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Preliminary communication

DIFFERENCES IN BEHAVIOUR OF ALKOXYCARBENE COMPLEXES TOWARDS NITROGEN ELECTROPHILES. THE REACTIONS OF A HETEROMETALLOCYCLIC CARBENE-THIO CHELATE WITH PRIMARY AND SECONDARY AMINES AND 1,1-DIMETHYLHYDRAZINE

HELGARD G. RAUBENHEIMER*, SIMON LOTZ

(Rand Afrikaans University, Auckland Park, Johannesburg 2000
(South Africa)

GERT KRUGER and GEOFFREY GAFNER

Council for Scientific and Industrial Research, Pretoria 0001
(South Africa)

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Summary

The heterometallocyclic complex *cis*-$[\mathrm{Cr\{C(OEt)C(OEt){=}CS(CH_2)_3S\}(CO)_4}]$ (I), reacts with ammonia and primary and secondary amines ($\mathrm{EtNH_2}$ and $\mathrm{Me_2NH}$) to give respectively (by aminolysis) an aminocarbene chelate *cis*-$[\mathrm{Cr\{C(NH_2)C(OEt){=}CS(CH_2)_3S\}(CO)_4}]$ (II), *syn* and *anti* aminocarbene complex isomers *cis*-$[\mathrm{Cr\{C(NHEt)C(OEt){=}CS(CH_2)_3S\}(CO)_4}]$ (IIIa, b) and (by deamination) the conformational *syn* and *anti* isomers of *cis*-$[\mathrm{Cr\{C(NHMe)C(OEt){=}CS(CH_2)_3S\}(CO)_4}]$ (IVa, b). The reaction of (I) with 1,1-dimethylhydrazine yields a series of structurally different compounds: (II), $[\mathrm{Cr\{S(CH_2)_3SC{=}C(OEt)CN\}(CO)_5}]$ (V), $[\mathrm{Cr\{NH{=}C(OEt)C(OEt){=}CS(CH_2)_3S\}(CO)_5}]$ (VI) and the chelate *cis*-

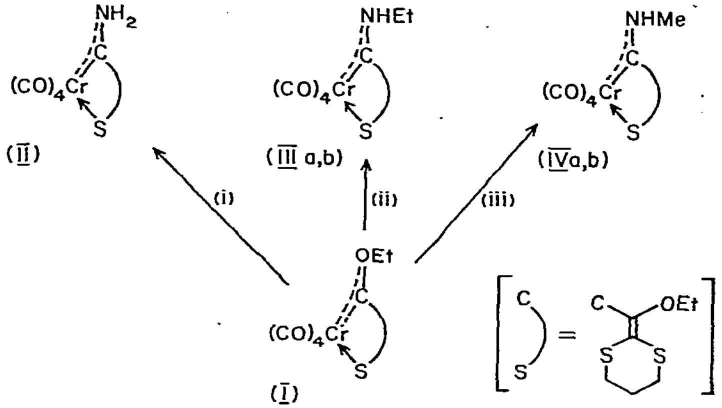
$[\mathrm{Cr\{NH{=}C(OEt)C(OEt){=}CS(CH_2)_3S\}(CO)_4}]$ (VII), which has been shown by X-ray crystallography to be coordinated through the nitrogen atom of an imidate moiety.

Reaction of the compounds $[\mathrm{Cr\{C(OR')R\}(CO)_4}]$ (R' = Me; R = alkyl or aryl) with various nitrogen electrophiles are known [1,2]. When however, the carbene carbon atom forms part of a metallocycle as in cis-$[\mathrm{Cr\{C(OEt)C(OEt){=}CS(CH_2)_3S\}(CO)_4}]$ (I) [3], significant deviations from the accepted reaction patterns occur with certain secondary amines and 1,1-dimethylhydrazine. The preliminary results reported in this communication not only illustrate the sensitivity of certain reactions towards steric influences, but once again emphasize the versatility of the carbene moiety in synthetic reactions.

Treatment of an ether solution of (I) with ammonia (Scheme 1) afforded (after chromatography) the expected [1] aminocarbene complex (II)[#] [yield 82%; m.p. 114 °C; m/z 367; ν(CO, hexane) 2022, 1955, 1910, 1863 $\mathrm{cm^{-1}}$]. Both the amines $\mathrm{EtNH_2}$ and $\mathrm{Me_2NH}$ yielded a pair of conformational isomers [4] (IIIa) [syn: yield 12%; m.p. 87 °C; m/z 395; ν(CO, hexane) 2016, 1950, 1903, 1868 $\mathrm{cm^{-1}}$; ν(NH,$\mathrm{CCl_4}$) 3358 $\mathrm{cm^{-1}}$; τ($\mathrm{CDCl_3}$) e.g. 1.60 (1H, NH), 6.08 (2H, $\mathrm{OCH_2}$)] and (IIIb) [anti; yield 32%; m.p. 111 °C; ν(CO, hexane) 2022, 1953, 1902, 1862 $\mathrm{cm^{-1}}$; ν(NH, $\mathrm{CCl_4}$) 3278 $\mathrm{cm^{-1}}$ τ($\mathrm{CDCl_3}$) 0.95 (1H, NH), 5.85 (2H, $\mathrm{OCH_2}$)], and (IVa) [syn; yield 27%; m.p. 99 °C; m/z 381; ν(CO, hexane) 2020, 1950, 1902, 1866 $\mathrm{cm^{-1}}$; ν(NH, $\mathrm{CCl_4}$) 3378 $\mathrm{cm^{-1}}$; τ($\mathrm{CDCl_3}$) 1.45 (1H, NH), 6.09 (2H, $\mathrm{OCH_2}$)] and (IVb) [anti; yield 53%; m.p. 127 °C; ν(CO,hexane) 2020, 1953, 1902, 1869 $\mathrm{cm^{-1}}$; ν(NH, $\mathrm{CCl_4}$) 3292 $\mathrm{cm^{-1}}$; τ($\mathrm{CDCl_3}$) e.g. 0.85

