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Studies of the stereoselective allylation of chiral benzaldimine chromium tricarbonyl complexes

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Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday.

Abstract

Highly stereoselective allylation of a series of chiral tricarbonylchromium benzaldimine complexes (**2a–c**) was achieved at −20°C and homoallyl amine complexes (**4a–c**) were isolated in good yields. In the case of homoallyl amine **4c**, obtained in 75% d.e., the degree of stereoselection depends on the catalyst and the reaction conditions. The crystal structure of the major diastereoisomer of racemic **4c** was determined by X-ray diffraction, which showed a (*S*,*S*) or (*R*,*R*) configuration, in agreement with the stereochemical model operating for the *ortho*-substituted tricarbonylchromium arene complexes.

Furthermore, the new tricarbonylchromium complex of *N*-(2-methoxybenzyliden)diphenyl phosphinamide **3** was prepared. This substrate is a stable analog of the normally unviable ammonia imine.

Keywords: Tricarbonylchromium arenes; Stereoselective allylation; Imines; Homoallylamines

1. Introduction

Optically active amines are important organic compounds that can be used as chiral building blocks, chiral auxiliaries or ligands for catalysts in the field of asymmetric synthesis. Furthermore, amines with an α-stereocenter are widely represented in bioactive and pharmacologically interesting molecules.

The stereoselective 1,2-nucleophilic addition of organometallic reagents to imines is a useful method for the synthesis of primary and secondary enantiopure amines [1]. In particular, the use of allylic organometallic compounds provides a route to homoallyl amines, which are valuable molecules due to the different possible transformations of the double bond. Chiral tricarbonyl(benzaldimine) chromium complexes have been widely used for the usually very highly stereoselective synthesis of various organic and organometallic compounds [2,3]. The addition of organometallic reagents to chiral arylimine complexes was studied some years ago by Solladié-Cavallo [3a], but to the best our knowledge no examples of the addition of allylic organometallics to such imines have yet been reported. Because enantiopure homoallyl amines are molecules of considerable interest, we decided to study the addition reaction of allylic organometallic reagents to chiral benzaldimine complexes.

2. Results and discussion

We report here the results of the stereoselective addition of allyl magnesium bromide to a series of chiral imine complexes **2** and **3** (Fig. 1).

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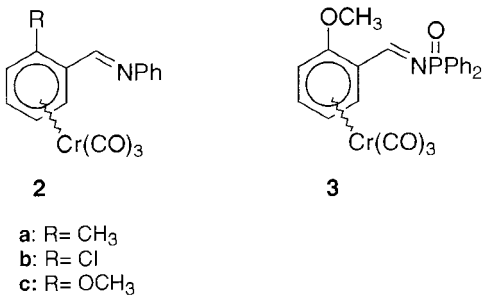
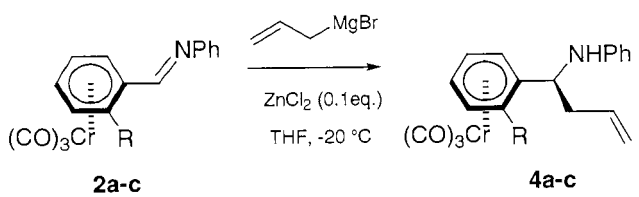


Fig. 1.

N-Phenyl benzaldimines **2a–c**, were prepared from the parent benzaldehyde complexes **1a–c** as previously described [2b,f]. The $Cr(CO)_3$ complex of *N*-diphenylphosphinylimine **(3),** prepared as reported below, is a new complex and particularly interesting substrate as it provides a stable analog of normally unviable ammonia imine [4].

We first studied the addition of allyl magnesium bromide to racemic *N*-phenyl benzaldimine complexes **2a–c.** The reaction was run in THF at -20°C in the presence of $ZnCl_2$ (0.1 equivalent). The color of the solution immediately changed from orange to yellow after the Grignard addition and the reaction was complete in about 20 min. Homoallyl amine complexes **4a–c** were isolated in very good yields (Scheme 1):



Scheme 1.

