Ethylene Trimerization with Mixed-Donor Ligand (N,P,S) Chromium Complexes: Effect of Ligand Structure on Activity and Selectivity

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Methylaluminoxane (MAO)-activated chromium(III) complexes of tridentate PNP and SNS ligands of the form $(R_2PCH_2CH_2)_2NR'$ (R = alkyl, aryl; R′ = H, Me, benzyl) and $(RSCH_2CH_2)_2NH$ (R = alkyl) have been prepared and tested for the trimerization of ethylene to 1-hexene. The effect of P or S donor substitution, nitrogen substitution, and chelate ring size has been examined. Sterically compact and basic P or S groups lead to the highest activities and selectivities, while a secondary amine central donor is crucial for high activity, raising the possibility that deprotonation of this group occurs during catalyst formation. Expanding the chelate ring size by introduction of a propyl spacer on one side of the SNS ligand gives $EtSC_3H_6N(H)C_2H_4SEt$, which leads to a trimerization catalyst with lower activity. The scope of S-donor-based ligands for ethylene trimerization was further studied by preparing and testing PSP and SPS tridentates of Cr^{III}. These complexes give rise to active oligomerization systems that give product distributions characteristic of both linear chain growth and selective trimerization.

Introduction

The oligomerization of ethylene is predominantly carried out using transition metal catalysts that produce a geometric distribution of linear alpha olefins (LAOs). While the C_6-C_{20} range is used on a large global scale as comonomers, as surfactant precursors, and in synthetic lubricant production,[1] such distributions of LAOs do not closely match market demand. In particular, 1-hexene and 1-octene are in high demand due to their use as comonomers for polyethylene production (LLDPE). This has led to considerable recent interest in the selective oligomerization of ethylene, particularly trimerization to 1-hexene.[2] Of the systems known to trimerize ethylene, the majority are based on Cr catalysts,[3−7] although other metals such as Ti[8] and Ta[9] have also been employed. A number of mechanistic studies, both experimental[10,11] and theoretical,[12] have also appeared recently, and all point toward a mechanism involving metallacycle formation and growth for the ethylene trimerization reaction. Additionally, the selective tetramerization of ethylene to 1-octene has recently been reported for the first time, catalyzed by highly active Cr-diphosphinoamine catalysts.[13]

We recently communicated on mixed-donor tridentate (PNP, SNS) complexes of Cr^{III}, which act as highly selective and efficient precatalysts for ethylene trimerization when activated with MAO.[14,15] Both the PNP

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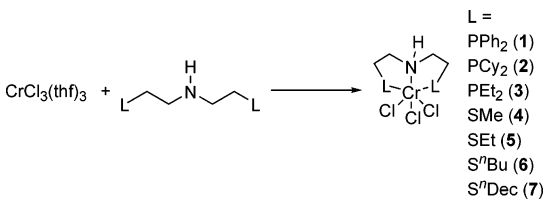
Scheme 1. Preparation of Complexes 1−7



and SNS systems were capable of total 1-hexene selectivities of over 97%, making them among the most selective systems available. As a result of its straightforward and inexpensive synthesis, the SNS system was optimized more extensively and was shown to give TOFs up to 260 000 h^{-1}. However, these initial reports focused only on the effect of substitution at the P or S donors. Herein we report full results on these systems, looking also at the effect of N substitution, chelate ring size, and changes to the tridentate donor set. In addition to new PNP and SNS Cr complexes, SPS and PSP complexes have also been prepared and characterized. These new complexes have been evaluated as ethylene oligomerization catalysts, and the factors required for selective trimerization with these systems are discussed.

