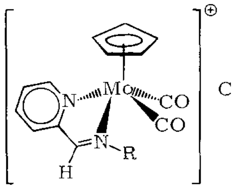
Synthesis and X-Ray Structure Analysis of a Mo Complex with η^2-Coordinated Benzaldehyde; Transformation of a CO Ligand by Double α-Addition[**]

By *Henri Brunner, Joachim Wachter, Ivan Bernal*, and *Michael Creswick*[*]

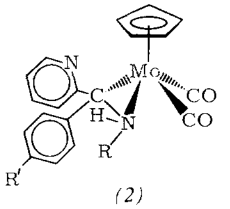
The chelate complexes *(1)*[1], accessible from the Schiff bases of 2-pyridinecarbaldehyde and $C_5H_5Mo(CO)_3Cl$ react with an excess of C_6H_5Li or p-$R'C_6H_4MgBr$ under ring contraction to give the neutral complexes *(2)*[2]. Reaction of the *N*-methyl compound *(1)* ($R=CH_3$) with p-$R'C_6H_4MgBr$ ($R'=H$, CH_3) in the molar ratio 1:2 does not stop at the stage of *(2)* but leads to *(3)* by reduction of a CO group. Whereas in the formation of a carbene ligand from a $M{-}C{\equiv}O$ group the nucleophile adds to the C atom and the electrophile to the O atom[3], the transformation of a $C{\equiv}O$ ligand into η^2-benzaldehyde, established for *(3a)* by X-ray structure analysis, requires double α-addition.

In the solid state *(3a)* occurs in two isomeric forms which can be separated manually. Both contain in the IR spectrum (KBr) the ν_{C-O} band at 1830 cm^{-1}; however, they differ in the frequency of the N—H stretching vibrations [*(3a')* 3203 cm^{-1}, *(3a'')* 3181 cm^{-1}]. The molecular structure of *(3a')* in the crystal (Fig. 1), determined by X-ray crystallography, is in accord with the ^1H- and ^{13}C-NMR spectra measured in solution at −10 °C (Table 1). Compared with *(2)*, in *(3a)* the $\delta(^{13}C)$ values for the MoCN three-membered ring ($\Delta=-23$) and the CO group ($\Delta=+13$) are shifted appreciably. In *(3b)* the p-CH_3 signals are nonequivalent.



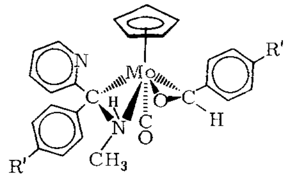
(1)

$R = CH_3, C_6H_5, CH(CH_3)_2, CH_2C_6H_5, CH(CH_3)C_6H_5$



(2)

$R' = H, CH_3, OCH_3, Cl$



(3a), $R' = H$, *(3b)*, $R' = CH_3$

At room temperature, the orange solutions of *(3)* in chloroform, benzene, and acetone soon turn blue with formation of extremely air sensitive and thermolabile complexes of still unknown structure.

Table 1. NMR data of complexes *(3a)* and *(3b)* ($CDCl_3$ solution, TMS int.) [a].

^1H-NMR	$C_6H_4CH_3$		NCH_3 ($J_{NH\ CH_3}$)	C_5H_5	CH	NH		C_5H_4N		C_6H_4R'
							H5	H4, H3	H6	
(3a)			^{2}2.63 (5.5)	^{1}4.76	^{1}5.22	^{m}6.30 [b]	^{m}6.49	^{m}6.98	^{m}8.39	^{m}7.32
(3b)	^{1}2.33, ^{1}2.36		^{2}2.56 (5.6)	^{1}4.73	^{1}5.21	^{m}6.24 [b]	^{m}6.54	[c]	^{m}8.31	^{m}7.14
^{13}C-NMR [d]	NCH_3	MoCN	MoCO [e]	C_5H_5	$C_5H_4N + C_6H_4R'$		C—O			
(3a)	39.3	76.9	81.6	100.6	120.0—147.3, 168.3		234.9			

[a] δ values, coupling constants in Hz; Varian T-60 and Bruker WH-90, temperature −10 °C. [b] Broad. [c] Signal obscured. [d] Broad band decoupled. [e] Doublet in the off-resonance spectrum.