4	R	Yield (%)	D.e.
a	CH_3	80	98
b	Cl	90	98
c	OCH_3	88	75

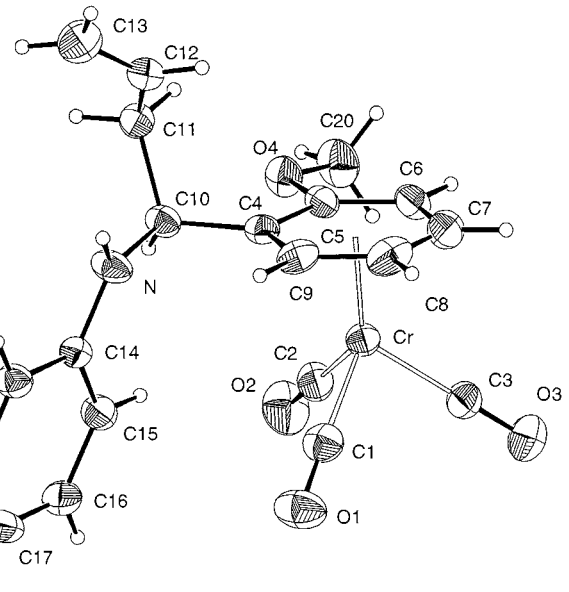
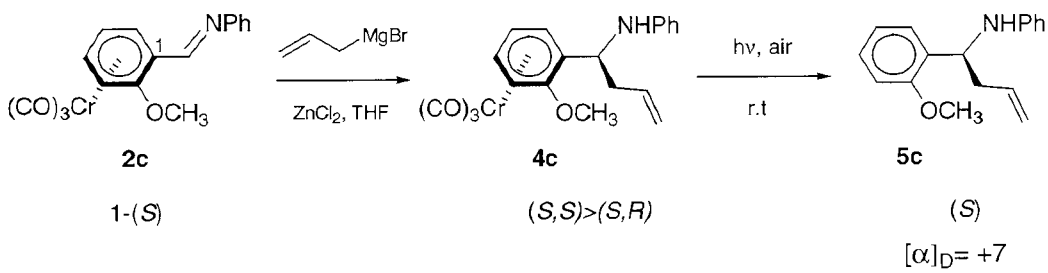


Fig. 2. View of the structure of the (*S*,*S*) enantiomer of the major diastereoisomer of racemic **4c.**The ellipsoids are drawn at the 30% probability level.

Complexes **4a** and **4b** were obtained with complete diastereoselection as determined by ^{1}H-NMR on the crude reaction mixture. Compound **4c** ($R = OCH_3$) showed a lower d.e. value (75%, Scheme 1), but the major diastereoisomer of racemic **4c,** was easily obtained after chromatographic separation of the crude reaction mixture. Furthermore (−)-**4c** was also obtained in enantiopure form, starting from optically pure (+)-1(*S*)-**2c** (see Section 4). Decomplexation of (−)-**4c** by means of air and sunlight gave the corresponding enantiopure homoallylimine (+)-**5c** in quantitative yields. (Scheme 2)

The determination of the crystal structure of **4c** by a X-ray diffraction showed that the configuration of the major diastereoisomer of **4c** is C4-(*S*), C10-(*S*) or C4-(*R*), C10-(*R*). The structure of the enantiomer C4-(*S*), C10-(*S*) is shown in Fig. 2 together with the atomic numbering system. Selected bond distances and angles in **4c** are given in Table 1.

The coordination around the Cr atom is of three legged piano stool type with the metal interacting in a



Scheme 2.

Table 1
Selected bond lengths (Å) and angles (°) for **4c**

Bond lengths			
Cr–C(1)	1.850(4)	(4)–C(20)	1.430(4)
Cr–C(2)	1.834(3)	N–C(14)	1.392(4)
Cr–C(3)	1.836(3)	N–C(10)	1.449(4)
Cr–C(4)	2.280(3)	C(4)–C(9)	1.401(4)
Cr–C(5)	2.263(3)	C(4)–C(5)	1.433(4)
Cr–C(6)	2.236(3)	C(4)–C(10)	1.531(4)
Cr–C(7)	.203(3)	C(5)–C(6)	1.399(4)
Cr–C(8)	2.217(3)	C(6)–C(7)	1.417(5)
Cr–C(9)	2.228(3)	C(7)–C(8)	1.386(6)
O(1)–C(1)	1.154(4)	C(8)–C(9)	1.417(5)
O(2)–C(2)	1.147(4)	C(10)–C(11)	1.552(4)
O(3)–C(3)	1.154(4)	C(11)–C(12)	1.485(5)
O(4)–C(5)	1.351(4)	C(12)–C(13)	1.303(5)
Bond angles			
C(2)–Cr–C(3)	88.16(15)	C(5)–C(4)–C(10)	119.7(3)
C(2)–Cr–C(1)	88.43(15)	O(4)–C(5)–C(6)	124.0(3)
C(3)–Cr–C(1)	88.29(15)	O(4)–C(5)–C(4)	115.2(3)
C(2)–Cr–C(8)	162.05(14)	C(6)–C(5)–C(4)	120.8(3)
C(1)–Cr–C(6)	165.51(14)	C(5)–C(6)–C(7)	119.3(3)
C(3)–Cr–C(4)	163.07(13)	C(8)–C(7)–C(6)	121.0(3)
C(5)–O(4)–C(20)	118.8(3)	C(7)–C(8)–C(9)	119.2(3)
C(14)–N–C(10)	125.5(2)	C(4)–C(9)–C(8)	121.6(3)
O(1)–C(1)–Cr	177.3(3)	N–C(10)–C(4)	112.7(3)
O(2)–C(2)–Cr	179.8(3)	N–C(10)–C(11)	109.1(2)
O(3)–C(3)–Cr	179.0(3)	C(4)–C(10)–C(11)	109.7(2)
C(9)–C(4)–C(5)	118.0(3)	C(12)–C(11)–C(10)	114.1(3)
C(9)–C(4)–C(10)	122.2(3)	C(13)–C(12)–C(11)	125.2(4)