Results and Discussion

The tridentate PNP and SNS ligands, in which the central donor is a secondary amine (H substitution), were prepared via literature procedures or through adaptation of these.[16,17] When reacted with $CrCl_3(thf)_3$, the immediate formation of complexes **1**−**7** was observed, which were isolated as blue-purple (**1**−**3**) or green (**4**−**7**) powders in high yield (80−100%, Scheme 1). The characterization of these complexes, including X-ray structural analysis of **1**, **2**, and **5**, has been reported previously.[14,15] The complexes display an octahedral geometry, as expected for Cr^{III}, with the ligands coordinated in a meridonal fashion. The structures of the PNP and SNS precatalysts are closely similar, indicating that the metal−ligand bonding for both families of ligands is also similar. The fact that both systems trimerize ethylene with very similar selectivities also supports a similar mode of binding for the PNP and SNS ligands. The same general procedure for complex preparation was followed for ligands with different N-substitution, different N−S spacer length, and different donor sets (see below; full details are given in the Experimental Section). Catalytic testing was carried out in a magnetically stirred 75 mL autoclave, immersed in an oil bath heated to 80−100 °C with toluene as solvent.[18] The ethylene pressure in the autoclave was 40 bar unless otherwise stated, and the cocatalyst employed in each case was MAO.

Effect of Substitution at Phosphorus or Sulfur. Selected results of ethylene trimerization with complexes **1**−**6** are shown in Table 1, which illustrate the effect of differing R groups on P and S and also serve as a benchmark for the results with different complexes. The marked effect of differing phosphorus substitution is shown in entries 1−3. Complex **1**, when activated with 120 equiv of MAO, was found to give a reasonable activity along with excellent selectivity toward 1-hexene. When bulky dicyclohexylphosphino substitution is introduced, the activity is greatly attenuated, and the main product formed is polyethylene (entry 2). However, with highly basic and sterically compact diethylphosphino substitution the activity of the system is doubled relative to catalyst **1**, and excellent selectivity to 1-hexene is restored. A greater loading of MAO (up to ca. 700 equiv) leads to higher activities (entry 5), and the optimal run temperature is within the range 80−100 °C. At lower temperatures the activity drops and a high polymer content results (entry 6), while at higher temperatures catalyst deactivation is observed and the formation of higher oligomers results (entry 7).

These results suggest that alkyl groups with a low steric demand (*n*-alkyl) lead to the most active catalysts with this ligand class. Such substitution was therefore employed on SNS complexes **4**−**7**. Entries 8−10 in Table 1 show that high trimerization activity results from substitution of phosphorus donors for sulfur and illustrates the effect that alkyl chain length has on activity and selectivity. Very similar results were obtained with either Me or Et groups on the S donors. With *n*-Bu groups on S, the selectivity is much the same; however a definite increase in activity is observed (entry 10). On going from shorter alkyl chain substitution to the *n*-Bu groups of complex **6**, a noticeable increase in solubility of the precatalyst was observed, which may account for this increase in activity to some extent.

The effect of *n*-alkyl chain length is further illustrated by comparative runs conducted under more optimal conditions with complexes **5** and **7** (Table 2).[19] A general trend of lower activities as a result of reduced amounts of MAO cocatalyst can be seen. Comparing complex **5**, with ethyl substitution, and complex **7**, which contains *n*-decyl substitution, it is evident that the longer alkyl chain leads to significantly enhanced activity. Employing complex **7**, it is possible to achieve high catalyst activity in the presence of very low loadings of MAO. For instance, a TOF of ca. 150 000 results from using only 30 equiv of MAO (entry 6). Table 2 also shows that an overall selectivity to 1-hexene of over 98% can be obtained with this system (entries 1 and 7).

Effect of Substitution at Nitrogen. Complexes **1**−**7** all contain a central secondary amine donor, and it is possible that during catalyst formation this is deprotonated to give an anionic amide ligand. This could be

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(18) Although higher activities and selectivities are achievable under conditions of better mass transfer and temperature control,[15] this system proved sufficient for comparing activities and selectivities of different catalysts.

(19) In these examples, a 300 mL Parr autoclave with gas entraining mechanical stirring was employed. The internal temperature was monitored and maintained at 90 °C.

