An Unusual Reaction in the Course of Fischer Carbene Synthesis: Preparation and Structure of Vinylidenemolybdenum Complexes

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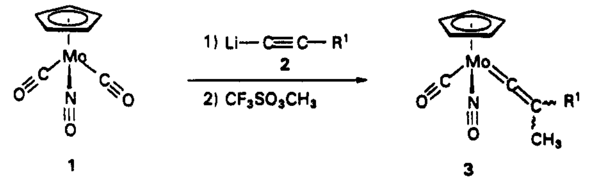
Summary: The reaction of [(η^5-C_5H_5)(CO)$_2$(NO)Mo] (1) with (phenylethynyl)lithium and subsequently with methyl trifluoromethanesulfonate led in 43% yield to {(η^5-C_5H_5)(CO)(NO)Mo[=C=C(CH_3)(Ph)]} (3a) as a 2:1 mixture of rotamers ($\Delta G^\ddagger$ = 20.5 (±0.3) kcal/mol). The anionic intermediate [(η^5-C_5H_5)(CO)(NO)(R^1CC)Mo]Li (7) is trapped by the reaction with HCl or acetic anhydride which yields vinylidene complexes {(η^5-C_5H_5)(CO)(NO)-Mo[=C=C(CH_3)(Ph)]} (5) and {(η^5-C_5H_5)(CO)(NO)-Mo[=C=C($COCH_3$)(Ph)]} (6) respectively. The X-ray analysis of {(η^5-C_5H_5)(CO)(NO)Mo[=C=C(CH_3)(Ph)]} is reported.

Introduction

The applications of Fischer-type metal carbene complexes in synthetic organic chemistry are manifold.[1] Not only the reactivity due to the metal–carbene functionality but also that of adjacent substituents[1] has shown possibilities of usefulness in a number of reactions. An area in need of further exploration is the use of chiral-at-metal carbene complexes in stereospecific synthesis.[2] In the course of an attempt to prepare the chiral carbene complexes 4 from molybdenum complex 1 by the general Fischer methodology for the preparation of alkoxycarbene complexes,[1] we have discovered an interesting pathway for the synthesis of vinylidenemetal complexes. In this communication we describe the synthesis of **3a**, **3b**, **5a**, and **6a** and the X-ray diffraction analysis of **3a**.

Results and Discussion

The reaction of acetylide **2a** with the molybdenum complexes 1 in THF at -30 °C led to a deep green solution. Treatment of this solution with trimethyloxonium tetrafluoroborate or preferentially with methyl trifluoromethanesulfonate afforded, after chromatography (silica gel; pentane:ether 3:1) and crystallization from pentane, vinylidene complex **3a** in 43% yield as an orange, air-stable crystalline product.[3] At room temperature, two rotamers are recognized in the product mixture with the ratio 2:1. This is evident from the ^1H NMR spectrum, which shows two signals for the CH_3 group at δ 2.01 and 2.09 (2:1), and from the ^{13}C NMR spectrum, with two distinct signals for C_α at δ 366.6 and 366.3, two CO signals at δ 217.1 and 217.7, and two C_β resonances at δ 134.3 and 134.7. **3a** shows a temperature-dependent ^1H NMR spectrum, and a $\Delta G^\ddagger$ = 20.5 (±0.3) kcal/mol was measured for the hindered rotation by dynamic NMR experiments. This amount of energy is considerably higher than those reported for comparable vinylidenemanganese complexes [(η^5-MeC_5H_4)Mn(CO)(PPh_3)(=C=CRR′)] (R = CH_3, R′ = H, 9.9 kcal/mol, R = CH_3, R′ = C_2H_5, 10.8 kcal/mol)[4] and is similar to the $\Delta G^\ddagger$ value for vinylidenerhenium compounds such as [(η^5-C_5H_5)Re^+(NO)(PPh_3)-(=C=CHR)] (R = C_6H_5, 21.5 ± 0.6 kcal/mol).[5] It is not possible to rigorously establish whether isomerization occurs via Mo=C_α or C_α=C_β bond rotation. However, since the alkene C=C rotation normally requires much higher temperatures, we assume that Mo=C_α bond rotation is occurring. It is interesting to note that the Fischer carbene complex **4a** could not be detected in this experiment.[6]



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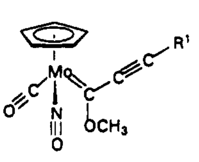

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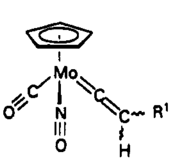