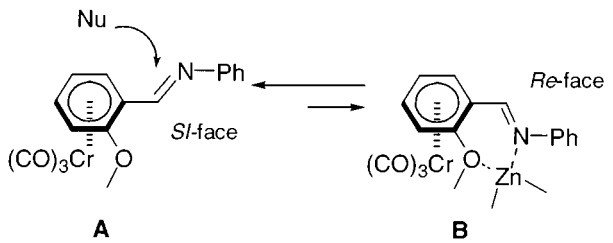


Fig. 3.

Table 2
Allylation of **2c** to give **4c**

Entry	T (°C)	$ZnCl_2$ (equivalents)	% Yield	% D.e.
1	0	1	90	62
2	0	0.1	90	70
3	0	0	74	90
4	−20	1	90	65
5	−20	0.1	88	75
6	−20	0	53	90
7	−78	0.1	75	93
8	−78	$BF_3{\cdot}OEt_2$ (1 equivalent)	79	98

slightly asymmetric η^6-fashion with the arene (Cr–C bond lengths in the range 2.203(3)–2.280(3) Å). The three carbonyls adopt a nearly eclipsed conformation with respect to the arene C5, C7, C9 carbon atoms, as shown by the torsion angle C1–Cr–CE–C9 = −10.3(3)°, C2–Cr–CE–C5 = −11.1(3)° and C3–Cr–CE–C7 = −13.5(3)° (CE is the centroid of the arene). The eclipsed orientation of the $Cr(CO)_3$ tripod with respect to the OMe substituent is in accord with literature results for arene complexes bearing electron donating groups. [5]

The 75% d.e obtained in the case of complex **4c** is lower than the d.e. usually reported in the literature when adding different nucleophiles to 2-methoxybenzaldehyde (85–100% [2a,c,f,5e] or 2-methoxybenzaldimine complexes (85–98%, [2b,c,f,6]), and so we decided to investigate further the stereochemical outcome of the reaction on 2-methoxybenzaldimine complex **2c**.

On the basis of the stereochemical model for the addition of a nucleophile to a prostereogenic unit of an *ortho*-substituted complex [6], the major (or exclusive) diastereoisomer is generated by the approach of the Grignard reagent from the opposite side to that of the $Cr(CO)_3$ group on the favourite conformation **A** of imine, in which the C=N group is *anti* with respect to the *ortho*-substituent (Fig. 3).

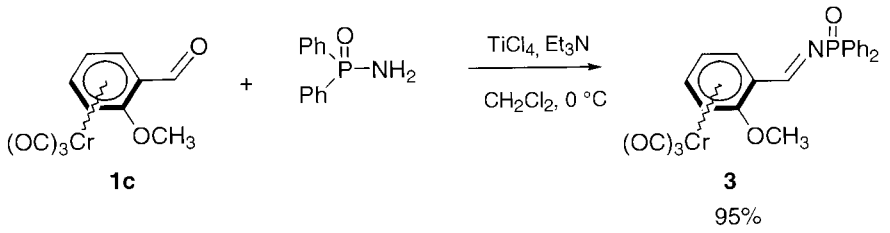
Considering the 1*S* enantiomer of **2c** (in which the *Si*-face is the favourite), the Grignard addition to conformer **A** leads to an *S* configuration for the new stereocenter, in agreement with the result of the X-ray analysis of **4c**. On the other hand, a possible Lewis acid chelation between the imine nitrogen and the oxygen of OCH_3 could stabilize the minor conformer **B**, thus leading to the formation of a certain amount of the opposite diastereoisomer.

This hypothesis suggests that the amount of the Lewis acid could be an important factor in driving the reaction towards one or the other of the two diastereoisomers (Fig. 3).

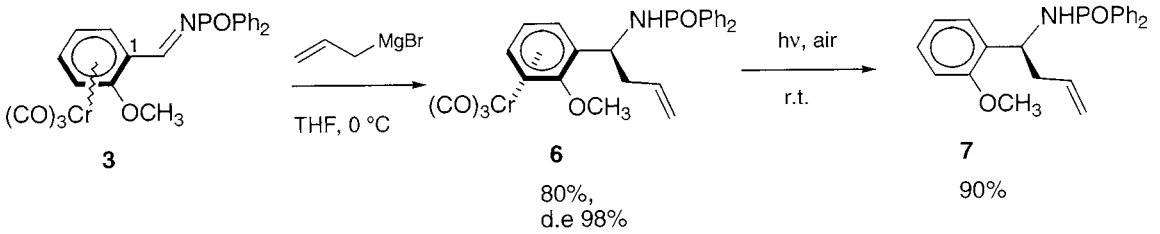
With the aim of thoroughly investigating the stereoselectivity of the allylation of 2-methoxybenzaldimine complex **2c**, the reaction was repeated under different experimental conditions, by changing the amount and nature of Lewis acid, as well as the reaction temperature (Scheme 2, Table 2)

