube and mounted on a Bruker SMART CCD X-ray diffractometer. Data were collected using Mo Kα radiation at 180 K (for **2**) and 150 K (for **4**). Cell dimensions were determined by least-squares refinement of the measured setting angles of 14 229 reflections with $3.5° < 2\theta < 55°$ (for **2**) and 31 027 reflections with $3.6° < 2\theta < 70.18°$ (for **4**). The structures were solved using direct methods (SHELXS-86) and refined by full-matrix least-squares techniques. ORTEP diagrams of structure **2** and **4** are presented in Figures 1 and 2. Crystallographic data for both structurally characterized compounds are given in Table 1, selected bond distances and angles are provided in Table 2.

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(1) (a) Wanzlick, H. W. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 75−80. (b) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530. (c) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(2) (a) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2163. (b) Huang, J.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 2674. (c) Huang, J.; Zhang, C.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804 and references therein. (d) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247.

(3) (a) Arduengo, A. J., III; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Khasnis, D.; Marshall, W. J.; Prakasha, T. K. *J. Am. Chem. Soc.* **1997**, *119*, 12742. (b) Analogous S derivatives have been prepared by other methods: Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J. P.; Ebel, K.; Brode, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1021.

(4) Capps, K. B.; Wixmerten, B.; Bauer, A.; Hoff, C. D. *Inorg. Chem.* **1998**, *37*, 2861.

(5) Bauer, A.; Capps, K. B.; Wixmerten, B.; Abboud, K. A.; Hoff, C. D. *Inorg. Chem.* **1999**, *38*, 2136.

(6) (a) Jason, M. E. *Inorg. Chem.* **1997**, *36*, 2641. (b) C.D.H. thanks Dr. Mark Jason (Solutia) for a gift of $Ph_3Sb{=}S$ and also helpful discussions.

(7) Huang, J.; Schanz, H. J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370.

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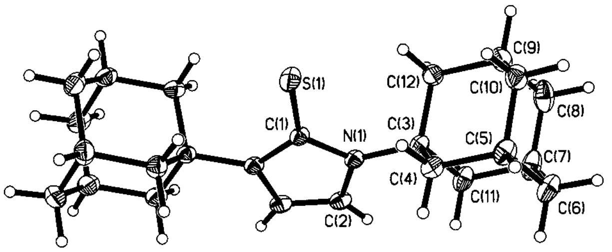
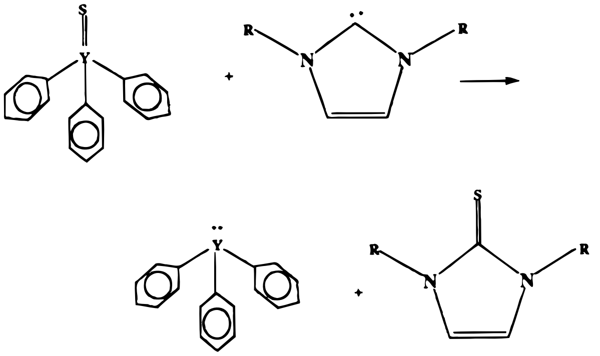


Figure 2. ORTEP diagram for **4**.

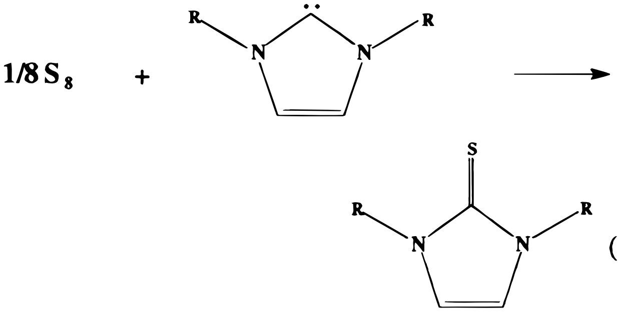
Results and Discussion

Synthesis and Calorimetry of IMes=S and IAd=S. Reactions of the adamantyl- and mesityl-substituted cyclic carbenes with sulfur transfer reagents were found to occur quantitatively in solution as shown in eq 3. Using the enthalpies of solution ($Ph_3As{=}S$, +4.4 ± 0.2 kcal/mol; $Ph_3Sb{=}S$, +5.3 ± 0.5 kcal/mol) and previously published enthalpies of sulfur atom transfer (SAT),[4] these data can be converted to enthalpies of reaction with elemental sulfur in toluene solution.