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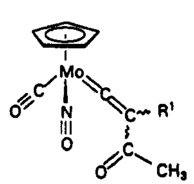

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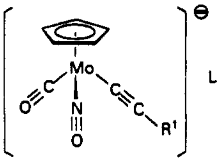
	R'
a	C_6H_5
b	p-Tolyl



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(3) A neutral vinylidenemolybdenum complex is prepared by the reaction of {Mo(≡$CCH_2{}^iPr$)[(P(OMe$_3$)]$_2$(η^5-C_5H_5)} with [4-$FC_6H_5N_2$]-[BF_4]; see: Baker, P. K.; Barker, G. K.; Gill, D. S.; Green, M.; Orpen, A. G.; Williams, D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* 1989, 1321–1331.

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The structure of product **3a** was further confirmed by X-ray crystallography. The ORTEP drawing is provided in Figure 1. Table 1 shows some data of the structure determination. In Tables 2 and 3 pertinent bond distances and angles are listed.

The bond distances and angles are comparable to other molybdenum vinylidene complexes like $\{(\eta^5\text{-}C_5H_5)Mo(C{=}CHPh)Br[P(OCH)_3]_2\}$.[7] Also the Mo—C(1) bond length of 1.937(4) Å is rather close to the Mo—vinylidene bond length in the former complex for which 1.917(5) Å is reported.

The formations of vinylidene complexes by alkylation or protonation of alkynyl transition metal compounds ($L_nMC{\equiv}CR$) or by a 1,2-hydrogen shift of η^2-alkyne complexes $L_nM(HC{\equiv}CR)$ are well recognized processes.[8,9] Considering the mild reaction conditions, an explanation for a low-energy pathway for dissociation of CO by the reaction of 18-electron complex **1** with acetylide **2a** is not obvious. We suggest that the reaction of **2a** with **1** proceeds *via* an associative or a single electron transfer (SET) induced dissociative process and produces ultimately after elimination of a CO molecule, the anionic alkynylmolybdenum complex **7** as an intermediate. This is subsequently alkylated by methyl trifluoromethanesulfonate to yield the vinylidene complex **3a**. The associative as well as the SET path could be facilitated owing to the strong π acceptor effect of the NO ligand of **1**.[10]

In analogy to the above transformation, the reaction of **1** with acetylide **2b** gave the vinylidene complex **3b** after alkylation with methyl trifluoromethanesulfonate in 53% yield. Although complexes **7a** or **7b** could not be isolated in the pure form due to their sensitivity, **7a** is trapped by using diluted HCl or acetic anhydride as the electrophile to give **5a** and **6a** in 41% and 19% yields, respectively.[11] As expected, due to the conjugation of the vinylidene CC double bond with the acetyl group, the vinylidene complex **6a** shows a lower activation energy for the hindered rotation ($\Delta G^{\ddagger} = 18.2 \pm 0.3$ kcal/mol).

Transition metal vinylidene complexes, $[L_nM{=}C{=}CRR']^{n+}$, have attracted considerable interest in the last decade.[8b,9] Surface bonded vinylidene complexes are postulated as intermediates in the Fischer–Tropsch process ("McCandlish mechanism"),[12] and they have been shown to be effective catalysts for acetylene polymerization[13] or condensation reactions.[14] Further, compounds containing metal–carbene double bonds exhibit unique and diverse reactivity.[1] However, compared to the use of the corresponding metal–carbene complexes, the application of transition metal vinylidene complexes in organic syntheses have only been limited to a few cases such as utilization in the preparation of β-lactams.[15] With the choice of the appropriate acetylides it is expected that synthetically useful vinylidene complexes of the group 6 elements can be prepared by this new method.

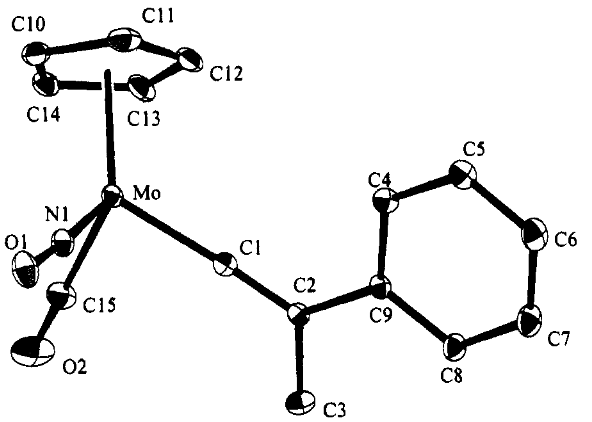

Figure 1. ORTEP structure of $\{(\eta^5\text{-}C_5H_5)(CO)(NO)Mo[{=}C{=}C(CH_3)(Ph)]\}$ (**3a**).