In a first set of experiments we studied the influence of the amount of $ZnCl_2$ on the stereoselectivity, working again at −20°C (entries 4–6). The reaction was first run using one equivalent of $ZnCl_2$ (Table 2, entry 4), but only a slight decrease in d.e. (10%) occurred (compare entry 4 with entry 5). A considerable increase in d.e. (90%) was found when the reaction was run without any catalyst (entry 6), but the product was obtained in lower yield (53%) even after addition of two further equivalents of Grignard reagent.

In a second set of experiments, we studied the effect of temperature on stereoselectivity by working at 0°C (entries 1–3). The same trend of stereoselection was



Scheme 3.



Scheme 4.

observed and, in the case of the reaction run in the absence of $ZnCl_2$ (Table 2, entry 3), the yield was better than at -20°C again with a good d.e. (90%). Finally, the reaction with 0.1 equivalent of $ZnCl_2$ was performed at -78°C (entry 7) and **4c** was obtained in higher stereoselection (93%) and quite good yields (75%).

These results suggest that the Lewis acid catalyst affects reaction yields, but has little effect on diastereoselectivity; the Zn chelation between OCH_3 and C=N only plays a marginal role in controlling stereoselection (as also found by Kündig [7]). It is likely that the angular geometry of the methoxy group reduces its steric hindrance (see X-ray, Fig. 2) and consequently the discrimination between the two conformers **A** and **B**. In line with this assumption, the bulkier *ortho*-substituents, such as CH_3 and Cl in **2a** and **2b**, gave the corresponding **4a** and **4b** with complete stereoselection (see Scheme 1).

The importance of the steric effect of the *ortho*-substituent is also supported by the result obtained in a further experiment (entry 8), in which a non-chelating $BF_3{\cdot}OEt_2$ Lewis acid was used. Product **4c** was recovered in good yield and with complete stereoselection. This is probably due to the fact that the coordination of BF_3 to the methoxy group greatly increases the size of this group and consequently the conformeric population **A.**

Given the promising results obtained for the allylation of *N*-phenyl substituted imine complexes **2**, the reaction was extended to the *N*-phosphinyl imine **3**. As mentioned above, after the removal of the phosphinyl group, this reaction can provide primary homoallylamines that are useful intermediates for the preparation of more elaborate organic compounds.

The racemic *N*-diphenylphosphinyl imine complex **3** was prepared in very good yields from tricarbonyl(2-methoxybenzaldehyde)chromium (**1c**), following a procedure described for uncomplexed substrates [8]. (Scheme 3)

The allylation reaction was run at 0°C without $ZnCl_2$ and gave the *N*-diphenylphosphinyl amine **6** in 80% yield and with complete stereoselection (Scheme 4) After decomplexing, the corresponding amine **7** was recovered in 90% yield.

The complete stereoselection obtained in this case (for sake of clarity only one enantiomer of **6** is shown) is probably due to the stereoelectronic effect of the nitrogen diphenylphospinyl substituent, which only allows an *anti* disposition of the imino moiety in **3**.

3. Conclusions

In conclusion we achieved a highly stereoselective synthesis of aromatic homoallyl amines, which can also be obtained in enantiomerically pure forms. The new chromiumtricarbonyl complex of *N*-diphenylphosphinyl imine **3** is a synthon of an ammonia imine and allows the preparation of primary homoallyl amines, which are very useful organic intermediates.

4. Experimental

4.1. General methods

All of the reactions were performed under nitrogen, with the exclusion of direct sunlight. Tetrahydrofuran was distilled from sodium benzophenone ketyl, and the

solvents purified according to standard procedures. Unless otherwise stated, all of the other reagents were used as obtained from commercial sources. Melting points were determined using a Büchi 510 M.P. apparatus and are uncorrected. The IR spectra were recorded on a Perkin-Elmer 1725X FTIR; the ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ using a Bruker AC300 spectrometer. Complexes **1** and **2** were prepared as described in the literature [2a,b,f].

4.2. Tricarbonyl[N-(η^6-2-methylbenzylidene)-aniline]chromium (**2a**)

M.p. 80–81°C (pentane). ^{1}H-NMR, δ: 2.42 (s, 3H, CH_3), 5.15 (d, 1H, arom.Cr(CO)$_3$, $J = 6.4$ Hz,), 5.3 (dd, 1H, arom.Cr(CO)$_3$, $J = 6.6$, 6.3 Hz), 5.58 (dd, 1H, arom.Cr(CO)$_3$, $J = 6.3$, 6.4 Hz), 6.41 (d, 1H, arom.Cr(CO)$_3$, $J = 6.6$ Hz,), 7.1–7.42 (m, 5H, arom.), 8.3 (s, 1H, CH=N). Anal. Calc. for $C_{17}H_{13}CrNO_3$: C, 61.63; H, 3.95; N, 4.23. Found: C, 61.65; H, 3.95; N, 4.24.

