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Synthesis of the first chiral phosphorous chelate aminophosphino–carbene complex and its applications in stereoselective addition reactions

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Abstract

The first phosphorous chelate chiral aminophosphinomethyl carbene complex **5** has been synthesized. Its conjugated base represents a new chiral α-unsubstituted amide enolate equivalent for stereoselective addition reactions. The structure of the major diastereoisomer of the aldol addition complex between **5** and pO_2N–C_6H_4–CHO, solved by X-ray diffraction, shows that the (*S*)-enantiomer of the conjugated base of **5** reacts preferentially with the *re* face of the carbonyl function.

Keywords: Carbene complexes; Diastereoselective aldol additions; Intramolecular phosphorous coordination

1. Introduction

Ever since their first preparation [1], Fischer-type carbene complexes have continued to reveal their particular and highly interesting chemical behavior, and are now routinely used as versatile organometallic reagents in organic synthesis [2]: for example, they can be used in both metal-centered cycloaddition reactions (i.e. benzannulation or cyclopropanation reactions) [2] and in carbene-centered reactions, in which exploitation of the reactivity of anions on the α-carbon atom (easily generated by treatment with bases) makes it possible to prepare differently functionalized carbene complexes [3]. The possibility of using them as chiral enol–acetate equivalents in stereoselective C–C bond formation in Michael addition reactions has also been envisaged, and good/excellent stereoselectivities have been obtained with cyclic enones [4a,b] and nitroolefins [5] using the chiral aminocarbene complexes **1** and **2** (Fig. 1).

The immobilization of a portion of the organic carbene ligand by means of chelation to the metal [6] is a recently introduced strategy in Fischer carbene chemistry which often profoundly modifies reactivity and allows many processes to be performed stereoselectively under milder conditions. The high levels of diastereoselection obtained in both aldol and Michael addition reactions by using the chiral chelated aminocarbene complex **3** [7,8] is a recent example of the application of this strategy (Fig. 1)[2,3].

Double bonds [10], sulfur [11] or phosphorous atoms [12] present in the carbenic ligand can be easily coordinated to the metal when placed at the right distance; furthermore, we have recently reported [13] that the nitrogen atom of hydrazinocarbenes can be easily coordinated to the metal to afford highly stable four-membered ring chelate complexes.

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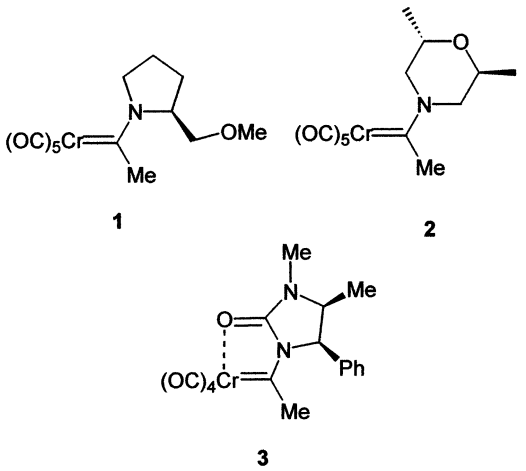


Fig. 1.

2. Results and discussion

The great potential offered by intramolecular coordination (especially in stereoselective processes) prompted us to investigate the process in more detail by extending it to different heteroatoms with the aim of preparing new chiral amino carbene complexes and exploiting them in stereoselective syntheses.

In particular, we concentrated on phosphorous atom chelate aminophosphinocarbene complexes with the general structure **4** (Fig. 2), which represent a new class of conformationally rigid chiral aminocarbene complexes. The complexes **4** were expected to have advantages over simple aminocarbenes or complex **3**, at least in terms of the reactivity of the corresponding conjugated base, because it has been reported [14] that the replacement of a CO ligand by a lower π-accepting phosphine in Fischer-type carbene complexes leads to a considerable reduction in the hydrogen acidity on the α-carbon atom at the carbenic center. Consequently, there is an increase in the nucleophilicity of the corresponding conjugated bases in their reactions with electrophiles. Furthermore, the presence in **4** of the magnetic spin active phosphorous atom introduces an additional parameter that may be useful in analysing the stereochemical outcome of stereoselective processes.

We report here the synthesis of the first chiral phosphorous-chelate aminophosphinocarbene complex **5**, the generation of its conjugated base, and some preliminary results concerning its use in stereoselective processes (Fig. 2).

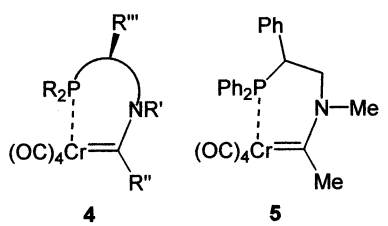


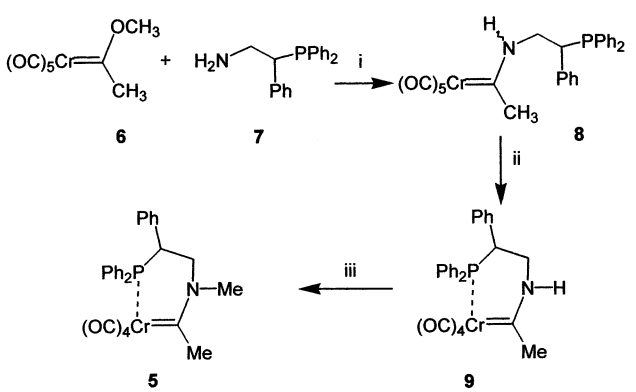
Fig. 2.

Complex **5** was synthesized in racemic form by means of aminolysis of the methoxymethylcarbene complex **6** with aminophosphine **7** in THF at −78°C. The aminophosphinocarbene complex **8**, obtained as a 3:1 *E*/*Z* mixture without any purification[4], was heated for 30 min in refluxing toluene to give the chelate complex **9** in an overall yield of 63% (from **7**). Finally, the nitrogen atom was methylated under phase transfer conditions to afford **5** in 93% yield (Scheme 1).

[2] The diastereoisomeric excess is almost always found on the corresponding α-hydroxyamides: i.e. after the removal of the metal-carbonyl moiety by oxidation with Ce^{+4} salts. Since the recovered organic material from this oxidation never reached 100; the reported diastereoselectivities represent only a qualitative and not a quantitative evaluation of the stereochemical outcome of the aldol addition process. D.e. has been evaluated using another chelated imidazolidinone complex on the aldol addition complex with a silylated hydroxy function; the absolute configuration of the new stereocenter of this latter complex has also been determined by X-ray analysis [8].

[3] Complex **1** has also been used in aldol addition reactions, but with modest or no diastereoselection [9]. Complex **2** was reacted with *p*-NO_2-benzaldehyde giving the corresponding aldol addition product in 67% yield and as a 1:1 diastereoisomeric mixture. (d.e. evaluated by ^{1}H NMR on aromatic hydrogen *ortho* to the carbinolic function).

