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New Chromium(II) Bidentate Phosphine Complexes: Synthesis, Characterization, and Behavior in the Polymerization of 1,3-Butadiene

Giovanni Ricci,*,[†] Alessandra Forni,[‡] Aldo Boglia,[†] and Mauro Sonzogni[†]

CNR, Istituto per lo Studio delle Macromolecole (ISMAC), Via E. Bassini 15, 20133 Milano, Italy, and CNR, Istituto di Scienze e Tecnologie Molecolari (ISTM), Via C. Golgi 19, 20133 Milano, Italy

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New chromium(II) bidentate phosphine complexes were synthesized by reacting $CrCl_2$(thf) with various bidentate phosphines [bis(dimethylphosphino)methane (dmpm); 1,2-bis(diethylphosphino)ethane (depe); 1,3-bis(diethylphosphino)propane (depp); 1,2-bis(dicyclohexylphpsphino)ethane (dcpe)] in toluene or diethyl ether as solvent. Single crystals of the complex $CrCl_2(depe)_2$ were obtained by recrystallization from toluene at low temperature; the structure of the complex was determined by X-ray diffraction and compared with that of the analogous methyl derivative $CrCl_2(dmpe)_2$ previously reported by Girolami et al. (dmpe = 1,2-bis(dimethylphosphino)ethane). All the complexes prepared were then used in combination with methylaluminoxane (MAO) for the polymerization of 1,3-butadiene. They were found to be very active catalysts, giving essentially 1,2-polybutadienes having a syndiotactic or isotactic structure depending on the type of phosphine bonded to the chromium atom. The results obtained also have some mechanistic implications and have been interpreted on the basis of the diene polymerization mechanism previously proposed.

Introduction

Chromium catalysts are reported to be specific systems for the 1,2 polymerization of butadiene.[1] The system $Cr(acac)_3-AlEt_3$, for example, gives a 1,2 polybutadiene having a syndiotactic or isotactic structure depending on the polymerization conditions (e.g., Al/Cr molar ratio); the activity of this system is however rather low.[2] More active and stereospecific catalysts have been recently obtained in our laboratory by combining $CrCl_2(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) with methylaluminoxane (MAO); this system gives from butadiene a highly stereoregular 1,2 syndiotactic polymer.[3] The same system is also able to polymerize isoprene and (*E*)-1,3-pentadiene, giving a 3,4 polymer and a *cis*-1,4 isotactic polymer,[3] respectively, indicating that monomer structure strongly affects polymer microstructure. We have now investigated the influence of the type of phosphine ligand on polymerization chemo- and stereoselectivity; it is well known that steric and electronic effects of phosphorus ligands strongly depend on the type of substituents on the phosphorus atom.[4] To this end, we have synthesized various new bidentate phosphine chromium(II) complexes, following the experimental procedures already reported for $CrCl_2(dmpe)_2$ [5] and $CrCl_2$(dippe) (dippe = 1,2-bis(diisopropylphosphino)ethane),[6] and we have used them in combination with MAO for the polymerization of butadiene. The most significant results obtained are reported in this paper.

Results and Discussion

Synthesis and Characterization of Cr(II) Complexes. The new Cr(II) complexes of this work were synthesized following the experimental procedures previously reported for analogous Cr(II) complexes.[5,6] $CrCl_2$(thf)[7] was reacted with different bidentate phosphines [bis(dimethylphosphino)methane (dmpm); 1,2-bis(diethylphosphino)ethane (depe); 1,3-bis(diethylphosphino)propane (depp); 1,2-bis(dicyclohexylphpsphino)ethane (dcpe)] using toluene or diethyl ether as solvent. The elemental analyses of the products obtained indicate that two ligands are bonded to the chromium atom in the case of dmpm, depe, and depp, while only one bidentate phosphine is bonded in the case of dcpe; this different behavior probably depends on the steric hindrance of the ligands, and it is in some way in agreement with the structures reported for $CrCl_2(dmpe)_2$[5] and $CrCl_2$(dippe).[6] Single crystals suitable for X-ray structure determination were obtained only in the case of $CrCl_2(depe)_2$ by recrystallization from toluene solution at low temperature (−30 °C). The molecular structure is shown in Figure 1, and selected bond lengths and angles are reported in Table 1, together with the

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* Corresponding author. E-mail: giovanni.ricci@ismac.cnr.it.

[†] ISMAC.

[‡] ISTM.

