Reactions of Complex Ligands, LXV[◇]

Vinylidene and Methoxy(alkynyl)carbene Molybdenum Complexes: Competitive Formation During Fischer Carbene Complex Synthesis and Crystal Structure Determination

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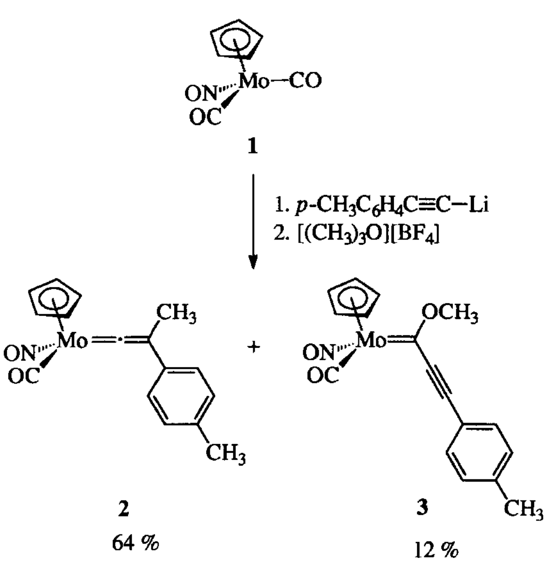
Reaction of $[(\eta^5\text{-}C_5H_5)(CO)_2(NO)Mo]$ (**1**) with alkynyllithium and $[(CH_3)_3O]BF_4$ affords the vinylidene-molybdenum complex **2** along with the methoxy(alkynyl)carbene molybdenum complex **3**. Both compounds are characterized by an X-ray crystal structure analysis. Due to axial and central chirality in the $L_nM{=}C{=}CR_2$ moiety complex **2** is formed as a 2:1 mixture of two diastereomers. The formation of **2** and **3** can be understood in terms of a competitive attack of alkynyllithium at the carbonyl ligand and the molybdenum center.

The manifold applications of Fischer-type carbene complexes in organic synthesis[2] have been extended to stereoselective synthesis by the use of compounds bearing chiral side chains at the carbene carbon center[3]. On the other hand carbene complexes with an α-alkynyl functionality have become valuable reagents for Michael-type addition and cycloaddition reactions[4]. We aimed at a combination of chirality and α-C≡C triple bond elements[5] and focussed our attention on half-sandwich molydenum complexes $CpMoL^1L^2L^3$ bearing a chiral metal center[6]. In a recent independent study, Ipaktschi et al.[7] have reported that the addition of arylalkynyllithium reagents to dicarbonyl(cyclopentadienyl)(nitrosyl)molybdenum **1** according to the customary Fischer methodology[8] does not generate the alkynylcarbene complex expected from nucleophilic addition to a carbonyl ligand but, surprisingly, instead affords vinylidene complexes with concomitant decarbonylation.

Preparative Results

In our hands, the addition of (*p*-tolyl)ethynyllithium to the dicarbonyl(nitrosyl) molybdenum complex **1** followed by alkylation with $[(CH_3)_3O]BF_4$ exhibits a competitive formation of both the vinylidene complex **2**[7,9] and the Fischer carbene complex **3** which were isolated in 64% and 12% yields after chromatographic workup. Both complexes were characterized by IR and NMR spectra. In comparison with **2**, the strong IR absorptions for **3** due to the CO and NO stretching vibrations are shifted to distinctly higher frequencies ($\Delta = 35\ cm^{-1}$) indicating that the alkynylcarbene ligand is a more potent donor than the vinylidene congener. The vinylidene complex **2** exhibits at room temperature a double set of signals in the ^1H- and ^{13}C-NMR spectra which demonstrates the existence of two diastereomers in a 2:1 ratio. This is due to the combination of two stereogenic elements along the $L^1L^2L^3Mo{=}C{=}CR^1R^2$ moiety of the molecule: the axial chirality of the metalla-allene unit and the central chirality at the metal. On the basis of dynamic NMR studies carried out on the phenyl homolog of **2** established a rotational barrier for the interconversion of both diastereomers involving a rotation around either the formal M=C or the C=C bond of $\Delta G^{\neq} = 20.5\ (\pm 0.3)$ kcal/mol[7].

