

# New synthesis of Fischer-type hydrazino(alkyl) complexes. First X-ray characterisation of a chelate hydrazino derivative

Emanuela Licandro,<sup>\*a</sup> Stefano Maiorana,<sup>a†</sup> Raffaella Manzotti,<sup>a</sup> Antonio Papagni,<sup>a</sup> Dario Perdicchia,<sup>a</sup> Mary Pryce,<sup>b</sup> Antonio Tiripicchio<sup>\*c</sup> and Maurizio Lanfranchi<sup>c</sup>

<sup>a</sup> Dipartimento di Chimica Organica e Industriale, Università degli Studi di Milano, via C. Golgi, 19, I-20133 Milan, Italy

<sup>b</sup> School of Chemical Sciences, Dublin City University, Dublin 9, Ireland

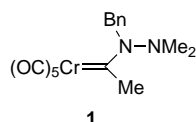
<sup>c</sup> Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Centro di Studio per la Strutturistica Diffraattometrica del CNR, viale delle Scienze, I-43100 Parma, Italy

The first Fischer-type hydrazino(methyl)carbene complex has been synthesized from the appropriate acetylhydrazine and  $\text{Na}_2\text{Cr}(\text{CO})_5$ ; the new complex has some peculiar features in comparison with aminocarbene complexes: (i) the *E* rotamer can be completely transformed into the *Z* rotamer through the formation of its anion, and (ii) as a result of a thermal reaction, the *Z* isomer affords a new unusual chelate hydrazino(methyl)carbene complex that can be mono- or dialkylated.

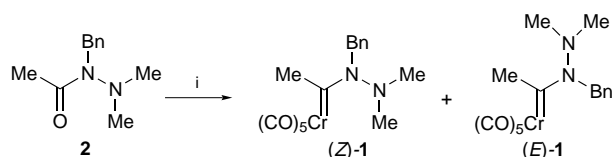
Only a few hydrazinocarbene complexes have so far been reported in the literature.<sup>1</sup> This is certainly due to the very limited applicability of the hydrazinolysis reaction of alkoxy-carbenes,<sup>2</sup> which seems to be partially successful only in the case of alkynyl carbene complexes.<sup>1b</sup>

Alkyl(hydrazino)carbene complexes are unknown and could in principle have some unique features due to the potential of the  $\beta$ -nitrogen of the hydrazine moiety as a coordinating group to the metal, and the influence of this coordination on the stereodynamic properties of the complex and the reactivity of the  $\alpha$ -carbanions.

We here report the synthesis of the first hydrazino(methyl)carbene complex **1**, its thermally promoted transformation, and the reaction of its anion with electrophiles. The

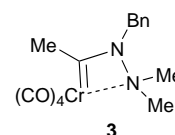


apparently simple but long-standing problem associated with the controlled synthesis of alkyl (hydrazino)carbene complexes has been solved by extending the known Hegedus method<sup>3</sup> for preparing amino carbene complexes from amides to hydrazide derivatives. The hydrazide **2** was reacted with disodium pentacarbonylchromate,<sup>3</sup> affording complex **1** as a 1:1.3 *E*:*Z* rotameric mixture (Scheme 1).<sup>‡</sup> The (*E*)-**1** and (*Z*)-**1** rotamers were fully characterized after chromatographic separation over silica gel. Rotamer (*E*)-**1** proved to be thermally stable,

