New Methodologies for Oxidizing Fischer Carbene Complexes: Synthesis of Hydrazides.

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SUPPORTING INFORMATION

General. Reagents obtained from commercial sources were used without further purification; $\text{Ca}(\text{OCl})_2$ (Fluka-RdH) was technical (about 65%). All of the reactions for the synthesis of the starting complexes were carried out under an atmosphere of dry nitrogen after the glassware had been flame-dried. Before being used, the THF was dried by distillation over sodium wires/benzophenone and the butyllithium solutions were titrated. Complexes **25** and **26** were prepared as reported in the literature¹. In order to monitor the progress of the reactions, thin layer chromatography (TLC) was performed using Merk silica gel 60 F254 precoated plates after eluting the indicated solvents, and visualized using a 254 nm UV lamp. Vacuum chromatography was performed using Merck silica gel 60, 230-400 mesh, and preparative layer chromatography (PLC) using Merck silica gel 60 F254 2-mm precoated plates. Melting points were determined by means of a Büchi 510 apparatus and are uncorrected. ^1H NMR (300 and 200 MHz, CDCl_3) and ^{13}C NMR (75 MHz, CDCl_3) spectra were recorded on Bruker AC 300, Bruker AC 200 and Bruker AMX 300. IR spectra were recorded on a Perkin-Elmer FT-IR 1725X. High-resolution EI mass spectra were recorded on a Vg Analytical 7070 EQ, and a $[\text{M}]^+$ or/and $[\text{M} + 1]^+$ peak was found.

Synthesis of starting complexes

Synthesis of tetracarbonyl[(*N*-benzyl-*N*',*N*'-dimethylhydrazinyl)-1-(ethyl-2-phenyl)carbene]chromium(0) (**18**) and tetracarbonyl[(*N*-benzyl-*N*',*N*'-dimethylhydrazinyl)-1-(ethyl-1-benzyl-2-phenyl)carbene]chromium(0) (**21**):

n-BuLi (2.95 mmol, 1.92 ml of a 1.54 M solution in hexane) was added dropwise to a -78°C cooled solution of complex **20**² (1.0014 g, 2.94 mmol) in 10 ml of THF. After 30', benzylbromide (0.7 ml, 5.8 mmol) was injected through a syringe. The mixture was left to react at -78°C for 30' and then at room temperature for 30'. After that time, 2 ml of water was added to the reaction mixture. The organic solvent was removed *in vacuo* and the residue was diluted with CH_2Cl_2 , dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The residue was purified by means of vacuum column chromatography over silica gel (40 g). Eluent: light petroleum for the benzylbromide and then light petroleum/ diethyl ether 8 : 2 to give 0.215 g of complex **21** (Rf: 0.47; yield 14%) and 0.8452 g of complex **18** (Rf: 0.38); yield 67%.

¹ Hoye, Thomas R.; Chen, Kejian; Vyvyan, James R. *Organometallics* **1993**, 12(7), 2806-9.

² Licandro, E.; Maiorana, S.; Perdicchia, D.; Baldoli, C.; Graiff, C.; Tiripicchio, A. *J. Organomet. Chem.* **2001**, 617-618, 399-411.

Data for **18**: orange solid; m.p. 116 °C (CH₂Cl₂/pentane). Anal. Found: C, 61.25; H, 5.32; N, 6.15. C₂₂H₂₂O₄N₂Cr calcd.: C, 61.38; H, 5.16; N, 6.51. ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.45-7.00 (10H, m, H_{arom.}), 4.49 (2H, s, CH₂Ph), 3.4-3.3 (2H, m, CrCCH₂), 3.1-2.9 (2H, m, CH₂CH₂Ph), 2.77 (6H, s, NMe₂); ¹³C NMR DEPT (CDCl₃, 75 MHz) δ (ppm) 292.7 (C_{carbene}), 231.9 (*trans* CO), 229.7, 218.6 (*cis* CO), 140.7 (C_q CH₂CH₂Ph), 133.5 (C_q NCH₂Ph), 129.5-125.1 (C Ph), 52.3 (NMe₂), 48.9 (NCH₂Ph); 43.5 (CrCCH₂), 34.4 (CH₂CH₂Ph); IR/FT (nujol) ν (cm⁻¹) 1998 (*trans* CO), 1865, 1829 (*cis* CO), 729, 698, 685 (γ CH_{arom.}).