Table 1. Ethylene Trimerization with Complexes 1−6[a]

entry	catalyst (amount μmol)	MAO (equiv)	temperature (°C)	PE (wt %)	C_6 (wt %)	1-C_6 (wt %)[b]	TOF (h^{-1})[c]	productivity (g/g Cr/h)
1	**1** (40.2)	120	100	0.1	98	99.2	8670	4680
2	**2** (42.3)	120	100	85.7	14	80.0	580	315
3	**3** (50.0)	100	100	0.2	98	99.2	17 300	9330
4	**3** (10.8)	690	100	0.7	98	98.9	58 570	31 600
5	**3** (11.0)	680	80	0.4	97	99.2	50 770	27 390
6	**3** (13.0)	600	50	21.9	78	98.8	2950	1590
7	**3** (11.3)	660	120	0.2	93	99.3	49 620	26 770
8	**4** (11.0)	600	80	0.11	94	99.7	77 050	41 570
9	**5** (11.0)	600	80	0.66	94	99.7	75 260	40 600
10	**6** (11.0)	600	80	0.97	93	99.3	95 470	51 510

[a] Conditions: 25 mL of toluene, 40 bar ethylene, 30 min. [b] Selectivity for 1-hexene as a percentage of total C_6 fraction. [c] Average TOF of ethylene conversion.

Table 2. Ethylene Trimerization with Complexes 5 and 7[a,19]

entry	catalyst (amount μmol)	MAO (equiv)	pressure (bar)	PE (wt %)	C_6 (wt %)	1-C_6 (wt %)	TOF (h^{-1})	productivity (g/g Cr/h)
1	**5** (4.6)	280	30	0.16	98.4	99.7	298 900	160 840
2	**5** (4.3)	120	30	0.38	97.1	99.8	104 870	56 260
3	**5** (12.0)	200	50	0.10	98.0	99.7	211 820	113 950
4	**5** (12.0)	50	45	1.92	99.8	∼100	13 640	7360
5	**7** (12.0)	100	45	0.30	97.2	99.7	263 757	142 035
6	**7** (12.0)	30	45	1.51	97.4	99.7	147 619	82 654
7	**7** (8.0)	50	45	1.11	98.7	99.8	153 482	85 950

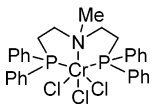
[a] Conditions: 100 mL of toluene, 90 °C, 30 min.

Table 3. Ethylene Oligomerization with Complexes 8−13[a]

entry	catalyst (amount μmol)	MAO (equiv)	pressure (bar)	PE (wt %)	C_6 (wt %)	1-C_6 (wt %)	TOF (h^{-1})	productivity (g/g Cr/h)
1	**8** (40.9)	120	40	30.6	40	∼100[b]	1708	922
2	**9** (41.5)	120	40	66.7	24	∼100[b]	360	194
3[c]	**10** (10.7)	670	40	1.4	81	97.9	27 380	14 770
4	**11** (42.0)	120	35	6.0	26[d]	82.6	9520	5130
5	**12** (51.5)	100	35	1.2	68	92.6	4380	2360
6	**12** (12.0)	620	35	14.9	26[e]	90.0	21 980	11 860
7	**13** (38.0)	130	40	4.4[f]	40[g]	67.2	13 740	7410
8	**13** (9.4)	790	40	7.8[f]	24[h]	88.9	38 760	20 910

[a] Conditions: 25 mL of toluene, 40 bar ethylene, 100 °C, 30 min. [b] C_6 isomers not detected. [c] 80 °C. [d] Schulz−Flory distribution, $K = 0.51$. [e] Schulz−Flory distribution, $K = 0.51$, C_6 24% enriched. [f] Wax. [g] Schulz−Flory distribution, $K = 0.56$, C_6 113% enriched. [h] Schulz−Flory distribution, $K = 0.67$, C_6 86% enriched.

achieved by direct action of MAO (or residual $AlMe_3$) on the amine or following alkylation of the Cr center. To probe the effect of alternative substitution on the central nitrogen, green PNP complexes **8** and **9** were prepared, which contain N-Me and N-benzyl substitution, respectively.