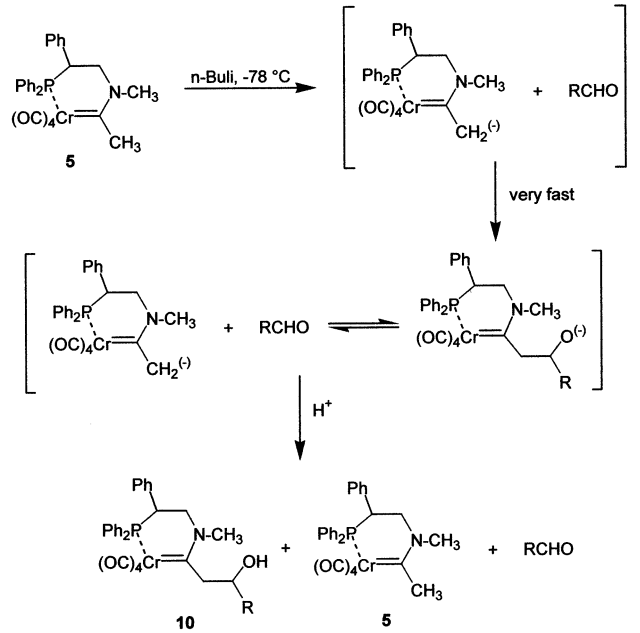
[4] The *E* and *Z* isomers of complex **8** can be separated by means of column chromatography. However both pure isomers were found to evolve into a 3:1 *E*/*Z* mixture (*Z* more rapidly) when left standing in a solution and dry state, and this hampers their full spectroscopic characterization. Furthermore, atmospheric oxygen must be carefully excluded in all manipulations of this complex in order to avoid the easy oxidation of the phosphine function to a phosphinoxide function.



Scheme 1. (i) THF, −78°C, 5 h; (ii) toluene reflux, 45 min; (iii) MeI (50 equiv.), benzene, NaOH 50; TBAB, 20 min.

Complex **5** is remarkably stable to air and silica gel, with a stability that is comparable with or better than that of simple aminocarbene complexes. The treatment of **5** with n-BuLi in THF at −78°C easily generates the corresponding conjugated base, and its reactivity was investigated in reactions with electrophiles (Table 1).

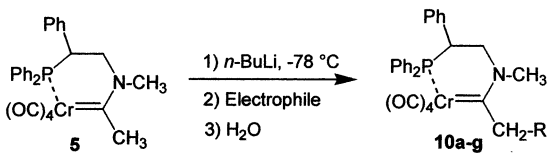
Various types of electrophiles were considered: alkylating reagents, aromatic and aliphatic aldehydes (linear and α-branched), and electron-poor olefins such as β-nitrostyrene and 2-cyclohexene-1-one. All of these electrophiles led to good reactivity at −78°C of the conjugated base of **5** to afford adducts **10** in good to excellent yields, with a conversion of over 90% in almost all cases (Table 1). A new stereocenter is produced in entries 2–10: the observed diastereoselectivities were fair to good with aromatic aldehydes (entries 2–5), and moderate with linear and α-branched aldehydes and in Michael reaction with 2-cycloexene-1-one (entries 6–8 and 10). No diastereoselection was observed with nitrostyrene (entry 9). In all cases, the diastereoselection could be easily determined on the crude reaction mixture by integrating the well-separated ^{31}P resonance signals for each diastereoisomers, and the resonances of the two aromatic hydrogen atoms falling within the range of 6.7–6.2 ppm were also particularly diagnostic.

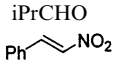
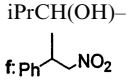


Scheme 2.

The reaction with isobutyrraldehyde was also performed at −100°C in order to check whether the diastereoselection was affected by temperature (entry 8,

Table 1
Reaction of the complex **5** with electrophiles [a,b]



Entry	Electrophile	R	Temp. (°C)	Time (min)	Yield [a] (%)	D.e. [b] (%)	^{31}P NMR (ppm)	
							major	minor
1	BnBr	**a**: Bn–	−78	200	85(5)	–	75.43	
2	Ph–CHO	**b**: Ph–CH(OH)–	−78	5	80(1)	60	75.19	78.33
3	Ph–CHO	Ph–CH(OH)–	−78	30	78(5)	60		
4	Ph–CHO	Ph–CH(OH)–	−78	200	73(15)	60		
5	$pNO_2C_6H_4$–CHO	**c**: $pNO_2C_6H_4$–CH(OH)–	−78	200	85(10)	74	73.26	78.03
6	EtCHO	**d**: EtCH(OH)–	−78	200	62(37)	34	74.79	78.77
7	iPrCHO	**e**: iPrCH(OH)–	−78	200	76(20)	44	75.17	78.71
8	iPrCHO	iPrCH(OH)–	−100	200	88(7)	40		
9		**f**: 	−78	200	85(6)	0	68.53	78.46
10		**g**: 	−78	200	92(2)	34	75.31	76.87

[a] Yields on isolated compounds. Between brakets recovering of unreacted **5**.
[b] D.e. evaluated on the crude reaction mixture by ^{1}H NMR and by ^{31}P NMR.

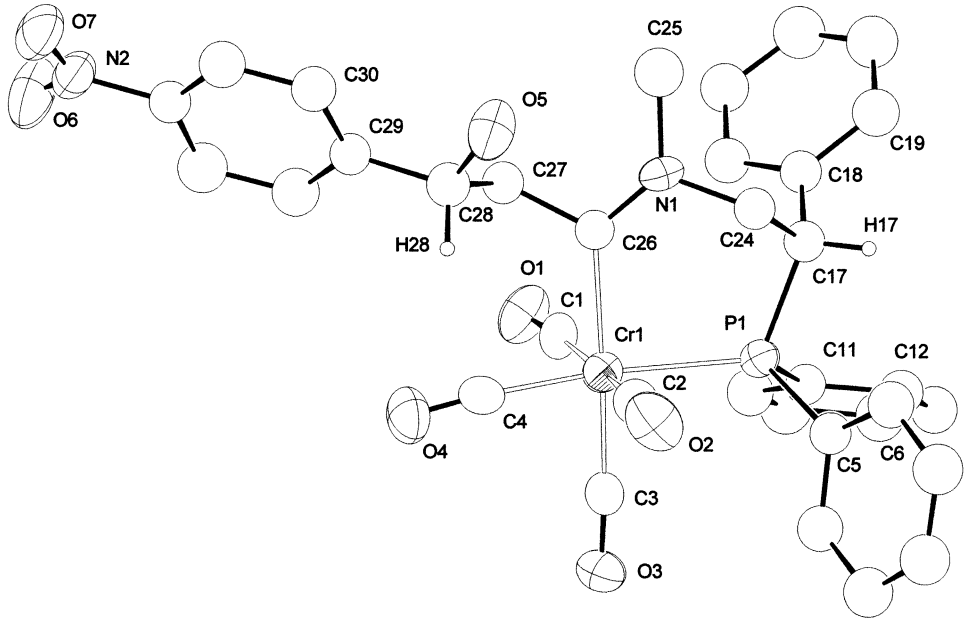


Fig. 3. ORTEP view of the structure of the (S_{C17},R_{C28})-enantiomer of the complex **10c** together with the atomic numbering scheme. The ellipsoids for the atoms are drawn at 30% probability level.

Table 1): the aldol addition complex was recovered with the the same level of diastereoselection as that observed at −78°C, but with a considerable improvement in chemical yield (88% versus 76%).

We have investigated the effect of the reaction time in the aldol addition process using benzaldehyde. By monitoring its reaction with **5** at different times (5, 30, 200 min, entries 2–4), it was possible to see that the addition of the conjugated base of **5** to the aldehyde is very fast (pratically complete within 5 min, with the unreacted **5** analyzed by ^{1}H NMR being less than 1%) and that, after the addition, equilibrium of the aldolate, the conjugated base of **5**, and the starting aldehyde seems to take place. These results, together with those obtained at different temperature, strongly suggest the reversibility of the aldol addition process, in which both temperature and reaction times play an important role in determining the chemical yields of aldol complexes **10** without affecting the diastereoselection (Scheme 2).

In the case of complex **10c**, we were able to isolate a pure sample of major diastereoisomer by means of preparative thin layer chromatography. Crystallization from dichloromethane/pentane affords crystals of the dichloromethane solvate of **10c** suitable for X-ray analysis. Because of the presence of an inversion center in the crystal structure the major diastereoisomer is present in both (*R*,*S*) or (*S*,*R*) configurations. Disordered molecules of dichloromethane are also present in the crystals.