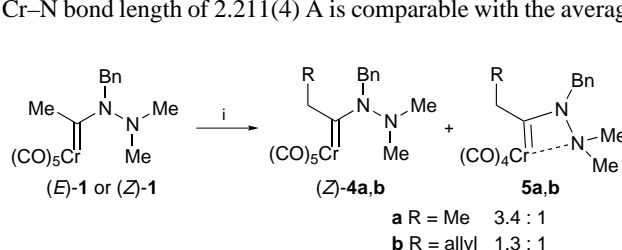


**Scheme 1** Reagents and conditions: i,  $\text{Na}_2\text{Cr}(\text{CO})_5$  (2 equiv.), anhydrous THF,  $\text{N}_2$ ,  $-78^\circ\text{C}$ , 40 min, allowed to warm to  $0^\circ\text{C}$ , 4 h, then cooled to  $-78^\circ\text{C}$ ,  $\text{Me}_3\text{SiCl}$  (3 equiv.),  $-78^\circ\text{C}$ , 30 min, then  $\text{Al}_2\text{O}_3$  (45 g on a base of 0.61 g of **2**), 45 min, then chromatographic separation on silica gel to give (*E*)-**1** (0.32 g) and (*Z*)-**1** (0.36 g), eluent light petroleum– $\text{CH}_2\text{Cl}_2$  8:2 (overall yield 59%)

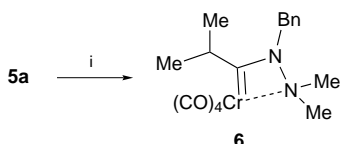
remaining unchanged after heating in hexane at  $50^\circ\text{C}$  for 2 h whereas, after heating at  $39^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$  for 3.5 h, (*Z*)-**1** was transformed into a new, red–orange solid complex, **3**<sup>‡</sup> with the



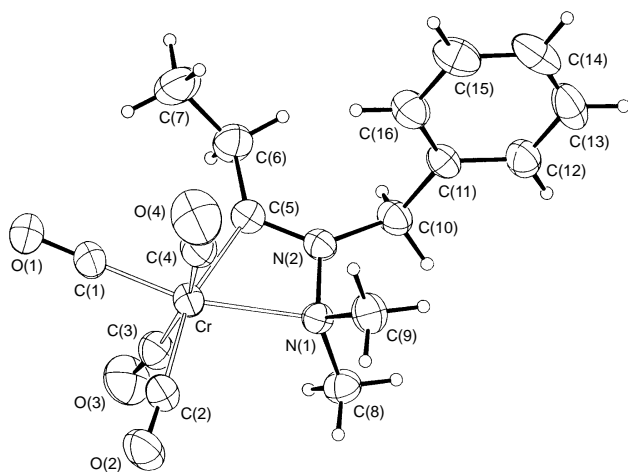
displacement of a CO ligand. As far as we know, only one example of an *N*-chelate complex with a four-membered ring has been previously reported.<sup>4</sup> The structure of **3** was supported by the X-ray analysis of the structure of the homologue **5a**<sup>§</sup> whose formation is described below (Scheme 2). The pure rotamers (*E*)-**1** and (*Z*)-**1** were treated with  $\text{Bu}^\text{n}\text{Li}$  at  $-70^\circ\text{C}$  and quenched with a saturated aq.  $\text{NH}_4\text{Cl}$ ; rotamer (*E*)-**1** was completely transformed into rotamer (*Z*)-**1**, whereas the latter proved to be configurationally stable. The complete conversion of (*E*)-**1** into (*Z*)-**1** is rather surprising since this transformation is usually incomplete in aminocarbene complexes and generally leads to a mixture of the two rotamers. The treatment of the anion generated from the pure (*E*)-**1** or (*Z*)-**1** rotamers with alkylating reagents such as iodomethane and allyl bromide gave the expected ethyl(hydrazino)carbene complexes (*Z*)-**4a** and (*Z*)-**4b**, together with the tetracarbonyl *N*-chelate derivatives **5a** and **5b** (Scheme 2).<sup>‡</sup> It can be seen that the formation of the coordinated derivatives **3**, **5a** and **5b** is easier as the bulk of the  $\alpha$ -substituent increases ( $\text{Me} < \text{Et} < \text{allyl}$ ). Column chromatography over silica gel gave pure samples of the complexes **5a** and **5b**, whereas complexes **4a** and **4b** were always recovered in the form of mixtures with **5a** and **5b** respectively.<sup>‡</sup> Unlike an amino(ethyl)carbene complex, the ethyl(hydrazino)carbene **5a** can easily be further alkylated with  $\text{MeI}$  to give complex **6** (Scheme 3).<sup>‡</sup> Compound **5a** is the first structurally characterized chelate hydrazinocarbene complex (see Fig. 1). The coordination around Cr is a distorted octahedron, with the organic moiety acting as a chelating ligand through N(1) and C(5). The four-membered ring is planar, and the chelation N(1)–Cr–C(5) angle is very narrow at  $62.9(2)^\circ$ . Although the Cr–N bond length of  $2.211(4) \text{ \AA}$  is comparable with the average