Scheme 1



Crystal Structure Determination

The molecular structures of **2** (Figure 1) and **3** (Figure 2) were confirmed by X-ray single-crystal structure analysis. The structure determination and refinement of **2** result in two independent molecules (Figure 1, annotations a and b, only one of two independent molecules is presented) per asymmetric unit which slightly differ in the trigonal-planar coordination of C(2). For both compounds a

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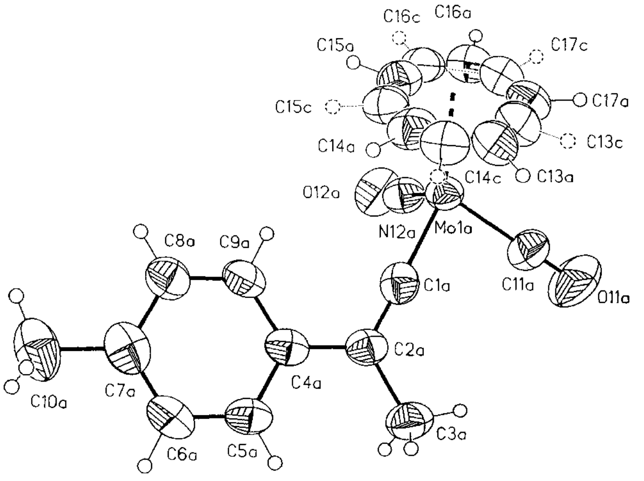
disorder of the cyclopentadienyl rings is observed (**2**: Figure 1, annotations c and d, a/c = 58 : 42, b/d = 65 : 35; **3**: Figure 2, annotations a and b, a/b = 52 : 48). A discrimination between the CO and NO ligands is based on their different bond lengths to molybdenum.

The bond lengths and bond angles in the vinylidene complex **2** are comparable to those reported for the corresponding phenyl derivative[7]. Both the Mo–C(1)–C(2) moiety in **2** and the alkyne fragment C(1)–C(2)–C(3)–C(4) in **3** are close to linear as previously observed for two other alkynylcarbene complexes[10] which have been structurally characterized. The carbene carbon atom is coordinated by Mo(1), C(2), and O(11) in a trigonal-planar fashion accompanied by a *Z* configuration across the carbene-oxygen bond.

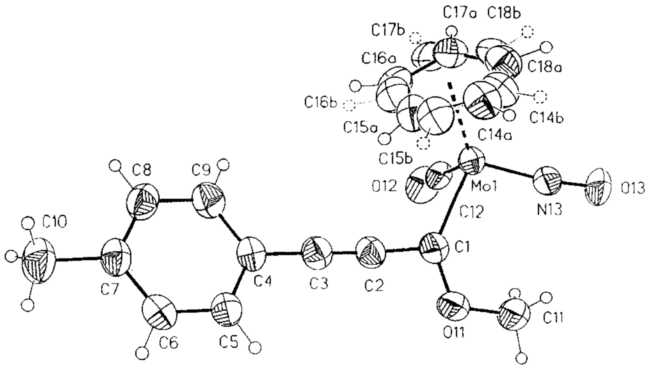
The superior donor ability of the alkynylcarbene ligand to the vinylidene ligand is also evident from the structural data obtained for the solid state: In comparison with **2**, the molybdenum-carbene bond in **3** is lenghtened by 0.11 Å while the molybdenum-carbonyl distance is slightly shortened.

Figure 1. Molecular structure of **2**. Cyclopentadienyl rings are disordered having two orientations [a/c = 58(1) : 42(1) and b/d = 65(1) : 35(1)].



Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°] in a and [b]: Mo(1a)–C(1a) 1.928(6) [1.929(6)], C(1a)–C(2a) 1.323(8) [1.324(7)], Mo(1a)–C(11a) 2.013(7) [2.035(7)], Mo(1a)–N(12a) 1.793(5) [1.804(5)], C(11a)–O(11a) 1.138(7) [1.115(7)], O(12a)–N(12a) 1.190(6) [1.192(6)], Mo(1a)–C(1a)–C(2a) 177.2(4) [175.2(5)], Mo(1a)–C(11a)–O(11a) 179.7(7) [178.7(6)], Mo(1a)–N(12a)–O(12a) 175.4(5) [174.3(4)].

