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Fischer-type alkyl(hydrazino)carbene complexes: new synthetic potential in comparison with aminocarbene complexes

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Abstract

A general picture is given of the reactivity of the two Fischer-type alkyl(hydrazino)carbene complexes $(CO)_5Cr{=}C(CH_3)N(Bn)N(CH_3)_2$ (**1**) and $(CO)_4Cr{=}C(CH_3)N(Bn)N(CH_3)_2$ (**3**). Unlike their organic isolobal hydrazide analogues, they easily yield the corresponding α-anions at −78°C, which react with various electrophiles. Furthermore, the tetracarbonyl chelate **3** (easily generated from **1**) has greater synthetic potential than aminocarbenes: for example, it can be alkylated stepwise twice in the α-position, thus making it possible to introduce a new stereogenic centre in the molecule.

Keywords: Hydrazino carbenes; Hydrazides; Alkylation; Chelate Fischer carbenes

1. Introduction

We have recently [1] published two complementary methodologies for the synthesis of alkyl(hydrazino)carbene complexes, a new class of nitrogen-stabilised Fischer-type carbenes (Chart 1).

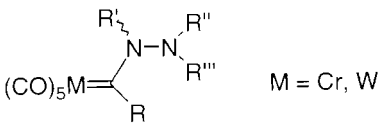

Chart 1.

As a result, we have been able to synthesise a large number of complexes, and this has opened up the possibility of systematically studying this new class of organometallics about which very little has so far been reported in the literature [2].

It is well known that the hydrogen atoms of aminocarbene complexes located in the α position with respect to the carbene carbon atom are acidic, and that these complexes can be efficiently deprotonated using strong bases at low temperature. The resulting anions easily react with electrophilic reagents, such as alkyl halides [3], epoxides [4], aldehydes [5] and Michael acceptors [6], and so the complexes have been widely (and also stereoselectively) functionalised, thus allowing the synthesis of a large number of interesting organic compounds.

The synthesis of alkyl(hydrazino)carbene complex **1** (Chart 2) made it possible to compare its reactivity with that of aminocarbenes; a further interesting point is that alkyl(hydrazino)carbenes can be used as synthetic hydrazide equivalents because hydrazides are the organic isolobal analogues of hydrazinocarbenes. We here show that the formal substitution of the pentacarbonylchromium moiety for the oxygen atom in the hydrazide leads to a fundamental differentiation in chemical reactivity. In this study, we chose to use the pentacarbonyl methyl(hydrazino)carbene of chromium(0) **1** as a model compound.

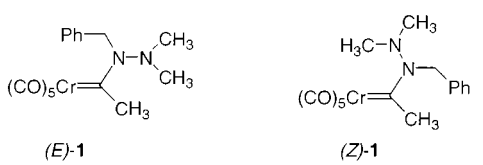

Chart 2.

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2. Results and discussion

2.1. Crystal structures and spectroscopic data of the complexes (Z)-1 and (E)-1

Compound **1** was synthesised as previously reported [1a][1]. The two rotational isomers (*Z*)-**1** and (*E*)-**1** can be easily separated by flash column chromatography and are configurationally stable (Chart 2).

The crystal structures of both isomers have been determined by X-ray diffraction methods. Views of the structures of (*Z*)-**1** and (*E*)-**1** are shown in Figs. 1 and 2, selected bond distances and angles in them in Tables 1 and 2, respectively. The structural features are typical of the Fischer-type pentacarbonylchromium aminocarbene complexes [7]. The structural parameters in the isomers are very similar, the only difference being in the carbenic Cr(1)–C(6) bond, which is slightly longer in (*E*)-**1**, 2.132(3) Å, than in (*Z*)-**1**, 2.108(2) Å. In both structures the N1N2C6C10 moiety is strictly planar, with the Cr and C7 atoms deviating on opposite sides by 0.206(1) and 0.095(4) Å in (*E*)-**1** and 0.265(1) and 0.169(3) Å in (*Z*)-**1**, respectively.

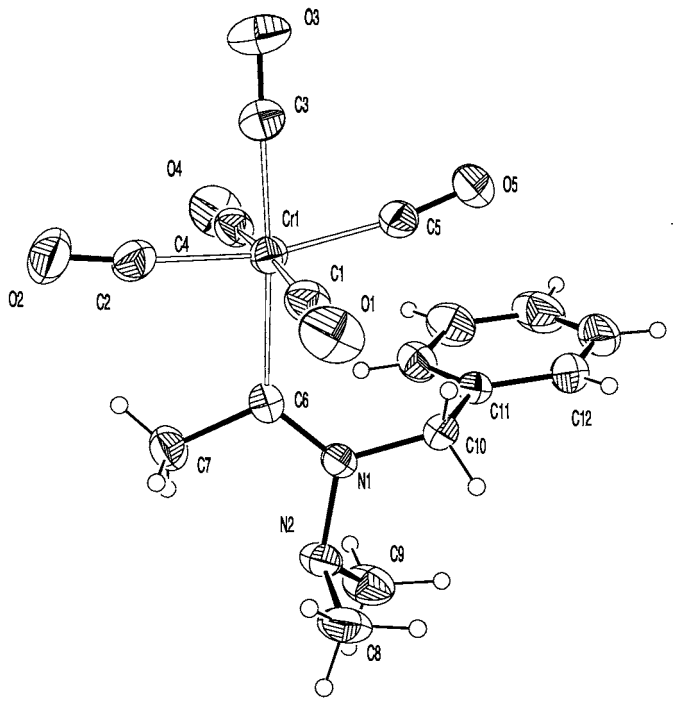


Fig. 1. ORTEP view of the structure of the complex (*E*)-**1** together with the atomic numbering scheme. The ellipsoids for the atoms are drawn at 30% probability level.

[1] The trisubstitued hydrazide necessary to the synthesis of compound **1** has been prepared following a general and efficient protocol we have set up. A patent application has been presented for this procedure.

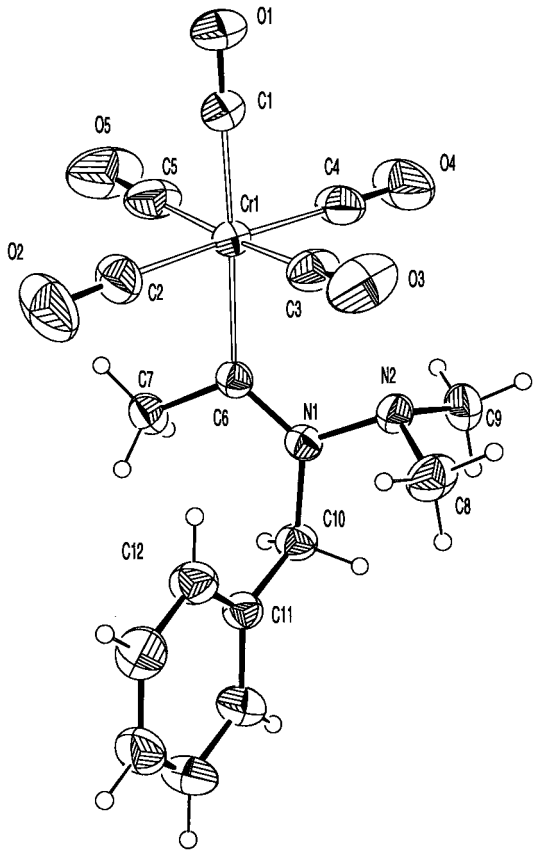


Fig. 2. ORTEP view of the structure of complex (*Z*)-**1** together with the atomic numbering scheme. The ellipsoids for the atoms are drawn at 30% probability level.

Comparison of the spectroscopic data of hydrazinocarbene complex (*E*)-**1** and aminocarbene complex (*Z*)-**2** (Chart 3) [7] reveals that the chemical shift values of the ^{1}H- and ^{13}C-NMR are very similar, thus indicating their qualitative analogy in terms of charge distribution. The structural parameters are also quite similar, including the carbenic Cr–C bond which is 2.134(3) Å in (*Z*)-**2**.

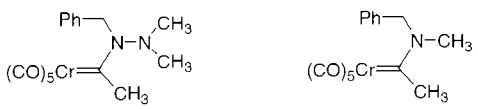


Chart 3.