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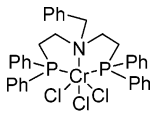

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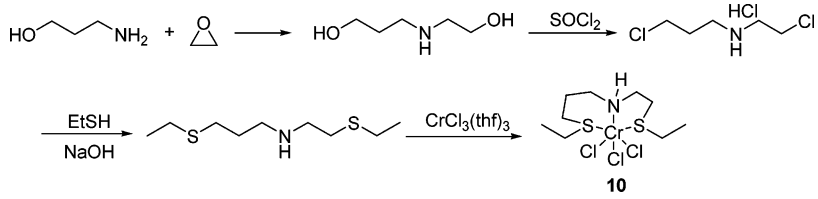
Table 3, entry 1 shows the results obtained when complex **8** was tested for trimerization activity and reveals that incorporation of an alkyl group on N leads to a dramatic decrease in both activity and selectivity. In this case, 30% of the product formed was polyethylene. Incorporation of a benzyl group (entry 2) leads to an even lower activity and a polymer content of 66%. With regards to selectivity within the liquid fraction (**8**, 57%; **9**, 71% 1-hexene), both catalysts produce more 1-hexene than is to be expected from a linear chain growth mechanism (Schulz−Flory), indicating that the catalysts are capable of following a trimerization mechanism. However, these results would seem to suggest that N−H functionality is essential for high activity and selectivity with this ligand system.

Effect of Chelate Ring Size. To evaluate the effect of expanding the chelate ring size on one side of the ligand, an asymmetric SNS ligand with a propyl spacer was prepared according to Scheme 2 and coordinated to Cr to yield complex **10**.

Complex **10** gives rise to an active trimerization catalyst as shown in Table 3, entry 3. However, the activity of this complex is less than half that of its symmetrical analogue **5** (Table 1, entry 9), and selectivity toward C_6 is likewise lower. This result is in contrast to those claimed for neutral tridentate ligand (PPP) Cr trimerization systems,[4] in which such a change leads to a large increase in activity (with little change in selectivity).

Effect of Donor Set: PSP and SPS Complexes. The utility of S-donor-containing ligands was further explored by preparing complexes of phosphine-sulfur tridentates. Such ligands represent sulfur-containing analogues of PPP trimerization systems.[4] The PSP complexes **11** and **12** were prepared according to Scheme 3, and results of catalytic tests are given in Table 3. Complex **11**, with diphenylphosphino substitution, does not lead to selective trimerization, but rather a Schulz−

Scheme 2. Preparation of Complex 10



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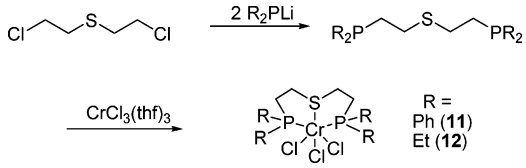
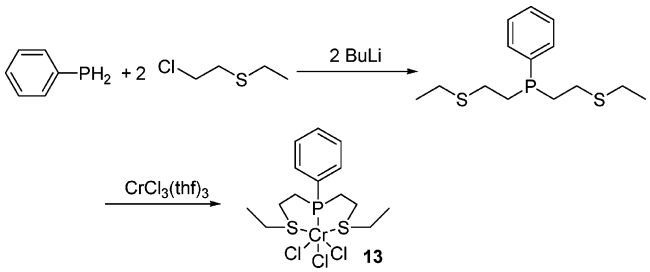
Scheme 3. Preparation of Complexes 11 and 12



Scheme 4. Preparation of Complex 13



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Flory distribution of olefins with a K^{20} value of 0.51 (entry 4). When diethylphosphino substitution is introduced, complex **12** gives predominantly 1-hexene, although the performance of this complex is poorer than the SNS and PNP catalysts (entry 5). When complex **12** is employed with more MAO, the activity increases; however this is at the expense of selectivity to C_6 (entry 6). In this instance, analysis of the C_8-C_{14} fraction reveals a Schulz–Flory distribution ($K = 0.51$); however the amount of C_6 is 24% higher than expected on the basis of such a distribution, suggesting that two active species (trimerization and linear chain growth) are present in the system.

