Transformation of a Pyrazolidene into a Tetrahydropyrimidinylidene Ligand by Deprotonation/Reprotonation

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In an unusual ring enlargement reaction the heterocyclic ligand in a pentacarbonyl(pyrazolidene) chromium complex is transformed in high yield into the corresponding tetrahydropyrimidinylidene ligands by a deprotonation/protonation (or deprotonation/alkylation) sequence.

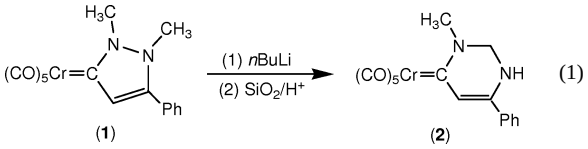
Key words: Carbene Complex, Pyrazolidene Complex, Tetrahydropyrimidinylidene Complex, Ring Enlargement

Introduction

N-Heterocyclic carbene (NHC) ligands such as imidazolinylidene and imidazolylidene have evolved into very powerful co-ligands for several transition metal complexes that are active homogeneous catalysts [1]. In several homogeneous catalysts – especially in those that are used in cross-coupling reactions – the traditional phosphane ligands are being increasingly replaced by *N*-heterocyclic carbenes. The donor/acceptor properties of NHC ligands and phosphanes are similar; however, the metal-carbene bond has turned out to be more stable than most metal-phosphane bonds [2]. Therefore, the development of new syntheses for NHC complexes and the investigation of their reactivity is currently a field of considerable active research. Until now the majority of studies are concerned with imidazolidene and imidazolylidene complexes although in recent years the coordination properties and the reactivity of complexes containing "alternative" heterocyclic ligands [3] or even carbocyclic ligands [4] have moved into the focus of attention. In catalytic processes these NHC ligands are generally regarded as inert spectator ligands. We now report on an unusal case of ring enlargement and on the transformation of a pyrazolidene ligand into a tetrahydropyrimidinylidene ligand.

Results and Discussion

On addition of an equimolar amount of *n*-butyllithium to a solution of pyrazolidene complex **1** in dry tetrahydrofuran at −78 °C the colour of the solution immediately changed from yellow to pale orange indicating a rapid reaction. The IR spectrum of the reaction mixture exhibited a ν(CO) absoption pattern typical for *pseudo*-octahedral pentacarbonyl complexes. The position of the ν(CO) absoptions at rather low wave numbers (2034 w, 1910 vs, 1864 m cm^{-1}) indicated the presence of an anionic complex. Filtration of the reaction mixture over a thin layer of silica at −20 °C followed by chromatography afforded the tetrahydropyrimidinylidene complex **2** in 91% yield (eq. 1).



(1) (2) (1)

Complex **2** was characterized by spectroscopic means, by an elemental analysis and, in addition, by an X-ray structural analysis. Based on the ν(CO) absorptions of **1** and **2**, the isomerization of the cyclic carbene ligand only marginally affects the σ donor/π acceptor properties of the ligand. In accord with the IR data the ^{13}C NMR resonances of the carbonyl carbon atoms in **1** and **2** are within error limit identical. However, the isomerization gives rise to a strong low-field shift of the carbene resonances ($\delta = 187.4$ in **1** and 231.4 in **2**) and a moderate high-field shift of the signal of the olefinic C$_\alpha$ atom (121.6 *versus* 116.6).

The X-ray structural analysis revealed very similar Cr–C(O) distances in **1** [5] and **2** (Fig. 1, Table 1) in agreement with the spectroscopic data. The significantly longer Cr–CO$_{trans}$ bonds compared to

Table 1. Crystal structure data for **2**.

