and the alkyl group was found.

1 catalyzed the polymerization of ethylene, albeit very slowly. We reasoned that binding of the olefin by substitution of a pyridine might be the rate-limiting step of this reaction and thus sought an analogue of **1** with more labile ligands. Addition of 2.0 equiv of $TlPF_6$ to a THF solution of $[Cp^*Cr(Me)Cl]_2$ followed by standard workup yielded dark purple crystals of $[Cp^*Cr(THF)_2Me]^+PF_6^-$ (**2**).[3b] To our surprise this compound proved stable enough for isolation and full characterization. However, when a solution of **2** in CD_2Cl_2 was exposed to 6 equiv of ethylene in a sealed NMR tube, no residual ethylene could be detected in the tube by the time the ^1H NMR was recorded. Instead two broad resonances at 1.52 and 1.23 ppm were observed, indicating the formation of long-chain saturated hydrocarbons, and a white solid (polyethylene) precipitated from the solution. Substitution of THF-d_8 for CD_2Cl_2 as a reaction medium substantially slowed the polymerization reaction, consistent with our notion that the olefin molecule must replace one of the ligands bound to chromium before insertion can take place. Unfortunately **2** also proved reactive enough to eventually self destruct. Solutions of it changed color from purple to a brilliant blue during the course of several hours. This decomposition involved attack on the hexafluorophosphate anion by the highly Lewis acidic chromium, leading to polynuclear chromium complexes held together by fluoride bridges (see Scheme I).[3c] In order to avoid this catalyst deactivation, the tetraphenylborate salt $[Cp^*Cr(THF)_2Me]^+BPh_4^-$ (**3**) was prepared by anion metathesis of **2** with $NaBPh_4$.[8] Solutions of **3** proved stable over several days, facilitating a more detailed study of the polymerization reaction.

Exposure of a solution of **3** (100 mg in 50 mL of CH_2Cl_2) to 1 atm of ethylene at room temperature initially resulted in a rapid uptake of the olefin, which eventually slowed down and came to a halt after approximately 3 h. At this point the color of the solution had changed to a blue shade of purple and 560 mg of a white solid had precipitated from the solution. The IR spectrum of this solid was indistinguishable from that of authentic high-density polyethylene, and its melting range was 123-124 °C. Gel permeation chromatography (GPC) analysis showed the sample to have a relatively narrow molecular weight distribution (M_w = 6530, M_n = 3025, d = 2.16). A similar experiment at higher ethylene pressure (3 atm) yielded 660 mg of polyethylene (mp 129-137 °C) with higher molecular weight and dispersity (M_w = 23200, M_n = 5690, d = 4.08). The activity of the catalyst was determined by monitoring the pressure drop in a large reaction volume charged initially with 1.5 atm of ethylene. At ambient temperature (22 °C) the initial rate of insertion was 0.24 turnovers/s. We believe that the eventual deactivation of the catalyst was caused by impurities in the ethylene (i.e., H_2O, O_2), because passing the ethylene through a bed of activated 4A molecular sieves led to a doubling in the yield of polyethylene.

The reaction of **3** with propene was much slower. ^1H NMR spectra of a sample containing ca. 10 equiv of propene in a sealed tube showed a gradual decrease in intensity of the olefinic signals accompanied by the appearance of signals for new hydrocarbons. However, the reaction stopped before the propene was consumed completely and the nature of the products (molecular weight, tacticity) remains to be established.

Several recent observations point toward cationic alkyls as the active species in Ziegler-Natta catalyst preparations based on group 4 elements.[9] Our results indicate that in chromium-based systems too, cationic metal sites may be responsible for the catalysis. The positive charge of such complexes may indeed be crucial for binding of the electron-rich olefin to a metal center that has little propensity for back-bonding. There remains the intriguing question how the support surface of actual heterogeneous catalysts stabilizes highly Lewis acidic and substitutionally labile metal complexes. We are currently studying this problem as well as the influence of the metal oxidation state on polymerization activity.

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Supplementary Material Available: Tables of crystal data and summary of data collection and refinement, fractional coordinates and thermal parameters, anisotropic thermal parameters, interatomic distances, and interatomic angles for **1** (8 pages); listing of structure factor magnitudes for **1** (10 pages). Ordering information is given on any current masthead page.