[#] All experiments and manipulations were conducted under an atmosphere of purified nitrogen. Satisfactory elemental analyses (Cr, C, H, N) were obtained for all the new complexes. Only some of the physical data obtained, are reported here.

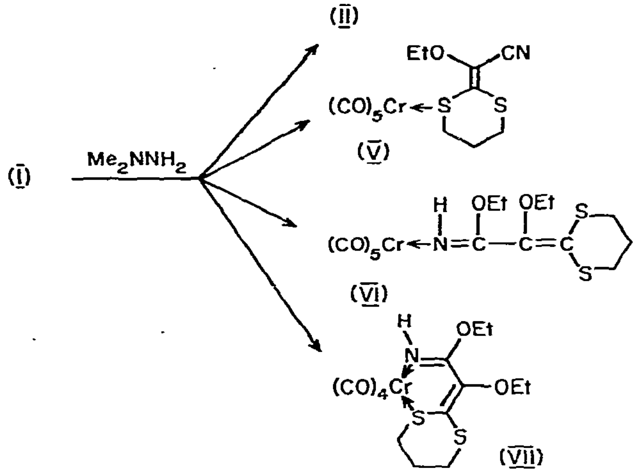
(1H, NH), 5.98 (2H, OCH_2)]. In contrast, the chromium alkyl or aryl alkoxycarbenes generally gave only one isomer (the <u>syn</u> form) with $EtNH_2$, and a complex of the type [$Cr\{C(NMe_2)R\}(CO)_5$] with Me_2NH [4,5]. The deamination which occurred in the present case with Me_2NH, is related to the elimination of an ethyl group in phenylethoxycarbenes containing metal-metal bonds [6], or the loss of the bulkier benzyl and isopropyl groups achieved before with pentacarbonylchromium compounds [7].



<u>Scheme 1</u>. (i) NH_3; (ii) NH_2Et; (iii) $NHMe_2$; a: <u>syn</u> form; b: <u>anti</u> form.

The fact that no reaction was observed between the chelate (I) and bulkier amines than $EtNH_2$, cannot necessarily be attributed to steric hindrance in the final product since the aminocarbene-thioether chelate <u>cis</u>-[$W\{C(NHBu^t)C(OEt)=CS(CH_2)_3S\}(CO)_4$], had been prepared before by successive treatment of [$W(S(CH_2)_3SCH_2)(CO)_5$] with BuLi, Bu^tNC and [$(C_2H_5)_3O$]BF_4 [8].

Scheme 2 reveals that the reaction of the heterometallocyclic complex (I) with $(CH_3)_2NNH_2$ modified the carbene moiety as previously reported [2] to give product (V) [yield, 7%; m.p. 68 °C; ν(CO, hexane) 2078, 1982, 1949, 1925 cm^{-1}; ν(CN, hexane) 2118 cm^{-1}; τ($CDCl_3$) e.g. 6.06 (2H, OCH_2)]. In addition however, the reaction followed other



Scheme 2.

unknown pathways to yield again the aminocarbene heterometallocycle (II) [yield 4%], another pentacarbonyl compound which, on the strength of spectroscopic data, was formulated as the imino-ether N-donor complex (VI) [yield 6%; m.p. 58 °C; ν(CO, hexane), 2076, 1986, 1936, 1909 cm^{-1}; ν(NH, CCl_4) 3410 cm^{-1}; τ($CDCl_3$) e.g. 3.00 (1H, NH), 5.77 (2H, $NCOCH_2$), 7.04 (2H, SCH_2)] and, by ring enlargement, compound (VII) as the main product in 35% yield. This complex [m.p. 80 °C; ν(CO, hexane) 2038, 1954, 1905, 1861 cm^{-1}; ν(NH, CCl_4) 3352 cm^{-1}; τ($CDCl_3$) e.g. 2.99 (1H, NH), 5.96 (2H, $NCOCH_2$); 6.16 (2H, $COCH_2$), 6.82 (SCH_2)], similar to (VI), gave m/z (max) 247 corresponding to the ionized ligand $NHC(OEt)C(OEt)\overline{CS(CH_2)_3S}^+$.

The crystal structure determination for VII, which will be reported in detail offers to our knowledge an unprecedented example of a low oxidation state metal complex containing the reactive imidate moiety [9]. The Cr-N bond length of 2.095(5) Å is longer than the 2.059(2) Å distance in $[Cr(NCSMe)(CO)_5]$ [10] but shorter than the corresponding (average) bond length (2.217 Å) in $[\underline{Cr\{N(Me)_2(CH_2)_2N}(Me)_2\}(CO)_4]$ [11].

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