Empirical formula	$C_{16}H_{12}CrN_2O_5$
Formula weight [g mol^{-1}]	364.28
Temperature [K]	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	6.860(1)
b [Å]	26.748(5)
c [Å]	8.855(2)
β [deg]	101.60(3)
Volume [Å^3]	1591.7(6)
Z	4
Calculated density [g cm^{-3}]	1.520
Absorption coefficient [mm^{-1}]	0.747
$F(000)$ [e]	744
θ Range for data collection [°]	3.39 to 29.29
Limiting indices	$-9 \le h \le 9$, $-36 \le k \le 35$, $-12 \le l \le 12$
Reflections collected	27062
Reflections unique, R(int)	4294, 0.0827
Refinement method	Full-matrix least-squares on F^2
Data / parameters	4294 / 217
Goodness-of-fit on F^2	1.039
Final R indices [$I \ge 2\sigma(I)$]	$R1 = 0.0462$, $wR2 = 0.1109$
R indices (all data)	$R1 = 0.0622$, $wR2 = 0.1177$
Largest diff. peak and hole [e A^{-3}]	0.439 / −0.974

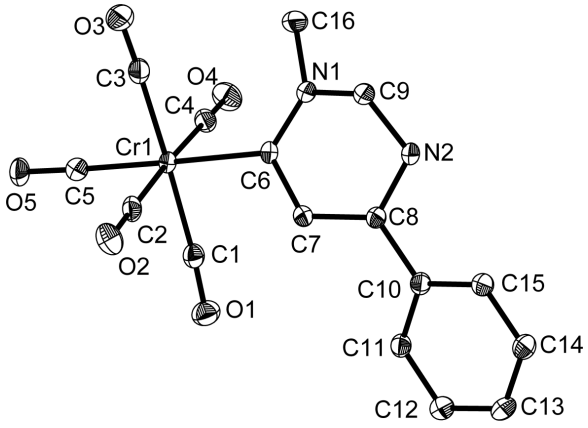
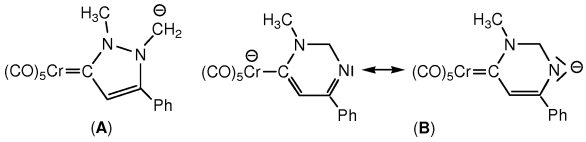


Fig. 1. Selected bond lengths (Å) and angles (°) in **2** (ellipsoids drawn at 50% level, hydrogen atoms omitted): Cr(1)–C(1) 1.912(2), Cr(1)–C(2) 1.897(2), Cr(1)–C(3) 1.915(2), Cr(1)–C(4) 1.908(2), Cr(1)–C(5) 1.854(2), Cr(1)–C(6) 2.144(2), C(6)–C(7) 1.446(3), C(7)–C(8) 1.378(3), C(8)–N(2) 1.357(3), C(9)–N(2) 1.435(3), C(9)–N(1) 1.474(3); Cr(1)–C(6)–C(7) 119.3(1), C(6)–C(7)–C(8) 120.5(2), C(7)–C(8)–N(2) 117.9(2), C(8)–N(2)–C(9) 114.6(2), N(2)–C(9)–N(1) 108.9(2), C(9)–N(1)–C(6) 117.6(2), N(1)–C(6)–Cr(1) 127.0(2).

the average of the Cr–CO_{cis} bonds in **1** and **2** illustrate the pronounced donor properties of both heterocyclic carbene ligands. For both complexes the Cr–C(carbene) distance is likewise identical whereas in **2** the C(carbene)–N bond is shorter and the C(carbene)–C(sp^2) bond is slightly longer indicating enhanced π interaction of the electron lone pair at the nitrogen atom with the p_z orbital at C6. The six-membered ring in **2** is stongly puckered and adopts a butterfly conformation with the vector C7···C9 forming the central axis of the butterfly.

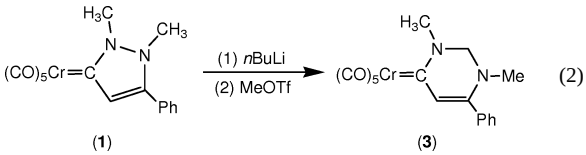
The deprotonation of **1** is regioselective. Only that product is obtained that is derived from deprotonation of the methyl group remote from the carbene carbon atom. On deprotonation of the methyl group adjacent to the carbene centre and subsequent reprotonation of the rearranged chromate anion the formation of a 3-methyl tetrahydropyrimidinylidene complex instead of the isolated 1-methyl tetrahydropyrimidinylidene complex would be expected.

