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Preliminary communication

Dihydropyridine-induced reductions of methyl(ethoxy)carbene complexes of chromium and tungsten: formation and X-ray crystal structure of the adduct between pyridine and the corresponding ethylidene carbene complexes

F. Cohen, R. Goumont, H. Rudler
Laboratoire de Chimie Organique, URA 408, Université Pierre et Marie Curie, T 44, 4 place Jussieu, 75252 Paris Cedex 05 (France)

J.C. Daran and R.A. Toscano
Laboratoire de Chimie des Métaux de Transition, URA 608, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05 (France)

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Abstract

The reactions of $[(CO)_5MC(OEt)Me]$ (1) (M = W or Cr) with 1,4-dihydropyridines $(R')C_5H_5N(R)$ (2) (R = H or Me; R′ = H or Me) give either the ylides $[(CO)_5\overline{M}CH(Me)(R)\overset{+}{N}C_5H_5(R')]$ (R = H, R′ = H or Me) (5) or the pyridinium tungstates and chromates $[(CO)_5MCH(Me)(OEt)]^-[(R)NC_5H_5(R')]^+$ (R = Me, R′ = H or 4-Me) (7) via hydride transfer to the carbene carbon atom. **5a** (R = H, R′ = 4-Me) was characterized spectrally and by single crystal X-ray diffraction.

During the course of our investigations on the synthesis and reactivity of aminocarbene complexes of tungsten and chromium [1], we studied the interaction of a series of 1,4-dihydropyridines of the general structure $(R')C_5H_5N(R)$ (R = H or Me; R′ = H or Me) with $[(CO)_5MC(OEt)Me]$ (1) (a, M = W; b, M = Cr). Although 1,4-dihydropyridines (R = H, R′ = H or Me) may react like other secondary amines to give, upon substitution of the alkoxy group, new aminocarbene complexes 3, a second reaction must also be considered, the transfer of a hydride from dihydropyridine to the carbene carbon atom. On the one hand, dihydropyridines are versatile reducing agents of carbonyl groups, both in classical organic reactions, as well as in biochemical reductions [2,3]. On the other hand, Fischer-type carbene complexes behave like carbonyl groups, especially towards nucleophiles.

Correspondence to: Dr. H. Rudler, Laboratoire de Chimie Organique, URA 408, Université Pierre et Marie Curie, T 44, 4 place Jussieu, 75252 Paris Cedex 05, France.

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Table 1

Interatomic distances (Å) for $C_{13}H_{11}CrNO_5$

Cr(1)-C(1)	2.250(6)		
Cr(1)-C(11)	1.848(6)	O(11)-C(11)	1.150(6)
Cr(1)-C(12)	1.872(6)	O(12)-C(12)	1.153(6)
Cr(1)-C(13)	1.890(6)	O(13)-C(13)	1.139(7)
Cr(1)-C(14)	1.879(7)	O(14)-C(14)	1.141(7)
Cr(1)-C(15)	1.901(7)	O(15)-C(15)	1.142(7)
N(1)-C(1)	1.489(7)	N(1)-C(3)	1.347(7)
N(1)-C(7)	1.349(7)	C(1)-C(2)	1.521(8)
C(3)-C(4)	1.365(8)	C(4)-C(5)	1.385(8)
C(5)-C(6)	1.390(8)	C(5)-C(8)	1.484(9)
C(6)-C(7)	1.372(8)		
C(1)-H(1)	0.98(7)	C(2)-H(21)	1.01(7)
C(2)-H(22)	0.96(5)	C(2)-H(23)	0.98(7)
C(3)-H(3)	0.87(7)	C(4)-H(4)	0.86(7)
C(6)-H(6)	0.92(7)	C(7)-H(7)	0.85(7)
C(8)-H(81)	0.78(7)	C(8)-H(82)	1.00(7)
C(8)-H(83)	1.05(7)		