(8) **3**: ^1H NMR (CD_2Cl_2) 9.0, 8.0, 7.36, 7.05, 6.93, -26.5 ppm; IR (KBr) 3051 (s), 2850 (s), 1940 (w), 1882 (w) 1821 (w), 1762 (w), 1700 (w), 1604 (s), 1578 (s), 1483 (s), 1443 (s), 1424 (s), 1379 (s), 1268 (m), 1214 (m), 1184 (m), 1149 (m), 1130 (s), 1066 (s), 1046 (s), 1032 (m), 1012 (s), 850 (s), 843 (s), 757 (vs), 731 (vs), 703 (vs), 639 (m), 611 (m), 477 (m), 438 (m) cm^{-1}; mp 135-138 °C. Anal. Calcd for $C_{43}H_{54}BCrO_2$: C, 77.58; H, 8.18. Found: C, 77.62; H, 8.21.

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The Relative Ease of Removing a Proton, a Hydrogen Atom, or an Electron from Carboxamides versus Thiocarboxamides

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Measurements of the acidities of acetamide and thioacetamide, their oxidation potentials, and those of their conjugate bases have revealed that the thiocarboxamide group gives up a proton more readily by about 10 kcal/mol, a hydrogen atom by about 16 kcal/mol, and an electron by about 50 kcal/mol (Table I). These differences are associated with the greater inherent ability of sulfur than oxygen to stabilize an anion, a radical, or a radical cation, which is exaggerated in the species derived from the amides by the weaker C=S than C=O bond.

Examination of Table I shows that replacement of the oxygen atom in carboxamides by a sulfur atom causes striking decreases in N-H bond pK_{HA}s,[10] in homolytic N-H bond dissociation energies (BDEs), and in the acidities of the corresponding radical cations ($pK_{HA}^{\cdot+}$). For $CH_3C(=X)NH_2$, $PhC(=X)NH_2$, and $H_2NC(=X)NH_2$ the ΔpK_{HA} values are 9.6, 8.8, and 8.1 kcal/mol, respectively, the ΔBDEs are 16.5, 16.5, and 18, respectively, and the $\Delta pK_{HA}^{\cdot+}$ values are 31.5, 23, and 23 kcal/mol, respectively. For the N-phenyl-substituted amides, $CH_3C(=X)NHPh$, and

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(5) These BDEs, which are believed to be accurate to about ±3 kcal/mol, are based on a thermodynamic cycle. This method has been used previously to estimate BDEs in the gas phase,[6] and a comparable method has been used to estimate the BDE of the O-H bond in hydroquinone and the hydroquinone radical.[7] BDE values for N-H bonds for carboxamides or thiocarboxamides do not appear to have been estimated hitherto; the BDE for the N-H bond in NH_3 is 107.4 ± 1.1.[8]
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(10) In the gas phase $CH_3C(=S)NH_2$ has a higher acidity than $CH_3C(=O)NH_2$ by 15 kcal/mol, showing that the sulfur effect on acidity is an intrinsic one.[11]

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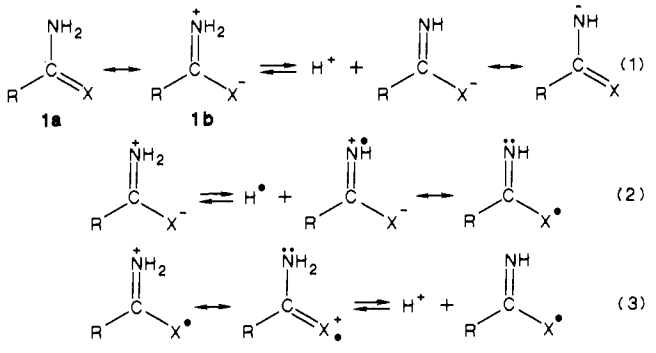
Table I. Acidities of Carboxamides and Thiocarboxamides and of the Radical Cations Derived Therefrom in Me_2SO at 25 °C

amide	pK_{HA}	$E_{ox}(A^-)^e$	$E_{ox}(HA)^f$	BDE[g]	$pK_{HA}^{\bullet+}$ [h]
CH_3CONH_2	25.5[a]	+0.725 (110)	+3.286 (250)	107.5	-18
CH_3CSNH_2	18.5[b]	+0.434 (110)	+1.212 (140)	91	+5
$CH_3CONHPh$	21.45[a,c]	+0.605 (70)	+2.140 (160)	99.5	-5
$CH_3CSNHPh$	14.7[b,d]	+0.670 (150)	+1.150 (120)	91.5	+7
$PhCONH_2$	23.35[a]	+0.824 (160)	+2.844 (120)	107	-11
$PhCSNH_2$	16.9[b]	+0.499 (70)	+1.157 (90)	90.5	+6
$(H_2N)_2C{=}O$	26.9[a]	+0.788 (170)	+3.104 (230)	111	-12
$(H_2N)_2C{=}S$	21.0[b]	+0.361 (110)	+1.074 (160)	93	+5
$(PhNH)_2C{=}O$	19.5[b]	+0.425 (70)	+1.951 (60)	92.5	-6
$(PhNH)_2C{=}S$	13.5[b]	+0.561 (50)	+1.117 (60)	87	+4