Data for **21**: orange solid; m.p. 117.5 °C (CH₂Cl₂/pentane). Anal. Found: C, 67.25; H, 5.72; N, 5.75. C₂₉H₂₈O₄N₂Cr calcd.: C, 66.90; H, 5.43; N, 5.38. ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.5-6.9 (15H, m, H_{arom.}), 3.77 (2H, s, CH₂Ph), 3.13 (4H, d, J = 6.7 Hz, CH(CH₂Ph)₂), 2.98 (1H, q, J = 6.7 Hz, CrCCH), 2.69 (6H, s, NMe₂); ¹³C NMR DEPT (CDCl₃, 75 MHz) δ (ppm) 293.2 (C_{carbene}), 232.1 (*trans* CO), 229.4, 219.4 (*cis* CO), 139.2 (C_q CH(CH₂Ph)₂), 134.0 (C_q NCH₂Ph), 129.5-125.7 (C Ph), 54.1 (CrCCH), 52.2 (NMe₂), 48.9 (NCH₂Ph); 39.6 (CH(CH₂Ph)₂); IR/FT (nujol) ν (cm⁻¹) 1996 (*trans* CO), 1865, 1834 (*cis* CO), 738, 687 (γ CH_{arom.}).

Synthesis of tetracarbonyl[(*N*-benzyl-*N*',*N*'-dimethylhydrazinyl)methylene-(1-hydroxy-cyclohexyl)carbene]chromium(0) (**22**)

n-BuLi (0.65 mmol, 0.42 ml of a 1.54 M solution in hexane) was added dropwise to a -78 °C cooled solution of complex **20** (0.2198 g, 0.646 mmol) in 7 ml of THF, and the mixture was allowed to react at the same temperature for 30'. Cyclohexanone (0.135 ml, 1.3 mmol) was then injected through a syringe, and the mixture stirred for 30', after which 0.5 ml of a NH₄Cl saturated aqueous solution was added. The organic solvent was evaporated at reduced pressure, and the residue diluted with CH₂Cl₂ and dried over Na₂SO₄. The solvent was evaporated at reduced pressure and the residue (0.3007 g) purified by means of vacuum chromatography over silica gel (15 g). Eluent: CH₂Cl₂ thus recovering a first fraction of unreacted complex **20** (0.0345 g) and a second fraction of complex **22** (0.2181 g); yield 77%.

Data for **22**: red solid; m.p. 110-111 °C (Et₂O/hexane). Anal. Found: C, 57.84; H, 5.62; N, 6.10. C₂₁H₂₆O₅N₂Cr calcd.: C, 57.53; H, 5.98; N, 6.39. ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.5-7.1 (5H, m, H_{arom.}), 4.78 (2H, s, CH₂Ph), 2.86 (2H, s, CrCCH₂), 2.83 (6H, s, NMe₂), 2.78 (1H, s, OH), 2-1.45 (10H, m, CH₂ cyclohexane); ¹³C NMR DEPT (CDCl₃, 75 MHz) δ (ppm) 287.3 (C_{carbene}), 257.2 (*trans* CO), 229.3, 217.8 (*cis* CO), 133.1 (C_q Ph), 129.4, 128.4, 125.8 (C Ph), 71.8 (COH), 52.6 (NMe₂), 49.7 (CrCCH₂ + NCH₂Ph), 38.4 (C(OH)CH₂CH₂), 25.4 (C(OH)CH₂CH₂), 21.9 (C(OH)CH₂CH₂CH₂); IR/FT (nujol) ν (cm⁻¹) 3469 (OH), 2001 (*trans* CO), 1875, 1823 (*cis* CO), 730, 685 (γ CH_{arom.}).

Synthesis of (*Z*)-pentacarbonyl[(*N*-benzyl-*N*-morpholin-4-yl)phenyl carbene]chromium(0) (**3**)

N-amino morpholine **23** (0.46 ml, 4.77 mmol) was added to a solution of LiCl (0.48 g, 11.3 mmol) in 15 ml of dry THF at room temperature, and a white slurry was formed. After cooling to -78°C, a solution of complex **24** (1.509 g, 4.83 mmol) in 8 ml of dry THF was added dropwise over 10 minutes; the reaction was checked by TLC and finished after 3 hours and 30 minutes. The organic solvent was evaporated at reduced pressure, and the residue diluted with CH₂Cl₂ and filtered on celite to remove the LiCl. After re-evaporation of the solvent, the residue, was purified by vacuum chromatography over silica gel (15 g). Eluent: light petroleum/ diethyl ether 6 : 4 to give 1.1886 g of complex **25** (Rf: 0.2); yield 65.2%. *n*-BuLi (3.43 mmol, 2.24 ml of a 1.53 M solution in hexane) was added dropwise to a -78°C cooled solution of complex **25** (1.3123 g, 3.435 mmol) in 25 ml of THF and the mixture was allowed to react at the same temperature for 30'. Benzylbromide (1.63 ml, 13.74 mmol) was added using a syringe. After reaching room temperature, the solution was heated at 40°C for two hours. The reaction was quenched with 1 ml of degassed water and the solvent was evaporated at reduced pressure; the residue was diluted with CH₂Cl₂, dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was purified by means of vacuum column chromatography over silica gel (15 g). Eluent: light petroleum/ diethyl ether 1 : 1 to give 1.312 g of complex **3**; yield 81%.