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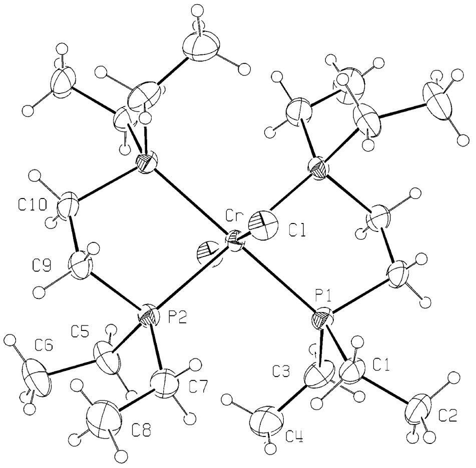

Figure 1. ORTEP plot[15] of $CrCl_2(depe)_2$ with atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $CrCl_2(depe)_2$ and $CrCl_2(dmpe)_2$

	$CrCl_2(depe)_2$[a]	$CrCl_2(dmpe)_2$[b]
Cr−P1	2.4067(7)	2.372, 2.371
Cr−P2	2.4056(7)	2.365, 2.368
Cr−Cl	2.3414(7)	2.351, 2.345
P1−C10	1.849(3)	1.834, 1.854
P2−C9	1.836(3)	1.842, 1.861
P1−C1	1.827(3)	1.808, 1.835
P1−C3	1.837(3)	1.804, 1.825
P2−C5	1.835(3)	1.816, 1.823
P2−C7	1.831(3)	1.860, 1.811
C9−C10	1.522(4)	1.380, 1.487
P1−Cr−P2	81.77(2)	82.9, 82.7
Cr−P1−C10	108.76(9)	108.2, 109.2
Cr−P2−C9	106.79(9)	107.9, 107.1
Cr−P1−C1	119.63(9)	120.6, 120.9
Cr−P1−C3	119.98(10)	120.3, 118.7
Cr−P2−C5	116.95(11)	119.3, 118.5
Cr−P2−C7	120.24(10)	119.4, 123.6
C1−P1−C3	104.03(15)	103.4, 100.7
C5−P2−C7	104.66(17)	101.6, 101.0
C1−P1−C10	101.72(14)	96.0, 104.3
C3−P1−C10	99.47(15)	104.8, 100.3
C5−P2−C9	103.25(15)	106.1, 101.8
C7−P2−C9	102.81(14)	100.4, 101.6
C2−C1−P1−C10	−47.4(3)	
C4−C3−P1−C10	175.9(3)	
C6−C5−P2−C9	−32.7(3)	
C8−C7−P2−C9	41.2(3)	

[a] Present work. [b] Ref 5. The asymmetric unit of this structure comprises two-half molecules.

corresponding values obtained for the analogous methyl derivative $CrCl_2(dmpe)_2$.[5] The two complexes are structurally very similar, as expected; nevertheless some small but significant differences can be detected. Among them, the most remarkable one concerns the Cr−P distances. By averaging all the Cr−P bonds in the two structures, a shortening of 0.037 Å is found on going from $CrCl_2(depe)_2$ to $CrCl_2(dmpe)_2$, indicating a weaker bond in the former complex. To ascertain the reliability of this small difference, theoretical calculations on the two complexes were performed. The computed average values of the Cr−P distances in $CrCl_2(depe)_2$ and $CrCl_2(dmpe)_2$, 2.419 and 2.334 Å, respectively, reproduced quite well the experimental ones and confirmed the observed shortening, though to a larger extent, of the Cr−P bonds on going from the former to the latter complex. On the other hand, theoretical calculations were not able to correctly reproduce the Cr−Cl distances, giving too high values in both compounds, 2.582 and 2.548 Å in $CrCl_2(depe)_2$ and $CrCl_2(dmpe)_2$, respectively. Moreover, at variance with the X-ray Cr−Cl distances, which are comparable within experimental error, the theoretical values decrease on going from the former to the latter complex, though to a lower extent with respect to what is computed for the Cr−P bonds.

A considerable difference between the X-ray structure of the two complexes is also observed in the C−C distance of the methylene moiety. While in $CrCl_2(depe)_2$ it assumes a standard value equal to 1.522 Å, the average value in $CrCl_2(dmpe)_2$ amounts to only 1.433 Å. However, this parameter has to be considered with caution, owing to high thermal motion which clearly occurs in at least one molecule of the asymmetric unit of $CrCl_2(dmpe)_2$, leading to artificially low C−C distances. The corresponding theoretical values, 1.528 and 1.536 Å in $CrCl_2(depe)_2$ and $CrCl_2(dmpe)_2$, respectively, are in fact comparable.