However, the isomers **1** have some steric peculiarities due to the presence of the second nitrogen atom. (i) The β-nitrogen lone pair in both the (*E*)- and (*Z*)-**1** isomers forms a dihedral angle of about 90° with the lone pair of the α-nitrogen, thus making it almost coplanar with the Cr–C–N(α) moiety. The same conformation is also found in trialkyl substituted hydrazides, and makes it possible to minimise the interaction between the two lone pairs [8]. Moreover, in contrast to hydrazinocarbenes, trialkyl substituted hydrazides only exist as (*E*)-iso-

mers, due to the steric repulsion between the oxygen and β-nitrogen lone pairs present in (*Z*)-isomers. (ii) In the (*Z*)-**1** isomer the β-nitrogen N2 is rather close to the chromium atom, the N2···Cr separation being 3.316(2) Å, with the lone pair pointing towards the metal atom. This fact could facilitate the elimination of a CO ligand and the chelation of the nitrogen atom. (iii) Some intramolecular interaction of the type $CO\cdots\pi_{arene}$ could be envisaged in the (*E*)-**1** isomer between the oxygen atom O5 of a carbonyl and the π electron cloud of the aromatic ring of the benzyl substituent. The structural parameters indicated by Gambaro et al. [9] to emphasise this type of interaction are: the C5–O5 line is almost parallel to the arene plane (deviation angle: 13.0(2)°), the distance between the O5 atom and the mean plane of the arene is 3.176(2) Å, the minimum and maximum distances from O5 to the carbon atoms of the six-membered of the arene ring (3.202(3) and 4.373(5) Å) and the distance from C5 to the nearest carbon atom of the arene ring (3.111(4) Å).

Table 1
Selected bond lengths (Å) and angles (°) for (*E*)-**1**

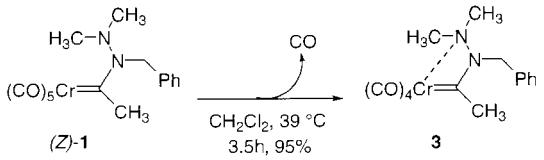
Bond distances	
Cr(1)–C(3)	1.863(3)
Cr(1)–C(4)	1.880(3)
Cr(1)–C(2)	1.878(4)
Cr(1)–C(1)	1.885(3)
Cr(1)–C(5)	1.890(3)
Cr(1)–C(6)	2.132(3)
O(1)–C(1)	1.147(3)
O(2)–C(2)	1.153(3)
O(3)–C(3)	1.147(4)
O(4)–C(4)	1.139(3)
O(5)–C(5)	1.144(3)
N(1)–C(6)	1.313(3)
N(1)–N(2)	1.449(3)
N(1)–C(10)	1.470(3)
C(6)–C(7)	1.508(4)
C(10)–C(11)	1.504(4)
Bond angles	
C(3)–Cr(1)–C(4)	91.19(14)
C(3)–Cr(1)–C(2)	85.24(14)
C(4)–Cr(1)–C(2)	91.96(13)
C(3)–Cr(1)–C(1)	95.65(13)
C(2)–Cr(1)–C(1)	88.69(14)
C(3)–Cr(1)–C(5)	81.38(14)
C(4)–Cr(1)–C(5)	89.94(13)
C(1)–Cr(1)–C(5)	91.01(13)
C(4)–Cr(1)–C(6)	85.97(12)
C(2)–Cr(1)–C(6)	91.85(13)
C(1)–Cr(1)–C(6)	87.20(12)
C(5)–Cr(1)–C(6)	101.60(12)
C(6)–N(1)–N(2)	120.0(2)
C(6)–N(1)–C(10)	124.2(2)
N(2)–N(1)–C(10)	115.8(2)
O(1)–C(1)–Cr(1)	178.0(3)
O(2)–C(2)–Cr(1)	174.3(3)
O(3)–C(3)–Cr(1)	176.4(3)
O(4)–C(4)–Cr(1)	178.9(3)
O(5)–C(5)–Cr(1)	170.6(3)
N(1)–C(6)–C(7)	114.0(3)
N(1)–C(6)–Cr(1)	128.9(2)
C(7)–C(6)–Cr(1)	117.1(2)
N(1)–C(10)–C(11)	114.7(3)

Table 2
Selected bond lengths (Å) and angles (°) for (*Z*)-**1**

Bond distances	
Cr(1)–C(1)	1.863(3)
Cr(1)–C(2)	1.875(3)
Cr(1)–C(3)	1.885(3)
Cr(1)–C(4)	1.887(3)
Cr(1)–C(5)	1.881(3)
Cr(1)–C(6)	2.108(2)
O(1)–C(1)	1.149(3)
O(2)–C(2)	1.147(3)
O(3)–C(3)	1.142(3)
O(4)–C(4)	1.139(3)
O(5)–C(5)	1.139(3)
N(1)–C(6)	1.317(3)
N(1)–C(10)	1.485(3)
N(1)–N(2)	1.422(2)
C(6)–C(7)	1.511(3)
C(10)–C(11)	1.520(3)
Bond angles	
C(1)–Cr(1)–C(2)	91.92(11)
C(1)–Cr(1)–C(5)	87.82(12)
C(2)–Cr(1)–C(5)	89.97(16)
C(1)–Cr(1)–C(4)	90.70(11)
C(5)–Cr(1)–C(4)	90.37(15)
C(1)–Cr(1)–C(3)	87.57(11)
C(2)–Cr(1)–C(3)	89.81(14)
C(4)–Cr(1)–C(3)	90.06(14)
C(2)–Cr(1)–C(6)	86.07(10)
C(5)–Cr(1)–C(6)	91.22(10)
C(4)–Cr(1)–C(6)	91.32(9)
C(3)–Cr(1)–C(6)	93.38(10)
C(6)–N(1)–N(2)	118.07(16)
C(6)–N(1)–C(10)	125.65(18)
N(2)–N(1)–C(10)	116.28(16)
O(1)–C(1)–Cr(1)	179.5(3)
O(2)–C(2)–Cr(1)	178.1(3)
O(3)–C(3)–Cr(1)	174.3(2)
O(4)–C(4)–Cr(1)	179.0(3)
O(5)–C(5)–Cr(1)	176.1(3)
N(1)–C(6)–C(7)	113.71(18)
N(1)–C(6)–Cr(1)	127.96(16)
C(7)–C(6)–Cr(1)	118.30(15)
N(1)–C(10)–C(11)	114.20(17)

2.2. General reactivity of complex **1**

The structural features of the two isomers **1** revealed by the X-ray studies described above suggested that they may have interesting and important a priori effects on reactivity: first of all, the lone pair of the β-nitrogen atom in the (*Z*)-rotamer is directed towards the metal atom, and therefore may be suitably oriented to coordinate to the metal by displacing a carbonyl ligand; furthermore, the lithium enolates of both the (*E*) and (*Z*) rotamers may have the same structure **4**, which



Scheme 1. Transformation of the (*Z*)-**1** complex into the chelate **3**.

would be stabilised by the chelation of the lithium cation by the nitrogen and chromium atoms. The reactivity of the isomers **1** completely confirmed both expectations: when heated in dichloromethane at reflux for 3.5 hours, compound (*Z*)-**1** is quantitatively transformed into the solid, red chelate complex **3** (Scheme 1) [1a].

Despite the presence of the strained four member ring, this new complex is much more stable to air than the starting compound **1** in solution and also in the solid state (see below for the oxidation conditions). On the contrary, (*E*)-**1** is thermally stable.

Treatment of the (*E*) and (*Z*) rotamers (alone or together) with *n*-BuLi in THF solution at −78°C, followed by quenching with water, quantitatively gives the (*Z*)-**1** isomer (Scheme 2).

This result is fully explained by the conformation of intermediate **4**[2], in which a five-member ring is formed as a result of the coordination of the lithium cation to both of the chromium and nitrogen atoms[3].

It is worth noting that, when treated with lithium bases, aminocarbenes lead to a mixture of the two rotamers, which in some cases reduces their usefulness in stereoselective synthesis.

2.3. Reactivity of complex *1* anion with electrophiles

The anion of complex **1**,[4] generated by treatment with *n*-BuLi as described above, is easily alkylated with methyl iodide, allyl bromide and *t*-butylbromoacetate, and gives quantitative yields of a mixture of the expected alkylated pentacarbonyl complexes **5–7** as *Z* rotamers, as well as the tetracarbonyl derivatives **8–10** (Scheme 3). The crystal structure of complex **8** has been previously reported by us [1a]. As shown in Scheme 3, the amount of tetracarbonyl derivatives **8–10** in the reaction mixtures increases with the bulkiness of the R group, probably because of a steric repulsion between the benzyl substituent on the nitrogen atom and the alkyl substituent on the α carbon atom (the alkyl substituent pushes the β-nitrogen close to the chromium atom, thus facilitating the elimination of a CO ligand and the chelation of the nitrogen atom).

The mixtures of penta- and tetracarbonyl complexes can be converted into tetracarbonyl derivatives **8–10** by means of heating in dichloromethane at 39°C (Scheme 3) and, once again, the chelate complex is more easily obtained as the bulkiness of the α substituent increases. We observed the transformation of *t*-butoxycarbonylmethyl derivative **7** into tetracarbonyl complex **10** at room temperature during purification over column chromatography of the mixture of the two complexes. Starting from complex **1**, the overall yields in compounds **8–10** are very high (see Scheme 3).