Data for **25**: yellow solid; m.p. 90-91 °C (CH₂Cl₂/pentane). Anal. Found: C, 50.49; H, 3.57; N, 7.25. C₁₆H₁₄O₆N₂Cr calcd.: C, 50.27; H, 3.69; N, 7.33. ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 8.78 (1H, broad s, NH), 7.5-6.9 (5H, m, H_{arom.}), 4.1-3.8 (4H, m, H₂COCH₂), 3.3-2.7 (4H, broad m, H₂CNCH₂); ¹³C NMR DEPT (CDCl₃, 75 MHz) δ (ppm) 275.1 (C_{carbene}), 234.4 (*trans* CO), 213.7 (*cis* CO), 135.8 (Cq Ph), 129.4, 128.5, 127.5 (C Ph), 68.1 (CH₂O), 56.6 (CH₂N); IR/FT (nujol) ν (cm⁻¹) 3158 (NH), 2055 (*trans* CO), 1932, 1898 (*cis* CO), 705, 672 (γ CH_{arom.}).

Data for **3**: yellow solid; m.p. 101-102 °C (Et₂O/pentane). Anal. Found: C, 58.58; H, 4.45; N, 5.91. C₂₃H₂₀O₆N₂Cr calcd.: C, 58.48; H, 4.27; N, 5.93. ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.5-6.5 (10H, m, H_{arom.}), 4.88 (2H, s, CH₂Ph), 4.03 (2H, td, J_{gem}=11.4 Hz, J_{vic}=2.3 Hz, OCH_{eq}), 3.91 (2H, dd, J_{gem}=11.4 Hz, J_{vic}=2.8 Hz, OCH_{ax}), 3.3-3.0 (4H, m, H₂CNCH₂); ¹³C NMR DEPT (CDCl₃, 75 MHz) δ (ppm) 284.5 (C_{carbene}), 225.0 (*trans* CO), 217.6 (*cis* CO), 150.9 (Cq NCH₂Ph), 135.4 (Cq Ph), 129.4-118.9 (C Ph), 65.5 (CH₂O), 53.3 (CH₂N), 51.5 (NCH₂Ph); IR/FT (nujol) ν (cm⁻¹) 2052 (*trans* CO), 1914 (*cis* CO), 736, 691 (γ CH_{arom.}).

Synthesis of (*E*)-pentacarbonyl[1-[(phenylmethyl)amino]pentylidene]chromium(0) (**7**)

Benzylamine (2.3 mmol, 0.25 ml) was added dropwise to a -78°C cooled solution of complex **26** (0.6429 g, 2.2 mmol) in 10 ml of THF; after 10 minutes, the temperature was allowed to reach to room temperature. The solvent was evaporated at reduced pressure and the residue was crystallized from ether-pentane to give 0.6869 g of complex **7**; yield 85%.

Data for **7**: yellow solid; m.p. 52-53 °C (Et₂O/pentane). Anal. Found: C, 55.62; H, 4.56; N, 4.10. C₁₇H₁₇O₅NCr calcd.: C, 55.59; H, 4.66; N, 3.81. ¹H NMR (CDCl₃, 200 MHz) δ (ppm) 8.88 (1H, broad s, NH), 7.5-7.2 (5H, m, H_{arom.}), 4.62 (2H, d, J=5.5 Hz, CH₂Ph), 3.1-2.9 (2H, m, CrCCH₂), 1.7-1.4 (4H, m, CH₃CH₂CH₂), 0.98 (3H, t, J=6.9 Hz, CH₃); IR/FT (nujol) ν (cm⁻¹) 3362 (NH), 2054 (*trans* CO), 1908 (*cis* CO), 741, 673 (γ CH_{arom.}).

Oxidation of complex **1** by CAN

A solution of CAN (0.652 g, 1.189 mmol) in 15 ml of acetone was added dropwise over 1 hour and 30' to a solution of complex **1**: the reaction was finished, but many by-products were obtained (by TLC; eluent: light petroleum/ diethyl ether 1 : 1). The solvent was evaporated at reduced pressure and, after the addition of 20 ml of water, extracted with diethyl ether (3 x 20 ml). The organic layer was separated and dried over Na₂SO₄, after which the solvent was removed *in vacuo* to give the crude product that was purified by means of preparative TLC (eluent: light petroleum/ diethyl ether 7 : 3; R_f hydrazide **2**: 0.21) to give 0.026 g of the hydrazide **2**²; yield 30%.

Oxidation of complexes by Ca(OCl)₂.

