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 $[(q^5\text{-C}_5\text{H}_5)](\text{CO})_2(\text{NO})\text{Mo} \quad (1)$ with alkynyllithium and $[(\text{CH}_3\text{O})\text{BF}_4]$ 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 $L,M=C=CR_2$ 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.

Preparative Results

In our hands, the addition of (p-tolyl)ethynyllithium to the dicarbonyl(nitrosyl)molybdenum complex 1 followed by alkylation with $[(\text{CH}_3\text{O})\text{BF}_4]$ exhibits a competitive formation of both the vinylidene complex 2 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 ($A = 35 \text{ cm}^{-1}$) 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 $^1\text{H}$- and $^{13}\text{C}$-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 $L_1L_2L_3\text{Mo}=C=CR_2R_2$ 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 $\text{M}=C$ or the $C=C$ bond of $\Delta G^*=20.5 \pm 0.3 \text{ kcal/mol}[7]$. 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
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(l), 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 lengthened by 0.11 Å while the molybdenum-carbonyl distance is slightly shortened.

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 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 which either may undergo decarbonylation to give the o-alkynyl species or again may lead to the acyl intermediate either via CO insertion into the molybdenum-alkynyl bond or via alkynyl migration to the carbonyl ligand\(^{(11)}\). The σ-alkynyl intermediate which also may be generated from the acyl molybdate by decarbonylation\(^{(12)}\) is known to undergo alkylation at the β-carbon atom\(^{(13)}\) giving rise to the formation of the vinylidene complex 3.

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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. – 1H and 13C NMR: Bruker AM 400. – IR: Nicolet Magna 550. – MS: Varian MAT CH7A. – Elemental analysis: Heraeus CHN-Rapid.

4-Methylphenylethynylidene[nitrosylmolybdenum(O)] and dicarbonylcyclopentadienylnitrosylmolybdenum(0) (1)[13] were synthesized according to literature procedures.

Procedure: 0.64 ml (0.58 g, 5.00 mmol) of 4-methylphenylethynylidene 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 -78°C. This mixture was stirred for 20 h while allowed to warm to room temp. After filtration (silica gel) 5519 reflections were collected, 5347 out of them were symmetry-independent reflections (Rint = 0.045). The structure was solved by direct methods (SHEXL-PLUS)


Crystal Data and Structure Refinement for 3[15]; C17H15MoNO2, M = 377.2, orange plates, crystal size 0.55 x 0.08 x 0.08 mm, monoclinic, space group P21/c (No. 14), a = 3.1914(4) Å, b = 6.128(2) Å, c = 22.909(2) Å, β = 104.22(3)°, V = 1607.69(2) Å3, Z = 4, dcalc = 1.56 g cm⁻³, µ(Mo-Kα) = 0.83 mm⁻¹, F(000) = 760. Data collection on a Nicolet R3m diffractometer at T = 293(2) K using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å, 2θmax = 50°, 0 ≤ θ ≤ 22, -27 ≤ θ ≤ 27, 0 ≤ ω ≤ 30°). Absorption correction was performed semiempirically from ψ scans (max. and min. transmissions: 0.899 and 0.818). Data / restraints / parameters: 5347 / 336 / 421; goodness-of-fit on F²: 0.89; final R indices wR2 = 0.114 [R1 = 0.046 for I > 2 σ(I)]; largest difference peak and hole: 0.69 and -0.65 e Å⁻³.


Crystal Data and Structure Refinement for 3[17]; C17H15MoNO2, M = 377.2, orange plates, crystal size 0.55 x 0.08 x 0.08 mm, monoclinic, space group P21/c (No. 14), a = 3.1818(5) Å, b = 6.128(2) Å, c = 22.909(2) Å, β = 104.22(3)°, V = 1607.69(2) Å3, Z = 4, dcalc = 1.56 g cm⁻³, µ(Mo-Kα) = 0.83 mm⁻¹, F(000) = 760. Data collection on a Nicolet R3m diffractometer at T = 293(2) K using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å, 2θmax = 50°, 0 ≤ θ ≤ 14, 0 ≤ k ≤ 7, -17 ≤ l ≤ 26, 0 ≤ ω ≤ 30°). Absorption correction was performed semiempirically from ψ scans (max. and min. transmissions: 0.899 and 0.818). Data / restraints / parameters: 5347 / 336 / 421; goodness-of-fit on F²: 0.89; final R indices wR2 = 0.081 [R1 = 0.030 for I > 2 σ(I)]; largest difference peak and hole: 0.69 and -0.65 e Å⁻³.