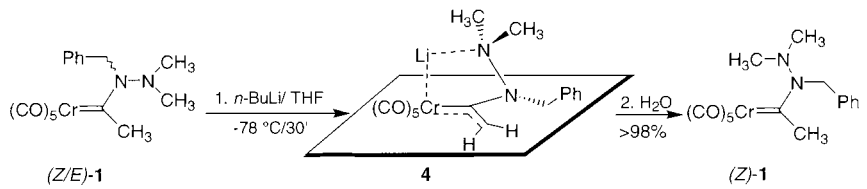
2.4. Reactivity of the complex *3* anion with electrophiles

The chelate complex **3** can be deprotonated using *n*-BuLi at −78°C, and the anion easily reacts with iodomethane at the same temperature to give compound **8** in quantitative yield (Scheme 4).

An explorative study using other electrophiles showed that the anion of **3** also reacts with ethylene and propylene oxides, cyclohexenone and benzaldehyde, respectively providing functionalised carbene complexes **11**, **12**, **13** and **14** in good yields (Scheme 5).

The reactions with epoxides were run in the presence of one equivalent of $BF_3{\cdot}Et_2O$ as a Lewis acid, following a protocol previously set up for aminocarbenes [4].

In these reactions, a new stereocentre is formed in the γ or β position with respect to the carbene carbon atom. The high chemical yields of the reactions and the stability of compounds **11–14** make the anion of chelate complex **3** a very interesting and useful d^2-synthon in the formation of new carbon–carbon bonds.

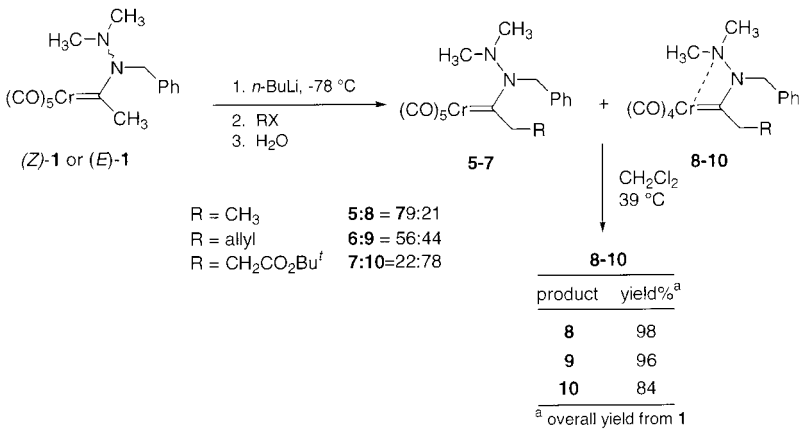


Scheme 2. Transformation of a (*Z*/*E*) mixture of complex **1** into the (*Z*)-**1**.

[2] The chelation of Li^+ to a CO ligand seems less probable because of the more constrained geometry of the resulting seven-membered ring.

[3] To support this hypothesis, we performed an experiment in which we added 12-crown-4 ether to the reaction mixture in order to disassociate the lithium chelate and, after quenching with water, recovered a mixture of the two (*E*) and (*Z*) rotamers.

[4] The pK_a of some of the synthesised hydrazino complexes was measured in collaboration with Professor Claude F. Bernasconi of the University of California (results to be published).



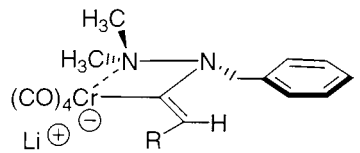
Scheme 3. Alkylation reactions of complex **1**.

2.5. Dialkylation reactions

One particularly interesting behaviour concerning the reactivity of chelate complex **8** is the fact that it can react further with electrophiles: the anion generated by using *n*-BuLi at −78°C can be alkylated with iodomethane or benzyl bromide to give the corresponding dialkylated complexes **15** and **16** in high yields (Scheme 6).

The most important consequence of this reactivity is the formation of a new stereogenic centre on the α carbon atom, as in compound **16**. This behaviour differentiates chelate complex **8** from the aminocarbenes bearing an alkyl group on the carbene carbon atom, which makes alkylation almost impossible [3]. The particular reactivity shown in Scheme 6 opens up the possibility of using type **8** chelate complexes in a new strategy for developing the stereoselective carbon-carbon bond forming reactions that are still impossible to develop using Fischer aminocarbene chemistry[5].

The different reactivity of the α-alkylation reactions between the amino- and chelate hydrazinocarbene can be attributed to the rigid structure of the latter, because the presence of the four-member ring in complex **8** forces the hydrazino moiety towards the metal atom. Unlike in the case of aminocarbenes, the α-carbon atom in 'enolate' **17** (Chart 4) is less sterically hindered and more accessible to electrophile attack, an explanation that is also supported by the fact that the pentacarbonyl ethyl(hydrazino)carbene **5** cannot be further alkylated on the α-carbon.



17

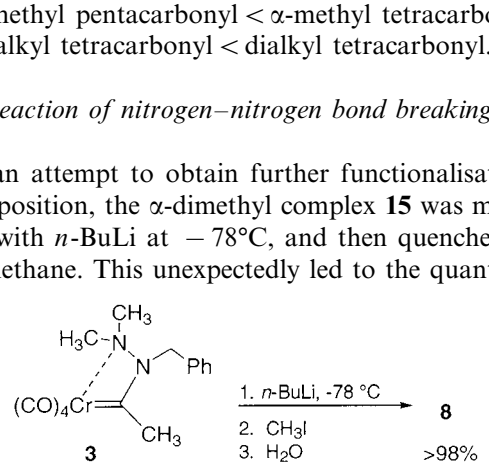
Chart 4.

The α-difunctionalised complexes **15** and **16** are very stable to air, as is shown by the time required for their oxidation to the corresponding hydrazides (Scheme 7): exposure to air and sunlight for 7 days transforms complex (*E*)-**1** into the organic isolobal hydrazide **18** in 90% yield, but it takes 78 days to transform chelate complex **15** into organic product **19** under the same conditions (Scheme 7).

In chelate and dialkylated complexes, there is probably great steric hindrance around the chromium atom and, furthermore, the presence of the two alkyl substituents in the α-position pushes the chelate β-nitrogen atom closer to the metal and thus stabilises the four-member ring. The qualitative order of increasing stability of hydrazinocarbene complexes to air and sunlight is: α-methyl pentacarbonyl < α-methyl tetracarbonyl < monoalkyl tetracarbonyl < dialkyl tetracarbonyl.

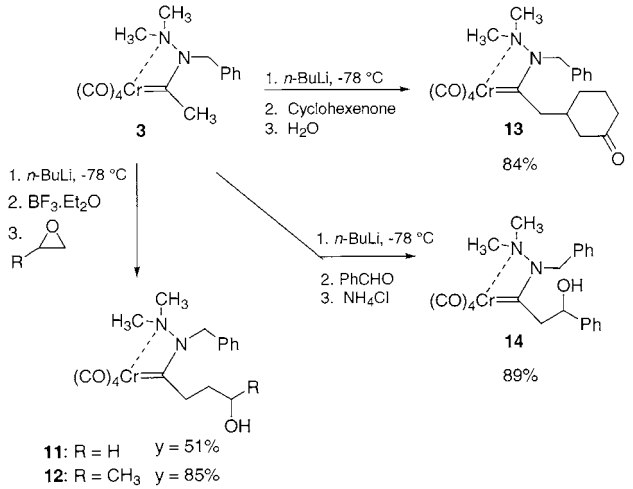
2.6. Reaction of nitrogen–nitrogen bond breaking

In an attempt to obtain further functionalisation at the α-position, the α-dimethyl complex **15** was made to react with *n*-BuLi at −78°C, and then quenched with iodomethane. This unexpectedly led to the quantitative

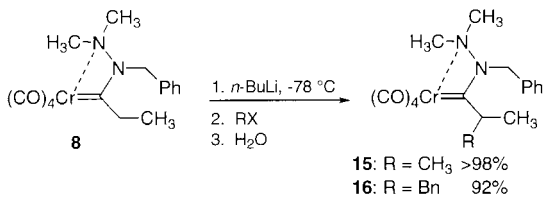


Scheme 4. Alkylation reaction of the chelate complex **3**.

[5] In this regard, diastereoselective aldol and Michael additions are currently in progress in our laboratory; and very high d.e. values are obtained (results to be published).



Scheme 5. Reactions of the chelate complex **3** with electrophiles.



Scheme 6. Alkylation reactions of complex **8**.