The structure of the (*S*,*R*) enantiomer of **10c** is shown in Fig. 3 together with the atomic numbering system and selected bond distances and angles are given in Table 2. The coordination around Cr is distorted octahedral with the organic moiety acting as a chelating ligand through the P1 and C26.

The six-membered chelation ring shows an envelope confomation with C24 out by 0.85(1) Å from the mean plane through the other five atoms, the chelation

Table 2
Selected bond lengths (Å) and angles (°) for **10c·0.75CH$_2$Cl$_2$**

Cr(1)–C(26)	2.121(6)
Cr(1)–P(1)	2.379(2)
P(1)–C(17)	1.858(6)
O(5)–C(28)	1.421(7)
N(1)–C(26)	1.314(7)
N(1)–C(25)	1.472(8)
N(1)–C(24)	1.490(8)
N(2)–C(32)	1.471(9)
C(17)–C(24)	1.543(9)
C(26)–C(27)	1.519(8)
C(27)–C(28)	1.531(9)
C(28)–C(29)	1.520(9)
C(26)–Cr(1)–P(1)	91.44(18)
C(17)–P(1)–Cr(1)	111.7(2)
C(26)–N(1)–C(25)	128.1(5)
C(26)–N(1)–C(24)	121.6(5)
C(25)–N(1)–C(24)	110.3(5)
C(24)–C(17)–P(1)	106.4(4)
N(1)–C(24)–C(17)	112.2(5)
N(1)–C(26)–C(27)	114.1(5)
N(1)–C(26)–Cr(1)	128.1(4)
C(27)–C(26)–Cr(1)	117.6(4)
C(26)–C(27)–C(28)	111.8(5)
O(5)–C(28)–C(29)	110.7(6)
O(5)–C(28)–C(27)	110.6(5)
C(29)–C(28)–C(27)	112.0(5)

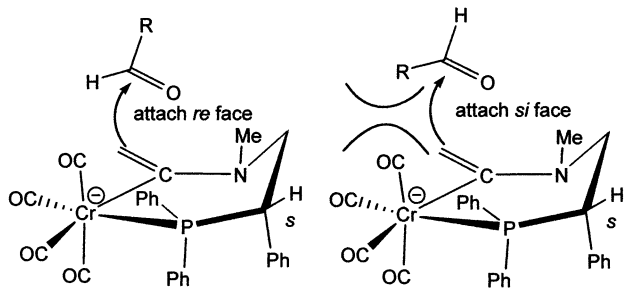


Fig. 4. Stereochemical model for the reaction between the conjugated base of (*S*)-**5** and aldehydes.

P1Cr1C26 angle being 91.44(18)°. The Cr1–C26, 2.121(6) Å, and C26–N1, 1.314(7) Å, bond lengths fall in the average values [(2.102(8) and 1.321(7) Å] found for the Cr–C and C–N bond lengths in the Cr–C–N fragments of aminocarbene complexes [15].

The X-ray analysis has confirmed the chelated nature of complex **5** and clearly shows that the major (*S*,*R*) diastereoisomer produced in the aldol addition process has originated by reaction of the (*S*)-enantiomer of **5** with the *re* face of the carbonyl function. It is likely that the configuration of the major diastereoisomer of aldol complexes **10b** and **10e** is also (*S*,*R*) [or (*R*,*S*)], and that of complex **10d** is (*S*,*S*) [or (*R*,*R*)]. In fact, the diastereoisomer nature of the above complexes can be inferred by comparison of their ^{31}P and ^{1}H NMR spectra with those of **10c**. X-ray analysis also shows two phenyl substituents (one bound to phopshorous atom and the other on the stereogenic center of the aminophospine moiety) shielding the bottom face of the chelate six-membered ring in its envelope conformation. If the conjugated base of **5** keeps in solution the same conformation, the approach of the aldehyde must preferentially occur from the opposite side of the two phenyl rings and with the bulky substituent far from the tetracarbonylchromium moiety. In Fig. 4, the approaching model of aldehydes to the conjugated base of the (*S*)-**5** enantiomer is represented.

3. Conclusions

We report here the synthesis of the first stable and chiral intramolecularly phosphorous chelated aminocarbene complex, and the generation and reactivity of the corresponding conjugated base towards electrophiles. These preliminary results indicate the better reactivity of this complex in comparison with simple aminocarbene complexes. The diastereoselectivity observed in aldol addition reaction were good only in the case of aromatic aldehydes, but it is likely that these can be improved by modifying the substitution pattern in the starting aminophosphine. In the case of an aldol addition reaction, the configuration of the newly formed stereocenter is, in almost all cases, opposite to that present in the aminophosphino moiety.

4. Experimental

4.1. General

The amino phosphine **7** and complex **6** were prepared using standard procedures [16,17]. The aliphatic aldehydes, benzaldehyde and 2-cyclohexene-1-one were purchased from Aldrich and distilled just before use; the *para*-nitrobenzaldehyde and β-nitrostyrene were purchased from Aldrich and used as received. The reagent n-BuLi (1.6 M hexane solution) was purchased from Merck and titred just before use. THF was dried by refluxing over Na/benzophenone ketyl. All of the manipulations were made under an inert atmosphere. Flash and dry chromatography were performed using silica gel 60 Merck 230–400 mesh. The melting points were measured using a Büchi 510 melting point apparatus and are uncorrected. The IR spectra were recorded on a Perkin–Elmer 1725X FT-IR spectrometer, and the NMR spectra were obtained using a Bruker AMX 300 and AC300; mass spectra (EI, FAB) were collected using a VG Analytical 7070 EQ instrument.

4.2. Synthesis of complex **9**

The aminophosphine **7** (4.4 mmol dissolved in 5 ml of dry THF) was added in 5 min to a THF solution (30 ml) of **6** (4 mmol) cooled to −78°C. The mixture was allowed to react for 5 h at −78°C, then the solvent was removed under reduced pressure to afford a crude reaction mixture containing complex **8** as the main reaction product (*E*/*Z* mixture, 3:1 ratio by ^{1}H NMR analysis). The crude reaction mixture was dissolved in dry toluene and refluxed for 45 min. The solvent was removed under reduced pressure and the dark orange oil purified by means of dry column chromatography (eluent: light petroleum/methylene chloride, 3:2) to afford **9** in 63% yield (based on starting complex **6**).

Complex **9**: yellow solid, m.p. 71°C (from methylene chloride/pentane). IR (Nujol) cm^{-1}: 3295 (*ν*N–H); 1995 (*ν*CO *trans*), 1989–1850 (broad, *ν*CO *cis*). ^{1}H NMR (300 MHz, $CDCl_3$) *δ* ppm: 2.89 (s, 3H, CH_3–C=Cr), 3.68 (m, 1H, Ph_2P–C*H*–CH_2–N), 4.10 [m, 1H, Ph_2P–CH–C(H)*H*–N], 4.40 [m, 1H, Ph_2P–CH–C*H*(H)–N], 6.57 (d, 2H arom, $J_{ortho} = 7.6$ Hz), 6.90–7.40 (m, 13H arom), 9.17 (bs, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) *δ* ppm: 39.97 (Ph_2P–*C*H + Cr=C–*C*H_3), 56.12 (d, Ph_2P–CH–*C*H_2–N, $J_{P-C} = 12.7$ Hz), 126.37 (CH, arom), 126.74 (CH, arom), 128.09 (CH, arom), 128.25 (CH, arom), 128.60 (CH, arom), 129.97 (CH, arom), 130.10 (CH, arom), 131.72 (d, C_q, $J_{P-C} = 30.5$ Hz), 135.51 (CH, arom), 138.09 (C_q),

139.75 (d, C_q, $J_{P-C} = 32.0$ Hz), 217 (bs, CO), 225 (bs, CO), 230 (bs, CO), 232 (bs, CO), 285 (bs, Cr=*C*–C). ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4 as external standard) δ ppm: 68.96. *Anal*. Found: C, 62.87; H, 4.29; N, 2.71%. Calc. for $C_{26}H_{22}CrNO_4P$, MW 495.44: C, 63.03; H, 4.48; N, 2.83%.