A single example of an SPS complex was prepared, as shown in Scheme 4. Qualitatively similar results are obtained with complex **13** (entries 7 and 8) as were obtained with complex **12**. With 130 equiv of MAO a Schulz–Flory distribution is obtained (C_8-C_{14}, $K = 0.56$) that contains over twice the expected amount of C_6. Employing more MAO (790 equiv) leads to a high activity; however the selectivity to C_6 drops. In this instance a K value of 0.67 is obtained for the oligomers, enriched in C_6 by 86%, giving an overall C_6 content of 24%.

It is evident from these results that PSP and SPS ligands are capable of catalyzing the trimerization of ethylene; however conventional chain-growth oligomerization occurs concurrently. Although it is possible that the conditions could be optimized to increase 1-hexene selectivity with these catalysts, it seems that in terms of both activities and selectivities observed, the SNS- and PNP-based catalysts are superior.

Conclusion

A number of novel Cr^{III} mixed-donor complexes of PNP, SNS, PSP, and SPS tridentates have been prepared and evaluated for ethylene trimerization. Replacement of phosphine donors with sulfur gave a series of easily and inexpensively prepared SNS complexes that exhibit extremely high activity and selectivity when activated with MAO. The effect of placing alkyl groups on the central nitrogen donor shows that H-substitution is an essential attribute of this ligand class for high activity. This raises the possibility that deprotonation to give an anionic ligand may be occurring, which is under further investigation. While expansion of the chelate ring on one side of the ligand does give rise to an active trimerization catalyst, the efficiency of the system is reduced with such a change. The range of ligands has also been extended to include PSP and SPS complexes, which give rise to active ethylene oligomerization catalysts. Although these new systems do not show the same high activity or selectivity toward 1-hexene as SNS complexes, they do further demonstrate the usefulness of S-donor ligands on early transition metals. Unlike the SNS ligands, they do not contain an easily abstractable proton and, as such, are perhaps more similar to PPP-Cr trimerization systems that have been reported.[4]

Further investigations of the PNP and SNS-Cr systems with regards to the mode of ligand binding in the active catalyst, oxidation state of the metal, and role of the cocatalyst are underway and will be reported in due course.

Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox, using solvents purified and dried by standard procedures. Nuclear magnetic resonance spectra were recorded at ambient temperature (300 MHz, ^1H; 75 MHz, ^{13}C; 121 MHz, ^{31}P), and peaks are labeled as singlet (s), doublet (d), multiplet (m), and broad (br).

Ethylene Trimerization. Trimerization was conducted in a 75 mL stainless steel autoclave, fitted with an addition funnel. The base of the autoclave was charged with MAO (Aldrich, 10 wt % in toluene) and the addition funnel with a 20 mL toluene solution of the catalyst. The autoclave was immersed in an oil bath at the desired temperature and allowed to equilibrate for 20 min, after which the autoclave was charged with ethylene and the catalyst solution added to the MAO solution. The reactor was maintained at constant pressure with the use of a ballast vessel. After the desired reaction time the autoclave was cooled to 0 °C and depressurized. The off-gas was collected and analyzed for 1-butene. Internal standard (nonane) was added to the reaction solution, which was then quenched with MeOH and 10% HCl. The organic phase was analyzed by GC and solid polyethylene collected by filtration, washed with MeOH, dried, and weighed.