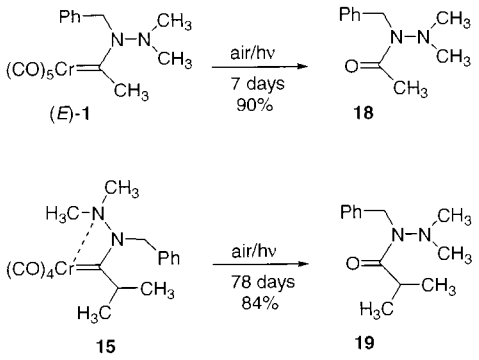
formation of the new complex **20** (Scheme 8), an aminocarbene arising from a nitrogen–nitrogen bond breaking and rearrangment that introduces a stereocentre between the two nitrogen atoms[6].

3. Conclusions

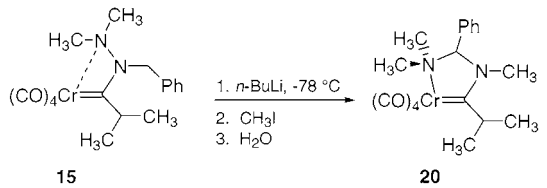
We here report the reactivity of the pentacarbonyl methyl(hydrazino)carbene **1** and tetracarbonyl derivative **3**, which were chosen as model compounds of the new class of hydrazinocarbene complexes. Both compounds have a high synthetic potential in carbon–carbon bond forming reactions. The most interesting characteristic, which is due to the presence of the β-nitrogen atom in complex **1**, is the possibility of generating rigid structures, such as the 'enolate' **4** or the chelate **3**. In particular, as a consequence of the decreased conformational freedom and easier accessibility to the α-carbon atom in chelate complexes, it is possible to alkylate the ethyl(hydrazino)carbene **8** and therefore generate a new stereogenic centre on the α-carbon atom.

Furthermore, both the penta- and tetracarbonyl derivatives proved to be very stable and easy to handle, thus making them simple and practical to use in synthesis.

[6] Further work is in progress in our laboratory concerning the study of the mechanism of this rearrangement and the synthetic potential.



Scheme 7. Oxidation reactions of complexes **1** and **15**.



Scheme 8. Rearrangment of complex **15** into aminocarbene **20**.

Finally, although hydrazinocarbenes are isolobal organic analogues of hydrazides, trialkyl hydrazide enolates have only been used for carbon–carbon bond forming reactions in rare and specific cases [10] because hydrazides do not react to or are unstable towards bases [8]. This means that they are not useful for synthetic purposes in reactions with bases, but hydrazinocarbenes can act as efficient synthetic equivalents.

The structural parameters inferred from the X-ray structures of both isomers anticipated and justified some of the behaviours we found for complexes **1** and **3**.

4. Experimental

4.1. General experimental considerations

All reactions were carried out under an atmosphere of dry argon or nitrogen; glasswares were flame-dried before use. THF was dried by distillation over sodium wires/benzophenone prior to use; butyllithium solutions were titrated prior to use. Flash and vacuum chromatography were performed with Merck silica gel 60, 230–400 mesh. Melting points (m.p.s) were determined with a Büchi 510 apparatus and are uncorrected. All samples were filtered over a celite pad before NMR spectroscopic registration. ^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectra were recorded on Bruker AC 300 and Bruker AMX 300. IR spectra were recorded on Perkin–Elmer FTIR 1725X. Mass spectra (EI, FAB) were recorded on Vg Analytical 7070 EQ.

4.2. Preparation of $Na_2Cr(CO)_5$ solution

To a mixture of naphtalene (21.08 g, 164 mmol) and finely cut metallic sodium (3.13 g, 136 mmol), 98 ml of THF was added. The mixture, deep green, was stirred at room temperature (r.t.) for 2.5 h. Using a double-tipped needle, the naphtalenide solution was dropped into a slurry of $Cr(CO)_6$ (14.06 g, 61.3 mmol) in 130 ml of THF at −78°C, during 2 h. The mixture was allowed to warm to r.t. and stirred overnight. The brown dianion solution (0.268 M) can be kept at −20°C for several weeks.

4.3. Synthesis of complex **1**

To 35.8 ml of the $Na_2Cr(CO)_5$ solution in THF (9.6 mmol, 1.5 equivalents) cooled to −78°C, a solution of the hydrazide **18** (6.4 mmol, one equivalent) in 4 ml of THF was added. The mixture was allowed to react at −78°C for 30 min and then at 0°C for 6.5 h. After cooling to −78°C, trimethylsilyl chloride (19.2 mmol, 3 equivalent) was added and the mixture allowed to react at −78°C for 30 min and then to r.t. for 30 min. Neutral alumina (16 g), degassed under vacuum, was then added to the reaction mixture and the solvent removed under reduced pressure. The residue was purified by column chromatography over silica gel; eluent light petroleum for the elution of naphtalene and then light petroleum–diethyl ether 8:2), thus recovering rotamer (*E*)-**1**, 0.713 g and rotamer (*Z*)-**1**, 0.715 g. Yield of the two rotamers 60.6%[7].

4.3.1. (E)-Pentacarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)methyl carbene]chromium(0) (1)

Yellow solid; m.p. 57°C (Et_2O–pentane). X-ray quality crystals were grown by slow diffusion of pentane into a saturated solution of the complex in diethyl ether.

MS (EI), *m*/*z* 368 (M^+); 340 (M^+–CO); 204 (M^+–3CO); 256 (M^+–4CO); 228 (M^+–5CO); 207 (M^+–3CO–C_6H_5); 184 (M^+–5CO–NMe_2); 176 (M^+–$Cr(CO)_5$); 132 (M^+–$Cr(CO)_5$–NMe_2).

4.3.2. (Z)-Pentacarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)methyl carbene]chromium(0) (1)

Yellow solid; m.p. 85°C (CH_2Cl_2–pentane). X-ray quality crystals were grown by slow diffusion of pentane into a saturated solution of the complex in CH_2Cl_2.

IR/FT (nujol) *v* (cm^{-1}) 2050 (CO *trans*), 1926, 1882 (CO *cis*); MS (EI), *m*/*z* 368 (M^+); 340 (M^+–CO); 204 (M^+–3CO); 256 (M^+–4CO); 228 (M^+–5CO); 207 (M^+–3CO -C_6H_5); 184 (M^+–5CO–NMe_2); 176 (M^+–$Cr(CO)_5$); 132 (M^+–$Cr(CO)_5$–NMe_2).

4.4. Synthesis of tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)methyl carbene]chromium(0) (3)

Complex (*Z*)-**1** (1.346 g, 3.658 mmol) was dissolved in 100 ml of dichloromethane and the solution degassed by ultrasound for 30 min. The mixture was then heated at reflux for 3 h. After cooling to r.t., the solvent was removed in vacuo. The residue (1.1761 g) was pure complex **3**. Yield 95%. Yellow–orange solid; m.p. 124°C (CH_2Cl_2–pentane). Anal. Found: C, 53.14; H, 5.05; N, 8.33. Calc. for $C_{15}H_{16}O_4N_2Cr$: C, 52.94; H, 4.74; N, 8.23%. ^{13}C-NMR ($CDCl_3$) δ (ppm) 289.5 ($C_{carbene}$), 232.2 (*trans* CO), 229.6 (*cis* CO), 218.4 (*cis* CO), 133.8 (C_q Ph), 129.5, 128.5, 126.1 (C Ph), 52.2 (NMe_2) 48.9 (CH_2Ph); 28.9 ($CrCCH_3$); IR/FT (nujol) *v* (cm^{-1}) 1997 (*trans* CO), 1888, 1868, 1830 (*cis* CO); MS (FAB$^+$), *m*/*z* 340 (M^+); 312 (M^+–CO); 284 (M^+–2CO); 256 (M^+–3CO); 228 (M^+–4CO); 91 ($C_7H_7^+$).

4.5. Isomerisation of complex (E)-1 into (Z)-1

n-BuLi (0.3 mmol, 0.18 ml of a 1.6 M solution in hexane) was added dropwise to a −78°C cooled solution of complex (*E*)-**1** (0.1 g, 0.27 mmol) in 4 ml of THF. After 30 min, 4 ml of water was added to the reaction mixture at the same temperature. The organic solvent was removed in vacuo and the residue extracted with dichloromethane. The organic layer was separated, dried over Na_2SO_4 and the solvent removed in vacuo, to give 0.099 g of pure complex (*Z*)-**1**. Yield >98%.