4.3. Synthesis of the complex **5**

NaOH 50% (6 ml) and tertrabutylammonium bromide (0.8 mmol) were added at room temperature to a benzene solution (30 ml) of **9** (4.2 mmol). Under vigorous stirring, MeI (50 mmol) was introduced by means of a syringe, and the mixture was allowed to react at room temperature. The reaction, which was monitored by means of TLC analysis (eluent: light petroleum/methylene chloride, 3:2), was completed after 30 min and quenched by adding water (10 ml); the organic solvent was removed under reduced pressure. The resulting suspension was extracted with methylene chloride (2×20 ml), and the organic phase was washed with water (2×10 ml), dried over Na_2SO_4 and the solvent evaporated under reduced pressure. The crude reaction mixture was purified by means of dry column chromatography (eluent: light petroleum/methylene chloride, 3:2) to afford complex **5** in 93% yield.

Complex **5**: yellow solid, m.p. 95°C (from toluene, the complex crystallized incorporating a molecule of toluene), m.p. 158°C (from methylene chloride/pentane). IR (Nujol) cm^{-1}: 1994 (*v*CO *trans*), 1986–1833 (broad, *v*CO *cis*). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.82 (s, 3H, CH_3–C=Cr), 3.29 (s, 3H, NCH_3), 3.76 [m, 1H, Ph_2P–C*H*–CH_2–N], 4.22 [ddd, 1H, $J_{P-H} = 29$ Hz, $J_{gem} = 13.5$ Hz, $J_{vic} = 2.1$ Hz, Ph_2P–CH–C(H)*H*–N], 4.78 [m, 1H, Ph_2P–CH–C*H*(H)–N], 6.68 (d, 2H arom, $J_{ortho} = 6$ Hz), 6.90–7.40 (m, 13H arom), 9.17 (bs, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 39.60 (Cr=C–*C*H_3), 39.72 Ph_2P–*C*H–CH_2), 48.84 (N–CH_3), 65.30 (d, Ph_2P–CH–*C*H_2–N, $J_{P-C} = 13.9$ Hz), 126.57 (CH, arom), 127.57 (CH, arom), 128.34 (CH, arom), 128.52 (CH, arom), 128.73 (CH, arom), 129.90 (CH, arom), 130.09 (CH, arom), 132.29 (d, C_q, $J_{P-C} = 32$ Hz), 135.61 (CH, arom), 138.16 (C_q), 140.43 (d, C_q, $J_{P-C} = 35$ Hz), 219.79 (CO), 224.53 (CO), 229.17 (CO), 230.14 (CO), 282.89 (Cr=*C*–C). ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4 as external standard) δ ppm: 73.89. MS (EI) *m*/*z*: 509 (M^+), 453 ($M^+ - 2$CO), 425 ($M^+ - 3$CO), 397 ($M^+ - 4$CO), 345 ($M^+ - 4$CO–Cr). *Anal*. Found: C, 63.30; H, 4.55; N, 2.58%. Calc. for $C_{27}H_{24}CrNO_4P$, MW 509.45: C, 63.65; H, 4.75; N, 2.75%.

4.4. General procedure for the preparation of the complexes **10a–g**

The electrophiles (1.2 equiv.) were added at −78°C to a tetrahydrofuran solution (10 ml) of the conjugated base of complex **5** (generated by treating 1 mmol of **5** with 0.7 ml of 1.6 M hexane solution of n-BuLi (1.1 mmol) at −78°C for 20 min) under an inert atmosphere. The mixture was allowed to react at −78°C and the progress of the reaction was monitored by TLC analysis (eluent: CH_2Cl_2/light petroleum 1:1). After the time reported in Table 1, the reaction was considered concluded. The reaction was quenched by adding 10 ml of a saturated ammonium chloride solution, followed by extraction with CH_2Cl_2 (2×50 ml). The organic phase was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by means of dry flash chromatography (eluent: light petroleum/methylene chloride, 3:2) to afford complexes **10a–g** (see Table 1 for yields). The diasteroisomeric mixture of complexes **10b** and **d–g** were unseparable using classical techniques. The pure major diastereoisomer of complex **10c** was obtained by means of preparative TLC (eluent: light petroleum/ethylacetate, 3:2) and crystallized from methylene chloride/pentane.

Complex **10a**: yellow solid, m.p. 211°C (dec.) (from methylene chloride). IR (Nujol) cm^{-1}: 1996 (*v*CO *trans*), 1897–1830 (broad, *v*CO *cis*). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.70 [dt, 1H, $J_{gem} = J_{vic1} = 12.5$ Hz, $J_{vic2} = 5.4$ Hz, Ph–C(H)*H*–CH_2–C=Cr], 2.90 [dt, 1H, $J_{gem} = J_{vic1} = 12.5$ Hz, $J_{vic2} = 5.2$ Hz, Ph–C*H*(H)–CH_2–C=Cr], 3.31 (s, 3H, NCH_3), 3.40 [dt, 1H, $J_{gem} = J_{vic1} = 12.5$ Hz, $J_{vic2} = 5.4$ Hz, Ph–CH_2–C(H)*H*–C=Cr], 3.50 [dt, 1H, $J_{gem} = J_{vic1} = 12.5$ Hz, $J_{vic2} = 5.2$ Hz, Ph–CH_2–C*H*(H)–C=Cr], 3.70 [m, 1H, Ph_2P–C*H*–CH_2–N], 4.10 [m, 1H, Ph_2P–CH–C(H)*H*–N], 4.78 [m, 1H, Ph_2P–CH–C*H*(H)–N], 6.60 (d, 2H arom, $J_{ortho} = 6$ Hz), 6.90–7.40 (m, 18H arom). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 31.64 (Cr=C–CH_2–*C*H_2–Ph), 39.38 (Ph_2P–*C*H–CH_2), 43.23 (N–CH_3), 54.50 (Cr=C–*C*H_2–CH_2–Ph), 65.04 (d, Ph_2P–CH–*C*H_2–N, $J_{P-C} = 14$ Hz), 126.41, 126.52, 127.48, 127.61, 128.29, 128.83, 129.96, 130.25, 135.50, 135.63 (CH, arom), 137.33 (C_q), 138.47 (C_q), 131.24 (d, C_q, $J_{P-C} = 30$ Hz), 140.38 (d, C_q, $J_{P-C} = 35$ Hz), 220.03 (CO), 224.60 (CO), 229.03 (CO), 230.05 (CO), 281.50 (Cr=*C*–C). ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4 as external standard) δ ppm: 75.43. *Anal*. Found: C, 67.89; H, 5.02; N, 2.15%. Calc. for $C_{34}H_{30}CrNO_4P$, MW 599.58: C, 68.11; H, 5.04; N, 2.34%.