The two complexes are very similar as far as the bond angles are concerned. The only detectable, though very small, difference can be found in the C−P−C angles involving the carbon atoms of the ethyl/methyl groups, whose average values amount to 104.3° and 101.7° (103.3° and 100.3° from theory) in $CrCl_2(depe)_2$ and $CrCl_2(dmpe)_2$, respectively. This difference can be ascribed to steric factors, owing to the greater bulkiness of the ethyl with respect to methyl groups.

Polymerization of 1,3-Butadiene. The results obtained by polymerizing butadiene with catalysts based on different Cr(II) complexes are reported in Table 2 (the results previously obtained with $CrCl_2(dmpe)_2$ are reported for comparison) and can be summarized as follows.

- The system $CrCl_2(dmpm)_2$−MAO (Table 1, runs 1−4) gives from butadiene polymers with an essentially 1,2 structure (∼90%), in which isotactic sequences are predominant (percentage of isotactic triads [mm] = ∼70%), as shown in Figure 2. The polymers are not crystalline by X-ray, and no melting point was observed. The molecular weight (MW) and the molecular weight distribution (MWD), determined by GPC analysis, are 470 000 g mol^{-1} and 2.1, respectively. The low MWD value is in agreement with the single-site nature of the system used.
- The system $CrCl_2(depe)_2$−MAO (Table 2, runs 8−12) gives from butadiene crystalline, essentially 1,2 syndiotactic polymers. The 1,2 content, determined by the ^1H NMR analysis (Figure 3), is around 90−98%, slightly increasing with a decrease in the polymerization temperature. The syndiotactic index [rrrr] (percentage of syndiotactic pentads) of the polymers, evaluated from the ^{13}C NMR spectrum (Figure 2) as reported in the Experimental Section, and the melting point, determined by DSC (Figure 4), are instead much more influenced, increasing with a decrease in the polymerization temperature. At the same polymerization conditions, the 1,2 content, the syndiotactic index, and the melting point of the polymers obtained with $CrCl_2(depe)_2$−MAO (Table 2, runs 8−11) are lower than the corresponding values of the polymers obtained with $CrCl_2(dmpe)_2$−MAO (Table 2, runs 5−7).

Table 2. Polymerization of 1,3-Butadiene with Different Cr(II) Catalysts

	catalyst				polymerization[a]			polymer microstructure[b]				
run	Cr compound	θ^c (deg)	mol ×10^5	Al/Cr (molar ratio)	temp (°C)	time (h)	conv (%)	*cis* (%)	1,2 (%)	rr/mr/mm (%)	rrrr (%)	mp[d](°C)
1	$CrCl_2(dmpm)_2$	203	0.3	3000	+20	0.5	100	9.1	90.9	17/13/70		
2			1	1000	+20	0.5	80.2	10.7	89.3	16/13/71		
3			1	100	+20	2	29.3	8.8	91.2	15/21/64		
4			2	1000	−30	192	21.6	15.9	84.1	11/22/67		
5	$CrCl_2(dmpe)_2$	214	1	1000	+20	1	39.5	5	~95	83/17/0	63	152
6			1	100	+20	1	17.0	5	~95	82/18/0	61	151
7			2	1000	−30	142	41.9		~97		95	200
8	$CrCl_2(depe)_2$	230	1	1000	+20	1	76.0	10.9	89.1	72/26/2	49	106
9			1	300	+20	1	36.9	8.2	91.8	72/25/3	49	105
10			1	100	+20	2	19.5	9.9	90.1	71/26/3	48	104
11			1	1000	−30	68	20.7	4.7	95.3	87/13/0	70	184
12			1	1000	−78	600	10.0		~98		~95	200
13	$CrCl_2(depp)_2$	235	1	1000	+20	2.7	31.1	15.2	84.8	67/30/3	45	104
14			1	100	+20	1.4	7.5	14.0	86.0	66/30/4	43	103
15	$CrCl_2(dcpe)$	284	1	1000	+20	1110	5.9	34	66			

[a] Polymerization conditions: butadiene, 2 mL; toluene, total volume 16 mL; methylaluminoxane as cocatalyst. [b] Determined by NMR (^1H and ^{13}C) analysis; rr/mr/rr = molar ratio of syndiotactic/atactic/isotactic triads; rrrr = syndiotactic index, percentage of syndiotactic pentads (refs 20b−f). [c] Phosphine cone angle, as reported by Tolman (ref 4). [d] Melting point, determined by DSC analysis.