4.6. Synthesis of tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)ethyl carbene]chromium(0) (8)

4.6.1. Starting from complex 1

n-BuLi (6.4 mmol, 4.2 ml of a 1.53 M solution in hexane) was added dropwise to a −78°C cooled solution of complex (*E*)-**1** (2.32 g, 6.3 mmol) in 20 ml of THF. After 30 min, iodomethane (0.79 ml, 12.69 mmol) was added by a syringe. The mixture was let to react at −78°C for 5 min and then at r.t. for 25 min. After that time, 15 ml of water was added to the reaction mixture. The organic solvent was removed in vacuo and the residue extracted with dichloromethane (3 × 50 ml). The organic layer was separated, dried over Na_2SO_4 and the solvent removed in vacuo to give the reaction product as a mixture of (*Z*)-**5** and **8** complexes. From the ^{1}H-NMR analysis of the crude, the ratio of (*Z*)-**5**/**8** was 79.3: 20.7. The mixture of the complexes was directly dissolved in 100 ml of CH_2Cl_2 and the solution was degassed under nitrogen by ultrasound for 30 min.

[7] For both (*E*) and (*Z*) rotamers of complex **1**, ^{1}H- and ^{13}C-NMR spectroscopic data have already been reported [1a].

The mixture was heated at reflux for 40 min, then cooled to r.t. and filtered over a celite pad. The solvent was removed in vacuo to give complex **8** (2.238 g, 6.32 mmol) as pure compound. Yield > 98%.

*4.6.1.1. Z-Pentacarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)ethyl carbene]chromium(0) (**5**-Z).* ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.50–7.00 (5H, m, $H_{arom.}$), 4.85 (2H, s, CH_2Ph), 3.01 (2H, q, $J = 7.6$ Hz, $CrCCH_2$), 2.59 (6H, s, NMe_2), 1.03 (3H, t, $J = 7.6$ Hz, CH_2CH_3); ^{13}C-NMR ($CDCl_3$) δ (ppm) 280.2 ($C_{carbene}$), 225.1 (*trans* CO), 218.6 (*cis* CO), 134.6 (C_q Ph), 129.3, 127.9, 125.2 (C Ph), 48.1 (CH_2Ph), 43.8 (NMe_2); 43.0 ($CrCCH_2$), 10.7 (CH_2CH_3); IR/FT (nujol) ν (cm^{-1}) 2043 (*trans* CO), 1900–1800 (*cis* CO).

*4.6.1.2. Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)ethyl carbene]chromium(0) (**8**).* Orange solid; m.p. 119°C (CH_2Cl_2–pentane). X-ray quality crystals were grown by slow diffusion of pentane into a saturated solution of the complex in toluene. IR/FT (nujol) ν (cm^{-1}); 1997 (*trans* CO), 1865, 1829 (*cis* CO), 727, 685 (γ CH_{arom}); MS (FAB$^+$), m/z 354 (M^+); 326 (M^+–CO); 298 (M^+–2CO); 270 (M^+–3CO); 242 (M^+–4CO); 206 (M^+–2CO–C_7H_8); 198 (M^+–4CO–NMe_2); 190 (M^+–$Cr(CO)_4$); 146 (M^+–$Cr(CO)_4$–NMe_2); 107 (M^+–4CO-NMe_2–$PhCH_2$); 91 ($C_7H_7^+$).

*4.6.2. Starting from complex **3***

n-BuLi (0.64 mmol, 0.41 ml of a 1.55 M solution in hexane) was added dropwise to a −78°C cooled solution of complex **3** (0.214 g, 0.63 mmol) in 5 ml of THF. After 30 min, iodomethane (0.08 ml, 1.28 mmol) was added by a syringe. The mixture was let to react at −78°C for 5 min and then at r.t. for 20 min. After that time, 4 ml of water was added to the reaction mixture. The organic solvent was removed in vacuo and the residue extracted with dichloromethane (3 × 15 ml). The organic layer was separated, dried over Na_2SO_4 and the solvent removed in vacuo to give the complex **8** (0.223 g, 0.63 mmol). Yield > 98%.

*4.7. Synthesis of (Z)-pentacarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)1-but-3-enyl carbene]chromium(0) (Z)-**6***

The same procedure as reported for complex **8** was used. In this case we started from the (*Z*)-**1** rotamer and the following amounts of reagents and solvent used: (*Z*)-**1** 0.1367 g, 0.371 mmol, 5 ml THF, 0.255 ml (0.41 mmol) of 1.6 M BuLi hexane solution, allyl bromide 0.047 ml, 0.56 mmol. After work-up, a crude of 0.1476 g was obtained, as a 56: 44 mixture of the two (*Z*)-**6** and **9** complexes. This mixture was quantitatively converted into complex **9** by dissolving in 50 ml of CH_2Cl_2 and heating at reflux for 30 min. Overall yield from **1**, 95.6%.

*4.7.1. Z-Pentacarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)1-but-3-enyl carbene]chromium(0) (Z)-**6***

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.45–7.00 (5H, m, $H_{arom.}$), 5.75 (1H, ddt, $CH_2CH{=}CH_2$, $J_{trans} = 16.9$; $J_{cis} = 10.17$; $J_{HC-CH2} = 6.6$), 5.06 (1H, dd, $CH_2CH{=}CH_2$ *cis*, $J_{tran} = 16.9$; $J_{gem} = 1.36$), 5.00 (1H, dd, $CH_2CH{=}CH_2$ *trans*, $J_{cis} = 10.17$, $J_{gem} = 1.36$), 4.89 (2H, s, CH_2Ph), 3.15–3.00 (2H, m, $CrCCH_2$), 2.60 (6H, s, NMe_2), 2.35–2.2 (2H, m, CH_2–CH=); IR/FT (neat) ν (cm^{-1}) 2049 (*trans* CO), 1800–1970 (*cis* CO).

*4.7.2. Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)1-but-3-enyl carbene]chromium(0) (**9**)*

Orange solid; m.p. 90–95°C (CH_2Cl_2–pentane). Anal. Found: C, 57.02; H, 5.16; N, 7.55. Calc. for $C_{18}H_{20}O_4N_2Cr$: C, 56.84; H, 5.26; N, 7.36%. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.45–7.00 (5H, m, H_{arom}), 6.0–5.8 (1H, m, $CH_2CH{=}CH_2$), 5.12 (1H, dd, $CH_2CH{=}CH_2$ *cis*, $J_{trans} = 16.9$; $J_{gem} = 1.25$), 5.05 (1H, dd, $CH_2CH{=}CH_2$ *trans*, $J_{cis} = 10.05$, $J_{gem} = 1.25$), 4.69 (2H, s, CH_2Ph), 2.80 (6H, s, NMe_2), 2.8–2.75 (4H, m, CH_2–CH_2); ^{13}C-NMR ($CDCl_3$) δ (ppm) 292.6 ($C_{carbene}$), 231.9 (*trans* CO), 229.8 (*cis* CO), 218.4 (*cis* CO), 137.1 (CH=), 133.4 (Cq Ph), 129.5, 128.5, 126.5 (C Ph), 116.1 (=CH_2), 52.4 (NMe_2) 49.2 (CH_2Ph); 40.8 ($CrCCH_2$), 32.5 (CH_2CH=); IR/FT (neat) ν (cm^{-1}) 1998 (*trans* CO), 1865, 1828 (*cis* CO); 1641 (C=C); 916 (=CH); MS (FAB$^+$), m/z 380 (M^+); 352 (M^+–CO); 324 (M^+–2CO); 296 (M^+–3CO); 268 (M^+–4CO).

*4.8. Synthesis of tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)2-terbutoxycarbonylethyl carbene]-chromium(0) (**10**)*

The same procedure as reported for complex **8** was used. The following amounts of reagents and solvent used: (*E*)-**1**, 0.207 g, 0.562 mmol, 5 ml THF, 0.38 ml (0.56 mmol) of 1.48 M BuLi–hexane solution, *tert*-butyl bromoacetate 0.165 ml, 1.1 mmol. After work-up, a crude of 0.2948 g was obtained, as a 22:78 mixture of the two (*Z*)-**7** and **10** complexes and the unreacted *tert*-butyl bromoacetate. This crude was purified by column chromatography over silica gel (30 g), eluent light petroleum–diethyl ether (1:1). The fraction of the (*Z*)-**7** complex was completely transformed into complex **10** within 1 h at r.t. Yield in complex **10**, 83.7%.

*4.8.1. Z-Pentacarbonyl[(N-benzyl-N′,N′-dimethyl-hydrazinyl)2-terbutoxycarbonylethyl carbene] chromium(0) (**7-Z**)*

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.5–7.00 (5H, m, H_{aromat}), 5.08 (2H, s, CH_2Ph), 3.12 (2H, t, $J = 7.6$ Hz, CrCCH_2), 2.60 (2H, t, $J = 7.6$ Hz, CH_2COO), 2.60 (6H, s, NMe_2), 1.39 (9H, s, OC(CH_3)$_3$).