Our preliminary results show that the corresponding tungsten complexes behave similarly by the reaction with acetylides.[16]

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of argon (by Messer-Griesheim, 99.99%) with the use of standard Schlenk techniques. Solvents were purified by standard methods and distilled under argon prior to use. Literature methods were used to prepare $(\eta^5\text{-}C_5H_5)(CO)_2(NO)Mo$.[17] All other compounds were commercially available. NMR spectra were obtained on a Bruker AM 400 and AC 200 spectrometer. Proton and carbon chemical shifts are referred to tetramethylsilane. MS measurements (70 eV) were performed on a Varian MAT 311-A. IR spectra were recorded on a Bruker FT-IR IFS 85. Microanalyses were done on a Carlo Erba 1104 elemental analyzer.

$\{(\eta^5\text{-}C_5H_5)(CO)(NO)Mo[{=}C{=}C(CH_3)(Ph)]\}$ (3a). At −30 °C, a solution of 7.5 mmol of (phenylethynyl)lithium in 15 mL of THF was added dropwise to an orange solution of **1** (1.24 g, 5 mmol) in THF (50 mL). The progress of the reaction was monitored by IR. After complete disappearance of **1**, at −30 °C a solution of $CF_3SO_3CH_3$ (0.85 mL, 7.5 mmol, in 4 mL of THF) was added to the deep green reaction mixture, whereby the color changed to brown. After 1 h, the solution was concentrated under vacuum, and the residue was partitioned between ether and saturated aqueous sodium bicarbonate. After usual workup the residue was chromatographed (silica gel; pentane:ether 3:1) to yield 720 mg (43%) of **3a**, as orange crystals, mp 103–104 °C dec from pentane. Anal. Calcd for $C_{15}H_{13}MoNO_2$: C, 53.75; H, 3.91; N, 4.18. Found: C, 53.81; H, 3.65; N, 4.18. Two rotamers (ratio 1:2): ^1H NMR ($CDCl_3$) δ 7.43–7.14 (m, 5 H), 5.82 (s, 5 H, Cp), 2.09 and 2.01 (two s, 1:2, CH_3); ^{13}C NMR ($CDCl_3$) δ 366.6 and 366.3 (two C_α), 217.7 and 217.1 (two C=O), 135.4 (arom C), 134.7 and 134.3 (two C_β), 128.4, 126.6, 125.3, 124.9 (arom C), 97.4 and 97.0 (two Cp), 14.8 and 13.0 (two CH_3); IR (KBr) $\bar{\nu}$ (cm^{-1}) 2015 (C=O), 1625 (N=O); MS (70 eV) *m/e* 335 (M^+, ^{96}Mo), 307 (M^+

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Table 1. Crystal Structure Determination and Refinement of $\{(\eta^5\text{-}C_5H_5)(CO)(NO)Mo[{=}C{=}C(CH_3)(Ph)]\}$ (3a)

cryst dimens (mm), color and habit	0.25 × 0.10 × 0.10, orange red, transparent; pinacoidal
cryst syst	monoclinic
space group	$C2/c$ (No. 15)
lattice constants (from single crystal data)	
a (Å)	15.496(1)
b (Å)	12.061(1)
c (Å)	15.849(1)
β (deg)	106.362(7)
vol (Å^3)	2962.1(6)
formula units per unit cell (Z)	8
d (calc) (g/cm^3)	1.566
linear abs coeff (cm^{-1})	μ(Mo Kα) = 8.18
diffractometer	four-circle (AED-2; Siemens)
radiation (λ (Å))	Mo Kα (0.710 73)
monochromator	graphite
data collection	ω-scan using "learnt-profile" method,[a] room temperature
scan range (deg)	$6.0 \le \theta \le 70.0$
ind collected	$-23 \le h \le 23$; $-20 \le k \le 20$; $0 \le l \le 26$
no. of reflns collcd	12 836
no. of ind reflns	5834
no. of ind reflns $F_0 > 4\sigma(F_0)$	3464
applied corrections	Lorentz and polarization coefficients, no absorption
structure determination and refinement	Mo positional parameters from Patterson synthesis (program SHELXS-86;[b] R(PATT) = 0.371); further atoms from ΔF synthesis (program SHELX-76[c]); full-matrix least-squares refinement; anisotropic displacement coefficients for all non-hydrogen atoms; atomic scattering coefficient from footnote d
extinction correction[e]	Ex = 0.00022(2) (program SHELX-76)
no. of params	173 ($N_o/N_v = 20$)
$R = \sum\lVert F_o\rvert - \lvert F_c\rVert/\sum\lvert F_o\rvert$	0.045
$R_w = \sum w\lVert F_o\rvert - \lvert F_c\rVert/\sum w\lvert F_o\rvert$[f]	0.037