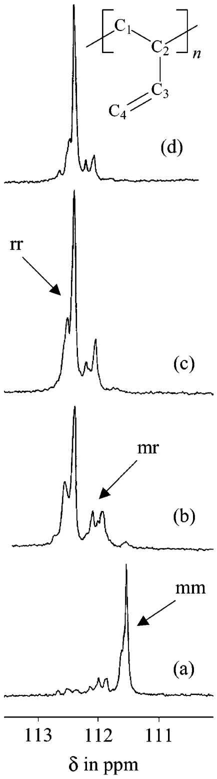

Figure 2. ^{13}C NMR spectra (olefinic region, C4 resonances; $C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of 1,2 polybutadienes obtained at +20 °C with (a) $CrCl_2(dmpm)_2$−MAO (Table 2, run 2), (b) $CrCl_2(depp)_2$−MAO (Table 2, run 13), (c) $CrCl_2(depe)_2$−MAO (Table 2, run 8), and (d) $CrCl_2(dmpe)_2$−MAO (Table 2, run 5).

• The system $CrCl_2(depp)_2$−MAO shows a polymerization behavior very similar to that of $CrCl_2(depe)_2$−MAO, even if the 1,2 content of the polymers obtained with the former system is slightly lower with respect to that of the latter one.

• The system $CrCl_2(dcpe)$−MAO, using much more hindered phosphine ligands (cone angle θ value of about 284°),[4] exhibits a very low activity with respect to the other systems; chemoselectivity too is much lower since polymers with a mixed *cis*-1,4/1,2 structure are obtained.

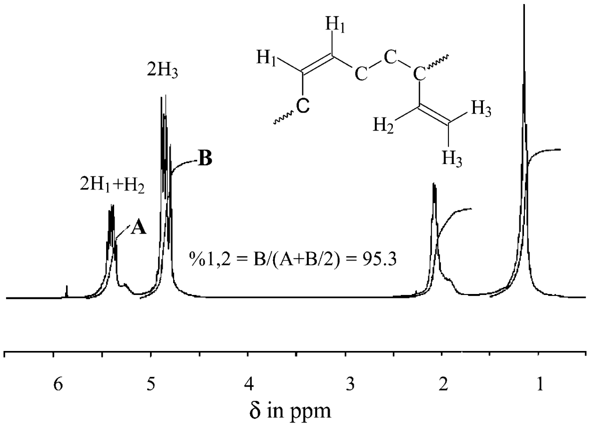

Figure 3. ^1H NMR spectrum ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of the 1,2 syndiotactic polybutadiene obtained with $CrCl_2(depe)_2$−MAO at −30 °C (Table 2, run 11) (A and B are the integrated areas of the resonances around 4.8 and 5.4 ppm, respectively).

• While the MAO/Cr molar ratio does not seem to affect the catalyst stereospecificity, it has some influence on the catalyst activity; in general catalysts prepared at higher Al/Cr molar ratio (1000) are more active than those prepared at lower molar ratio (Al/Cr = 100). This is probably due to the formation of a lower number of active sites at low Al/Cr molar ratio.

• In general, at the same polymerization conditions, the 1,2 content of the polybutadienes decreases with an increase in the steric hindrance of the phosphine ligand bonded to the chromium atom, indicating that the type of ligand has some influence on the chemoselectivity. Only the system $CrCl_2(dmpm)_2$−MAO makes an exception to this rule, but we have to consider that this catalyst is in some way different from the other ones since it gives a predominantly isotactic polymer while the other systems give a syndiotactic polymer. This last result seems to suggest that the type of ligand affects not only the chemoselectivity but also the stereoselectivity.