(3)

R	Y	ΔH (kcal/mol)
Adamantyl	As	-15.9 ± 1.0
Mesityl	As	-25.8 ± 1.1
Mesityl	Sb	-30.5 ± 1.4



(4)

For the adamantyl carbene, the calculated enthalpy of reaction 4 is −24.1 ± 1.5 kcal/mol. The mesityl-subsituted carbene has enthalpies of reaction of −34.1 ± 1.3 kcal/mol when reacted with $Ph_3As{=}S$ and −35.8 ± 1.9 kcal/mol when $Ph_3Sb{=}S$ is used as the SAT reagent. There is reasonable agreement between the two values, which yield an average of −35 ± 2 kcal/mol.

Structures of IMes=S and IAd=S. The crystal structures of two thiocarbonyl compounds are shown in Figures 1 and 2, and selected data are shown in Tables 1 and 2. Full data are available as Supporting Information. Two key factors warrant comment regarding the structures of the thiocarbonyls shown in Figures 1 and 2. The first is that the imidazole ring and sulfur atom are essentially coplanar and that direct π interactions of the aromatic rings of the mesityl derivative appear to be precluded since they are nearly perpendicular to the plane of the imidazole ring. The second is the apparent lack of steric crowding relative to corresponding metal complex structures that have been reported recently.[7] In keeping with the stronger carbon−sulfur bond strength (≈10 kcal/mol), the carbon−sulfur bond of **2** is 0.0114(30) Å shorter than that in **4** as shown in Table 2.

Table 1. Crystallographic Data for the Compounds IMes=S (**2**) and IAd=S (**4**)

	2	**4**
empirical formula	$C_{21}H_{24}N_2S{\cdot}{}^1/_2C_6D_6$	$C_{23}H_{32}N_2S$
fw	375.54	368.57
color	colorless	colorless
space group	monoclinic, $P2_1/c$	trigonal, $P6_22_1$
a, Å	11.9887(4)	7.0433(14)
b, Å	12.0792(4)	7.0433(14)
c, Å	14.9021(4)	34.011(8)
α, deg	90	90
β, deg	104.2470(10)	90
γ, deg	90	120
μ(Mo), cm^{-1}	1.65	1.75
Z	4	3
R	0.1096	0.0428
R_w	0.0849	0.0766
no. of refined params	352	183
no. of data collected	14 229	31 027
no. of unique data, $I > 3\sigma$	4698	4191
R_{merge}	0.0495	0.0696

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **2** and **4**

	2	**4**
C−S	1.6756(18)	1.6860(12)
C(S)−N	1.371(2), 1.367(2)	1.3716(10)
C(H)−N	1.386(2), 1.385(2)	1.3837(11)
C(H)−C(H)	1.332(3)	1.3401(18)
C(R)−N	1.452(2), 1.447(2)	1.4897(11)
N−C(S)−N	104.59(15)	106.14(10)
N−C(S)−S	127.01(14), 128.40(15)	126.93(5)
N−C(H)−C(H)	107.3(2), 107.74(19)	107.95(5)
C(S)−N−C(H)	110.24(16), 110.11(15)	108.98(7)
C(S)−N−C(R)	124.91(16), 124.52(16)	127.12(7)

Absolute $R_2(C_2H_2N_2C){=}S$ Bond Strengths. The enthalpies of reaction 4 in toluene solution can be used to derive estimates of the $R_2(C_2H_2N_2C){=}S$ bond strengths. Assuming that gas-phase enthalpies are similar to those in solution (there do not appear to be any significant solvation energies for the species in eq 4), addition of the enthalpy of formation of one S atom from $^1/_8S_8$ (+ 67 kcal/mol)[8] to the enthalpies of reaction 4 give rise to estimates of the absolute C=S bond strengths of 102 kcal/mol for IMes=S and of 91 kcal/mol for IAd=S. These values can be compared with literature data for other C=S complexes: O=C=S (74.2 kcal/mol), S=C=S (94.5 kcal/mol), and $H_2C{=}S$ (124 kcal/mol).[9] The low value for O=C=S is directly attributable to the fact that C≡O is formed with a net increase in the carbon−oxygen bond strength upon loss of C=S. More subtle changes in $R_2C{=}S$ involving π-bonding effects may play an important role in thermochemistry of carbene ligands, but

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(8) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2. (b) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.