$(Ph_2PCH_2CH_2)_2NMe$. A 4 mL (35 mmol) sample of *N*-methyldiethanolamine was added dropwise to 10 mL (138 mmol) of $SOCl_2$, after which the solution was stirred for 15 min. Excess $SOCl_2$ was removed under vacuum and the residue washed with ether to give a powder, bis(2-chloroethyl)-

(20) $K = k_{prop}/(k_{prop} + k_{ch\ transfer}) = \text{mol } C_{n+2}/\text{mol } C_n$.

methylamine hydrochloride. A solution of the amine hydrochloride (2.11 g, 10.9 mmol) in water was treated with 1 equiv of NaOH, extracted into ether, and dried over $MgSO_4$. After filtration the solvent was removed to yield 1.137 g (7.28 mmol) of liquid. This was taken up in 5 mL of THF and added to a solution of Ph_2PLi (prepared from 2.918 g, 15.67 mmol of Ph_2PH and 15.7 mmol of BuLi in 10 mL of THF) at −50 °C. The solution was allowed to warm to RT and then heated to 60 °C overnight. After cooling, 20 mL of water was added and the organics were separated, dried over $MgSO_4$, and filtered. The solvent was removed under vacuum and the product heated to 100 °C under vacuum to afford a thick oil. Yield: 2.475 g (50% from amine hydrochloride). ^{1}H NMR (C_6D_6): 7.51 (m, 8H, phenyl*H*); 7.17 (m, 12H, phenyl*H*); 2.56 (m, 4H, CH_2); 2.24 (m, 4H, CH_2); 2.13 (s, 3H, NCH_3). ^{31}P NMR (C_6D_6): −18.5.

(EtSCH$_2$CH$_2$CH$_2$)N(H)(CH$_2$CH$_2$SEt). *N*-Propanolamine (55 g, 0.73 mol) was taken up in 50 mL of THF in a glass pressure reactor and 16.8 g (0.38 mol) of ethylene oxide condensed in. After stirring for 2 days at RT the mixture was fractionally distilled at 0.1 mm. (HOCH$_2$CH$_2$CH$_2$)N(H)(CH$_2$CH$_2$OH) distilled at 124 °C. Yield: 25.72 g (57%). ^{1}H NMR (CD_3CN): 3.63 (t, J = 6 Hz, 2H, NCH_2CH$_2$CH$_2$OH); 3.55 (t, J = 5 Hz, 2H, NCH_2CH$_2$OH); 2.90 (s, br, 3H, NH + OH); 2.74 (t, J = 6 Hz, 2H, NCH$_2$CH$_2$CH_2OH); 2.65 (t, J = 5 Hz, 2H, NCH$_2$CH_2OH); 1.65 (m, J = 6 Hz, 2H, NCH$_2$CH_2CH$_2$OH). ^{13}C NMR (CD_3CN): 61.3, 60.3 (N*C*H$_2$); 51.1, 47.5 (HO*C*H$_2$); 31.4 (CH$_2$*C*H$_2$CH$_2$). The diol-amine (16.49 g, 0.134 mol) was added dropwise to 70 mL (0.96 mol) of $SOCl_2$ and the solution stirred for 6 days, after which the solvent was removed under vacuum and the residue triturated with 80 mL of ether to give a white powder. The product was washed with more ether (2 × 60 mL) and dried under vacuum to give (ClCH$_2$CH$_2$CH$_2$)N(H)(CH$_2$CH$_2$Cl)·HCl. Yield: 24.01 g (93%). ^{1}H NMR (D_2O): 3.78 (t, J = 5 Hz, 2H, NCH_2CH$_2$Cl); 3.59 (t, J = 6 Hz, 2H, NCH_2CH$_2$CH$_2$Cl); 3.38 (t, J = 5 Hz, 2H, NCH$_2$CH_2Cl); 3.18 (t, J = 6 Hz, 2H, NCH$_2$CH$_2$CH_2Cl); 2.09 (m, J = 6 Hz, 2H, NCH$_2$CH_2CH$_2$Cl). ^{13}C NMR (D_2O): 49.2, 45.6 (N*C*H$_2$); 41.8, 39.5 (HO*C*H$_2$); 28.5 (CH$_2$*C*H$_2$CH$_2$). The hydrochloride (5.32 g, 27.6 mmol), ethanethiol (5.32 g, 85.6 mmol), and NaOH (3.46 g, 86.5 mmol) were combined in 100 mL of ethanol and left to stir for 2 days. The solution was filtered and the solvent removed under vacuum. Water was added, the mixture was extracted four times with ether and filtered, and the solvent was removed to leave a pale yellow liquid, (EtSCH$_2$CH$_2$CH$_2$)N(H)(CH$_2$CH$_2$SEt). Yield: 4.106 g (72%). ^{1}H NMR ($CDCl_3$): 2.79 (t, J = 7 Hz, 2H SCH_2); 2.70 (2t, J = 7 Hz, 6 Hz, 4H, NCH_2); 2.55 (m, 6H, SCH_2); 1.76 (m, J = 7 Hz, 2H, SCH$_2$CH_2CH$_2$N); 1.51 (s, br, 1H, NH); 1.24 (t, J = 7 Hz, 6H, SCH$_2$CH_3). ^{13}C NMR ($CDCl_3$): 48.9 (N*C*H$_2$); 32.3, 30.2, 29.8, 26.3, 26.2 (*C*H$_2$); 15.3, 15.1 (SCH$_2$*C*H$_3$).