Synthesis of the 2-benzyl-3-phenyl-propionic acid *N*-benzyl-*N*',*N*'-dimethyl-hydrazide (**27**)

Hydrazinocarbene complex **21**: 0.1769 g, 0.34 mmol, 1 eq.; NaHCO₃: 0.2861 g, 3.4 mmol, 10 eq.; TBAB: 0.006 g, 0.0176 mmol, 5.1 mol%; Ca(OCl)₂: 0.1124 g, 0.51 mmol, 3 eq.; water: 10 ml; AcOEt: 10 ml; 0.1168 g of hydrazide **27** was obtained; yield 92.2%.

Data for **27**: colourless oil; HRMS (EI) for C₂₅H₂₈ON₂: (M + 1)⁺ calc.: 373.22798, found: 373.2278. ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.3-6.85 (15H, m, H_{arom.}), 4.37 (2H, s, NCH₂Ph), 4.18 (1H, tt, J_{vic1}=10 Hz, J_{vic2}=5 Hz, OCCH), 3.02 (2H, dd, J_{gem}=13 Hz, J_{vic}=10 Hz, CH(CH₂Ph)₂), 2.79 (2H, dd, J_{gem}=13 Hz, J_{vic}=5 Hz, CH(CH₂Ph)₂), 1.77 (6H, s, NMe₂); ¹³C NMR DEPT (CDCl₃, 75 MHz) δ (ppm) 177.0 (CO), 140.2 (C_q CH(CH₂Ph)₂), 138.7 (C_q NCH₂Ph), 130-126 (C Ph), 45.0 (CH), 44.1 (NMe₂), 41.2 (NCH₂Ph), 39.7 (CH(CH₂Ph)₂); IR/FT (neat) ν (cm⁻¹) 1651 (ν CO), 1949, 1879, 1808, 1728 (δ oop ArC-H), 1605, 1496 (ArC-C), 1455 (δ CH₂), 741, 673 (γ CH_{arom.}); MS (EI), *m/z* 373 (M⁺ + 1); 372 (M⁺); 329 (M⁺ + 1 - NMe₂); 281 (M⁺ - PhCH₂); 238 (M⁺ - NMe₂ - PhCH₂); 223 (COCH(CH₂Ph)₂⁺); 149 (M⁺ - COCH(CH₂Ph)₂); 91 (C₇H₇⁺).

Synthesis of the 2-methyl-3-phenyl-propionic acid *N*-benzyl-*N*',*N*'-dimethyl-hydrazide (**29**)

Hydrazinocarbene complex **28**: 0.0835 g, 0.1878 mmol, 1 eq.; NaHCO₃: 0.1582 g, 1.878 mmol, 10 eq.; TBAB: 0.0032 g, 0.009 mmol, 5 mol%; Ca(OCl)₂: 0.062 g, 0.28 mmol, 3 eq.; water: 6 ml; AcOEt: 6 ml; 0.0537 g of hydrazide **29** was obtained; yield 96.6%.

Data for **29**: colourless oil; HRMS (EI) for C₁₉H₂₄ON₂: (M)⁺ calc.: 296.18886, found: 296.1869, (M + 1)⁺ calc.: 297.196688, found: 297.1928. ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.3-7.0 (10H, m, H_{arom.}), 4.65 (1H, d, J_{gem}=15.77 Hz, NCH₂Ph), 4.42 (1H, d, J_{gem}=15.77 Hz, NCH₂Ph), 3.9-3.8 (1H, m, COCH), 3.02 (1H, dd, J_{gem}=13.16 Hz, J_{vic}=9.1 Hz, CHCH₂Ph), 2.656 (1H, dd, J_{gem}=13.16 Hz, J_{vic}=6.1 Hz, CHCH₂Ph), 2.47 (3H, s, NMe₂), 2.11 (3H, s, NMe₂), 1.19 (3H, d, J=6.88 Hz, CHMe); ¹³C NMR DEPT (CDCl₃, 75 MHz) δ (ppm) 178.6 (CO), 140.7 (C_q CHCH₂Ph), 139.0 (C_q NCH₂Ph), 130-125 (C Ph), 44.6 (NMe₂), 41.2 (NCH₂Ph), 40.4 (CHCH₂Ph), 37.2 (CH), 18.12 (CHMe); IR/FT (neat) ν (cm⁻¹) 1651 (ν CO); 1949, 1878, 1808, 1729 (δ oop ArC-H); 1605, 1496, (ArC-C); 1455 (δ CH₂); 1353 (δ sy CH₃ of the CHMe); 911, 699 (δ and γ CH_{arom.}); 744 (γ CH₂). MS (EI), m/z 297 (M⁺ + 1); 296 (M⁺); 253 (M⁺ + 1 - NMe₂); 205 (M⁺ - PhCH₂); 162 (M⁺ + 1 - NMe₂ - PhCH₂); 150 (M⁺ + 1 - COCHCH₃(CH₂Ph)); 149 (M⁺ - COCHCH₃(CH₂Ph)); 148 (COCHCH₃(CH₂Ph)⁺); 119 (CHCH₃(CH₂Ph)⁺); 106 (M⁺ + 1 - COCHCH₃(CH₂Ph) - NMe₂); 92 (C₇H₈⁺); 91 (C₇H₇⁺); 79 (C₆H₇⁺); 77 (C₆H₅⁺); 65 (C₅H₅⁺).