(9) Bond strength estimates for CS_2 and COS were calculated on the basis of data from ref 11. Data for $H_2C{=}S$ were taken from the following references: (a) Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105. (b) Roy, M.; McMahon, T. B. *Org. Mass. Spectrom.* **1982**, *17*, 392. (c) Kutina, R. E.; Edwards, A. K.; Goodman, G. L.; Berkowitz, J. *J. Chem. Phys.* **1982**, *77*, 5508.

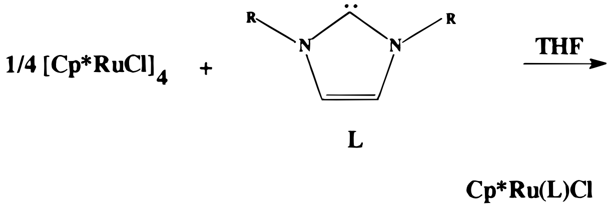
Table 3. Enthalpies of Reaction (kcal/mol) of Phosphine and Carbene Ligands with $^1/_8S_8$ and $^1/_4[Cp^*RuCl]_4$

L	$\Delta H°(^1/_8S_8)^a$	$\Delta H°(^1/_4[Cp^*RuCl]_4)^b$
IMes	−35.0	−15.6
PCy_3	−30.9	−10.5
IAd	−24.1	−6.8
$PMePh_2$	−23.8	*c*
PPh_3	−21.5	*c*

[a] In toluene solution. Data for phosphine sulfides were taken from ref 4. [b] In THF solution. Data taken from ref 7. [c] Data for these complexes are not directly comparable since the smaller phosphine ligands bind in a 2/1 rather than a 1/1 ligand/metal ratio.

understanding the role of heteroatom π-bonding effects in the special Arduengo carbenes remains a challange.[10] The absolute values of the $R_2(C_2H_2N_2C){=}S$ bond energies determined here appear to place them in the middle of the literature values discussed above. Extension of this work aimed at better understanding of these effects for both metals and chalcogens is in progress.[11]

Comparison of Relative Enthalpies of Formation of $R_2C{=}S$ and $(R_2C)Ru(Cl)Cp^*$. The enthalpies of binding of the carbene ligands to metal complexes have been recently investigated[7] for reactions such as that shown in eq 5. These results showed that the carbenes are among the strongest ligands known for Ru(II) and that their bond strengths compare well to Ru(II)−PR_3 bond strengths. As shown in Table 3, the relative enthalpies of reaction with sulfur (eq 4) correlate well with the enthalpies of binding to the organoruthenium complex (eq 5).



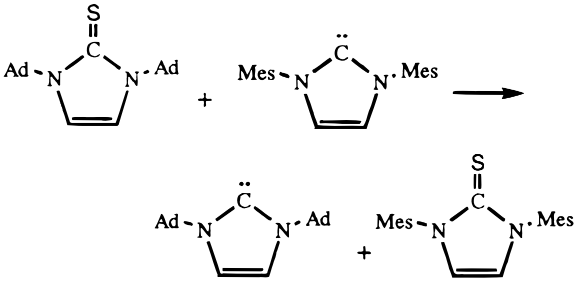
(5)

There is only one phosphine ligand that is common to both sets of data [smaller phosphine ligands coordinate in a 2/1 PR_3/Ru ratio[7] and are thus not directly comparable to the carbene ligands]. Even though only one phosphine serves as an “anchor point” in Table 3, it can be assumed that data for other phosphine ligands would show the normal pattern of binding which Angelici has shown to parallel that of enthalpies of protonation[12] and which we have shown to also parallel that of enthalpies of sulfurization.[4] This **may** indicate that the ability to donate electrons to H^+, ML_n, and S, which appear to show similar trends for phosphines, may also apply to the Arduengo carbenes. Work to further test this hypothesis is in progress.[11]