Figure 2. Molecular structure of **3**. Cyclopentadienyl ring is disordered having two orientations [a/b = 52(2) : 48(2)].

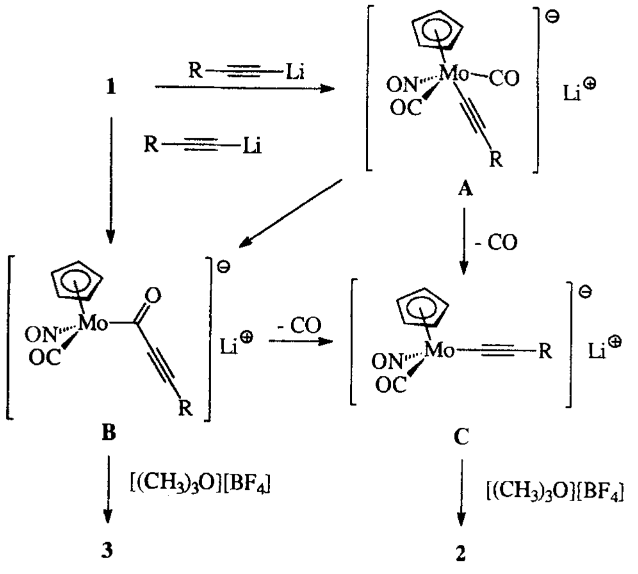


Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Mo(1)–C(1) 2.043(3), Mo(1)–C(12) 1.997(4), Mo(1)–N(13) 1.790(3), C(1)–C(2) 1.425(5), C(2)–C(3) 1.199(5), C(3)–C(4) 1.437(5), C(1)–O(11) 1.344(4), C(12)–O(12) 1.149(4), N(13)–O(13) 1.193(3), Mo(1)–C(1)–C(2) 117.2(2), Mo(1)–C(1)–O(11) 134.9(2), Mo(1)–C(12)–O(12) 177.5(3), Mo(1)–N(13)–O(13) 172.3(2), C(2)–C(1)–O(11) 107.8(3), C(1)–C(2)–C(3) 176.5(4), C(2)–C(3)–C(4) 177.6(4).

Discussion of the Reaction Mechanism

One mechanistic rationale for the formation of the alkynylcarbene complex **3** according to the customary Fischer synthesis along with the vinylidene complex **2** can be based on a competitive addition of the organolithium nucleophile to the molybdenumcarbonyl complex **1** (Scheme 2): Nucleophilic alkynylation of the carbonyl ligand affords the acyl molybdate **B** which is subsequently alkylated at the oxygen terminus to give the Fischer type carbene complex **3**. Alternatively, an attack of the alkynyllithium reagent at the metal center is expected to generate a labile 20-electron intermediate **A** which either may undergo decarbonylation to give the σ-alkynyl species **C** or again may lead to the acyl intermediate **B** either via CO insertion into the molybdenum-alkynyl bond or via alkynyl migration to the carbonyl ligand[11]. The σ-alkynyl intermediate **C** which also may be generated from the acyl molybdate **B** by decarbonylation[12] is known to undergo alkylation at the β-carbon atom[13] giving rise to the formation of the vinylidene complex **3**.

Scheme 2



R = p-$CH_3C_6H_4$-

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Experimental

All operations were carried out in flame-dried glassware under argon. Tetrahydrofuran (THF) was freshly distilled from potassium sodium alloy before use. – Column chromatography was accomplished with Merck silica gel (Type 60, 0.063–0.200 mm) and petroleum ether (PE) fraction 40–60°C. – ^{1}H and ^{13}C NMR: Bruker AM 400. – IR: Nicolet Magna 550. – MS: Varian MAT CH7A. – Elemental analysis: Heraeus CHN-Rapid.

4-Methylphenylethyne[14] and dicarbonylcyclopentadienylnitrosylmolybdenum(0) (**1**)[15] were synthesized according to literature procedures.