The formation of 1,2 polybutadienes having different types and levels of tacticity (iso- and syndiotactic) by varying the type of phosphine ligand and the polymerization conditions (e.g., the polymerization temperature)

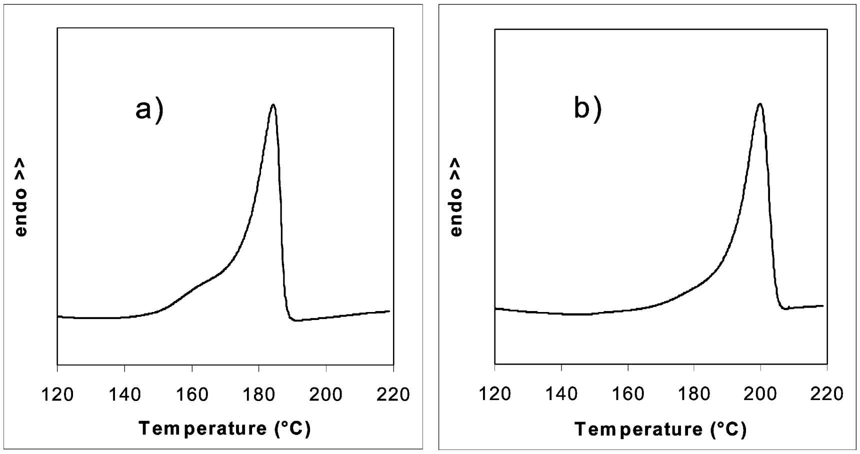

Figure 4. DSC curves of the polybutadienes obtained with $CrCl_2(depe)_2$−MAO at (a) −30 (Table 2, run 11) and (b) −78 °C (Table 2, run 12).

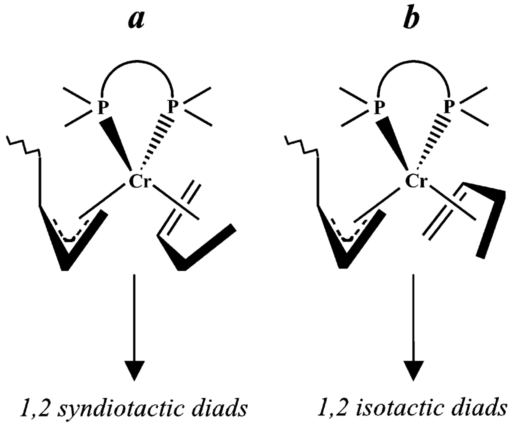

Figure 5. Scheme for formation of syndiotactic and isotactic diads in the polymerization of butadiene with Cr(II) catalysts.

can be interpreted on the basis of the diolefin polymerization mechanism previously proposed.[8]

In the case of the chromium catalyst of this paper, the catalytic site is most probably that shown in Figure 5, with only one bidentate phosphine ligand coordinated to the metal. When the new monomer reacts at C3 of the allylic unit, a 1,2 unit is formed: if the monomer and the allylic unit are oriented as shown in Figure 5a, a syndiotactic diad is obtained; if they are oriented as in Figure 5b, an isotactic diad is formed. Most probably in the case of hindered ligands (e.g., dmpe, depe, depp) the orientation as in Figure 5a is much more favored and 1,2 syndiotactic sequences are formed; when the ligand bulkiness is low (e.g., dmpm), both orientations are possible, even if that in Figure 5b is more favored, and predominantly isotactic sequences containing a certain amount of steric errors are formed.

The same scheme is also able to explain the formation, at low polymerization temperature, of more syndiotactic (higher percentage of rrrr pentads) polybutadienes with the systems $CrCl_2(L)_2$−MAO (L = dmpe, depe, depp) and of a less isotactic (lower percentage of mm triads and higher percentage of mr triads) polymer with the system $CrCl_2(dmpm)_2$−MAO. Most probably the probability of the orientation as in Figure 5a increases at low temperature and the amount of syndiotactic diads formed is larger with respect to that formed at room temperature; it follows that the syndiotactic polymers obtained with $CrCl_2(depe)_2$−MAO, for example, will contain a smaller number of stereoerrors, while in the isotactic polymer obtained with $CrCl_2(dmpm)_2$−MAO a larger number of stereoerrors will be present.

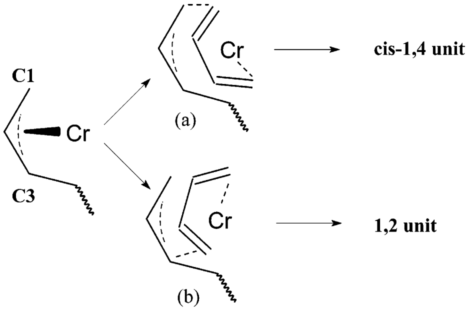

Figure 6. Scheme for formation of *cis*-1,4 units vs 1,2 units.