Complex **10b**: yellow solid, m.p. 161°C (from methylene chloride/pentane, mixture of two diastereoisomers). IR (Nujol) cm^{-1}: 3555, 3470 (*v*OH major diast. and minor diast.), 1998 (*v*CO *trans*, both diast.), 1896–1826 (broad, *v*CO *cis*, both diast.). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 1.85 (d, $J_{OH-H} = 3.6$ Hz, OH, major diast.), 1.90 (d, $J_{OH-H} = 3.5$ Hz, OH, minor diast.), 3.28 (s, 3H, CH_3N, major diast.), 3.45–3.65 [m, 5H, NCH_3 (minor diast.) + PhCH(OH)–

CH_2–C≡Cr (major diast. + minor diast.)], 3.75 (m, 1H, Ph_2P–CH–CH_2–N, major diast. + minor diast.), 4.10 [m, 1H, Ph_2P–CH–C(H)H–N, major diast. + minor diast.], 4.75 [m, 1H, Ph_2P–CH–CH(H)–N, major diast. + minor diast.], 5.47 [dt, 1H, $J_{vic1} = 9.3$ Hz, $J_{vic2} = 3.6$ Hz, $J_{H-OH} = 3.6$ Hz, PhCHOH, major diast.], 5.68 (m, 1H, PhCHOH, minor diast.), 6.55 (d, 2H arom, $J_{ortho} = 7.2$ Hz, minor diast.), 6.61 (d, 2H arom, $J_{ortho} = 7.0$ Hz, major diast.), 6.90–7.60 (m, 18H arom, major diast. + minor diast.). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 39.20 (Ph_2P–CH–CH_2, major diast. + minor diast.), 45.60 (N–CH_3, major diast. + minor diast.), 60.09 [Cr≡C–CH$_2$–CH(OH)Ph, major diast. + minor diast.], 65.43 (Ph_2P–CH–CH$_2$–N, major diast. + minor diast.), 72.82 [Cr≡C–CH$_2$–CH(OH)Ph major diast. + minor diast.], 125.52, 126.39, 127.51, 127.54, 127.82, 128.18, 128.35, 128.63, 128.83, 129.89, 130.03, 130.31, 135.51, 135.83 (CH, arom, major diast. + minor diast.), 131.72 (d, C_q, $J_{P-C} = 30.4$ Hz), 138.35 (C_q, major diast. + minor diast.), 139.04 (d, C_q, $J_{P-C} = 35.4$ Hz), 144.46 (C_q, major diast. + minor diast.), 220.69, 220.81, 224.19, 224.38, 224.53, 228.98, 229.18, 229.44 (CO major diast. + minor diast.), 281.75 (Cr=C–C, minor diast.), 281.94 (Cr=C–C, major diast.). ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4 as external standard) δ ppm: 78.33 (minor diast.), 75.19 (major diast.). *Anal*. Found: C, 66.55; H, 5.12; N, 2.10%. Calc. for $C_{34}H_{30}CrNO_5P$, MW 615.59: C, 66.34; H, 4.91; N, 2.28%.

Complex **10c**: orange solid, m.p. 155°C (dec.) (from methylene chloride/pentane, mixture of two diastereoisomers). Data for the major diastereoisomer: m.p. 170°C (dec.) (from methylene chloride/pentane). IR (Nujol) cm^{-1}: 3470 (νOH), 1991 (νCO *trans*), 1866–1826 (broad, νCO *cis*). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.10 (d, $J_{OH-H} = 3.5$ Hz, OH), 3.34 (s, 3H, N–CH_3), 3.45 [dd, 1H, $J_{gem} = 12.6$ Hz, $J_{vic} = 10.3$ Hz, PhCH(OH)–C(H)H–C≡Cr], 3.65 [dd, 1H, $J_{gem} = 12.6$ Hz, $J_{vic} = 3.7$ Hz, PhCH(OH)–CH(H)–C≡Cr], 3.83 (m, 1H, Ph_2P–CH–CH_2–N), 4.23 [ddd, 1H, $J_{P-H} = 29$ Hz, $J_{gem} = 13.5$ Hz, $J_{vic} = 1.6$ Hz, Ph_2P–CH–C(H)H–N], 4.76 [m, 1H, Ph_2P–CH–CH(H)–N], 5.65 [dt, 1H, $J_{vic1} = 10.1$ Hz, $J_{vic2} = J_{H-OH} = 3.5$ Hz, pNO$_2$Ph-CH(OH)–CH$_2$–], 6.65 (d, 2H arom, $J_{ortho} = 6.8$ Hz), 6.90–7.50 (m, 13H arom), 7.67 (bd 2H, system AA′, $J_{ortho} = 8.7$ Hz, pNO$_2$Ph–), 8.25 (bd 2H, system BB′, $J_{ortho} = 8.7$ Hz, pNO$_2$Ph. ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 39.45 (d, $J_{P-C} = 8$ Hz Ph_2P–CH–CH$_2$), 46.20 (N–CH_3), 59.95 [Cr≡C–CH$_2$–CH(OH)Ar], 66.17 (d, $J_{P-C} = 13$ Hz Ph_2P–CH–CH$_2$–N), 72.61 [Cr≡C–CH$_2$–CH(OH)Ar], 122.73, 124.32, 126.72, 127.03, 127.99, 128.12, 128.74, 128.87, 129.40, 130.45, 130.64, 130.76, 135.65, 135.82 (CH, arom), 131.70 (d, C_q, $J_{P-C} = 30$ Hz), 138.50 (C_q), 140.04 (d, C_q, $J_{P-C} = 35$ Hz), 148.10 (C_q, Ar), 151.10 (C_q, Ar), 220.3, 224.75, 229.87, 230.05 (CO), 288.40 (Cr = C–C). ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4 as external standard) δ ppm: 73.26. *Anal*. Found: C, 61.55; H, 4.72; N, 4.37%. Calc. for $C_{34}H_{29}CrN_2O_7P$, MW 615.59: C, 61.82; H, 4.42; N, 4.24%.