Synthesis of the propionic acid *N*-benzyl-*N*',*N*'-dimethyl-hydrazide (**31**)

Hydrazinocarbene complex **30**: 0.1028 g, 0.29 mmol, 1 eq.; K₂HPO₄: 0.5088 g, 2.92 mmol, 10 eq.; KH₂PO₄: 0.3977 g, 2.92 mmol, 10 eq.; TBAB: 0.0056 g, 0.009 mmol, 5.7 mol%; Ca(OCl)₂: 0.0643 g, 0.29 mmol, 2 eq.; water: 8 ml; AcOEt: 8 ml; 0.0541 g of hydrazide **31** was obtained; yield 90.4%.

Data for **31**: colourless oil; HRMS (EI) for C₁₂H₁₈ON₂: (M)⁺ calc.: 206.14191, found: 206.1396. ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.3-7.2 (5H, m, H_{arom.}), 4.60 (2H, s, NCH₂Ph), 2.62 (2H, q, J=7.5 Hz, COCH₂), 2.47 (6H, s, NMe₂), 1.16 (3H, t, J=7.5 Hz, Me); ¹³C NMR DEPT (CDCl₃, 75 MHz) δ (ppm) 175.7 (CO), 138.8 (C_q NCH₂Ph), 127.5, 126.7, 125.9 (C Ph), 43.5 (NMe₂), 40.5 (NCH₂Ph), 25.6 (CH₂CO), 8.8 (Me); IR/FT (neat) ν (cm⁻¹) 1661 (ν C=O); 1605, 1497 (arC-C); 909, 724, 694 (δ e γ CH aromat.). MS (EI), m/z 206 (M⁺); 163 (M⁺ - CH₂NMe₂); 149 (M⁺ - C₂H₅CO); 115 (M⁺ - CH₂Ph); 106 (M⁺ - C₂H₅CO - CH₂NMe₂); 91 (C₇H₇⁺); 77 (C₆H₅⁺); 65 (C₅H₅⁺).

Synthesis of the (1-Hydroxy-cyclohexyl)-acetic acid *N*-benzyl-*N*',*N*'-dimethyl-hydrazide (**32**)

Hydrazinocarbene complex **22**: 0.1468 g, 0.3348 mmol, 1 eq.; K₂HPO₄: 0.5893 g, 3.38 mmol, 10.1 eq.; KH₂PO₄: 0.4619 g, 3.39 mmol, 10.1 eq.; TBAB: 0.0065 g, 0.019 mmol, 5.7 mol%; Ca(OCl)₂: 0.0748 g, 0.34 mmol, 2 eq.; water: 9 ml; AcOEt: 9 ml; after work-up, 0.0692 g of the crude product was purified by gravimetric chromatography over silica gel (15 g). Eluent: light petroleum/ CH₂Cl₂ 1 : 1 to give 0.0271 g of the hydrazide **32**; yield 28%.

Data for **32**: colourless oil; HRMS (EI) for C₁₇H₂₆O₂N₂: (M)⁺ calc.: 290.19942, found: 290.1990, (M + 1)⁺ calc.: 291.207253, found: 291.2068. ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.35-7.1 (5H, m, H_{arom.}), 5.06 (1H, broad s, OH), 4.60 (2H, s, NCH₂Ph), 2.79 (2H, s, COCH₂), 2.45 (6H, s, NMe₂), 1.8-1.1 (10H, m, CH₂ cyclohexyle); ¹³C NMR DEPT (CDCl₃, 75 MHz) δ (ppm) 175.7 (CO), 138.7 (C_q NCH₂Ph), 128.4, 127.1, 126.9 (C Ph), 70.2 (COH), 44.4 (NMe₂), 41.3 (NCH₂Ph, CH₂CO), 37.9 ((CH₂)₂COHCH₂), 25.8, 22.1 (3CH₂ cyclohexyle); IR/FT (neat) ν (cm⁻¹) 3414 (ν OH); 1626 (ν C=O); 1496 (arC-C); 1445 (δ CH₂); 1353 (δ sy CH₃); 919, 726, 699 (δ e γ CH_{arom.}). MS (EI), *m/z* 291 (M⁺ + 1); 290 (M⁺); 247 (M⁺ + 1 - NMe₂); 229 (M⁺ + 1 - NMe₂ - H₂O); 199 (M⁺ - PhCH₂); 150 (M⁺ + 1 - COCH₂COH(CH₂)₅); 149 (M⁺ - COCH₂COH(CH₂)₅); 106 (M⁺ + 1 - COCH₂COH(CH₂)₅ - NMe₂); 91 (C₇H₇⁺); 79 (C₆H₇⁺); 77 (C₆H₅⁺); 65 (C₅H₅⁺).