The data reported in Table 2 show that the chemoselectivity too (formation of *cis*-1,4 or 1,2 units) is influenced by the type of phosphine ligand: in general the *cis* content increases with increasing steric hindrance of the ligand, as indicated by the fact that $CrCl_2(dmpe)_2$−MAO gives a polymer with a 1,2 content of about 95%, while $CrCl_2(dcpe)$−MAO gives a polybutadiene with a mixed *cis*-1,4/1,2 structure (34:66 molar ratio).

Again, the diene polymerization mechanism previously proposed[8] can help us in interpreting such behavior. The type of ligand can affect the orientation of the incoming monomer with respect to the allylic unit of the polymer growing chain, favoring the insertion of the new monomer at C1 of the allylic unit (with formation of a *cis*-14 unit) or at C3 (with formation of a 1,2 unit) (Figure 6). The amount of *cis*-1,4 or 1,2 content depends on the probability of the two orientations (Figure 6a and 6b); when the probability is almost the same, an equibinary *cis*-1,4/1,2 polybutadiene can form, as occurred for instance in the polymerization of butadiene with the systems $Co(acac)_3$−$AlEt_3$−H_2O,[9] $MoCl_3(OR)_2$−AlR_3,[10] and $Fe(acac)_3$−$Al(iBu)_3$−bipy.[11]

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Conclusions

We have synthesized some new Cr(II) phosphine complexes which associated with MAO were found to be highly active and stereospecific for the 1,2 polymerization of butadiene. Depending on the type of phosphine ligand, they were able to give highly syndiotactic 1,2 polybutadiene or 1,2 isotactic polybutadiene: 1,2 syndiotactic polybutadiene is one of the only two diene polymers of industrial interest, the other one being *cis*-1,4 polybutadiene, while 1,2 isotactic polybutadiene was obtained only once several years ago by Porri.[2]

Moreover, the results obtained have clearly pointed out the influence of the ligand on chemo- and stereoselectivity, confirming the validity of the diene polymerization mechanism previously proposed.[8]

Experimental Section

Materials and Methods. Bis(dimethylphosphino)methane (dmpm) (Strem, 98% pure), 1,2-bis(diethylphosphino)ethane (depe) (Strem, 98% pure), 1,3-bis(diethylphosphino)propane (depp) (Fluka, 97% pure), 1,2-bis(dicyclohexylphosphino)-ethane (dcpe) (Strem, min 98% pure), and methylaluminoxane (MAO) (Crompton, 10 wt % solution in toluene) were used as received. Toluene (Fluka, >99.5% pure) was refluxed over Na for ca. 8 h, then distilled and stored over molecular sieves under dry nitrogen; pentane (Fluka, ≥99% pure) was refluxed over K for ca. 8 h, then distilled and stored over molecular sieves under dry nitrogen; diethyl ether (Fluka, ≥99.5% pure) was refluxed over Na/K benzophenone for ca. 8 h, then distilled and stored over molecular sieves under dry dinitrogen. 1,3-Butadiene (Air Liquide, >99.5% pure) was evaporated from the container prior to each run, dried by passing through a column packed with molecular sieves, and condensed into the reactor, which had been precooled to −20 °C. $CrCl_2(thf)$[7] and $CrCl_2(dmpe)_2$[5] were prepared as reported in the literature; the other chromium complexes were prepared in a similar way as reported above. The elemental analyses of the chromium complexes were performed by the analytical laboratories of Polimeri Europa-Centro Ricerche Novara-"Istituto Guido Donegani"; infrared spectra were recorded as KBr disks with a Bruker IFS 48 instrument.

Synthesis of $CrCl_2(dmpm)_2$. $CrCl_2(thf)$ (0.69 g, 3.5 mmol) and toluene (20 mL) were introduced in a 50 mL Schlenck flask. The suspension obtained was kept under stirring at room temperature, then bis(dimethylphospine) (1.0 g, 7.3 mmol) was added. The suspension immediately became dark green; after stirring for ca. 4 h, it was filtered. The green residue on the filter was first washed with small amounts of pentane, dried in a vacuum at room temperature, and then extracted continuously with boiling toluene for several days. In the end a green microcrystalline powder is filtered off from the solution. Yield: 0.97 g [70% conversion based on $CrCl_2(thf)$]. Anal. Calcd for $C_{10}H_{28}CrCl_2P_4$: Cr, 13.16; Cl, 17.95; P, 31.36. Found: Cr, 13.3; Cl, 18.1; P, 31.3. Spectroscopic data: IR (KBr) ν (cm^{-1}) 1410m, 1371w, 1300m, 1285w, 1261w, 942s, 898s, 866w, 846w, 792m, 752m, 728w.