4.3. Tricarbonyl[N-(η^6-2-chlorobenzylidene)aniline]-chromium (**2b**)

M.p. 83–84 °C (pentane). ^{1}H-NMR, δ: 5.20 (dd, 1H, arom.Cr(CO)$_3$, $J = 6.4$, 6.3 Hz), 5.46 (d, 1H, arom.Cr(CO)$_3$, $J = 6.5$ Hz,), 5.58 (ddd, 1H, arom.Cr(CO)$_3$, $J = 6.5$, 6.3, 1.0 Hz), 6.56 (dd, 1H, $J = 6.5$, 1.0 Hz, arom.Cr(CO)$_3$), 7.15–7.45 (m, 5H, arom.), 8.53 (s, 1H, CH=N). Anal. Calc. for $C_{16}H1_0ClCrNO_3$: C, 54.64; H, 2.86; N, 3.98. Found: C, 54.71; H, 2.88; N, 3.97.

4.4. Tricarbonyl[N-(η^6-2-methoxybenzylidene)-aniline]chromium (**2c**)

M.p. 138–140°C (pentane). ^{1}H-NMR, δ: 3.81 (s, 3H, OCH_3), 5.05 (dd, 1H, arom.Cr(CO)$_3$, $J = 6.4$, 6.5Hz), 5.13 (d, 1H, arom.Cr(CO)$_3$, $J = 6.8$ Hz,), 5.74 (ddd, 1H, arom.Cr(CO)$_3$, $J = 6.8$, 6.4, 1.2 Hz,), 6.65 (dd, 1H, aromCr(CO)$_3$, $J = 6.5$, 1.2 Hz), 7.35–7.5 (m, 5H, arom.), 8.5 (s, 1H, CH=N). Anal. Calc. for $C_{17}H_{13}CrNO_4$: C, 58.79; H, 3.77; N, 4.03. Found: C, 58.49; H, 3.79; N, 4.05. (+)-1(*S*)-**2c**, $[\alpha]_D = +390$ ($c = 0.1$, $CHCl_3$).

4.5. Tricarbonyl[N-(η^6-2-methoxybenzylidene)-diphenylphosphinamide]chromium (**3**)

Triethylamine (0.74 ml, 4.4 mmol) was added dropwise to a stirred solution of tricarbonyl(2-methoxybenzaldehyde) chromium (**1c**) (0.4 g, 1.47 mmol) and *N*-diphenylphosphinamide (0.38 g, 1.76 mmol) in CH_2Cl_2 (6 ml). The mixture was cooled to 0°C and $TiCl_4$ (0.88 mmol, 0.88 ml of 1 M sol. in CH_2Cl_2) was slowly added. After 4 h (TLC: AcOEt:Et_3N, 10:1), the mixture was filtered over Celite® and washed with 30 ml of a saturated solution of $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2 (3 × 30 ml) and, after evaporation of the solvent, the red residue was purified by flash column chromatography (eluent: AcOEt:Et_3N, 10:1). Yield: 95%; m.p.: 131–132°C (diisopropyl ether). IR (nujol): *v*, 1968, 1885, 1605, 1198 cm^{-1}. ^{1}H-NMR, δ: 3.82 (s, 3H, OCH_3), 5.02 (dd, 1H, arom.Cr(CO)$_3$, $J = 6.5$, 6.4 Hz), 5.06 (d, 1H, arom.Cr(CO)$_3$, $J = 6.9$ Hz), 5.83 (ddd, 1H, arom.Cr(CO)$_3$, $J = 6.9$, 6.4, 1.1 Hz), 6.65 (dd, 1H, arom.Cr(CO)$_3$, $J = 6.5$, 1.1 Hz), 7.4–7.5 (m, 6H, arom.), 7.9 (m, 4H, arom.), 9.4 (d, 1H CH=N, $J_{H-P} = 30.8$ Hz). ^{31}P-NMR, δ: 26.37. EI-MS *m*/*z*: 471 (M^+), 415 (M^+2CO), 387 (M^+–3CO).

4.6. Allylation of benzaldimine complexes. General procedure

Allyl magnesium bromide (1 mmol, 1 ml of 1 M sol. in Et_2O) was added dropwise to a solution of the proper imine complex **2a–c** (0.6 mmol) and $ZnCl_2$ (see Table 1) in THF (6 ml) cooled to the appropriate temperature. The color of the solution rapidly changed from orange to yellow and, after 20 min (TLC: CH_2Cl_2:petroleum ether, 1:1), the mixture was quenched by adding 15 ml of 1/1, H_2O/MeOH solution. The mixture was passed through a pad of Celite®, extracted with CH_2Cl_2 (3 × 15 ml), and the solvent was evaporated. The crude mixture was purified by means of column chromatography (eluent: petroleum ether:Et_2O, 3:2) affording complexes **4a–c** as yellow solids.