*4.8.2. Tetracarbonyl[(N-benzyl-N′,N′-dimethyl-hydrazinyl)2-terbutoxycarbonyletyl carbene]chromium(0) (**10**)*

Red oil; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.5–7.1 (5H, m, H_{aromat}), 4.87 (2H, s, CH_2Ph), 3.1–3.0 (2H, m, CrCCH_2), 2.9–2.8 (2H, m, CH_2COO), 2.80 (6H, s, NMe_2), 1.45 (9H, s, OC(CH_3)$_3$); ^{13}C-NMR ($CDCl_3$) δ (ppm) 290.2 ($C_{carbene}$), 231.7 (*trans* CO), 229.5 (*cis* CO), 218.0 (*cis* CO), 172.0 (COO), 133.8 (Cq Ph), 129.3, 128.1, 126.9 (C Ph), 80.8 (*C*(Me)$_3$), 52.0 (NMe_2) 49.2 (*C*H_2Ph); 36.1 (CrC*C*H_2), 33.8 (*C*H_2COO), 27.9 (C(*C*H_3)$_3$); IR/FT (neat) ν (cm^{-1}) 2000 (*trans* CO), 1871, 1833, (*cis* CO), 1723 (COO′Bu); 731, 686 (γ CH_{arom}).

*4.9. Synthesis of tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(propyl-3-hydroxy) carbene]-chromium(0) (**11**)*

n-BuLi (0.34 mmol, 0.215 ml of a 1.58 M solution in hexane) was added dropwise to a −78°C cooled solution of complex **3** (0.1045 g, 0.307 mmol) in 5 ml of THF. After 30 min, $BF_3{\cdot}Et_2O$ (0.045 ml, 0.35 mmol) was added by a syringe and gaseous ethylene oxide was bubbled for 5 min. After stirring for 5 h at −78°C, 0.5 ml of $NaHCO_3$ saturated aqueous solution was added at the same temperature. The solvent was then evaporated at reduced pressure and the crude mixture purified by column chromatography over silica gel; eluent CH_2Cl_2 for recovering unreacted complex **3** (0.0415 g) and then CH_2Cl_2–MeOH (9.5:0.5) for complex **11** (0.0602 g); yield 51%.

*4.9.1. Complex **11***

Yellow–orange oil; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.5–7.1 (5H, m, H_{arom}), 4.74 (2H, s, CH_2Ph), 3.9–3.7 (2H, m, CH_2OH), 2.9–2.7 (2H, m, CrCCH_2), 2.80 (6H, s, NMe_2), 2.4–2.1 (2H, m, CH_2); ^{13}C-NMR ($CDCl_3$) δ (ppm) 292.8 ($C_{carbene}$), 232.2 (*trans* CO), 229.6 (*cis* CO), 218.6 (*cis* CO), 218.4 (*cis* CO), 133.5 (Cq Ph), 129.4, 128.4, 126.0 (C Ph), 62.1 (CH_2OH), 52.3 (NMe_2), 49.2 (*C*H_2Ph), 37.8 (CrC*C*H_2), 31.4 (CH_2); IR/FT (neat) ν (cm^{-1}) 3369 (ν OH), 1997 (ν *trans* CO), 1865, 1828 (ν *cis* CO), 728, 686 (γ CH_{arom}); MS (FAB$^+$), *m*/*z* 384 (M$^+$); 356 (M$^+$–CO); 328 (M$^+$–2CO); 300 (M$^+$–3CO); 272 (M$^+$–4CO); 248 (M$^+$–Cr–3CO).

*4.10. Synthesis of tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(butyl-3-hydroxy) carbene]chromium(0) (**12**)*

The reaction was run as reported for complex **11**, using the following amounts of reagents and solvent: complex **3**, 0.1014 g, 0.298 mmol; BuLi, 0.21 ml, 0.33 mmol of a 1.58 M solution in hexane; $BF_3{\cdot}OEt_2$, 0.045 ml, 0.35 mmol; propylene oxide, 0.045 ml, 0.35 mmol. After 4 h at −78°C, 0.4 ml of $NaHCO_3$ saturated aqueous solution was added at the same temperature. The solvent was then evaporated at reduced pressure and the crude mixture purified by column chromatography over silica gel; eluent CH_2Cl_2 for recovering unreacted complex **3** (0.0153 g) and then CH_2Cl_2–MeOH (9.5:0.5) for complex **12** (0.1008 g); yield 85%.

*4.10.1. Complex **12***

Orange oil; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.45–7.1 (5H, m, H_{arom}), 4.79, 4.69 (2H, AB sistem, $J = 17.2$ Hz, CH_2Ph), 4–3.8 (1H, m, C*H*OH), 2.9–2.7 (2H, m, CrCCH_2), 2.81, 2.79 (6H, s, NMe_2), 2.35–2.2 (1H, m, CH_2CHOH), 2.1–1.5 (1H, m, CH_2CHOH), 1.3 (1H, s br., OH), 1.27 (3H, d, $J = 6.2$ Hz, CH_3); ^{13}C-NMR ($CDCl_3$) δ (ppm) 292.5 ($C_{carbene}$), 232.1 (*trans* CO), 229.6 (*cis* CO), 218.3 (*cis* CO), 133.6 (Cq Ph), 129.4, 128.4, 126.0 (C Ph), 67.5 (CHOH), 52.2 (NMe_2), 49.2 (*C*H_2Ph), 37.6 (CrC*C*H_2), 37.4 (CH_2), 23.7 (CH_3); IR/FT (neat) ν (cm^{-1}) 3397 (ν OH), 1997 (ν *trans* CO), 1870, 1828 (ν *cis* CO), 729, 686 (γ CH_{aromat}); MS (FAB$^+$), *m*/*z* 398 (M$^+$); 370 (M$^+$–CO); 342(M$^+$–2CO); 314 (M$^+$–3CO); 286(M$^+$–4CO).

*4.11. Synthesis of tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)metylene-(3-cycloesanone) carbene]chromium(0) (**13**)*

n-BuLi (0.327 mmol, 0.2 ml of a 1.645 M solution in hexane, 1.1 equivalents) was added dropwise to a −78°C cooled solution of complex **3** (0.101 g, 0.297 mmol, one equivalent) in 5 ml of THF and the mixture allowed to react at the same temperature for 30 min; cyclohexenone (0.035 ml, 0.363 mmol, 1.22 equivalents) was then added by a syringe. After stirring for 3 h at −78°C, 0.25 ml of water was added at the same temperature. The organic solvent was removed in vacuo and the residue taken up with CH_2Cl_2 and dried over Na_2SO_4. The solvent was then evaporated at reduced pressure giving a crude, as a red oil, of 0.126 g which was purified by column chromatography over silica gel (15 g); eluent: Et_2O thus recovering a first fraction of unreacted complex **3**, 0.01 g, and a second fraction of complex **13**, 0.1099 g; yield 84%.

4.11.1. Complex ***13***

Orange solid; m.p. 143°C (CH_2Cl_2–pentane). Anal. Found: C, 57.40; H, 5.90; N, 6.21. Calc. for $C_{21}H_{24}O_5N_2Cr$: C, 57.79; H, 5.54; N, 6.42%. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.5–7.1 (5H, m, H_{arom}), 4.71 (2H, s, CH_2Ph), 2.9–2.8 (1H, m, CrCCH_2), 2.80 (3H, s, NMe_2), 2.81 (3H, s, NMe_2), 2.65–2.50 (1H, m, CrCCH_2, 2H, m, CHCH_2CO), 2.45–2.30 (1H, m, COCH_2CH$_2$CH$_2$ ax.), 2.30–2.15 (1H, m, COCH_2-CH$_2$CH$_2$ eq., 1H, m, COCH$_2$CH_2CH$_2$ ax.), 2.15–2.00 (CHCH$_2$CO), 2.00–1.90 (1H, m, COCH$_2$CH_2CH$_2$ eq.), 1.90–1.70 (1H, m, COCH$_2$CH$_2$CH_2 ax.), 1.50–1.30 (1H, m, COCH$_2$CH$_2$CH_2 eq.); ^{13}C-NMR ($CDCl_3$) δ (ppm) 291.0 ($C_{carbene}$), 231.4 (*trans* CO), 229.5 (*cis* CO), 218.5 (*cis* CO), 218.1 (*cis* CO), 210.4 (CO ketone), 133.1 (Cq Ph), 129.4, 128.5, 125.9 (C Ph), 52.3 (NMe_2), 49.4 (*C*H$_2$Ph), 48.0 (*C*H$_2$CO), 47.3 (CrC*C*H$_2$), 41.1 (*C*H$_2$CO), 38.5 (CH), 31.4 (*C*H$_2$CH$_2$CO), 24.4 (CH*C*H$_2$CH$_2$); IR/FT (nujol) ν (cm^{-1}) 1996 (*trans* CO); 1891, 1869, 1819 (*cis* CO); 1708 (CO ketone); 726, 686 (γ CH_{aromat}); MS (FAB^+), m/z 436 (M^+); 380 (M^+–2CO); 364 (M^+–1CO–NMe_2); 352 (M^+–3CO); 324 (M^+–4CO); 307 (M^+–3CO–$HNMe_2$); 279 (M^+–4CO–$HNMe_2$); 233 (M^+–4CO–$PhCH_2$); 91 ($C_7H_7^+$).