Synthesis of $CrCl_2(depe)_2$. The synthesis was carried out following the procedure reported in the literature for $CrCl_2(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane].[5] To a suspension of $CrCl_2(thf)$ (0.45 g, 2.3 mmol) in toluene (20 mL) was added 1,2-bis(diethylphosphino)ethane (1.0 g, 4.85 mmol). A practically homogeneous green-yellow solution is immediately formed. After 5 h, the solution was filtered, to remove unreacted $CrCl_2$ traces, and cooled to −30 °C. After 24 h at low temperature large yellow-green prisms were collected and further crops of crystals were obtained by concentration and cooling of the supernatant. Yield: 0.95 g [77% conversion based on $CrCl_2(thf)$]. Anal. Calcd for $C_{20}H_{48}CrCl_2P_4$: Cr, 9.71; Cl, 13.24; P, 23.14. Found: Cr, 9.8; Cl, 13.3; P, 23.2. Spectroscopic data: IR (KBr) ν (cm^{-1}) 1459s, 1416s, 1373m, 1043s, 1033s, 984w, 869m, 813m, 759s, 726s, 691m, 676m, 660w, 613w.

Synthesis of $CrCl_2(depp)_2$. To a suspension of $CrCl_2(thf)$ (0.41 g, 2.1 mmol) in toluene (25 mL) was added bis(diethylphospohino)propane (1.0 g, 4.6 mmol). An almost homogeneous blue solution is formed with time; after 6 h under stirring at room temperature, it was filtered. The blue solution obtained was reduced in volume under vacuum, then a large amount of pentane was added, causing the formation of a blue precipitate. The solid was separated by filtration, washed with pentane (2 × 5 mL), then dried in a vacuum at room temperature. Yield: 1.01 g [85.4% conversion based on $CrCl_2(thf)$]. Anal. Calcd for $C_{22}H_{52}CrCl_2P_4$: Cr, 9.23; Cl, 12.58; P, 21.99. Found: Cr, 9.4; Cl, 12.8; P, 21.7. Spectroscopic data: IR (KBr) ν (cm^{-1}) 1458s, 1415s, 1272m, 1197m, 1043s, 985m, 961m, 875w, 833m, 764s, 741m, 707w.

Synthesis of $CrCl_2(dcpe)$. To a suspension of $CrCl_2(thf)$ (0.43 g, 2.20 mmol) in diethyl ether (30 mL) was added bis(dicyclohexylphosphino)ethane (1 g, 2.3 mmol). A blue solid slowly formed; after stirring for 1 day the suspension was filtered, and the residue on the filter washed with diethyl ether and then dried under vacuum at room temperature. The solid obtained was then extracted continuously with boliling diethyl ether; after 24 h the diethyl ether blue solution was concentrated and a large amount of pentane was added. The precipitate was separated by filtration and dried under vacuum at room temperature. Yield: 1.1 g [91.7% conversion based on $CrCl_2(thf)$]. Anal. Calcd for $C_{26}H_{48}CrCl_2P_2$: Cr, 9.54; Cl, 13.00; P, 11.36. Found: Cr, 9.4; Cl, 12.9; P, 11.5. Spectroscopic data: IR (KBr) ν (cm^{-1}) 2930s, 2853s, 1449s, 1415w, 1349w, 1328w, 1299w, 1263m, 1218m, 1045m, 1008m, 947w, 918m, 894m, 857m, 823m, 804m, 767m, 695w.

X-ray Structure Determination of $CrCl_2(depe)_2$. A summary of the experimental details is reported in Table 3. The crystal used for the data collection was entirely covered with perfluorinated oil to reduce crystal decay. X-ray data were collected on a Bruker Smart Apex CCD area detector equipped with a fine-focus sealed tube operating at 50 kV and 30 mA. The first 100 frames were collected also at the end of the data collection to monitor crystal decay. Data reduction was made using SAINT programs; absorption corrections based on multiscan were obtained by SADABS.[12] The structure was solved by SIR92[13] and refined on F^2 by full-matrix least-squares using SHELX97.[14] For molecular graphics the program ORTEP-III[15] was used.