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Table 2. Selected Bond Distances (Å) for $\{(\eta^5\text{-}C_5H_5)(CO)(NO)Mo[{=}C{=}C(CH_3)(Ph)]\}$

Mo–C(1)	1.937 (4)	C(4)–C(9)	1.406 (5)
Mo–C(10)	2.375 (4)	C(5)–C(6)	1.408 (5)
Mo–C(11)	2.357 (5)	C(6)–C(7)	1.397 (5)
Mo–C(12)	2.366 (4)	C(7)–C(8)	1.409 (7)
Mo–C(13)	2.382 (4)	C(8)–C(9)	1.418 (6)
Mo–C(14)	2.385 (4)	C(10)–C(11)	1.427 (7)
Mo–C(15)	2.007 (5)	C(10)–C(14)	1.401 (7)
Mo–N(1)	1.787 (4)	C(11)–C(12)	1.439 (7)
C(1)–C(2)	1.316 (5)	C(12)–C(13)	1.423 (7)
C(2)–C(9)	1.488 (5)	C(13)–C(14)	1.435 (7)
C(2)–C(3)	1.522 (5)	C(15)–O(2)	1.134 (6)
C(4)–C(5)	1.403 (6)	N(1)–O(1)	1.198 (6)

Table 3. Selected Angles (deg) for $\{(\eta^5\text{-}C_5H_5)(CO)(NO)Mo[{=}C{=}C(CH_3)(Ph)]\}$

C(1)–Mo–C(10)	149.9 (2)	C(14)–Mo–C(15)	91.1 (2)
C(1)–Mo–C(11)	116.4 (2)	C(14)–Mo–N(1)	126.3 (2)
C(1)–Mo–C(12)	92.6 (2)	C(15)–Mo–N(1)	91.9 (2)
C(1)–Mo–C(13)	102.8 (2)	Mo–C(1)–C(2)	177.6 (5)
C(1)–Mo–C(14)	136.9 (2)	C(1)–C(2)–C(9)	121.2 (4)
C(1)–Mo–C(15)	87.0 (2)	C(3)–C(2)–C(9)	119.9 (4)
C(1)–Mo–N(1)	96.8 (2)	C(5)–C(4)–C(9)	120.8 (4)
C(10)–Mo–C(15)	116.7 (2)	C(2)–C(9)–C(4)	121.1 (4)
C(10)–Mo–N(1)	100.5 (2)	C(11)–C(10)–C(14)	109.4 (5)
C(11)–Mo–C(15)	149.2 (2)	C(10)–C(11)–C(12)	106.5 (5)
C(11)–Mo–N(1)	103.9 (2)	C(11)–C(12)–C(13)	108.6 (4)
C(12)–Mo–C(15)	131.8 (2)	C(12)–C(13)–C(14)	107.3 (5)
C(12)–Mo–N(1)	135.8 (2)	C(10)–C(14)–C(13)	108.2 (5)
C(13)–Mo–C(15)	98.4 (2)	Mo–C(15)–O(2)	179.4 (5)
C(13)–Mo–N(1)	158.3 (2)	Mo–N(1)–O(1)	175.9 (5)

– CO), 277 (M$^+$ – CO – NO); high resolution mass spectrum calcd for $C_{15}H_{13}{}^{100}MoNO_2$ (M$^+$) *m/e* 339.0021, found *m/e* 339.0037.