Synthesis of the N-Benzyl-N-morpholin-4-yl-benzamide (**4**)

Hydrazinocarbene complex **3**: 0.1684 g, 0.356 mmol, 1 eq.; NaHCO₃: 0.3026 g, 3.6 mmol, 10 eq.; TBAB: 0.0064 g, 0.0188 mmol, 5.3 mol%; Ca(OCl)₂: 0.1559 g, 0.708 mmol, 4 eq.; water: 10 ml; AcOEt: 10 ml; 0.1014 g of hydrazide **4** was obtained; yield 96.1%.

Data for **4**: colourless oil; HRMS (EI) for C₁₈H₂₀O₂N₂: (M)⁺ calc.: 296.15247, found: 296.1511. ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.6-7.1 (10H, m, H_{arom.}), 4.81 (2H, broad s, NCH₂Ph), 3.8-3.5 (2H, m, OCH_{eq}), 3.4-3.1 (2H, m, OCH_{ax}), 2.94 (2H, broad s, NCH_{eq}), 2.60 (2H, broad s, NCH_{ax}); ¹³C NMR DEPT (CDCl₃, 75 MHz) δ (ppm) 172.7 (CO), 169.3 (C_q OCP_h), 138.5 (C_q NCH₂Ph), 130-126 (C Ph), 66.4 (CH₂O), 52.7 (CH₂N), 43.9 (NCH₂Ph); IR/FT (neat) ν (cm⁻¹) 1646 (ν CO); 1603, 1495, (ArC-C); 920, 698 (δ e γ CH_{arom.}). MS (EI), *m/z* 297 (M⁺ + 1); 296 (M⁺); 211 (M⁺ + 1 - O(CH₂)₄N); 205 (M⁺ - PhCH₂); 191 (M⁺ - C₆H₅); 105 (C₆H₅⁺); 91 (C₇H₇⁺); 77 (C₆H₅⁺); 65 (C₅H₅⁺).

Synthesis of the 1-morpholin-4-yl-1,3,4,7-tetrahydro-azepin-2-one (**6**)

Hydrazinocarbene complex **5**: 0.1358 g, 0.3647 mmol, 1 eq.; NaHCO₃: 0.3108 g, 3.7 mmol, 10.1 eq.; TBAB: 0.0065 g, 0.0191 mmol, 5.2 mol%; Ca(OCl)₂: 0.1607 g, 0.729 mmol, 4 eq.; water: 10 ml; AcOEt: 10 ml; 0.0443 g of the crude hydrazide **4** was obtained; yield <30% (from NMR).

Synthesis of the pentanoic acid benzylamide (**8**)

Aminocarbene complex **7**: 0.2393 g, 0.651 mmol, 1 eq.; NaHCO₃: 0.552 g, 6.57 mmol, 10 eq.; TBAB: 0.0113 g, 0.033 mmol, 5.1 mol%; Ca(OCl)₂: 0.2155 g, 0.979 mmol, 3 eq.; water: 18 ml; AcOEt: 18 ml; 0.1226 g of the amide **8**³ was obtained; yield 98.5%.

Oxidation of complexes by NaBO₃/KI.

Synthesis of the 2-methyl-3-phenyl-propionic acid *N*-benzyl-*N*',*N*'-dimethyl-hydrazide (**29**)

Hydrazinocarbene complex **28**: 0.1657 g, 0.3728 mmol, 1 eq.; KH₂PO₄: 0.5075 g, 3.728 mmol, 10 eq.; NaBO₃·4H₂O: 0.2939 g + 0.1 g after 1^h30', 2.51 mmol, 5 + 1.7 eq.; KI: 0.007 g, 0.042 mmol, 11 mol%; water: 10 ml; AcOEt: 10 ml; 0.1058 g of hydrazide **29** was obtained; yield 95.7%.

Synthesis of the (3-oxo-cyclohexyl)-acetic acid *N*-benzyl-*N*',*N*'-dimethyl-hydrazide (**34**)

Hydrazinocarbene complex **33**: 0.1057 g, 0.242 mmol, 1 eq.; KH₂PO₄: 0.3297 g, 2.42 mmol, 10 eq.; NaBO₃·4H₂O: 0.1954 g + 0.0607 g after 1^h30', 1.63 mmol, 5.1 + 1.6 eq.; KI: 0.0036 g, 0.021 mmol, 9 mol%; water: 6 ml; AcOEt: 6 ml; 0.067 g of hydrazide **34** was obtained; yield 96%.