The orange rhombs of *(3a')* crystallize in the space group $P\bar{1}$, $Z=2$, cell constants $a=9.035(6)$, $b=12.314(6)$, $c=13.220(5)$ Å, $\alpha=65.91(4)$, $\beta=71.40(4)$, $\gamma=72.42(4)°$; $V=1246.97$ Å^3, $\varrho_{calc}=1.311$ $g\cdot cm^{-3}$. From 3154 measured reflections (MoK_α radiation, $\lambda=0.71073$ Å) 2128 with $I>2\sigma(I)$ were used for the refinement of the structure [R(F) value 4.59%].

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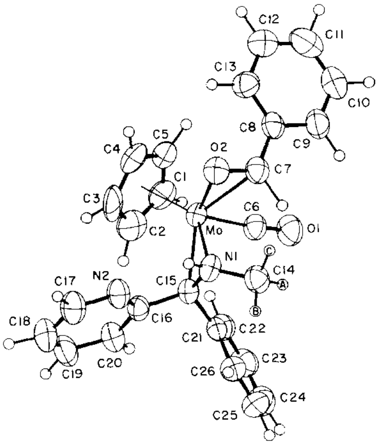

Fig. 1. ORTEP diagram of *(3a')*. Bond lengths: Mo–C6 1.900(11), C6–O1 1.182(13), Mo–C7 2.258(14), C7–O2 1.333(12), Mo–O2 2.071(8), Mo–N1 2.137(9), N1–C15 1.436(17), Mo–C15 2.203(9), Mo–Cp (average) 2.35(3) Å; bond angles: C7–Mo–O2 35.4, Mo–C7–O2 64.5, N1–Mo–C15 38.7, Mo–N1–C15 73.2, Mo–C6–O1 171.7, C6–Mo–C7 69.7, C6–Mo–O2 104.6, C6–Mo–N1 93.4, C6–Mo–C15 88.9°.

Similarly as in *(2)*, in the MoCN three-membered ring of *(3a')* the pyridyl substituent at C15 and the hydrogen atom at N1 lie at the side of the C_5H_5 ring; a hydrogen bridge is formed between N1 and N2[2]. The C_6H_5 substituent at the MoCO three-membered ring is also orientated to the C_5H_5 ring. The plane of the C_5H_5 ring forms angles of 60.36 and 33.58° with the planes of the MoCN and MoCO three-membered rings, whereby in the MoCN ring C15 and in the MoCO ring O2 are closer to the C_5H_5 plane. With an angle of 77.56° the planes of both three-membered rings are nearly perpendicular to each other. With 110.6(8)° the angle C16—C15—C21 is close to the tetrahedral angle. The η^2-bonding of the benzaldehyde in *(3a')* corresponds to the coordination of formaldehyde in $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$[4] and benzaldehyde in $Ni(PPh_3)_2(\eta^2\text{-}C_6H_5CHO)$[5]. Considering the η^2-benzaldehyde a two-electron ligand and the η^2-aminomethyl group a three-electron ligand, *(3a')* can be regarded as a derivative of $C_5H_5Mo(CO)_2(NO)$[6].

Procedure

A solution of p-$R'C_6H_4MgBr$ ($R' = H$ or CH_3) (11.6 mmol) in 50 ml THF is added dropwise to a suspension of 2.2 g (5.9 mmol) *(1)* ($R = CH_3$) in 100 ml THF at room temperature. After refluxing for 30 minutes the solvent is evaporated off and the residue dissolved in 15 ml benzene. On chromatography on SiO_2 (column 3 × 20 cm) with benzene two very weak zones develop. These are discarded. Thereafter a broad greenish-blue zone develops which contains *(3a)*, *(3b)* and their subsequent reaction products; this is eluted with benzene/ether (1:1). Recrystallization at $-35\,^\circ C$ from 100 ml acetone and 20 ml ether affords red orange crystals in 23–25% yield. On further recrystallization from ether/pentane (10:1) analytically pure compounds can be obtained: orange rhombs of *(3a')* (dec. 155 °C, $\nu_{NH} = 3203\ cm^{-1}$)[7], red prisms of *(3a'')* (dec. 154 °C, $\nu_{NH} = 3181\ cm^{-1}$), and red prisms of *(3b)* (dec. 170 °C, $\nu_{NH} = 3181\ cm^{-1}$), respectively.