$\{(\eta^5\text{-}C_5H_5)(CO)(NO)Mo[{=}C{=}C(CH_3)(p\text{-tolyl})]\}$ (3b). The preparation of **3b** is analogous to that for **3a**, instead of (phenylethynyl)lithium (*p*-tolylethynyl)lithium was used. Yield: 925 mg (53%). Mp: 89–90 °C dec. Anal. Calcd for $C_{16}H_{15}MoNO_2$: C, 55.03; H, 4.33; N, 4.01. Found: C, 55.42; H, 4.12; N, 4.01. Two rotamers: ^{1}H NMR (CDCl$_3$) δ 7.32–7.1 (m, 4 H), 5.81 (s, 5 H, Cp), 2.33 and 2.31 (two s, 2:1, CH$_3$), 2.07 and 2.00 (two s, 2:1, CH$_3$); ^{13}C NMR (CDCl$_3$) δ 366.9 and 366.6 (two C$_\alpha$), 217.9 and 217.3 (two C=O), 136.4 (arom C), 134.7 and 134.3 (two C$_\beta$), 132.3, 129.2, 125.2, 124.9 (arom C), 97.4 and 97.0 (two Cp), 21.1 (CH$_3$), 14.8 and 13.0 (two CH$_3$); IR (CCl$_4$) $\tilde{\nu}$ (cm^{-1}) 2018 (C=O), 1657 (N=O), 1622 (C=C); MS (70 eV) *m/e* 349 (M$^+$, ^{96}Mo), 321 (M$^+$ – CO), 291 (M$^+$ – CO – NO); high resolution mass spectrum calcd for $C_{16}H_{15}{}^{92}MoNO_2$ (M$^+$) *m/e* 345.0171, found *m/e* 345.0141.

$\{(\eta^5\text{-}C_5H_5)(CO)(NO)Mo[{=}C{=}C(H)(Ph)]\}$ (5). The procedure was analogous to that for **3a**; instead of CF$_3$SO$_3$CH$_3$, 1 mL of concentrated HCl diluted with 20 mL of water was added. Yield: 660 mg (41%). Mp: 101–102 °C dec. Anal. Calcd for $C_{14}H_{11}MoNO_2$: C, 52.35; H, 3.45; N, 4.36. Found: C, 52.73; H, 3.20; N, 4.35. Two rotamers: ^{1}H NMR (CDCl$_3$) δ 7.30–7.11 (m, 5 H), 6.95 and 6.90 (two s, 2:3, C$_\beta$-H), 5.85 and 5.83 (two s, 3:2, Cp); ^{13}C NMR (CDCl$_3$) δ 366.7 and 366.5 (two C$_\alpha$), 217.3 and 215.9 (two C=O), 133.4, 128.7 (arom C), 129.1 and 128.6 (two C$_\beta$), 126.7, 126.0, 125.8 (arom C), 97.4 and 97.3 (two Cp); IR (KBr) $\tilde{\nu}$ (cm^{-1}) 2028 (C=O), 1646 (N=O); MS (70 eV) *m/e* 321 (M$^+$, ^{96}Mo), 293 (M$^+$ – CO), 263 (M$^+$ – CO – NO).

$\{(\eta^5\text{-}C_5H_5)(CO)(NO)Mo[{=}C{=}C(COCH_3)(Ph)]\}$ (6). The procedure was analogous to that for **5**; instead of diluted HCl, 1 mL of acetic anhydride was added at –70 °C. After warming to room temperature in 12 h, the solution was concentrated under vacuum and the brown residue was suspended in 100 mL of ether. After filtration this solution was concentrated under vacuum and chromatographed (silica gel; pentane:ether 10:1 and 1:1) to yield 335 mg (19%) of **6**; mp 94–95 °C dec. Anal. Calcd for $C_{16}H_{13}MoNO_3$: C, 52.91; H, 3.61; N, 3.86. Found: C, 53.43; H, 3.30; N, 3.88. Two rotamers: ^{1}H NMR (CDCl$_3$) δ 7.41–7.19 (m, 5 H), 5.88 and 5.74 (two s, 3:2, Cp), 2.48 and 2.41 (two s, 3:2, CH$_3$); ^{13}C NMR (CDCl$_3$) δ 375.4 and 374.0 (two C$_\alpha$), 215.2 and 213.9 (two C=O), 194.7 (C=O), 144.9, 131.9, and 130.9 (two C$_\beta$), 128.9, 128.1, 127.2, 98.1, and 97.6 (two Cp), 30.4 and 30.3 (two CH$_3$); IR (CCl$_4$) $\tilde{\nu}$ (cm^{-1}) 2030 (C=O), 1674 (N=O); MS (70 eV) *m/e* 363 (M$^+$, ^{96}Mo), 335 (M$^+$ – CO), 305 (M$^+$ – CO – NO); high resolution mass spectrum calcd for $C_{16}H_{13}{}^{92}MoNO_3$ (M$^+$) *m/e* 358.9964, found *m/e* 358.9979.

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Supplementary Material Available: Tables of atomic coordinates and bond lengths and angles for **3a** (2 pages). Ordering information is given on any current masthead page.

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