Complex **10d**: yellow solid, m.p. 153°C (from methylene chloride/pentane, mixture of two diastereoisomers); IR (Nujol) cm^{-1}: 3605, (νOH, both diast.), 1995 (νCO *trans*, both diast.), 1896–1836 (broad, νCO *cis*, both diast.). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 1.0 [m, 3H, –CH(OH)–CH$_2$CH_3], 1.43 (d, 1H, $J_{OH-H} =$ 5.1 Hz, OH, major diast.), 1.65 [m, 2H, CH(OH)–CH_2CH$_3$ + OH minor diast.], 3.20 [m, 1H, EtCH(OH)–C(H)H–C≡Cr, major diast. + minor diast.], 3.37 (s, 3H, CH_3N, major diast.), 3.45–3.65 [m, 1H, EtCH(OH)–C(H)H–C≡Cr (major diast. + minor diast.) + s, 3H, NCH_3 (minor diast.)], 3.59 (m, 1H, Ph_2P–CH–CH_2–N minor diast.), 3.75 (m, 1H, Ph_2P–CH–CH_2–N, major diast.), 3.90–4.15 [m, 1H, Ph_2P–CH–C(H)H–N, major diast. + minor diast.], 4.20–4.40 [EtCH(OH)–CH$_2$–C≡Cr (major diast. + minor diast.)], 4.65–4.85 [m, 1H, Ph_2P–CH–CH(H)–N, major diast. + minor diast.], 6.52 (d, 2H arom, $J_{ortho} =$ 7.2 Hz, minor diast.), 6.63 (d, 2H arom, $J_{ortho} = 6.5$ Hz, major diast.), 6.90–7.60 (m, 13H arom, major diast. + minor diast.). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 10.37 [(CH(OH)–CH$_2$CH_3, major diast.], 10.43 [(CH(OH)–CH$_2$CH_3 minor diast.], 32.00 [(CH(OH)–CH_2CH$_3$, minor diast.], 32.11 [(CH(OH)–CH_2CH$_3$, major diast.], 39.61 (Ph_2P–CH–CH$_2$–, minor diast.), 39.72 (Ph_2P–CH–CH$_2$–, major diast.), 45.81 (N–CH_3, minor diast.), 46.34 (N–CH_3, major diast.), 58.04 [Cr≡C–CH_2–CH(OH)–CH$_2$CH$_3$, minor diast.], 58.39 [Cr≡C–CH_2–CH(OH)–CH$_2$CH$_3$, major diast.] 65.80 (Ph_2P–CH–CH_2–N, minor diast.), 65.97 (Ph_2P–CH–CH_2–N, major diast.), 72.36 [Cr≡C–CH$_2$–CH(OH)–CH$_2$CH$_3$, major diast.], 72.59 [Cr≡C–CH$_2$–CH(OH)–CH$_2$CH$_3$, minor diast.], 126. 78, 126.87, 127.88, 128.00, 128.26, 128.60, 128.68, 128.79, 129.24, 130.27, 130.46, 130.70, 130.81, 130.92, 135.75, 135.91, 136.11, 136.28 (CH, arom, both diast.), 131.61 (d, C_q, $J_{P-C} = 30.1$ Hz, Ph–P–, minor diast.), 132.40 (d, C_q, $J_{P-C} = 30.4$ Hz, Ph–P–, major diast.), 138.68 (d, $J_{P-C} = 5.2$ Hz, C_q, Ph, major diast.), 139.27 (d, $J_{P-C} = 34.6$ Hz, C_q, Ph–P–, minor diast.), 139.32 (d, $J_{P-C} = 7.3$ Hz, C_q, Ph, minor diast.), 140.11 (d, C_q, $J_{P-C} = 33.4$ Hz, Ph–P–, major diast.), 220.64 (d, $J_{P-C} = 8.8$ Hz, CO, minor diast.), 221.24 (d, $J_{P-C} = 9.8$ Hz, CO, major diast.), 224.76 (d, $J_{P-C} = 13.3$ Hz, CO, major diast.), 225.96 (d, $J_{P-C} =$ 13.2 Hz, CO, minor diast.), 229.66, 229.85, 229.98, 230.47 (CO, major diast. + minor diast.), 283.45 (d, $J_{P-C} = 11.6$ Hz Cr=C–C, minor diast.), 283.64 (d, Cr=C–C, $J_{P-C} = 16.3$ Hz, major diast.). ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4 as external standard) δ ppm: 78.76 (minor diast.), 74.79 (major diast.). *Anal*. Found: C, 63.25; H, 5.25; N, 2.36%. Calc. for $C_{30}H_{30}CrNO_5P$, MW 567.55: C, 63.49; H, 5.33; N, 2.47%.

Complex **10e**: yellow solid, m.p. 110°C (from methylene chloride/pentane, mixture of two diastereoisomers); IR (Nujol) cm^{-1}: 3601, (νOH, both diast.), 1988 (νCO *trans*, both diast.), 1890–1840 (broad, νCO *cis*, both diast.). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 0.94 [d, 3H, $J_{vic} = 3.6$ Hz, –CH(OH)–CH(CH_3)CH_3, major diast.], 0.99 [d, 3H, $J_{vic} = 3.6$ Hz, –CH-(OH)–CHCH_3(CH_3), major diast.], 1.01 [d, 3H, $J_{vic} =$ 4.3 Hz, –CH(OH)–CHCH_3(CH_3), minor diast.], 1.04 [d, 3H, $J_{vic} = 4.3$ Hz, –CH(OH)–CHCH_3(CH_3), minor diast.], 1.37 (d, 1H, $J_{OH-H} = 4.7$ Hz, OH major diast.), 1.48 (d, 1H, $J_{OH-H} = 5.1$ Hz, OH diast. minor), 1.80 [m, 1H, CH(OH)–CH(CH_3)$_2$], 3.20 [m, 1H, (CH_3)$_2$CH-(OH)–C(H)H–C≡Cr (major diast. + minor diast.)], 3.37 (s, 3H, CH_3N, major diast.), 3.45–3.65 [m, 1H, (CH_3)$_2$CH(OH)–C(H)H–C≡Cr (major diast. + minor diast.) + s, 3H, NCH_3 (minor diast.)], 3.59 (m, 1H, Ph_2P–CH–CH_2–N minor diast.), 3.74 (m, 1H, Ph_2P–CH–CH_2–N, major diast.), 3.90–4.20 [m, 1H, Ph_2P–CH–C(H)H–N, major diast. + minor diast.], 4.25–4.35 [(CH_3)$_2$CH(OH)–CH_2–C ≡ Cr (major diast. + minor diast.)], 4.60–4.80 [m, 1H, Ph_2P–CH–CH(H)–N, major diast. + minor diast.], 6.53 (d, 2H arom, $J_{ortho} = 7.2$ Hz, minor diast.), 6.62 (d, 2H arom, $J_{ortho} = 6.7$ Hz, major diast.), 6.90–7.60 (m, 13H arom, major diast. + minor diast.). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 17.71, 18.98, 19.25 [(CH(OH)–CH(*C*H_3)$_2$, major diast. + minor diast.], 35.50 [(CH(OH)–*C*H(CH_3)$_2$, major diast.], 35.55 [(CH(OH)–*C*H(CH_3)$_2$, minor diast.] 39.70 (Ph_2P–*C*H–CH_2–, minor diast.), 39.78 (Ph_2P–*C*H–CH_2–, major diast.), 45.78 (N–CH_3, major diast.), 46.25 (N–CH_3, minor diast.), 55.17 [Cr≡C–*C*H_2–CH(OH)–CH(CH_3)$_2$, minor diast.], 55.69 [Cr≡C–*C*H_2–CH(OH)–CH(CH_3)$_2$, major diast.] 65.76 (Ph_2P–CH–*C*H_2–N, minor diast.), 65.94 (Ph_2P–CH–*C*H_2–N, major diast.), 75.40 [Cr≡C–CH_2–*C*H(OH)–CH(CH_3)$_2$, minor diast.], 75.55 [Cr≡C–CH_2–*C*H(OH)–CH(CH_3)$_2$, major diast.], 126. 75, 126.82, 127.83, 127.96, 128.25, 128.57, 128.65, 128.77, 129.23, 130.25, 130.44, 130.73, 130.79, 130.84, 130.91, 135.77, 135.93, 136.11, 136.28 (CH, arom, both diast.), 131.68 (d, C_q, $J_{P-C} = 29.8$ Hz, Ph–P–, major diast.), 132.38 (d, C_q, $J_{P-C} = 30.3$ Hz, Ph–P–, minor diast.), 138.77 (d, $J_{P-C} = 5.1$ Hz, C_q, Ph, minor diast), 139.29 (d, $J_{P-C} =$ 35.1 Hz, C_q, Ph–P–, major diast.), 139.37 (d, $J_{P-C} = 7.2$ Hz, C_q, Ph, minor diast.) 140.08 (d, C_q, $J_{P-C} = 33.7$ Hz, Ph–P–, major diast.), 220.72 (d, $J_{P-C} = 8.5$ Hz, CO, major diast.), 221.34 (d, $J_{P-C} = 9.8$ Hz, CO, minor diast.), 224.80 (d, $J_{P-C} = 13.2$ Hz, CO, minor diast.), 226.04 (d, $J_{P-C} = 13.4$ Hz, CO, major diast.), 229.54, 229.76, 229.92 (CO, major diast. + minor diast.), 230.46 (CO, major diast.), 283.95 (d, $J_{P-C} = 14.0$ Hz Cr≡*C*–C, major diast.), 284.14 (d, Cr≡*C*–C, $J_{P-C} = 14.8$ Hz, minor diast.). ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4 as external standard) δ ppm: 78.71 (minor diast.), 75.18 (major diast.). *Anal.* Found: C, 64.02; H, 5.55; N, 2.41%. Calc, for $C_{31}H_{32}CrNO_5P$, MW 581.56: C, 63.59; H, 5.63; N, 2.34%.