For the anionic intermediate formed on deprotonation of **1** essentially two structures are conceivable: **A** and **B**. Structure **B** is derived from **A** by insertion of the N–CH_2 group into the N–N bond. When considering the ν(CO) absoptions at very low wave numbers structure **B** seems more likely.



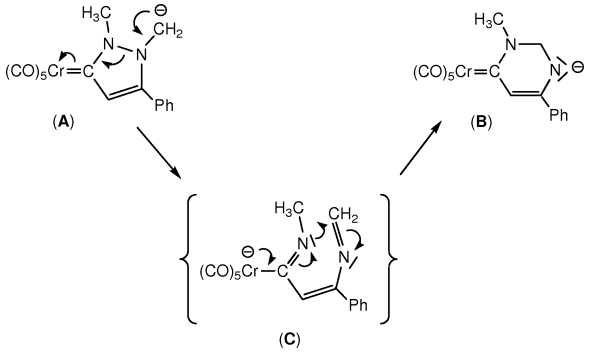
To distinguish between the two structures experimentally the anionic intermediate was treated with trifluorosulfonic acid methylester. Addition of $[CH_3]^+$ to **A** should give the N(2)–ethyl derivative of **1**, addition of $[CH_3]^+$ to **B** should give the N,N'-dimethyl derivative of **2**.

The alkylation of the anionic intermediate with methyl triflate and chromatographic workup of the reaction mixture afforded the N,N'-dimethyl compound **3** in 87% yield (eq. 2) thus confirming structure **B** for the intermediate.



(2)

A possible mechanism for the rearrangement of **A** into **B** is depicted in Scheme 1. Deprotonation and subsequent opening of the pyrazolidene ring in **A** gives the *C*-iminyl chromate **C** containing an additional terminal imine functionality. Nucleophilic addition of the



Scheme 1.

iminyl-nitrogen to the terminal CH_2 group affords **B**, protonation (or alkylation) of **B** finally gives the isolated complexes **2** and **3**.

Pentacarbonyl tetrahydropyrimidinylidene complexes are rare. A few tungsten complexes have been synthesized by reaction of aminocarbene complexes with dichloromethane or dibromomethane under phase transfer conditions [6] or by cycloaddition of urea with alkynyl(alkoxy)carbene complexes [7]. The formation of a tetrahydropyrimidinylidene ligand by ring enlargement of a pyrazolidene ligand is, to the best of our knowledge, without precedence. However, a somewhat related ring expansion of N,N'-dialkyl substituted indazoles to dihydroquinazolinones under basic conditions has been described [8].

Experimental Section

All operations were performed in an inert gas atmosphere using standard Schlenk techniques. The solvents were dried by distillation from CaH_2 (CH_2Cl_2), $LiAlH_4$ (pentane) and sodium (THF). The silica gel used for chromatography (Baker, silica for flash chromatography) was argon-saturated. The yields refer to analytically pure substances and are not optimized. Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were recorded with Jeol JNX 400 and Varian Inova 400 spectrometers at ambient temperature. Chemical shifts are relative to the residual solvent peak. IR: Biorad FTS 60. MS: Finnigan MAT 312. Elemental analysis: Heraeus CHN-O-Rapid. Complex **1** was prepared as reported earlier [5, 9]. All other chemicals were used as obtained from commercial suppliers.

*Pentacarbonyl(3-methyl-6-phenyl-1,2,3,4-tetrahydropyrimidin-4-ylidene)chromium (**2**)*