Data for **34**: colourless oil; HRMS (EI) for C₁₇H₂₄O₂N₂: (M)⁺ calc.: 288.1837783, found: 288.1839. ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.35-7.1 (5H, m, H_{arom.}), 4.60 (2H, s, NCH₂Ph), 2.75-2.55 (2H, m, COCH₂), 2.46 (6H, s, NMe₂), 2.55-2.3 (3H, m, COCH₂CH₂ + CH), 2.3-1.9 (4H, m, COCH₂CH + CHCH₂CH₂ eq + COCH₂CH₂ eq), 1.8-1.6 (1H, m, COCH₂CH₂ ax), 1.5-1.35 (1H, m, CHCH₂CH₂ ax); ¹³C NMR DEPT (CDCl₃, 75 MHz) δ (ppm) 211.2 (CO), 173.8 (NCO), 139.2 (C_q NCH₂Ph), 128.4, 127.4, 126.8 (C Ph), 47.9 (CH₂CHCH₂CO), 44.5 (NMe₂), 41.5 (NCH₂Ph), 41.3 (CH₂CH₂CO), 38.9 (CH₂CON), 35.5 (CH₂CHCH₂CO), 31.1 (CH₂CH₂CH₂CO), 24.9 (CH₂CH₂CH₂CO); IR/FT (neat) ν (cm⁻¹) 1709 (ν CO); 1651 (ν NC=O); 1495 (arC-C); 1455 (δ

³ The melting point and the NMR spectra were identical to those previously reported: A. R. Katritzky, Jean-Luc Montou, Y. Zhijun, *Org. Prep.*, 27, 3, **1995**, 361-366

CH₂); 1352 (δ sy CH₃); 913, 731, 701 (δ e γ CH_{arom.}). MS (EI), m/z 289 ($M^+ + 1$); 288 (M^+); 245 ($M^+ + 1 - NMe_2$); 197 ($M^+ - PhCH_2$); 150 ($M^+ + 1 - COCH_2COCH(CH_2)_4$); 149 ($M^+ - COCH_2COCH(CH_2)_4$); 106 ($M^+ + 1 - COCH_2COCH(CH_2)_4 - NMe_2$); 91 (C₇H₇⁺); 79 (C₆H₇⁺); 77 (C₆H₅⁺); 65 (C₅H₅⁺).

Synthesis of the (1-hydroxy-cyclohexyl)-acetic acid *N*-benzyl-*N,N'*-dimethyl-hydrazide (**32**)

Hydrazinocarbene complex **22**: 0.1655 g, 0.377 mmol, 1 eq.; KH₂PO₄: 0.5148 g, 3.78 mmol, 10 eq.; NaBO₃·4H₂O: 0.2958 g after 1^h30', 1.88 mmol, 5 eq.; KI: 0.002 g, 0.012 mmol, 3.2 mol%; water: 10 ml; AcOEt: 10 ml; 0.0925 g of hydrazide **32** was obtained; yield 84.5%.

Oxidation of complexes by I₂.

Synthesis of the pent-4-enoic acid but-3-enyl-morpholin-4-yl-amide (**16**)

Hydrazinocarbene complex **15**: 0.1256 g, 0.325 mmol, 1 eq.; NaHCO₃: 0.2730 g, 3.25 mmol, 10 eq.; I₂: 0.0919 g, 0.362 mmol, 1.1 eq.; water: 9 ml; AcOEt: 9 ml; 0.0680 g of hydrazide **16** was obtained; yield 87.8%.

Data for **16**: colourless oil; HRMS (EI) for C₁₃H₂₂O₂N₂: (M)⁺ calc.: 238.16813, found: 238.1687. ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 5.9-5.65 (2H, m, CH=CH₂), 5.1-4.9 (4H, m, CH=CH₂), 3.87(2H, dd, $J_{gem}=11.1$, $J_{vic\ eq,eq}=3.2$, OCH_{eq}), 3.63 (2H, td, $J_{gem}=J_{vic\ ax,eq}=11.1$, $J_{vic\ ax,ax}=2.2$, OCH_{ax}), 3.4-3.3 (2H, m, NCH₂), 2.93 (2H, td, $J_{gem}=J_{vic\ eq,ax}=11.1$, $J_{vic\ eq,eq}=3.2$, NCH_{eq}), 2.65-2.55 (4H, m, CH₂CO + CH_{ax}N), 2.4-2.25 (4H, m, CH₂CH=CH₂); ¹³C NMR DEPT (CDCl₃, 75 MHz) δ (ppm) 174.6 (CO), 137.9; 135.3 (CH=CH₂), 116.5; 114.8 (CH=CH₂), 66.8 (CH₂O), 52.8 (CH₂N morpholin), 39.3 (NCH₂CH₂CH=CH₂), 33.7 (NCH₂CH₂CH=CH₂), 32.5 (COCH₂), 29.6 (COCH₂CH₂); IR/FT (neat) ν (cm⁻¹) 3078 (ν =CH₂); 1657 (ν C=O); 1114 (ν_{as} C-O); 998, 917 (δ out of plane CH=CH₂). MS (EI), m/z 239 ($M+1$); 238 (M); 155 ($M - COCH_2CH_2CH=CH_2$); 152 ($M - O(CH_2)_2N$); 86 (O(CH₂)₂N); 83 (COCH₂CH₂CH=CH₂); 69 (NCH₂CH₂CH=CH₂).