Table 2

Bond angles (°) for $C_{13}H_{11}CrNO_5$

O(11)-C(11)-Cr(1)	177.2(5)	O(12)-C(12)-Cr(1)	178.2(5)
O(13)-C(13)-Cr(1)	176.6(6)	O(14)-C(14)-Cr(1)	177.8(6)
O(15)-C(15)-Cr(1)	177.0(6)		
C(11)-Cr(1)-C(1)	178.4(3)	C(12)-Cr(1)-C(1)	92.5(2)
C(12)-Cr(1)-C(11)	87.9(2)	C(13)-Cr(1)-C(1)	91.6(2)
C(13)-Cr(1)-C(11)	90.0(3)	C(13)-Cr(1)-C(12)	90.4(2)
C(14)-Cr(1)-C(1)	87.8(2)	C(14)-Cr(1)-C(11)	90.6(3)
C(14)-Cr(1)-C(12)	92.9(3)	C(14)-Cr(1)-C(13)	176.7(3)
C(15)-Cr(1)-C(1)	87.7(2)	C(15)-Cr(1)-C(11)	92.0(3)
C(15)-Cr(1)-C(12)	178.4(3)	C(15)-Cr(1)-C(13)	88.0(3)
C(15)-Cr(1)-C(14)	88.8(3)		
C(3)-N(1)-C(1)	122.0(5)	C(7)-N(1)-C(1)	119.8(5)
C(7)-N(1)-C(3)	118.1(5)	N(1)-C(1)-Cr(1)	111.1(3)
C(2)-C(1)-Cr(1)	115.5(4)	C(2)-C(1)-N(1)	110.7(5)
C(4)-C(3)-N(1)	122.2(5)	C(5)-C(4)-C(3)	121.1(5)
C(6)-C(5)-C(4)	116.0(6)	C(8)-C(5)-C(4)	122.1(6)
C(8)-C(5)-C(6)	121.9(6)	C(7)-C(6)-C(5)	121.2(6)
C(6)-C(7)-N(1)	121.5(5)		
H(1)-C(1)-Cr(1)	110.1(39)	H(1)-C(1)-N(1)	103.3(40)
H(1)-C(1)-C(2)	105.2(39)	H(21)-C(2)-C(1)	104.3(40)
H(22)-C(2)-C(1)	116.6(30)	H(22)-C(2)-H(21)	113.8(47)
H(23)-C(2)-C(1)	112.3(40)	H(23)-C(2)-H(21)	108.3(52)
H(23)-C(2)-H(22)	101.6(48)	H(3)-C(3)-N(1)	116.5(45)
H(3)-C(3)-C(4)	121.3(45)	H(4)-C(4)-C(3)	118.7(46)
H(4)-C(4)-C(5)	119.8(46)	H(6)-C(6)-C(5)	122.0(44)
H(6)-C(6)-C(7)	116.7(44)	H(7)-C(7)-N(1)	116.3(46)
H(7)-C(7)-C(6)	122.2(46)	H(81)-C(8)-C(5)	105.1(53)
H(82)-C(8)-C(5)	103.0(40)	H(82)-C(8)-H(81)	143.2(63)
H(83)-C(8)-C(5)	122.3(39)	H(83)-C(8)-H(81)	87.8(56)
H(83)-C(8)-H(82)	96.9(50)		