A solution of 0.63 mL of *n*-BuLi (1.6 M in *n*-hexane) was added at −80 °C to 0.36 g (1 mmol) of complex **1** in 30 mL of THF. The solution was stirred for 10 min at −80 °C and then filtered over a short layer (*ca.* 3 cm) of silica at −20 °C using CH_2Cl_2 as the eluent. Evaporation of the solvent and chromatography on silica at −20 °C with pentane/CH_2Cl_2 (2 : 1) gives 0.33 g (0.90 mmol; 90%) of **2** as a yellow solid. M. p. 97 – 98 °C. – IR (THF): ν(CO) = 2047 m, 1919 vs, 1902 sh cm^{-1}. – ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 3.66 (s, 3H, NCH_3), 4.55 (d, $^3J_{HH}$ = 5.5 Hz, 2H, NCH_2N), 6.64 (s, 1H, $C_\beta H$), 6.80 (s, 1H, NH), 7.37 (m, 3H, ArH), 7.64 (m, 2H, ArH). – ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 46.7 (NCH_3), 61.5 (NCH_2N), 116.6 (C_β), 129.1, 129.7, 132.0, 134.0 (4 ArC), 141.2 (C_γ), 220.0 (*cis*-CO), 224.6 (*trans*-CO), 231.4 (C_α). – MS (FAB): *m*/*z* (%) = 364 (16) [M$^+$], 336 (27) [(M – CO)$^+$], 308 (42) [(M – 2CO)$^+$], 280 (26) [(M – 3CO)$^+$], 252 (84) [(M – 4CO)$^+$], 224 (100) [(M – 5CO)$^+$]. – $C_{16}H_{12}CrN_2O_5$ (364.28): calcd. C 52.76, H 3.32, N 7.69; found C 53.03, H 3.57, N 7.65.

*Pentacarbonyl(1,3-dimethyl-6-phenyl-1,2,3,4-tetrahydropyrimidin-4-ylidene)chromium (**3**)*

A solution of 0.63 mL of *n*-BuLi (1.6 M in *n*-hexane) was added at −80 °C to 0.36 g (1 mmol) of complex **1** in 30 mL of THF. The solution was stirred for 10 min at −80 °C and then 0.124 mL (1.1 mmol) of MeOTf was added in one portion. After 10 min at −80 °C the crude reaction mixture was filtered over a short layer (*ca.* 3 cm) of silica at −20 °C using CH_2Cl_2 as the eluent. Evaporation of the solvent and chromatography on silica at −20 °C with pentane/CH_2Cl_2 (3 : 1) gives 0.33 g (0.87 mmol; 87%) of **3** as a yellow solid. M. p. 93 – 94 °C. – IR (THF): ν(CO) = 2048 m, 1920 vs, 1903 sh cm^{-1}. – ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 2.80 (s, 3H, NCH_3), 3.69 (s, 3H, NCH_3), 4.59 (d, $^3J_{HH}$ = 5.5 Hz, 2H, NCH_2N), 6.44 (s, 1H, $C_\beta H$), 7.40 (m, 3H, ArH), 7.51 (m, 2H, ArH). – ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 38.0 (NCH_3), 47.2 (NCH_3), 69.1 (NCH_2N), 121.0 (C_β), 129.5, 130.3, 131.3, 134.0 (4 ArC), 144.6 (C_γ), 219.7 (*cis*-CO), 224.4 (*trans*-CO), 229.9 (C_α). – MS (FAB): *m*/*z* (%) = 378 (14) [M$^+$], 350 (31) [(M – CO)$^+$], 322 (39) [(M – 2CO)$^+$], 294 (35) [(M – 3CO)$^+$], 266 (96) [(M – 4CO)$^+$], 238 (100) [(M – 5CO)$^+$]. – $C_{17}H_{14}CrN_2O_5$ (378.31): calcd. C 53.97, H 3.73, N 7.40; found C 54.14, H 4.04, N 7.46.

*X-ray structural analysis of **2***

Single crystals (0.4 × 0.3 × 0.2 mm, yellow blocks) suitable for X-ray structural analysis were obtained by slow diffusion of *n*-hexane into a solution of **2** in CH_2Cl_2 at 4 °C. The measurements were performed with a crystal mounted on a glass fibre on a Stoe IPDS II diffractometer (graphite monochromator, Mo Kα, radiation, λ = 0.71073 Å). The structures were solved by direct methods using the SHELXTL-97 program package [10]. The position of

the hydrogen atoms were calculated by assuming ideal geometry, and their coordinates were refined together with those of the attached carbon atoms as riding model. All other atoms were refined anisotropically.

CCDC 617017 contains the supplementary crystallographic data for complex **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

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