[a] Reference 1. [b] Algrim, D. J. Ph.D. Dissertation, Northwestern University, 1981. [c] pK_{HA} = 13.8 in H_2O (ref 2). [d] pK_{HA} = 11.6 in H_2O (ref 2). [e] Measured in Me_2SO (V) versus a Ag/AgI electrode by cyclic voltammetry (CV) by using the method described previously[3] and referenced to the standard hydrogen electrode (SHE_{aq}); wave widths in mV are given in parentheses. [f] Measured in MeCN (V) by CV and referenced to SHE_{aq}. [g] Estimated by using the following equation:[4,5] BDE (kcal/mol) = $1.37pK_{HA} + 23.06E_{ox}(A^-) + 55.86$. [h] Estimated to be accurate to about ±2 units by using the equation $pK_{HA}^{\bullet+} = pK_{HA} + [E_{ox}(A^-) - E_{ox}(HA)]23.06/1.37$.[9]

PhNHC(=X)NHPh, the ΔpK_{HA} values remain about the same (9.3 and 8.2 kcal/mol), but the ΔBDE values are decreased sharply (8.0 and 5.5 kcal/mol), as are the $\Delta pK_{HA}^{\bullet+}$ values (16 and 14 kcal/mol).

The large differences in the properties of carboxamides and their thio analogues can be rationalized in part by the superior ability of sulfur, relative to oxygen, in stabilizing $RC(=X)NH^-$ anions (eq 1), $RC(=NH)X^\bullet$ radicals (eq 2), and $RC(=X)NH_2^{+\bullet}$ radical cations (eq 3).



When X in eq 1 and 2 is changed from O to S, the equilibria shift to the right because of the superior ability of sulfur in stabilizing the negative charge or odd electron, but in eq 3 the equilibrium shifts to the left (Table I) because the stabilizing effect of S versus O is greater on the radical cation than on the radical.

The inherent greater ability of sulfur than oxygen to accommodate a negative charge is suggested by the greater acidity of PhSH than PhOH by 10.7 kcal/mol in Me_2SO and 8.5 kcal/mol in the gas phase, which can be explained by a decrease in lone pair–lone pair interactions in the larger S^- ion.[12a] An adjacent PhS function is also far more effective in stabilizing a carbanion than is a PhO function.[12b] There is qualitative evidence that PhS• radicals are more stable than PhO• radicals, and there is ESR data to indicate that RS functions are better than RO functions at stabilizing either adjacent[13] or para[14] carbon-centered radicals. Finally, in gas phase, there is evidence that MeS is superior to MeO in stabilizing the positive charge in $MeXCH_2^+$ cations.[15] The superiority of sulfur over oxygen in these respects is greatly exaggerated in thiocarboxamides versus carboxamides because the C=S bond is weaker than the C=O bond by about 30 kcal/mol,[16] which increases the contribution of **1b**, relative to **1a**, more for X = S than for X = O. For the thioamides this leads to IR stretching frequencies for CN typical of C=N, to CS IR frequencies normally associated with C-S, to higher C=N rotational barriers (15.4 versus 7.5 kcal/mol), and to higher dipole moments.[2]

Replacement of a hydrogen atom on nitrogen by a phenyl substituent has about an equal effect in increasing the acidities of the carboxamides and thiocarboxamides, probably because the negative charge in the anions is localized primarily on oxygen or sulfur, and delocalization of the charge to nitrogen is encouraged to about an equal degree by phenyl substitution. On the other hand, phenyl substitution has a much greater effect in lowering the BDE of the N-H bond in carboxamides and in decreasing the acidities of the radical cations derived therefrom than for the thiocarboxamides, probably because the radicals (eq 2) and radical cations (eq 3) for X = S are already effectively stabilized by localization of the odd electron and positive charge on the sulfur atom but less so for the oxygen atom where X = O.

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Nickel-Catalyzed Intramolecular [4 + 4] Cycloadditions. 4. Enantioselective Total Synthesis of (+)-Asteriscanolide

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We recently reported the development of methodology, based on nickel-catalyzed intramolecular [4 + 4] cycloadditions of unactivated bis-dienes, which provides practical access to fused and bridged ring systems incorporating eight-membered carbocycles.[1] Described herein is the application of this methodology to the first synthesis of the recently characterized sesquiterpene lactone (+)-asteriscanolide (**1**).[2] This study establishes the first asymmetric synthesis of a cyclooctane-containing terpenoid[3] and

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