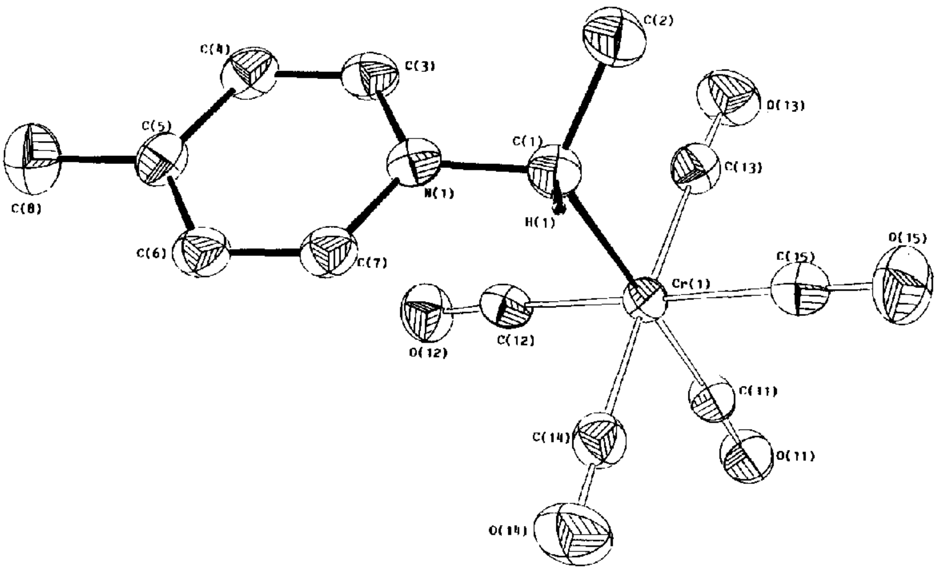
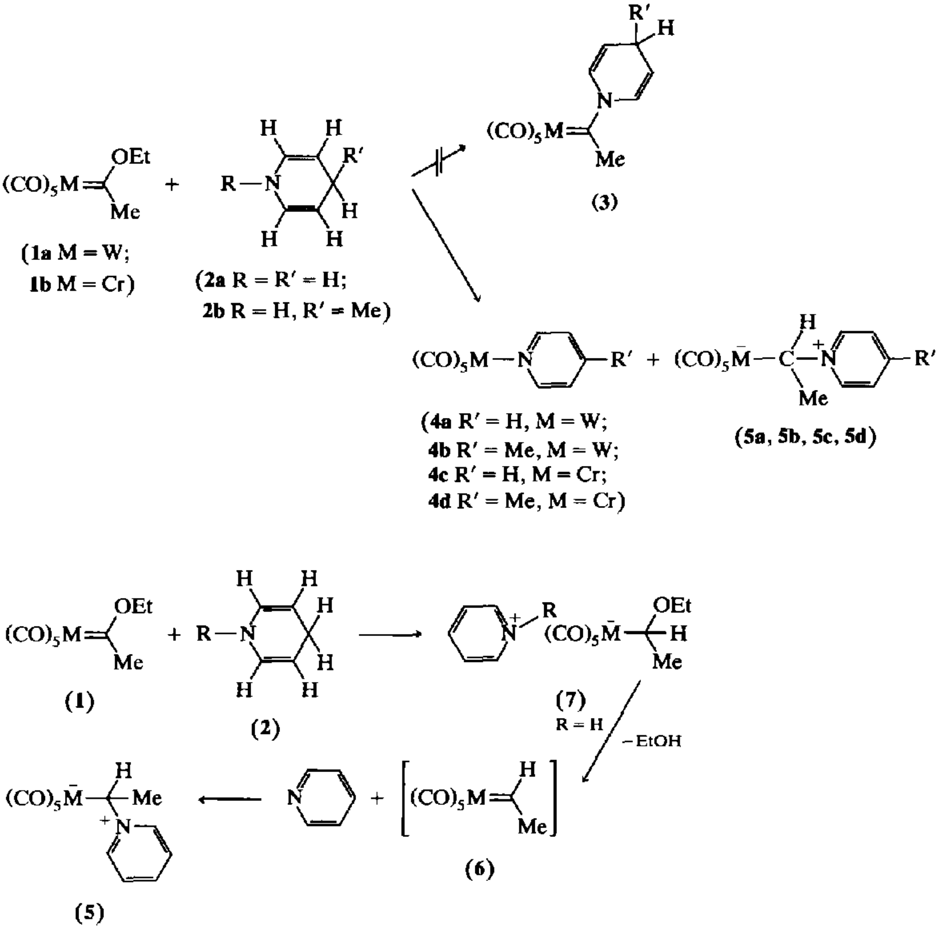


Fig. 1. ORTEP view of complex **5a** with the atom labelling scheme. Selected bond distances (Å) and angles (°): Cr(1)–C(1) 2.250(6); C(1)–N(1) 1.489(7); C(1)–C(2) 1.521(8); C(1)–H(1) 0.98(7); Cr(1)–C(1)–N(1) 111.1(3); Cr(1)–C(1)–C(2) 115.5(4); Cr(1)–C(1)–H(1) 110.1(39).

This communication shows that the second reaction, the hydride transfer, is observed, and reports the synthesis and X-ray crystal structure of $[(CO)_5WCH(Me)NC_5H_5\text{-}Me]$, which can be considered as the product of the interaction of methylpyridine with $[(CO)_5W{=}CH(Me)]$ (**6**).