Procedure: 0.64 ml (0.58 g, 5.00 mmol) of 4-methylphenylethyne was lithiated with 5.00 mmol (3.13 ml of a 1.6 M solution in hexane) of *n*-butyllithium in 20 ml of THF at –50°C. This mixture was added to a solution of 1.23 g (5.00 mmol) of molybdenum complex **1** in 10 ml of THF at –78°C. The colour of the mixture changed immediately from orange to dark brown. After stirring for 1 h at –78°C the reaction mixture was warmed up to –10°C and then stirred for further 30 min. After removal of the solvent at 0°C the residue was dissolved in 20 ml of CH_2Cl_2, and 1.47 g (10.0 mmol) of trimethyloxonium tetrafluoroborate was added at –50°C to the solution. The mixture was stirred for 20 h while allowed to warm to room temp. After filtration (silica gel) 5 g of silica gel was added and the solvent was removed in vacuo. The residue was put on top of a column filled with silica gel, and 60 mg (0.24 mmol, 5%) of the starting material **1** (orange crystals) was eluted as the first orange band with PE/CH_2Cl_2 (3 : 1) at 0°C. Further elution and stepwise change of the solvent to PE/CH_2Cl_2 (1 : 1) yielded 1.11 g (3.18 mmol, 64%) of vinylidene complex **2** (orange crystals) as the second band. Finally, 230 mg (0.61 mmol, 12%) of the carbene complex **3** (orange crystals) was eluted.

Single crystals of **2** and **3** were obtained by slow diffusion of PE into ethereal solutions at –20°C via the gas phase.

Carbonylcyclopentadienyl[2-(4-methylphenyl)-1-propene-1-ylidene]nitrosylmolybdenum(0) (**2**): IR (PE): $\tilde{\nu}$ = 2017 s (CO), 1670 s (NO) cm^{-1}. – MS (70 eV, reg. ^{98}Mo), *m*/*z* (%): 351 (9) [M$^+$], 323 (47) [M$^+$ – CO], 293 (100) [M$^+$ – CO – NO], 286 (20) [M$^+$ – C_5H_5], 258 (3) [M$^+$ – C_5H_5 – CO]. – ^{1}H NMR ($CDCl_3$), isomer A: δ = 2.01 (s, 3H, 3-CH_3), 2.36 (s, 3H, $C_6H_4CH_3$), 5.83 (s, 5H, C_5H_5), 7.12–7.15 (m, 2H, C_6H_4), 7.29–7.33 (m, 2H, C_6H_4). – Isomer B: δ = 2.09 (s, 3H, 3-CH_3), 2.33 (s, 3H, $C_6H_4CH_3$), 5.83 (s, 5H, C_5H_5), 7.12–7.15 (m, 2H, C_6H_4), 7.29–7.33 (m, 2H, C_6H_4). – Isomer A/isomer B = 65 : 35 (by integration of the 3-CH_3 signals). – ^{13}C{^{1}H} NMR, ($CDCl_3$), isomer A: δ = 366.83 (C-1), 217.30 (CO), 136.30 (*para*-C), 134.15 (C-2) 132.17 (*ipso*-C), 129.10 (*meta*-CH), 124.72 (*ortho*-CH), 97.31 (C_5H_5), 21.00 ($C_6H_4CH_3$), 14.75 (3-CH_3). – Isomer B: δ = 366.49 (C-1), 217.94 (CO), 136.27 (*para*-C), 134.55 (C-2) 132.17 (*ipso*-C), 129.10 (*meta*-CH), 125.08 (*ortho*-CH), 96.98 (C_5H_5), 21.06 ($C_6H_4CH_3$), 12.94 (3-CH_3). – $C_{16}H_{15}MoNO_2$ (349.24): Mol. mass 351 (MS, reg. ^{98}Mo).