*4.12. Synthesis of tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(ethyl-2-phenyl-2-hydroxy) carbene]chromium (0) (**14**)*

n-BuLi (0.347 mmol, 0.23 ml of a 1.51 M solution in hexane, 1.1 equivalents) was added dropwise to a −78°C cooled solution of complex **3** (0.115 g, 0.313 mmol, one equivalent) in 6 ml of THF and the mixture allowed to react at the same temperature for 30 min. Benzaldehyde (0.49 mmol, 1.58 eq) was then added by a syringe; the mixture was stirred for 4.5 h and during this time the temperature was slowly allowed to reach −30°C. A total of 0.25 ml of a NH_4Cl saturated aqueous solution was then added at −30°C. The organic solvent was then evaporated at reduced pressure and the residue taken up with CH_2Cl_2 and dried over Na_2SO_4. The solvent was then evaporated at reduced pressure and the residue, 0.163 g, was purified by column chromatography over silica gel (15 g); eluent: light petroleum–CH_2Cl_2 (1:1) thus recovering a first fraction of unreacted complex **3**, 0.01 g, and CH_2Cl_2 for the second fraction of complex **14**, 0.127 g; yield 89.2%.

4.12.1. Complex ***14***

Red viscous oil; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.5–7.1 (10H, m, H_{aromat}), 5.72 (1H, dd, J_1 = 9.45 Hz, J_2 = 3.16 Hz, OHC*H*Ph), 4.87, 4.60 (2H, AB system, J = 17.2 Hz, CH_2Ph), 3.17 (1H, dd, J_{gem} = 14.9 Hz, J_{vic} = 3.16 Hz, CrCCH$_2$), 3.02 (1H, dd, J_{gem} = 14.9 Hz, J_{vic} = 9.45 Hz, CrCCH$_2$), 2.86, 2.76 (6H, s, NMe_2), 2.55 (1H, s br., OH); ^{13}C-NMR ($CDCl_3$) δ (ppm) 288.4 ($C_{carbene}$), 231.9 (*trans* CO), 229.3 (*cis* CO), 218.5 (*cis* CO), 218.2 (*cis* CO), 143.5 (Cq CHOH*Ph*), 133.4 (Cq NCH$_2$*Ph*), 129.4, 128.4, 125.5 (C Ph), 73.2 (CHOH), 52.6, 52.2 (NMe_2), 50.8 (CrC*C*H$_2$), 49.3 (N*C*H$_2$Ph); IR/FT (neat) ν (cm^{-1}) 3402 (OH), 2000 (*trans* CO), 1865, (*cis* CO), 728, 701, 685.7 (γ CH_{aromat}); MS (EI), m/z 446 (M^+); 429 (M^+–OH); 334 (M^+–4CO); 289 (M^+–4CO–$HNMe_2$); 107 ($PhCH{=}OH^+$); 91 ($C_7H_7^+$); 79 ($C_6H_7^+$); 69 ($C_5H_9^+$).

*4.13. Synthesis of tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)isopropyl carbene] chromium(0) (**15**)*

n-BuLi (0.6 mmol, 0.4 ml of a 1.5 M solution in hexane) was added dropwise to a −78°C cooled solution of complex **8** (0.2106 g, 0.595 mmol) in 5 ml of THF. After stirring for 1 h at the same temperature, iodomethane (0.075 ml 1.2 mmol) was added by a syringe and the mixture allowed to react at −78°C for 1 h and then at r.t. for 30 min. The reaction was quenched by adding 0.2 ml of water and the organic solvent removed in vacuo. The residue was taken-up with CH_2Cl_2 and dried over Na_2SO_4. The solvent was evaporated giving pure complex **15**, 0.2188 g; yield >98%.

4.13.1. Complex ***15***

Orange solid; m.p. 122–123°C (CH_2Cl_2–pentane). Anal. Found: C, 55.26; H, 5.35; N, 7.33. Calc. for $C_{17}H_{20}O_4N_2Cr$: C, 55.43; H, 5.47; N, 7.61%. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.5–7.1 (5H, m, H_{arom}), 4.68 (2H, s, CH_2Ph), 2.80 (6H, s, NMe_2), 2.75 (1H, J = 6.45 Hz, CrCCH), 1.35 (6H, d, J = 6.45 Hz, CH(CH_3)$_2$); ^{13}C-NMR ($CDCl_3$) δ (ppm) 296.5 ($C_{carbene}$), 232.2 (*trans* CO), 229.9 (*cis* CO), 218.6 (*cis* CO), 133.6 (Cq Ph), 129.4, 128.5, 126.0 (C Ph), 52.3 (NMe_2) 48.7 (*C*H$_2$Ph); 38.0 (CrC*C*H), 21.2 (CH(*C*H$_3$)$_2$); IR/FT (neat) ν (cm^{-1}) 1996 (*trans* CO), 1888, 1834, 1820 (*cis* CO), 734, 685 (γ CH_{arom}); MS (EI), m/z 368 (M^+); 340 (M^+–CO); 312 (M^+–2CO); 295 (M^+–CO–NMe_2); 284 (M^+–3CO); 267 (M^+–2CO–NMe_2); 256 (M^+–4CO); 239 (M^+–3CO–NMe_2); 232 (M^+–Cr–3CO); 211 (M^+–4CO–NMe_2); 204 (M^+–Cr–4CO); 160 (M^+–Cr–4CO–$MeN{=}CH_2$).

*4.14. Alkylation of the mixture of (Z)-**5** and **8** complexes*

The reaction was run as reported for complex **5**, using the following amounts of reagents and solvent: mixture of (*Z*)-**5** and **8**, 0.244 g, **5**-*Z*:**8** = 58%: 42%, 0.622 mmol; THF, 5 ml; BuLi, 1.578 M, 0.66 mmol; 0.08 ml of MeI, 1.28 mmol; after work-up 0.230 g of crude was obtained.

Ratio of compounds (from the ^{1}H-NMR of the crude) (*Z*)-**5**:**8**:**15** = 47.5:22.2:30.3; overall yield 99.3%.

4.15. Synthesis of tetracarbonyl[(*N*-benzyl-*N*′,*N*′-dimethylhydrazinyl)ethyl-1-benzyl carbene]chromium(0) (**16**)

The reaction was run as reported for complex **15** using the following amounts of reagents and solvent; complex **8**, 0.2096 g, 0.59 mmol; THF, 5 ml; *n*-BuLi, 0.598 mmol, 0.42 ml of a 1.425 M solution in hexane); benzylbromide, 0.145 ml. The reaction mixture was stirred at −78°C for 2 h, and then at 0°C for 40 min; after the work-up, the crude was purified by under vacuum column chromatography over silica gel (20 g); eluent: light petroleum for benzylbromide, then light petroleum/diethyl ether 1: 1 to give complex **16**, 0.2417 g; yield 92%.

4.15.1. Complex **16**

Orange solid; m.p. 117°C (CH_2Cl_2–pentane). Anal. Found: C, 62.33; H, 5.27; N, 6.44. Calc. for $C_{23}H_{24}O_4N_2Cr$: C, 62.12; H, 5.44; N, 6.30. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.4–7.1 (10H, m, H_{aromat}), 4.20 (2H, s, NCH_2Ph), 3.15 (1H, dd, J_{gem} = 13.4 Hz, J_{vic} = 7.9 Hz, CHCH_2Ph), 3.02 (1H, dd, J_{gem} = 13.4 Hz, J_{vic} = 5.8 Hz, CHCH_2Ph), 2.9–2.8 (1H, m, CrCCH), 2.74, (3H, s, NMe_2), 2.69 (3H, s, NMe_2), 1.44 (3H, d, J_{vic} = 6.4 Hz, CH_3CH); ^{13}C-NMR ($CDCl_3$) δ (ppm) 294.3 ($C_{carbene}$), 232.2 (*trans* CO), 229.6 (*cis* CO), 219.5 (*cis* CO), 218.5 (*cis* CO) 139.1 (Cq CHCH_2*Ph*), 133.7 (Cq NCH_2*Ph*), 129.3, 128.5, 128.4, 126.6, 125.7 (C Ph), 52.3, 52.1 (NMe_2), 48.8 (NCH_2Ph); 46.0 (CrC*C*H), 41.9 (CH*C*H_2Ph), 19.9 (*C*H_3CH); IR/FT (neat) ν (cm^{-1}) 1997 (*trans* CO), 1865, 1829 (*cis* CO), 738, 680 (γ CH_{aromat}).