**Scheme 2** Reagents and conditions:  $\text{Bu}^\text{n}\text{Li}$  (1 equiv.), THF,  $\text{N}_2$ ,  $-78^\circ\text{C}$ , 30 min, then RX,  $-78^\circ\text{C}$ , 10 min,  $0^\circ\text{C}$ , 30 min



**Scheme 3** Reagents and conditions: Bu<sup>n</sup>Li (1 equiv.), THF, N<sub>2</sub>, −78 °C, 30 min, then MeI, −78 °C, 10 min then 0 °C, 20 min, then room temp., 10 min



**Fig. 1** View of the molecular structure of complex **5a** together with the atomic numbering system. Selected bond distances (Å) and angles (°): Cr–C(5) 2.028(4), Cr–N(1) 2.221(4), C(5)–N(2) 1.308(7), N(1)–N(2) 1.451(5), N(2)–C(10) 1.481(6), C(5)–C(6) 1.494(7); N(1)–Cr–C(5) 62.9(2), Cr–C(5)–N(2) 101.3(3), Cr–N(1)–N(2) 88.5(2), N(1)–N(2)–C(5) 107.3(3), N(1)–N(2)–C(10) 120.8(3), C(5)–N(2)–C(10) 131.8(4).

value found in complexes of Cr<sup>0</sup> with tertiary amines (2.21 Å), the 2.028(4) Å Cr–C(5) bond length is much shorter than those found in aminocarbene complexes of Cr<sup>0</sup> (in the range of 2.123–2.156 Å).<sup>5</sup> This means that the Cr–C(5) bond has a more noticeably double bond character than the other aminocarbene complexes. It is also worth noting that the 1.813(6) Å Cr–C(1) bond involving the carbonyl *trans* to the aminic N(1) atom is shorter than other Cr–C(carbonyl) bonds [in the range 1.871(5)–1.882(5) Å].

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## Notes and References

† E-mail: maior@icil64.cilea.it

‡ Selected data for (*E*)-**1**: mp 57 °C (decomp.); δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>) 2.45 [s, 6 H, N(CH<sub>3</sub>)<sub>2</sub>], 3.05 (s, 3 H, CH<sub>3</sub>), 5.55 (s, 2 H, CH<sub>2</sub>Ph), 7.40–7.20 (m,