Carbonylcyclopentadienyl[methoxy(4-methylphenyl)ethynylcarbene]nitrosylmolybdenum(0) (**3**): IR (PE): $\tilde{\nu}$ = 1982 s (CO), 1645 s (NO) cm^{-1}. – MS (70 eV, reg. ^{98}Mo), *m*/*z* (%): 379 (31) [M$^+$], 351 (55) [M$^+$ – CO], 336 (29) [M$^+$ – CO – CH_3], 321 (26) [M$^+$ – CO – NO], 308 (98) [M$^+$ – CO – $COCH_3$], 293 (31) [M$^+$ – CO – $COCH_3$ – CH_3], 278 (100) [M$^+$ – CO – NO – $COCH_3$]. – ^{1}H NMR ($CDCl_3$): δ = 2.36 (s, 3H, $C_6H_4CH_3$), 4.37 (s, 3H, OCH_3), 5.78 (s, 5H, C_5H_5), 7.14–7.17 (m, 2H, C_6H_4), 7.31–7.35 (m, 2H, C_6H_4). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 292.01 (Mo=C), 223.29 (CO), 140.20 (*para*-C), 131.39 (*meta*-CH), 130.58 ($C{\equiv}C{-}C_6H_4$), 129.44 (*ortho*-CH), 118.98 (*ipso*-C), 99.02 (C_5H_5), 97.54 ($C{\equiv}C{-}C_6H_4$), 65.47 (OCH_3), 21.64 ($C_6H_4CH_3$). – $C_{17}H_{15}MoNO_3$ (377.25): Calcd. C 54.13, H 4.01, N 3.71; found C 54.02, H 4.29, N 3.64. – Mol. mass calcd. 379.0106, found 379.0118 (HRMS, reg. ^{98}Mo).

Crystal Data and Structure Refinement for **2**[16]: $C_{16}H_{15}MoNO_2$, M = 349.2, orange plates, crystal size 0.55 × 0.50 × 0.10 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 18.964(4), b = 11.109(2), c = 14.354(3) Å, β = 92.89(2)°, V = 3020(1) Å^3, Z = 8, $d_{\text{calcd.}}$ = 1.54 g cm^{-3}, μ(Mo-K$_\alpha$) = 0.87 mm^{-1}, $F(000)$ = 1408. The data set was collected on a Nicolet R3m diffractometer at T = 293(2) K by using graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å, 2 $\theta_{\text{max.}}$ = 50°, $0 \le h \le 22$, $-13 \le k \le 0$, $-17 \le l \le 17$, ω scans, 3 standard reflections measured after every 147 reflections as an intensity check, variation of standards ±1%). A total of 5519 reflections were collected, 5347 out of them were symmetry-independent reflections (R_{int} = 0.045). The structure was solved by direct methods (SHELXTL-PLUS)[17] and the refinement was done by the SHELXL-93 program[18] using full-matrix least-squares refinement on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms and hydrogens were refined by using a riding model. Disordered cyclopentadienyl groups were refined by use of ideal geometry contraints (C–C distances 1.42 Å, angles 108.0°). Absorption correction was performed semiempirically from ψ scans (max. and min. transmissions: 0.989 and 0.818). Data / restraints / parameters: 5347 / 336 / 421; goodness-of-fit on F^2: 0.89; final R indices w$R2$ = 0.114 [R_1 = 0.046 for $I > 2\sigma(I)$]; largest difference peak and hole: 0.69 and –0.65 eÅ^{-3}.

Crystal Data and Structure Refinement for **3**[16]: $C_{17}H_{15}MoNO_3$, M = 377.2, orange plates, crystal size 0.80 × 0.45 × 0.08 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 11.814(4), b = 6.128(2), c = 22.906(8) Å, β = 104.22(3)°, V = 1607.6(9) Å^3, Z = 4, $d_{\text{calcd.}}$ = 1.56 g cm^{-3}, μ(Mo-K$_\alpha$) = 0.83 mm^{-1}, $F(000)$ = 760. Data collection on a Nicolet R3m diffractometer at T = 293(2) K using graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å, 2 $\theta_{\text{max.}}$ = 50°, $0 \le h \le 14$, $0 \le k \le 7$, $-27 \le l \le 26$, ω scans, 3 standard reflections measured after every 147 reflections, variation of standards ±1%). 2977 reflections were collected, 2830 out of them were symmetry-independent reflections (R_{int} = 0.026). Structure solution and refinement identical with compound **2**. Semiempirical absorption correction from ψ scans (max. and min. transmissions: 0.849 and 0.756). Data / restraints / parameters: 2830 / 180 / 228; goodness-of-fit on F^2: 1.00; final R indices w$R2$ = 0.081 [R_1 = 0.030 for $I > 2\sigma(I)$]; largest difference peak and hole: 0.51 and –0.73 eÅ^{-3}.

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