4.7. Tricarbonyl[N-1-((η^6-2-methylphenyl)-but-3-enyl) aniline]chromium (**4a**)

Yield: 80%; m.p.: 103–104°C (diisopropyl ether). IR (nujol): *v*, 3410, 1880, 1860, 1600 cm^{-1}. ^{1}H-NMR, δ: 2.3 (s, 3H, CH_3,), 2.5 (m, 2H, CH_2), 3.75 (brs, 1H, NH), 4.38 (t, 1H, CHN, $J = 6.1$ Hz), 4.98 (d, 1H, arom.Cr(CO)$_3$, $J = 6.2$ Hz), 5.06 (dd, 1H, arom.Cr(CO)$_3$, $J = 6.4$, 6.3 Hz), 5.15 (d, 1H, CH_2=, $J = 17.0$ Hz), 5.16 (d, 1H, CH_2=, $J = 10.7$ Hz) 5.49 (dd, 1H, arom.Cr(CO)$_3$, $J = 6.3$, 6.2 Hz), 5.73 (m, 1H, CH=), 5.76 (d, 1H, arom.Cr(CO)$_3$, $J = 6.4$ Hz), 6.75 (m, 3H, arom.), 7.2 (m, 2H, arom.). Anal. Calc. for $C_{20}H_{19}CrNO_3$: C, 64.34; H, 5.13; N, 3.75. Found: C, 64.40; H, 5.15; N, 3.77.

4.8. Tricarbonyl[N-1-(η^6-2-chlorophenyl)-but-3-enyl) aniline]chromium (**4b**)

Yield: 90%; m.p.: 94–95°C (pentane). IR (nujol): *v*, 3393, 1971, 1874, 1650, 1048 cm^{-1}. ^{1}H-NMR, δ: 2.5

(m, 1H, CH_2), 2.65 (m, 1H, CH_2), 3.85 (brs, 1H, NH), 4.72 (m, 1H, CHN), 4.9 (dd, 1H, arom.$Cr(CO)_3$, J = 6.2, 6.1 Hz), 5.16 (d, 1H, CH_2=, J = 17.6 Hz), 5.18 (d, 1H, CH_2=, J = 10.1 Hz), 5.28 (d, 1H, arom.$Cr(CO)_3$, J = 6.2 Hz), 5.5 (dd, 1H, arom.$Cr(CO)_3$, J = 6.1, 6.4 Hz), 5.73 (m, 1H, CH=), 5.75 (d, 1H, arom.$Cr(CO)_3$, J = 6.4 Hz), 6.75 (m, 3H, arom.), 7.2 (m, 2H, arom.). Anal. Calc. for $C_{19}H_{16}ClCrNO_3$: C, 57.54; H, 4.09; N, 3.57. Found: C, 57.90; H, 4.05; N, 3.57.

4.9. Tricarbonyl[N-1-(η^6-2-methoxyphenyl)-but-3-enyl) aniline]chromium (**4c**)

Yield: 88% (Table 1, entry 5). After column chromatography (eluent: petroleum ether:Et_2O, 3:2).

4.9.1. I diast.

(*S**,*R**) (r.f. 0.36), yield: 12%; m.p.: 157°C dec.(diisopropyl ether). IR (nujol): ν, 3435, 1940, 1856, 1642 cm^{-1}. ^{1}H-NMR, δ: 2.35 (ddd, 1H, CH_2, J = 14.7, 5.1, 3.7 Hz), 2.9 (ddd, 1H, CH_2, J = 14.7, 8.7, 10.1 Hz), 3.88 (s, 3H, OCH_3), 3.98 (brs, 1H, NH), 4,38 (dd, 1H, CHN, J = 3.7, 10.1 Hz), 4.7 (dd, 1H, arom.$Cr(CO)_3$, J = 6.3, 6,4 Hz), 5.05 (d, 1H, arom.$Cr(CO)_3$, J = 6.8 Hz), 5.18 (d, 1H, CH_2=, J = 10.2 Hz), 5.25 (d, 1H, CH_2=, J = 17.1), 5.58 (ddd, 1H, arom.$Cr(CO)_3$, J = 6.4, 6.5, 1,0 Hz), 5.87 (dddd, 1H, CH=, J = 10.2, 17.1, 8.7, 5.1 Hz), 5.97 (dd, 1H, arom.$Cr(CO)_3$, J = 6.5, 1.0 Hz), 6.45 (d, 2H, arom., J = 9.4 Hz), 6.7 (t, 1H, arom., J = 8.0 Hz), 7.1 (t, 1H, arom., J = 9.4 Hz). ^{13}C-NMR, δ: 44.25 (CH_2), 50.18 (CHN), 55.87 (OCH_3), 72.44, 82.86, 95.46, 97.69, (CH, arom.$Cr(CO)_3$), 103.94 (C_q, arom.$Cr(CO)_3$), 113.23 (CH, arom.), 117.96 (CH, arom.), 118.38 (CH_2=), 129.23 (CH, arom.), 135.1 (CH=), 141.9 (C_q, arom.$Cr(CO)_3$), 146.5 (C_q, arom.), 233.38 (CO). EI-MS *m/z*:389 (M^+), 361 (M^+–CO), 333 (M^+–2CO), 305 (M^+–3CO). From (+)-1(*S*)-**2c**: (+)-(*S*,*R*)-**4c**, 161–163°C (pentane), $[\alpha]_D$ = +76 (c = 0.12, $CHCl_3$).