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CAS Registry numbers:
(1), $R = CH_3$, 41308-25-2; *(3a)*, 71888-50-1; *(3b)*, 71888-49-8; C_6H_5Br, 108-86-1; p-$CH_3C_6H_4Br$, 106-38-7

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[1] *H. Brunner, W. A. Herrmann*, Chem. Ber. *105*, 3600 (1972).

[2] *H. Brunner, H. Schwägerl, J. Wachter, G. M. Reisner, I. Bernal*, Angew. Chem. *90*, 478 (1978); Angew. Chem. Int. Ed. Engl. *17*, 453 (1978); *H. Brunner, H. Schwägerl, J. Wachter*, Chem. Ber. *112*, 2079 (1979).

[3] *E. O. Fischer*, Angew. Chem. *86*, 651 (1974); Adv. Organomet. Chem. *14*, 1 (1976).

[4] *K. L. Brown, G. R. Clark, C. E. L. Headford, K. Marsden, W. R. Roper*, J. Am. Chem. Soc. *101*, 503 (1979).

[5] *D. Walther*, Z. Chem. *15*, 490 (1975); *T. T. Tsou, J. C. Huffman, J. K. Kochi*, Inorg. Chem. *18*, 2311 (1979).

[6] *M. G. Reisner, I. Bernal, H. Brunner, J. Doppelberger*, J. Chem. Soc. Dalton Trans. *1979*, 1664; *J. L. Atwood, R. Shakir, J. T. Malito, M. Herberhold, W. Kremnitz, W. P. E. Bernhagen, H. G. Alt*, J. Organomet. Chem. *165*, 65 (1979).

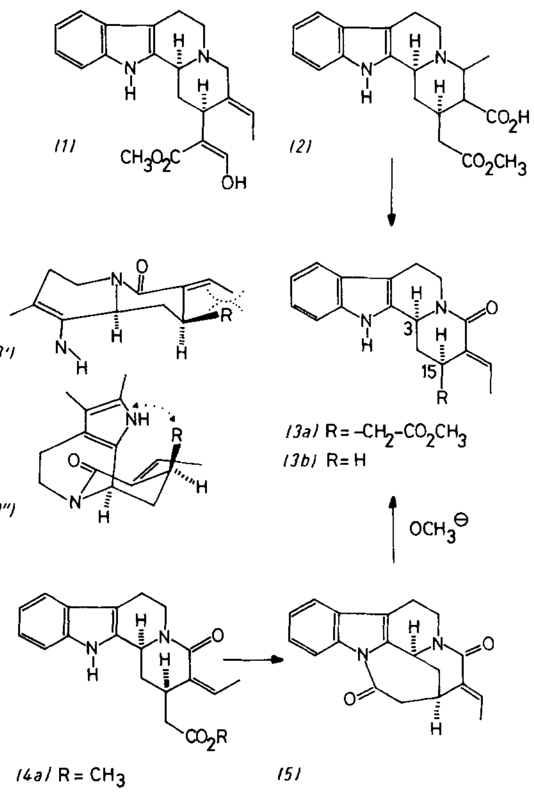
[7] The 70 eV mass spectra of *(3a)* and *(3b)* contain as fragments of highest mass number $[M - C_6H_6 - CO]^+$. The molecular ions can be observed in the F-D spectrum (Varian 311 A). We thank Dr. *K. K. Mayer* and *F. Fischer* for recording the spectra.

Thermodynamically Controlled Stereoselective Synthesis of Geissoschizine[**]

By *Werner Benson* and *Ekkehard Winterfeldt*[*]

Dedicated to Professor Wolfgang Lüttke on the occasion of his 60th birthday

We have previously described a total synthesis[1] of the biogenetically important alkaloid[2] geissoschizine *(1)*. The stereoselective methylene-lactam rearrangement of amino acids of type *(2)* may be regarded as the key reaction, which affords the *E*-configurated lactam *(3a)* as main product.



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