The absolute values of the enthalpies of reaction of the ligands in Table 3 cannot be compared directly since the relevant bond strengths derived from enthalpies of eqs 4 and 5 depend on knowledge of the enthalpies of fragmentation of $^1/_8S_8$ and $^1/_4[Cp^*RuCl]_4$. The enthalpy of dissociation of the transition metal tetramer is not known. The relative values in Table 3, however, do show a surprising correlation. Bonding in the metal complexes has been analyzed in terms of contributions from both steric and electronic factors.[7] There are no signs in the crystal structures in Figures 1 and 2 of significant steric strain in the carbene sulfides.

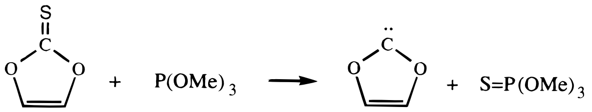
The fact that the mesityl-substituted carbene is the strongest donor for both metal and sulfur, by nearly 10 kcal/mol, shows a rather strong influence of a group that is two atoms away from the site of reactivity. Furthermore, on the basis of σ inductive effects, the adamantyl-substituted carbene would be expected to be a better donor. Replacement of an alkyl by an aryl group in reactions of R_3P, for example, results in a less exothermic enthalpy of reaction with sulfur.[4] For the metal complex, steric factors may play a role in the relative ordering of these ligands,[7] but as discussed above, this seems less likely for sulfur. It seems possible that electronic factors, depending on how π-bonded delocalization energy in the imidazole ring influences its ability to function as a σ donor, are the origin of this difference.

Kinetic Barriers to Sulfur Atom Transfer (SAT). The large thermodynamic difference between the mesityl- and adamantyl-substituted carbenes led to calculations showing that reaction 6 should be exothermic by over 10 kcal/mol. Reaction 6 was attempted, but at room temperature over 24 h reaction did not occur to any detectable amount. This is in keeping with relatively large barriers to transfer of S atoms between phosphines reported earlier by Baechler and co-workers.[13] The mechanisms of these SAT reactions are not well understood but are under continued investigation.



(6)

Given the similarity in $R_3P{=}S$ and $R_2C{=}S$ bond strengths, it is of interest to note that the carbene shown in reaction 7 was proposed as a possible intermediate by Corey[14] in 1963. The reaction conditions (refluxing trimethyl phosphite, 70−80 h) are in keeping with a large kinetic barrier to this proposed intermediate and reminiscent of the conditions used by Baechler and co-workers[13] in a study of SAT reactions with tertiary phosphines. Thermochemical data indicate comparable C=S and P=S bond strengths and support that reaction 7 should be approximately thermoneutral.



(7)

Conclusion

The enthalpies of formation of $R_2C{=}S$ have been measured by solution calorimetry and used to derive carbon to sulfur double-bond strength estimates of 102 kcal/mol (for IMes=S) and 91 kcal/mol (for IAd=S). These data, summarized in Table 3, show the carbene ligands to be thermochemically comparable

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(10) For two recent theoretical papers relevant to this subject, see: (a) Heineman, C.; Muller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023. (b) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039.

(11) Nolan, S. P.; Hoff, C. D. Work in progress.

(12) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51.

(13) Baechler, R. D.; Stack, M.; Stevenson, K.; Vanvalkenburgh, V. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *48*, 49.

(14) Corey, E. J.; Winter, R. A. E. *J. Am. Chem. Soc.* **1963**, *85*, 2677−2678.

to phosphine ligands with respect to enthalpy of oxidative addition of sulfur as well as formation of ligand−metal complexes.

The ≈10 kcal/mol weaker nature of the IAd bond compared to the IMes bond could be attributed to steric interactions in formation of the ruthenium complex; however, the crystal structures in Figures 1 and 2 show no apparant signs of strain energy for formation of the cyclic thiocarbonyls. In view of the expected greater σ inductive effect of the adamantyl group, changes in π-bond order are most likely the origin of the stronger binding to IMes compared to IAd for reaction with sulfur, and possibly for reaction with metals as well. Additional studies aimed at determining the thermochemical factors controlling reactivity of these and related systems are in progress.[11]

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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