4.9.2. II diast.

(*S**,*S**) (r.f. 0.26), yield: 80%; m.p.: 103°C (pentane). IR (nujol): ν, 3047, 1956, 1875, 1639 cm^{-1}. ^{1}H-NMR, δ: 2.6 (m, 2H, CH_2), 3.78 (s, 1H, NH), 3.82 (s, 3H, OCH_3), 4,67 (dd, 1H, CHN, J = 7.2, 4.7 Hz), 4.78 (t, 1H, arom.$Cr(CO)_3$, J = 6.2 Hz), 4.98 (d, 1H, arom.$Cr(CO)_3$, J = 6.8 Hz), 5.14 (m, 2H, CH_2=), 5.52 (dd, 1H, arom.$Cr(CO)_3$, J = 6.2, 6.8 Hz), 5.73 (dddd, 1H, CH=, J = 2.5, 7.0, 9.9, 13.6 Hz), 5.8 (d, 1H, arom.$Cr(CO)_3$, J = 6.2 Hz), 6.75 (m, 3H, arom.), 7.18 (m, 2H, arom.). ^{13}C-NMR, δ: 41.58 (CH_2), 51.08 (CHN), 55.72 (OCH_3), 72.57, 83.23, 94.73, 94.78, (CH, arom.$Cr(CO)_3$), 102.14 (C_q, arom.$Cr(CO)_3$), 114.02 (CH, arom.), 118.13 (CH, arom.), 118.84 (CH_2=), 129.14 (CH, arom.), 133.68 (CH=), 141.3 (C_q, arom.$Cr(CO)_3$), 146.5 (C_q, arom.), 232.91 (CO). EI-MS *m/z*: 389 (M^+), 361 (M^+–CO), 333 (M^+–2CO), 305 (M^+–3CO). From (+)-1(*S*)-**2c**: (−)-(*S*,*S*)-**4c**, m.p. 114°C (pentane), $[\alpha]_D$ = −302 (c = 0.12, $CHCl_3$).

4.10. N-(1-(-2-methoxyphenyl)-but-3-enyl) aniline (**5c**)

A solution of racemic **4c** in CH_2Cl_2 was exposed to air and sunlight until the yellow color had completely disappeared. The solvent was evaporated and the residue, taken up with Et_2O, was filtered over a pad of Celite® to yield **5c** as nearly analitically pure colorless oil. IR (neat): ν, 3410, 3075, 3050,1600 cm^{-1}. ^{1}H-NMR, δ: 2.45 (m, 1H, CH_2), 2.64 (m, 1H, CH_2), 3.9 (s, 3H, OCH_3), 4.20 (brs, 1H, NH), 4,8 (dd, 1H, CHNH, J = 7.8, 4.9 Hz), 5.1 (d, 1H, CH_2=, J = 10.1 Hz), 5.15 (d, 1H, CH_2=, J = 17.2 Hz), 5.78 (m, 1H, CH=), 6.45–6.65 (m, 3H, arom.), 6.83–7.31(m, 6H, arom.). From (−)-(*S*,*S*)-**4c**: (+)-(*S*)-**5c**, $[\alpha]_D$ = −302 (c = 0.12, $CHCl_3$). (e.e. ≥ 98, by ^{1}H-NMR, using Eu(hfc)$_3$ as chiral shift reagent).