Computational Details. Geometries of complexes $CrCl_2(depe)_2$ and $CrCl_2(dmpe)_2$ were fully optimized using density functional theory (DFT) with Becke's three-parameter hybrid functional using the LYP correlation functional (B3LYP).[16] The D95 basis set[17] was used for carbon and hydrogen atoms, and the Los Alamos effective core potential plus DZ (LanL2DZ)[18]

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Table 3. Crystal Data, Details of Data Collection, and Results of the Refinement for $CrCl_2(depe)_2$

formula	$C_{20}H_{48}Cl_2CrP_4$
M_r	535.36
cryst syst	monoclinic
space group	$P2_1/n$
Z	2
D_{calc}, g cm^{-3}	1.277
a, Å	10.965(2)
b, Å	9.608(2)
c, Å	14.152(2)
β, deg	110.92(1)
V, Å^3	1392.6(4)
cryst size, mm	0.45 × 0.30 × 0.25
color, habit	dark yellow, rhombic prism
μ, mm^{-1}	0.838
radiation	Mo Kα
T, K	293(2)
$2\theta_{max}$, deg	60.10
h, k, l ranges	$-15 \rightarrow 15$; $-13 \rightarrow 13$; $-19 \rightarrow 19$
intensity decay, %	1.86
absorp corr	multiscan (Bruker SADABS)
T_{min}, T_{max}	0.907, 1.000
no. of measd reflns	27 233
R_{int}	0.0605
no. of indep reflns	4089
no. of reflns with $I > 2\sigma(I)$	2711
no. of params	124
$R(F^2)$, $R_w(F^2)$	0.0799, 0.1120
$R[F^2>2\sigma(F^2)]$, $R_w[F^2>2\sigma(F^2)]$	0.0404, 0.0912
goodness-of-fit	1.044
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.434, −0.384

for chromium, phosphorus, and chlorine atoms. All calculations were performed with the GAUSSIAN 98 program.[19]

Polymerization. All operations were carried out under an atmosphere of dry dinitrogen. A standard procedure is reported. 1,3-Butadiene (2 mL) was condensed into a 25 mL dried glass reactor kept at −20 °C, then toluene was added and the solution obtained was brought to the desired polymerization temperature. Methylaluminoxane (MAO) and the chromium compound were then added, as toluene solutions, in that order. The polymerization was stopped with methanol containing a small amount of hydrochloric acid, and the polymer was coagulated and repeatedly washed with methanol, then dried in a vacuum at room temperature.

Polymer Characterization. ^{13}C and ^1H NMR measurements were performed with a Bruker AM 270 instrument. The spectra were obtained in $C_2D_2Cl_4$ at 103 °C (hexamethyldisiloxane, HMDS, as internal standard). The concentration of polymer solutions was about 10 wt %. Differential scanning calorimetry (DSC) scans were carried out on a Perkin-Elmer Pyris 1 instrument. Typically, ca. 10 mg of polymer was analyzed in each run, while scan speed was ca. 20 K/min under a dinitrogen atmosphere. X-ray diffraction powder spectra of the polymers were recorded on an Italstructure θ/θ diffractometer. The infrared spectra were performed with a Bruker IFS 48 instrument, using polymer films on KBr disks. The films were obtained by deposition from solutions in benzene or hot (ca. 100 °C) solutions in 1,2,4-trichlorobenzene. MW and MWD were determined by GPC analysis using the Universal Calibration method. The GPC system was composed by a Agilent 1100 pump, an IR Agilent 1100 detector, and PL Mixed-A columns; tetrahydrofuran (1 mL/min) was used as solvent at 25 °C. Polymer microstructure was determined as reported in the literature.[20] The 1,2 content was determined by ^1H NMR analysis (see Figure 3) from the integrated areas of the resonances around 4.8 and 5.4 ppm. The syndiotactic index [rrrr] (percentage of syndiotactic pentads) was determined by ^{13}C NMR analysis from the integrated areas of the resonances around 112 ppm (peak at 112.30 ppm in Figure 2 corresponds to rrrr pentad); the percentage of the different triads (rr, mr, and mm) was evaluated in an analogous way as shown in Figure 2.

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Supporting Information Available: X-ray powder spectrum and ^{13}C NMR spectrum of the 1,2 syndiotactic polybutadiene obtained with $CrCl_2(depe)_2$−MAO at −30 °C; tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, and bond distances and angles for $CrCl_2(depe)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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