(Et$_2$PCH$_2$CH$_2$)$_2$S. A THF solution of Et_2PLi (6.2 mL of 0.67 M, 4.1 mmol) was added dropwise to a solution of S(CH$_2$CH$_2$Cl)$_2$ (0.323 g, 2.03 mmol) in 5 mL of THF at −50 °C. After warming to RT the solution was heated to 60 °C for 90 min before 10 mL of water was added, and the organics were separated, dried over $MgSO_4$, and filtered. Removal of the solvent under vacuum gave a clear oil. Yield: 0.491 g (91%). ^{1}H NMR (C_6D_6): 2.71 (m, 4H, SCH_2); 1.73 (m, 4H, CH_2P); 1.29 (m, 8H, PCH_2); 1.06 (m, 12H, PCH$_2$CH_3). ^{13}C NMR (C_6D_6): 29.6, 27.7 (2d, J_{CP} = 19 Hz, 18 Hz, SCH_2*C*H$_2$P); 19.6 (d, J_{CP} = 13 Hz, P*C*H$_2$); 10.2 (d, J_{CP} = 13 Hz, PCH$_2$*C*H$_3$). ^{31}P NMR (C_6D_6): 21.1.

(Ph$_2$PCH$_2$CH$_2$)$_2$S was prepared in the same manner as above. ^{1}H NMR (C_6D_6): 7.45 (m, br, 8H, phenyl*H*); 7.16 (br, 12H, phenyl*H*); 2.62 (m, 4H, SCH_2); 2.31 (m, 4H, CH_2P). ^{13}C NMR (C_6D_6): 139.3 (d, J_{CP} = 15 Hz, phenyl*C*$_{ipso}$); 133.4 (d, J_{CP} = 18 Hz, phenyl*C*); 129.2, 129.1 (phenyl*C*); 29.2 (m, *C*H$_2$*C*H$_2$). ^{31}P NMR (C_6D_6): −15.8.