4.16. Synthesis of tetracarbonyl[(*N*-benzyl-(1-dimethylamino)-*N*-methylamino)isopropyl carbene]chromium(0) (**20**)

The reaction was run as reported for the synthesis of complex **8** using the following amounts of reagents and solvent; idrazino carbene **15**, 0.1427 g, 0.388 mmol; THF, 5 ml; BuLi, 1.48 M, 0.3 ml, 0.44 mmol; MeI, 0.027 ml, 0.43 mmol; after the work-up, 0.1504 g of the complex **20** were obtained. Yield >98%.

4.16.1. Complex **20**

Yellow–orange solid; m.p. 136–140°C (Et_2O–pentane); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.5–7.2 (5H, m, H_{aromat}), 4.99 (1H, s, C*H*Ph), 3.02 (1H, ept., J = 6.6 Hz, CrCCH), 3.02 (3H, s, $CrCNCH_3$), 2.70 (3H, s, NNMe anti to Ph), 2.20 (3H, s, NNMe syn to Ph), 1.58 (3H, d, J = 6.6 Hz, CrCCH(CH_3)$_2$), 1.34 (3H, d, J = 6.6 Hz, CrCCH(CH_3)$_2$). A NMR NOESY experiment was also performed; ^{13}C-NMR ($CDCl_3$) δ (ppm) 305.5 ($C_{carrbene}$), 230.1 (*trans* CO), 229.0 (*cis* CO), 218.9 (*cis* CO), 130.2, 128.6, (C Ph), 129.3 (Cq Ph), 55.8 (NNMe anti to Ph), 50.4 (NNMe syn to Ph), 42.1 (CrC*C*H), 38.9 (CrCN*Me*), 22.9, 20.4 (CH(*C*H_3)$_2$). The assignment of the peaks was done by two-dimensional heteronuclear (H,C)-correlated NMR Spectroscopy. IR/FT (neat) ν (cm^{-1}) 1993 (*trans* CO); 1860, 1816 (*cis* CO); 739, 688 (γ CH_{aromat}); MS (EI), m/z 382 (M^+); 354 (M^+–CO); 326 (M^+–2CO); 298 (M^+–3CO); 270 (M^+–4CO); 225 (M^+–4CO–$HNMe_2$); 174 (M^+–4CO–Cr–NMe_2); 158 (M^+–4CO–Cr–NMe_2–CH_4); 134 (PhCH=NMe_2^+); 132 (M^+–4CO–Cr–NMe_2–C_3H_6); 91 ($C_7H_7^+$).

4.17. Oxidation of complex (*E*)-**1** into hydrazide **18**

A solution of complex (*E*)-**1** (0.213 g, 0.579 mmol) in 30 ml of ethyl acetate was exposed to air and sunlight for 7 days at r.t. The precipitate was eliminated by filtration over a celite pad and the solvent removed in vacuo. The residue, colourless oil, was pure hydrazide **18** [11], 0.0998 g; yield 89.7%.

4.18. Oxidation of complex **15** into hydrazide **19**

A solution of complex **15** (0.1532 g, 0.417 mmol) in 40 ml of ethyl acetate was exposed to air and sunlight for 78 days at r.t. The precipitate was eliminated by filtration over a celite pad and the solvent removed in vacuo. The residue, colourless oil, was pure hydrazide **19**, 0.0771 g; yield 84.3%.

4.18.1. 1-Benzyl-1-isopropionyl-2,2-dimethyl hydrazine **19**

Colorless oil; HRMS (EI) for $C_{13}H_{20}ON_2$: M^+ Calc. = 220.15756, Found = 220.1629; $M^+ + 1$ Calc. = 221.16538, Found = 221.1691; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.4–7.1 (5H, m, H_{aromat}), 4.60 (2H, s, CH_2Ph), 3.41 (1H, ept, J = 6.86 Hz, COCH), 2.48 (6H, s, NMe_2), 1.14 (6H, d, J = 6.86 Hz, CH(CH_3)$_2$; ^{13}C-NMR ($CDCl_3$) δ (ppm) 179.9 (CO), 139.4 (Cq Ph), 128,4, 127.1, 126.6 (C Ph), 44.7 (NMe_2), 41.2 (*C*H_2Ph), 29.9 (*C*H(Me)$_2$), 19.5 (CH(*C*H_3)$_2$); IR/FT (neat) ν (cm^{-1}) 1656 (ν CO), 1605, 1497, (ArC–C), 1352 (δ sy CH_3 of the $CHMe_2$), 1151 (γ CH_3 of the $CHMe_2$), 911, 698 (δ e γ CH_{aromat}); MS (EI), m/z 221 ($M^+ + 1$); 220 (M^+); 178 (M^+–C_3H_6); 177 ($M^+ + 1$–NMe_2); 176 (M^+–NMe_2); 149 (M^+–CO–C_3H_6); 129 (M^+–$PhCH_2$); 92 ($C_7H_8^+$); 91 ($C_7H_7^+$); 79 ($C_6H_7^+$); 65 ($C^5H_5^+$).

Table 3
Crystal data and structure refinement for (*E*)-**1** and (*Z*)-**1**.

	(*E*)-**1**	(*Z*)-**1**
Formula	$C_{16}H_{16}CrN_2O_5$	$C_{16}H_{16}CrN_2O_5$
Formula weight	368.31	368.31
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
Unit cell dimensions		
a (Å)	9.214(5)	25.746(5)
b (Å)	15.990(5)	10.281(3)
c (Å)	12.401(5)	16.391(4)
β (°)	103.47(5)	125.19(2)
Volume	1777(1)	3546(1)
Z	4	8
D_{calc} (Mg m^{-3})	1.377	1.380
Absorption coefficient (cm^{-1})	6.70	6.71
F(000)	760	1520
Crystal size (mm)	$0.23\times0.33\times0.41$	$0.32\times0.26\times0.18$
θ range (°)	3.06–24.95	1.94–28.23
Index ranges	$-10\le h\le10$, $-5\le k\le18$, $-14\le l\le14$	$-33\le h\le28$, $-13\le k\le13$, $-13\le l\le21$
Reflections collected	3236	10494
Independent reflections	3093 [$R_{int}=0.0176$]	3966 [$R_{int}=0.0249$]
Observed reflections [$I>2\sigma(I)$]	1669	2762
Data/restraints/parameters	3093/0/282	3966/0/221
Goodness-of-fit on F^2	0.821	1.017
Final R indices [$I>2\sigma(I)$]	[a] $R_1=0.0346$, [b] $wR_2=0.0792$	$R_1=0.0401$, $wR_2=0.1051$
R indices (all data)	$R_1=0.0803$, $wR_2=0.0898$	$R_1=0.0643$, $wR_2=0.1156$

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

4.19. X-ray structure determination of (E)-1 and (Z)-1

The intensity data of both complexes were collected at r.t. on a Philips PW 1100 ((*E*)-**1**) and on an Bruker AMX SMART 1000, equipped with an area detector((*Z*)-**1**) diffractometer using a graphite-monochromated Mo–K_α radiation. Crystallographic and experimental details for both structures are summarised in Table 3. A correction for absorption was made for (*Z*)-**1** complexes using the Bruker software for absorption correction.

The structures were 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 cycles of refinement for all the non-hydrogen atoms.

In both structures the hydrogen atoms were introduced into the geometrically calculated positions and refined *riding* on the corresponding parent atoms. In the final cycles of refinement a weighting scheme $w=1/[\sigma^2F_o^2+(0.0523\quad P)^2]$ ((*E*)-**1**) and $w=1/[\sigma^2F_o^2+(0.0619P)^2+0.2221P]$ ((*Z*)-**1**) where $P=(F_o^2+2F_c^2)/3$ was used.

All calculations were carried out on the DIGITAL AlphaStation 255 computers of the 'Centro di Studio per la Strutturistica Diffrattometrica' del CNR, Parma, using the SHELX-97 crystallographic computer program systems [12].

5. Supplementary material

The supplementary material for the structures include lists of atomic coordinates for the non-H atoms, calculated coordinates for the hydrogen atoms, anisotropic thermal parameters and complete lists of bond lengths and angles. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 151799 for (*E*)-**1** and CCDC no. 151800 for (*Z*)-**1**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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