Synthesis of the 1-morpholin-4-yl-1,3,4,7-tetrahydro-azepin-2-one (**6**)

Hydrazinocarbene complex **17**: 0.110 g, 0.319 mmol, 1 eq.; NaHCO₃: 0.2680 g, 3.19 mmol, 10 eq.; I₂: 0.0891 g, 0.351 mmol, 1.1 eq.; water: 9 ml; AcOEt: 9 ml; 0.0549 g of hydrazide **6** was obtained; yield 87.7%.

Data for **6**: colourless oil; HRMS (EI) for C₁₀H₁₆O₂N₂: (M)⁺ calc.: 196.12118, found: 196.1209. ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 5.85-5.6 (2H, m, CH=CH), 4.1-4.0 (2H, m, NCH₂CH=), 3.75-3.6 (4H, m, NCH₂CH₂O), 3.2-2.9 (4H, m, NCH₂CH₂O), 2.64 (2H, t, J=6.5 Hz, CH₂CO), 2.45-2.3 (2H, m, CH₂CH₂CO); IR/FT (neat) ν (cm⁻¹) 3026 (ν HC=); 1651 (ν CO, C=C); 1455 (δ CH₂); 737 (γ CH₂); 698, 676 (δ out of plane HC=); MS (EI), *m/z* 197 (M+1), 196 (M), 110 (M-O(CH₂)₂N).

Synthesis of the 3-phenyl-propionic acid *N*-benzyl-*N*',*N*'-dimethyl-hydrazide (**19**)

Hydrazinocarbene complex **18**: 0.1270 g, 0.295 mmol, 1 eq.; NaHCO₃: 0.2536 g, 3 mmol, 10.1 eq.; I₂: 0.0824 g, 0.324 mmol, 1.1 eq.; water: 8 ml; AcOEt: 8 ml; 0.0691 g of hydrazide **19** was obtained; yield 83%.

Data for **18**: colourless oil; HRMS (EI) for C₁₈H₂₂ON₂: (M)⁺ calc.: 282.17321, found: 282.1721. ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.4-7.1 (10H, m, H_{arom.}), 4.62 (2H, s, NCH₂Ph), 3.05-2.9 (4H, m, CH₂CH₂CO), 2.41 (6H, s, NMe₂); 3.02 (1H, dd, J_{gem}=13.16 Hz, J_{vic}=9.1 Hz, CHCH₂Ph), 2.656 (1H, dd, J_{gem}=13.16 Hz, J_{vic}=6.1 Hz, CHCH₂Ph), 2.47 (3H, s, NMe₂), 2.11 (3H, s, NMe₂), 1.19 (3H, d, J=6.88 Hz, CHMe); ¹³C NMR DEPT (CDCl₃, 75 MHz) δ (ppm) 175.1 (CO), 139.1 (C_q Ph), 130-125 (C Ph), 44.4 (NMe₂), 41.4 (NCH₂Ph), 34.6 (CH₂CH₂Ph), 31.5 (CH₂CH₂Ph); IR/FT (neat) ν (cm⁻¹) 1657 (ν CO); 1949, 1880, 1804, 1722 (δ out of plane ArC-H); 1604, 1496, (ArC-C); 1455 (δ CH₂); 1353 (δ sy CH₃); 699 (δ e γ CH_{arom.}); 752 (γ CH₂). MS (EI), *m/z* 283 (M⁺ + 1); 282 (M⁺); 239 (M⁺ + 1 - NMe₂); 191 (M⁺ - PhCH₂); 150 (M⁺ + 1 - COCH₂CH₂Ph); 149 (M⁺ - COCH₂CH₂Ph); 148 (M⁺ + 1 - NMe₂ - PhCH₂); 133 (COCH₂CH₂Ph⁺); 106 (M⁺ + 1 - COCH₂CH₂Ph - NMe₂); 105 (CH₂CH₂Ph⁺); 92 (C₇H₈⁺); 91 (C₇H₇⁺); 79 (C₆H₇⁺); 77 (C₆H₅⁺); 65 (C₅H₅⁺).