Complex **10f**: yellow solid, m.p. 163°C (from methylene chloride/pentane, mixture of two diastereoisomers). IR (Nujol) cm^{-1}: 1994 (νCO *trans*, both diast.), 1986–1833 (broad, νCO *cis*, both diast.), 1554 (ν_{as} NO_2, both diast.). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.7 (s, 3H, NCH_3, one diast.), 2.93 (s, 3H, NCH_3, one diast.), 3.20–3.30 [m, 2H, Cr≡C–C(H)H–CH(Ph)–CH_2–, + Cr≡C–C(H)$_2$CH(Ph)–CH_2– both diast.], 3.48 [m, 1H, Cr≡C–CH(H)–CH(Ph)–CH_2–, one diast.], 3.55–4.10 [m, 6H, Cr≡C–C(H)H–CH-(Ph)–CH_2– + Ph_2P–CH–C(H)H–N + Ph_2P–CH–CH_2–N, both diast.], 4.30 [m, 1H, Ph_2P–CH–CH(H)–N], 4.82 [m, 2H, Cr≡C–CH_2–CH(Ph)–CH_2–NO_2, one diast.], 5.02 [m, 2H, Cr≡C–CH_2–CH(Ph)–CH_2–NO_2, one diast.], 6.48 (bd, 2H, $J_{ortho} = 7.5$ Hz, one diast.) 6.68 (bd, 2H arom, $J_{ortho} = 7.5$ Hz, one diast.), 6.90–7.40 (m, 18H arom both diast.). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 38.24 (d, $J_{P-C} = 15.5$ Hz, Ph_2P–*C*H–CH_2–, one diast.), 38.68 (Ph_2P–*C*H–CH_2–, one diast.), 42.56 [(Ph–*C*H–CH_2NO_2, both diast.), 43.32 (N–CH_3, one diast.)], 45.93 (N–CH_3, one diast.), 60.24 [Cr≡C–*C*H_2–CH(Ph)–CH_2, both diast.], 65.43 (Ph_2P–CH–*C*H_2–N, both diast.), 79.00 [Cr≡C–CH_2–CH(Ph)–*C*H_2–NO_2, one diast.], 79.35 [Cr≡C–CH_2–CH(Ph)–*C*H_2–NO_2, one diast.], 126.46, 126.81, 127.43, 127.64, 127.80, 128.10, 128.21, 128.43, 129.02, 129.18, 129.94, 130.21, 130.37, 134.89, 135.04, 135.63, 135.78 (CH, arom, both diast.), 130.78 (d, C_q, $J_{P-C} = 30.3$ Hz, one diast.), 132.06 (d, C_q, $J_{P-C} = 30.3$ Hz, one diast.), 137.01 (C_q one diast.), 138.19, 138.49, 138.67, 138.81 (C_q, both diast.), 140.05 (d, C_q, $J_{P-C} = 35.4$ Hz, one diast.), 218.92, 220.68, 223.13, 225.09, 228.90, 228.97, 229.27, 230.12 (CO both diast.), 284.21 (d, $J_{P-C} = 14.9$ Hz Cr = *C*–C, one diast.), 285.49 (d, Cr=*C*–C, $J_{P-C} = 15.1$ Hz, one diast.). ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4 as external standard) δ ppm: 68.53 (one diast.), 78.45 (one diast.). *Anal.* Found: C, 63.65; H, 4.84; N, 4.04%. Calc. for $C_{35}H_{31}CrN_2O_5P$, MW 658.62: C, 63.83; H, 4.74; N, 4.25%.

Complex **10g**: yellow solid, m.p. 124°C (from methylene chloride/pentane, mixture of two diastereoisomers). IR (Nujol) cm^{-1}: 1991 (νCO *trans*, both diast.), 1986–1833 (broad, νCO *cis*, both diast.), 1709 (νC=O, both diast.). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 1.60–2.50 (m, 7H, cyclohexyl, major diast. + minor diast.), 3.10 [dd, 1H, $J_{gem} = 13.0$ Hz, $J_{vic} = 5.3$ Hz, Cr≡C–C(H)H–cyclohexyl], 3.27 (s, 3H, NCH_3, minor diast.), 3.30 (s, 3H, NCH_3, major diast.), 3.32–3.80 [m, 2H, Cr≡C–C(H)H–cyclohexyl + Ph_2P–CH–CH_2–N, minor diast. + major diast.], 4.05 [m, 1H, Ph_2P–CH–C(H)H–N], 4.66 [m, 1H, Ph_2P–CH–C(H)H–N, minor diast. + major diast.], 4.78 [m, 1H, Ph_2P–CH–CH(H)–N, minor diast. + major diast.], 6.56 (d, 2H arom, $J_{ortho} = 7.3$ Hz, major diast.), 6.61 (d, 2H arom,

Table 3
Crystal data and structure refinement for **10c·0.75CH_2Cl_2**

Formula	$C_{34}H_{29}CrN_2O_7P{\cdot}0.75CH_2Cl_2$
Formula weight	724.26
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	18.255(6)
b (Å)	11.792(5)
c (Å)	8.533(4)
α (°)	68.22(3)
β (°)	81.66(4)
γ (°)	81.51(4)
Volume (Å^3)	1678.9(12)
Z	2
Density (calc., Mg m^{-3})	1.433
Absorption coefficient, (μ, mm^{-1})	0.559
F(000)	747
Crystal size	0.21 × 0.34 × 0.35 mm
θ range (°)	3.08–25.00
Index ranges	$-21 \le h \le 21$, $-12 \le k \le 14$, $0 \le l \le 10$
Reflections collected	5893
Independent reflections	5893
Observed reflections [$I > 2\sigma(I)$]	3167
Refinement method	Based on F^2
Data/restraint/parameters	5893/0/290
Flack index	−0.09(4)
Goodness-of-fit on F^2	0.769
Final R indices [$I > 2\sigma(I)$] [a]	$R_1 = 0.0769$, $wR_2 = 0.2087$
R indices (all data)	$R_1 = 0.1652$, $wR_2 = 0.2405$
Largest difference peak and hole (e Å^{-3})	0.740 and −0.429

[a] $R_1 = \Sigma\,|F_o - F_c| / |\Sigma(F_o)|$; $wR_2 = [\Sigma\,[w(F_o^2 - F_c^2)^2] / \Sigma\,[w(F_o^2)^2]]^{1/2}$.