5 H, arom); δ<sub>C</sub> (300 MHz, CDCl<sub>3</sub>) 39.6 (q, CH<sub>3</sub>), 44.3 [q, N(CH<sub>3</sub>)<sub>2</sub>], 56.2 (t, CH<sub>2</sub>), 126.6, 128.0, 128.8 (arom), 135.6 (s, arom), 217.6 (s, CO *cis*), 223.4 (s, CO *trans*), 277.5 (s, C=Cr); *m/z* (EI) 368 [M<sup>+</sup>]. For (*Z*)-**1**: mp 85 °C; δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>) 2.65 [s, 6 H, N(CH<sub>3</sub>)<sub>2</sub>], 2.70 (s, 3 H, CH<sub>3</sub>), 4.95 (s, 2 H, CH<sub>2</sub>Ph), 7.40–7.20 (m, 5 H, arom); δ<sub>C</sub> (300 MHz, CDCl<sub>3</sub>) 39.1 (q, CH<sub>3</sub>), 44.2 [q, N(CH<sub>3</sub>)<sub>2</sub>], 48.9 (t, CH<sub>2</sub>), 125.2, 127.8, 129.3 (arom), 133.5 (s, arom), 218.4 (s, CO *cis*), 225.2 (s, CO *trans*), 280.6 (s, C=Cr); *m/z* (EI) 368 [M<sup>+</sup>]. For **3**: mp 123–6 °C; ν(Nujol)/cm<sup>−1</sup> 1997, 1888–1830 (CO); δ<sub>H</sub> (80 MHz, CDCl<sub>3</sub>) 2.73 (s, 3 H, CH<sub>3</sub>), 2.78 [s, 6 H, N(CH<sub>3</sub>)<sub>2</sub>], 4.65 (s, 2 H, CH<sub>2</sub>Ph), 7.05–7.55 (m, 5 H, arom); *m/z* (FAB<sup>+</sup>) 340 [M<sup>+</sup>]. For **5a**: mp 120 °C (decomp.); ν(Nujol)/cm<sup>−1</sup> 1998 (CO *trans*), 1917–1803 (CO *cis*); δ<sub>H</sub> (80 MHz, CDCl<sub>3</sub>) 1.50 (t, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 2.65 (q, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 2.80 [s, 6 H, N(CH<sub>3</sub>)<sub>2</sub>], 4.65 (s, 2 H, CH<sub>2</sub>Ph), 7.10–7.45 (m, 5 H, arom); δ<sub>C</sub> (300 MHz, CDCl<sub>3</sub>) 13.0 (q, CH<sub>3</sub>), 34.7 (q, CH<sub>3</sub>), 49.1 (t, CH<sub>2</sub>), 52.3 [q, N(CH<sub>3</sub>)<sub>2</sub>], 126.1, 128.5, 129.5 (arom), 133.5 (s, arom), 218.5 (s, 2CO *cis*), 230.1 (s, CO *cis*), 232.2 (s, CO *trans*), 294.7 (s, C=Cr); *m/z* (FAB<sup>+</sup>) 354 [M<sup>+</sup>]. Spectroscopic and analytical data for complexes **4a**, **4b**, **5b** and **6** are in line with the reported structure.

§ Crystal data for **5a**: C<sub>16</sub>H<sub>18</sub>CrN<sub>2</sub>O<sub>4</sub>, *M<sub>r</sub>* = 354.32, monoclinic, space group C2/c, *a* = 21.346(6), *b* = 12.782(4), *c* = 14.136(4) Å, β = 113.70(2)°, *V* = 3532(2) Å<sup>3</sup>, *Z* = 8, ρ<sub>calc</sub> = 1.333 Mg m<sup>−3</sup>, *F*(000) = 1472, λ = 1.54184 Å, μ(Cu-Kα) = 5.507 mm<sup>−1</sup>. Crystal dimensions: 0.15 × 0.21 × 0.33 mm. The intensity data were collected by means of a Siemens AED diffractometer using the θ–2θ scan technique at room temperature. 3494 reflections were measured (with θ in the range 3–70°) of which 3357 were independent and included in the structural refinement. Correction for absorption was applied (maximum and minimum values for the transmission coefficient were 1.000 and 0.637). The structure was solved by means of direct and Fourier methods, and refined using full-matrix least-squares procedures (based on *F*<sub>o</sub><sup>2</sup>), with anisotropic thermal parameters in the last cycles of refinement for all of the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the parent atoms. The refinement converged at *wR*<sub>2</sub> = 0.1579 for all data, and 209 variables [*R*<sub>1</sub> = 0.0506 for 1603 reflections with *I* > 2σ(*I*)] min/max residual electron density: −0.356/0.408 e Å<sup>−3</sup>. The SHELXS-86 and SHELXL-93 computer programs were used (ref. 6). CCDC 182/726.

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