(EtSCH$_2$CH$_2$)$_2$PPh. Diphenylphosphine (0.927 g, 8.42 mmol) was taken up in 10 mL of THF and treated with BuLi (10.5 mL of 1.6 M, 16.8 mmol) at 0 °C. After stirring for 1 h at RT, the mixture was cooled to −70 °C and a solution of 2-chloroethyl ethyl sulfide (2.014 g, 16.2 mmol) in 5 mL of THF added dropwise. After warming to RT the solution was heated to 60 °C overnight and hydrolyzed with 10 mL of water, and the organics were dried over $MgSO_4$. After filtration the solvent was removed under vacuum to give a colorless liquid. Yield: 1.609 g (69%). ^{1}H NMR (C_6D_6): 7.51 (m, 2H, phenyl*H*); 7.20 (m, 3H, phenyl*H*); 2.56 (m, 4H, PCH$_2$CH_2); 2.31 (q, J = 7 Hz, 4H, SCH_2CH$_3$); 2.00 (m, 4H, PCH_2CH$_2$); 1.10 (t, J = 7 Hz, 6H, SCH$_2$CH_3). ^{13}C NMR (C_6D_6): 133.1 (d, J_{CP} = 19 Hz, phenyl*C*); 129.7, 129.3, 129.2 (phenyl*C*); 29.5, 28.8 (2d, J_{CP} = 16 Hz, 19 Hz, SCH_2*C*H$_2$P); 26.4 (S*C*H$_2$CH$_3$); 15.2 (SCH$_2$*C*H$_3$). ^{31}P NMR (C_6D_6): −24.1.

Synthesis of Complexes 8−13. The complexes were all prepared via a similar procedure, in yields of 80−100%, illustrated below for **9**.

CrCl$_3$[(Ph$_2$PCH$_2$CH$_2$)$_2$NBz] (9). $CrCl_3(thf)_3$ (0.191 g, 0.510 mmol) was taken up in 10 mL of THF, and a solution of (Ph$_2$PCH$_2$CH$_2$)$_2$NBz (0.276 g, 0.52 mmol) in 5 mL of THF added. The solution was stirred for 20 min, over which time a green precipitate formed. The solvent was evaporated to about half the original volume and 10 mL of ether added to complete precipitation. The product was collected by filtration, washed with 10 mL of ether, and dried under vacuum. Yield: 0.359 g (102%). MS (FAB): *m/z* 690 (10%, [M]$^+$); 653 (80%, [M − Cl]$^+$). Anal. Calcd for $C_{35}H_{35}NP_2Cl_3Cr$ (found): C, 60.93 (60.91); H, 5.11 (5.48); N, 2.03 (1.71).

CrCl$_3$[(Ph$_2$PCH$_2$CH$_2$)$_2$NMe] (8). MS (FAB): *m/z* 612 (5%, [M]$^+$); 577 (40%, [M − Cl]$^+$). Anal. Calcd for $C_{29}H_{31}NP_2Cl_3Cr$ (found): C, 56.74 (56.58); H, 5.09 (5.43); N, 2.28 (2.18).

CrCl$_3$[(EtSCH$_2$CH$_2$CH$_2$)N(H)(CH$_2$CH$_2$SEt)] (10). Anal. Calcd for $C_9H_{21}NS_2Cl_3Cr$ (found): C, 29.55 (29.56); H, 5.79 (5.94); N, 3.83 (3.72).

CrCl$_3$[(Ph$_2$PCH$_2$CH$_2$)$_2$S] (11). MS (FAB): *m/z* 580 (30%, [M − Cl]$^+$).

CrCl$_3$[(Et$_2$PCH$_2$CH$_2$)$_2$S] (12). MS (FAB): *m/z* 388 (100%, [M − Cl]$^+$). Anal. Calcd for $C_{12}H_{28}SP_2Cl_3Cr$ (found): C, 33.94 (33.61); H, 6.65 (6.86).

CrCl$_3$[(EtSCH$_2$CH$_2$)$_2$PPh] (13). MS (FAB): *m/z* 408 (40%, [M − Cl]$^+$). Anal. Calcd for $C_{14}H_{23}S_2PCl_3Cr$ (found): C, 37.81 (37.79); H, 5.21 (5.49).

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