J_{ortho} = 7.8 Hz, minor diast.), 6.90–7.40 (m, 13H arom). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 25.84 (O=C–CH_2–CH_2–*C*H_2–, minor diast.), 25.99 (O=C–CH_2–CH_2–*C*H_2–, major diast.), 31.95 (O=C–CH_2–*C*H_2–CH_2–, major diast.), 32.22 (O=C–CH_2–*C*H_2–CH_2–, minor diast.) 38.62 (Ph_2P–*C*H–CH_2–, minor diast.), 38.76 (Ph_2P–*C*H–CH_2–, major diast.), 39.20 (bs, O=C–CH_2–*C*H–CH_2–, both diast.), 41.61 (O=C–*C*H_2–CH_2–CH_2–, minor diast.), 41.72 (O=C–*C*H_2–CH_2–CH_2–, major diast.), 43.32 (N–CH_3, one diast.), 44.79 (N–CH_3, major diast.), 45.05 (N–CH_3, minor diast.), 48.32 (O=C–*C*H_2–CH–CH_2, minor diast.), 48.54 (O=C–*C*H_2–CH–CH_2, major diast.), 58.63 [bs, Cr=C–*C*H_2–CH–CH_2–C=O, both diast.], 65.53 (Ph_2P–CH–*C*H_2–N, minor diast.), 65.72 (Ph_2P–CH–*C*H_2–N, major diast.), 126.90, 127.88, 128.00, 128.37, 128.53, 128.68, 128.77, 128.88, 130.40, 130.57, 130.70, 135.80, 135.89, 135.97, 136.04 (CH, arom, both diast.), 131.87 (d, C_q, J_{P-C} = 30.7 Hz, Ph–P–, major diast.), 132.03 (d, C_q, J_{P-C} = 30.8 Hz, Ph–P–, minor diast.), 138.58 (d, J_{P-C} = 6.1 Hz, C_q, Ph, minor diast.), 138.58 (d, J_{P-C} = 5.4 Hz, C_q, Ph, major diast.), 139.48 (d, J_{P-C} = 34.8 Hz, C_q, Ph–P–, major diast.), 139.78 (d, C_q, J_{P-C} = 34.0 Hz, Ph–P–, major diast.), 211.09 (CH_2–*C*=O, both diast.), 215.83 (CO both diast.), 220.09 (d, J_{P-C} = 9.5 Hz, CO, major diast.), 220.23 (d, J_{P-C} = 12.0 Hz, CO, minor diast.), 224.73 (d, J_{P-C} = 13.6 Hz, CO, minor diast.), 225.07 (d, J_{P-C} = 13.3 Hz, CO, major diast.), 229.92 (CO, major diast.), 230.10 (CO, minor diast.), 288.71 (d, J_{P-C} = 16.0 Hz Cr=*C*–C, minor diast.), 288.92 (d, Cr=*C*–C, J_{P-C} = 15.4 Hz, major diast.). ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4 as external standard) δ ppm: 75.31 (minor diast.), 76.88 (major diast.). *Anal.* Found: C, 64.88; H, 5.48; N, 2.20%. Calc. for $C_{33}H_{32}CrNO_5P$, MW 605.58: C, 65.45; H, 5.33; N, 2.31%.

4.5. Crystal structure determination of the complex **10c·0.75CH_2Cl_2**

The intensity data of **10c·0.75CH_2Cl_2** were collected at room temperature (22°C) on a Siemens AED single-crystal diffractometer using the graphite-monochromated Mo Kα radiation and the θ–2θ scan technique. Final unit cell parameters were obtained from a least-squares refinement using 24 reflections. Crystallographic and experimental details are summarized in Table 3.

Data were corrected for Lorentz and polarization effects in the usual manner. A correction for absorption was made for both complexes (maximum and minimum value for the transmission coefficient was 1.000 and 0.6873 [18]).

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) with anisotropic thermal parameters in the last cicles of refinement for the Cr, P, N, O and C1–C4 atoms only. Molecules of the dichloromethane solvent are also present in the crystals. These have been found disordered and distributed around the inversion center in three positions, two of which having the carbon atom in common. The hydrogen atoms (excepting those of the disordered solvent molecules) were introduced into the geometrically calculated positions and refined *riding* on the atoms to which they are attached. In the final cycles of refinement a weighting scheme $w = 1/[\sigma^2 F_o^2 + (0.1603\ P)^2]$ (**10c·0.75CH_2Cl_2**), where $P = (F_o^2 + 2F_c^2)/3$ was used.

All calculations were carried out on the CNRDIF computers of the 'Centro di Studio per la Strutturistica Diffrattometrica' del CNR, Parma, using the SHELXL-97 system of crystallographic computer programs [19].

5. Supplementary material

The supplementary material for the structure includes the lists of atomic coordinates for the non-H atoms, of calculated coordinates for the hydrogen atoms, of anisotropic thermal parameters. The details of the crystal

structure investigation are deposited to the Cambridge Crystallographic Data Center as supplementary publications (copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336 033; e-mail: deposit@ccdc.cam.ac.uk.

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References

[1] E.O. Fischer, A. Maasbol, Angew. Chem., Int. Ed. Engl. 3 (1964) 580.
[2] (a) K.H. Dötz, Angew. Chem., Int. Ed. Engl. 23 (1984) 587. (b) W.D. Wullf, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Pergamon, New York, 1995, vol. 12, p. 469; (c) L.S. Hegedus, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Pergamon, New York, 1995, vol. 12, p. 549. (d) D.F. Harvey, D.M. Sigano, Chem. Rev. 96 (1996) 271. (e) A. de Meijere, Pure Appl. Chem. 68 (1996) 61. (f) J. Barluenga, Pure Appl. Chem. 68 (1996) 543. (g) L.S. Hegedus, Tetrahedron 53 (1997) 4105.
[3] W.D. Wulff, B.A. Anderson, A.J. Toole, Y.-C. Xu, Inorg. Chim. Acta 220 (1994) 215.
[4] (a) W.D. Wulff, B.A. Anderson, A.J. Rahm, J. Am. Chem. Soc. 115 (1993) 4602. (b) C. Baldoli, E. Licandro, P. Del Buttero, S. Maiorana. A. Papagni, A. Zanotti-Gerosa, J. Organomet. Chem. 486 (1995) 279.
[5] E. Licandro, S. Maiorana, L. Capella, R. Manzotti, A. Papagni, M. Pryce, C. Graiff, A. Tiripicchio, Eur. J. Org. Chem. (1998) 2127.
[6] (a) D.B. Grotjahn, K.H. Dötz, Synlett (1991) 381. (b) C.A. Merlic, D. Xu, B.G. Gladstone, J. Org. Chem. 58 (1993) 538.
[7] W.D. Wulff, Organometallics 17 (1998) 3116.
[8] T.S. Powers, Y. Shi, K.J. Wilson, W.D. Wulff, J. Org. Chem. 59 (1994) 6882.
[9] Y. Shi, Ph.D. Thesis, The University of Chicago, Chicago IL, 1995, p. 28.
[10] U. Schick, L. Jordi, S. Ricard, J. Veciana, K.H. Dötz, J.M. Moretò, J. Am. Chem. Soc. 120 (1998) 2283.
[11] (a) T. Weidmann, K. Sunker, W. Beck, J. Organomet. Chem. 459 (1993) 219. (b) M. Duetsch, F. Stein, R. Lackmann, E. Pohl, R. Herbst-Irmer, A. de Meijere, Chem. Ber. 125 (1992) 2051. (c) H. Fischer, K. Treier, C. Troll, Chem. Ber. 125 (1995) 883.
[12] H.G. Raubenheimer, G.J. Kruger, W.H. Viljoen, S. Lotz, J. Organomet. Chem. 314 (1986) 281.
[13] E. Licandro, S. Maiorana, R. Manzotti, A. Papagni, D. Perdicchia, M. Pryce, A. Tiripicchio, M. Lanfranchi, J. Chem. Soc. Chem. Commun. (1998) 383.
[14] (a) Y-C. Xu, W.D. Wulff, J. Org. Chem. 52 (1987) 3263. (b) R.P. Hsung, Y-C. Xu, W.D. Wulff, Tetrahedron Lett. 36 (1995) 8159. (c) K.H. Dötz, R. Dietz, Chem. Ber. 110 (1997) 1555.
[15] Cambridge Structural Database (CSD, october 1998).
[16] K. Issleib, P.V. Malotki, J. Prakt. Chem. (1973) 463.
[17] R. Aumann, E.O. Fischer, Chem. Ber. 101 (1968) 954.
[18] (a) N. Walker, D. Stuart, Acta Crystallogr., Sect. A 39 (1983) 158. (b) F. Ugozzoli, Comput. Chem. 11 (1987) 109.
[19] G.M. Sheldrick, 'SHELX-97', Program for the Crystal Structure Determination, Universität Göttingen, Germany, 1986.