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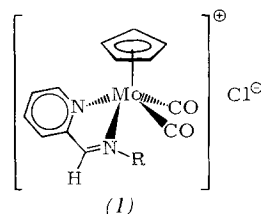
Synthesis and X-Ray Structure Analysis of a Mo Complex with η^2 -Coordinated Benzaldehyde; Transformation of a CO Ligand by Double α -Addition^[**]

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

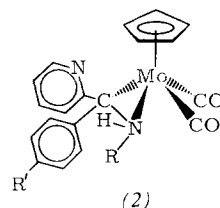
The chelate complexes (1)^[1], accessible from the Schiff bases of 2-pyridinecarbaldehyde and $C_5H_5Mo(CO)_3Cl$ react with an excess of C_6H_5Li or $p-R'C_6H_4MgBr$ under ring contraction to give the neutral complexes (2)^[2]. Reaction of the *N*-methyl compound (1) ($R=CH_3$) with $p-R'C_6H_4MgBr$ ($R'=H, CH_3$) 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.

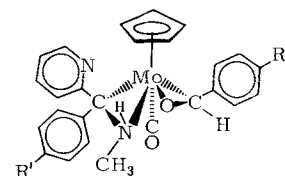
In the solid state (3a) occurs in two isomeric forms which can be separated manually. Both contain in the IR spectrum (KBr) the $\nu_{C=O}$ band at 1830 cm^{-1} ; however, they differ in the frequency of the N—H stretching vibrations [(3a') 3203 cm^{-1} , (3a'') 3181 cm^{-1}]. The molecular structure of (3a') in the crystal (Fig. 1), determined by X-ray crystallography, is



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



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



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

in accord with the 1H - and ^{13}C -NMR spectra measured in solution at $-10^\circ C$ (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.

At room temperature, the orange solutions of (3) in chloroform, benzene, and acetone soon turn blue with formation of

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	H 5	C_5H_4N H 4, H 3	H 6	C_6H_4R'
(3a)		δ 2.63 (5.5)	δ 4.76	δ 5.22	δ 6.30 [b]	δ 6.49	δ 6.98	δ 8.39	δ 7.32
(3b)	δ 2.33, δ 2.36	δ 2.56 (5.6)	δ 4.73	δ 5.21	δ 6.24 [b]	δ 6.54	[c]	δ 8.31	δ 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 $-10^\circ C$. [b] Broad. [c] Signal obscured. [d] Broad band decoupled. [e] Doublet in the off-resonance spectrum.

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extremely air sensitive and thermolabile complexes of still unknown structure.

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, $\alpha=65.91(4)$, $\beta=71.40(4)$, $\gamma=72.42(4)^\circ$; $V=1246.97$ Å³, $\rho_{calc}=1.311\text{ g}\cdot\text{cm}^{-3}$. 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%].

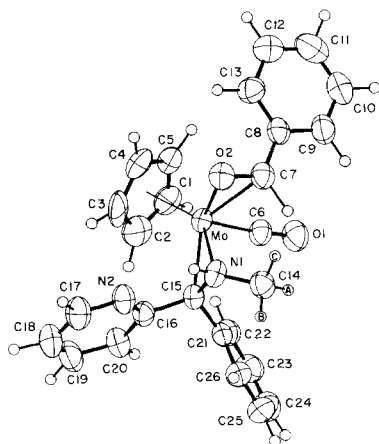


Fig. 1. ORTEP diagram of $(3a')$. Bond lengths: Mo—C6 1.900(11), C6—O1 1.182(13), Mo—C7 2.258(14), C7—O2 1.333(12), Mo—O2 2.071(8), Mo—N1 2.137(9), N1—C15 1.436(17), Mo—C15 2.203(9), Mo—Cp (average) 2.35(3) Å; bond angles: C7—Mo—O2 35.4, Mo—C7—O2 64.5, N1—Mo—C15 38.7, Mo—N1—C15 73.2, Mo—C6—O1 171.7, 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 $Os(\eta^2-CH_3O)(CO)_2(PPh_3)_2$ ^[4] and benzaldehyde in $Ni(PPh_3)_2(\eta^2-C_6H_5CHO)$ ^[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 $p\text{-R}'C_6H_4MgBr$ ($R' = H$ 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. $155^\circ C$, $\nu_{NH} = 3203\text{ cm}^{-1}$)^[7], red prisms of $(3a'')$ (dec. $154^\circ C$, $\nu_{NH} = 3181\text{ cm}^{-1}$), and red prisms of $(3b)$ (dec. $170^\circ C$, $\nu_{NH} = 3181\text{ cm}^{-1}$), respectively.

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(1), $R = CH_3$, 41308-25-2; (3a), 71888-50-1; (3b), 71888-49-8; C_6H_5Br , 108-86-1; $p\text{-CH}_3C_6H_4Br$, 106-38-7

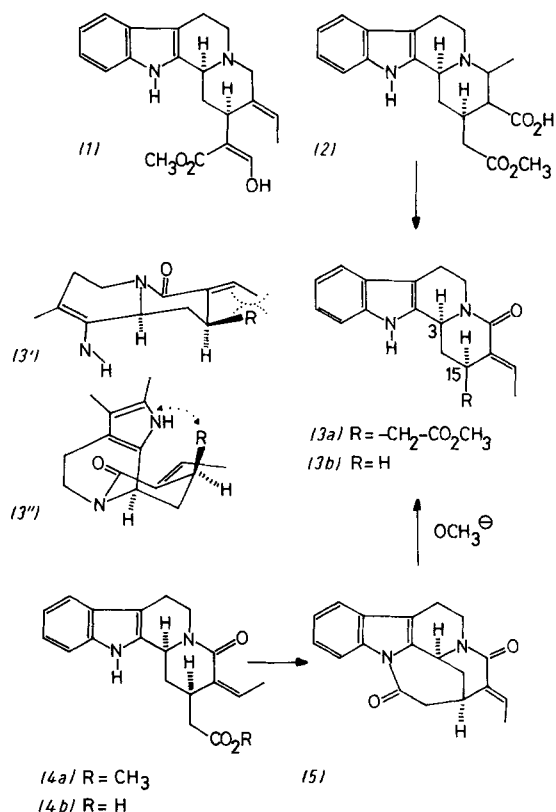
- [1] H. Brunner, W. A. Herrmann, Chem. Ber. 105, 3600 (1972).
- [2] H. Brunner, H. Schwägerl, J. Wachter, G. M. Reisner, I. Bernal, Angew. Chem. 90, 478 (1978); Angew. Chem. Int. Ed. Engl. 17, 453 (1978); H. Brunner, H. Schwägerl, J. Wachter, Chem. Ber. 112, 2079 (1979).
- [3] E. O. Fischer, Angew. 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 $[M - C_6H_5 - CO]^+$. 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*-configured lactam $(3a)$ as main product.



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