When a solution of dihydropyridine **2a** [3] (R = H, R′ = H) in diethyl ether was added, at room temperature, to a solution of complex **1a** (M = W) in the same solvent, a deep-red color developed instantaneously. Two new more polar complexes were formed during the reaction, as determined by TLC. Evaporation of the solvent *in vacuo* followed by chromatography of the residue on silica gel, allowed their isolation and full characterization.

Besides complex **1a** (60% recovered), complex **4a** was obtained as yellow crystals, m.p. 114°C (7.5%). Both the elemental analysis and the ^1H and ^{13}C NMR spectra were consistent. The second complex, orange crystals (m.p. 127°C, 25%), appeared much more polar than classical aminocarbene complexes, and was given structure **5a** on the following grounds. The elemental analysis was consistent with replacement of the alkoxy group by 1,4-dihydropyridine. The ^1H NMR spectrum confirmed the disappearance of the ethoxy group and the presence of a pyridine group, with signals at δ 8.53 (d, 2H), 7.82 (t, 1H) and 7.58 (t, 2H). Moreover, the presence of a doublet at δ 2.33 (3H, $J = 7$ Hz) and a quartet at δ 4.88 (1H, $J = 7$ Hz) confirmed the addition of the hydride to the carbene carbon. The ^{13}C NMR spectrum, which displayed signals at 204.5, 201.9 (CO's), 139.2, 136.1, 126.6 (pyridine), 57.1 and 30.7 (CHMe), supported structure **5a**. Similar results were obtained from complex **1b** (M = Cr) which gave **5c** (18%), or from methyl-4 dihydropyridine **2b** and **1a** or **1b**, which led to **5b** (25%) and to **5d** (23%), respectively.



Scheme 1.

Crystals of **5b** (m.p. 62°C) suitable for an X-ray diffraction were grown from methylene chloride/hexane solutions. The structure (Fig. 1) * suggests a zwitterionic species, resulting formally from the interaction of **6** with methyl pyridine. In order to gain some insight into the mechanism of this reaction and on the sequence of the hydride-transfer and pyridine 1-addition steps, we synthesized *N*-methyl dihydropyridine **2c** and allowed it to react in methylene chloride with complex **1a**: again a fast reaction took place, leading to an orange oil. Since no crystals of this new complex have yet been obtained, its structure was established by NMR spectroscopy: a doublet associated with a methyl group, at δ 0.91 ppm, and a quartet for one proton at δ 3.10 ppm confirmed the transfer of a hydride

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* *Crystal data:* Compound **5d**: $C_{13}H_{11}CrNO_5$, $M = 313.2$, space group $P\bar{1}$, a 8.078(3), b 8.724(2), c 10.688(1) Å, α 105.85(2), β 100.45(2), γ 98.80(2)°, $Z = 2$, $\mu(\text{Mo-}K_\alpha)$ 8.17 cm^{-1}, D_0 1.49 g cm^{-3}. 2449 independent reflections were collected on a PW 1100 Philips diffractometer, 1698 reflections with $I > 3\sigma(I)$ were used to solve and refine the structure with the CRYSTALS package. Final $R = 0.0526$ and $R_W = 0.0537$. Full lists of structure factors, bond lengths and angles, and atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre.

from dihydropyridine to the carbene carbon. Moreover, the ethoxy group is still present in the new complex, with signals at δ 1.10 ppm (t, 3H) and at δ 3.57 and 3.23 (m, 2H) for the two diastereotopic hydrogen atoms. Thus dihydropyridines, like the complex hydride K $[HB(OR)_3]$, used by Casey *et al.* to reduce $[(CO)_5WC(Ph)OMe]$ to K $[(CO)_5WC(OMe)(Ph)H]$ [4], first transfer a hydride to the carbene carbon to give similar adduct **7**. However, when R = H, a concerted or non-concerted rearrangement with elimination of ethanol, lead finally to complex **5** (Scheme 1), probably via **6**.

Work is in progress to establish the exact mechanism of these new metal-carbene reduction reactions, and to try to use this approach for the preparation of cyclopropanes via (alkyl) H-substituted mononuclear carbene complexes [5].

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