4.11. Tricarbonyl[N-(1-(η^6-2-methoxyphenyl)-but-3-enyl)diphenylphosphinamide (**6**)

M.p. 106–107°C (dec.) (diisopropyl ether). IR (nujol): ν, 3160, 1970, 1955, 1867, 1183 cm^{-1}. ^{1}H-NMR, δ: 2.34 (dd, 1H, NH, J = 3.5, 10.1 Hz), 2.62–2.88 (m, 2H, CH_2), 3.7 (s, 3H, OCH_3), 4.3 (m, 1H, CHNH), 4.78 (dd, 1H, arom.$Cr(CO)_3$, J = 6.2, 6.3 Hz), 4.94 (d, 1H, arom.$Cr(CO)_3$, J = 6.5 Hz), 5.1 (d, 1H, CH_2=, J = 10.9 Hz), 5.12 (d, 1H,CH_2=, J = 15.0 Hz), 5.54 (d, 1H, arom.$Cr(CO)_3$, J = 6.2 Hz), 5.56 (dd, 1H, arom.$Cr(CO)_3$, J = 6.3, 6.5 Hz), 5.65 (m, 1H, CH=), 7.1–7.6 (m, 6H, arom.), 7.8–8.05 (m, 4H, arom). ^{13}C-NMR, δ: 42.7 (CH_2), 50.8 (CHN), 55.7 (OCH_3), 72.6, 83.4, 94.9, 95.7, (CH, arom.$Cr(CO)_3$), 103 (C_q, arom.$Cr(CO)_3$), 119.6, (CH_2=), 128.6, 128.7, 131.8, 132, 132.5, 132.6, (CH, arom.), 133.4 (CH=), 141.6 (C_q, arom.$Cr(CO)_3$), 151.5 (C_q, arom.), 233 (CO). Anal. Calc. for $C_{26}H_{24}CrNO_5P$: C, 60.82; H, 4.71; N, 2.73. Found: C, 60.89; H, 4.72; N, 2.73.

4.12. N-(1-(2-methoxyphenyl)-but-3-enyl)-diphenylphosphinamide (**7**)

A solution of racemic **6** in CH_2Cl_2 was exposed to air and sunlight until the yellow color had completely disappeared. The solvent was evaporated and the residue, taken up with Et_2O, was filtered over a pad of Celite® to yield **7** as white solid (90%): m.p. 119–120°C (diisopropyl ether). IR (nujol): ν, 3138, 1600, 1493, 1245, 1194 cm^{-1}. ^{1}H-NMR, δ: 2.7 (m, 2H, CH_2), 3.72 (s, 3H, OCH_3), 3.94 (dd, 1H, NH, J = 11.0, 8.2 Hz), 4.32–4.46 (m, 1H, CHN), 4.95 (d, 1H, CH_2=, J = 8.2 Hz), 5.0 (d, 1H, CH_2=, J = 15.4 Hz), 5.5–5.64 (m, 1H, CH=), 6.8–7.0 (m, 3H, arom.), 7.2–7.5 (m, 8H, arom.), 7.7–7.9 (m, 3H, arom.).

Table 3
Crystal data and structure refinement for **4c**

Empirical formula	$C_{20}H_{19}CrNO_4$
Formula weight	389.36
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	
a (Å)	12.257(5)
b (Å)	9.338(2)
c (Å)	17.143(6)
β (°)	105.29(2)
Volume (Å^3)	1892.7(11)
Z, calculated density (Mg m^{-3})	4, 1.366
Absorption coefficient (mm^{-1})	0.628
$F(000)$	808
Crystal size (mm)	$0.15\times0.25\times0.38$
θ range for data collection (°)	3.22–30.03
Index ranges	$-17\le h\le16$, $0\le k\le13$, $0\le l\le24$
Reflections collected/unique	5675/5518 [$R_{int}=0.0318$]
Reflections observed [$I>2\sigma(I)$]	3130
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5518/0/255
Goodness-of-fit[a] on F^2	1.150
Final R indices [$I>2\sigma(I)$]	R_1[b] $=0.0475$, wR_2[c] $=0.1230$
R indices (all data)	$R_1=0.1188$, $wR_2=0.1850$
Largest difference peak and hole (e Å^{-3})	0.404 and −0.872

[a] GoF $=[\Sigma[w(F_o^2-F_c^2)^2]/(n-p)]^{1/2}$.
[b] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[c] $wR_2=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$, where $P=[\max(F_o^2,0)+2F_c^2]/3$.

4.13. X-ray data collection, structure determination, and refinement of (**4c**)

The crystallographic data are summarized in Table 3. Accurate unit-cell parameters were determined by least-squares refinement of the setting angles of 30 randomly distributed and carefully centered reflections with · in the range 11–19°. One standard reflection was monitored every 100 measurements, no significant decay was noticed over the time of data collection. Intensities were corrected for Lorentz and polarization effects and reduced to F_o^2. No absorption correction was applied to the data. The structure was solved by direct methods (SIR92) [9] and refined by full-matrix least-squares on F^2 using SHELXL-97 [10], first with isotropic thermal parameters and then with anisotropic thermal parameters for all the non-hydrogen atoms. All the hydrogen atoms were placed at their geometrically default-distances calculated positions and refined 'riding' on their parent atoms. All calculations were carried out on the DIGITAL AlphaStation 255 of the 'Centro di Studio per la Strutturistica Diffrattometrica' del CNR, Parma.

5. Supplementary material

The supplementary material for the structure includes the lists of atomic coordinates for the non-H atoms, of coordinates for the hydrogen atoms, and of anisotropic thermal parameters. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 130237. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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