2566 *Organometallics* **1994**, *13*, 2566-2568

Synthesis and Reactivity of $[MoCl(CO)_2(\eta^3\text{-}CH_2C(COCl)C{=}CH_2)L_2]$ (L_2 = 2,2′-Bipyridine, 1,10-Phenanthroline): Crystal Structure of $[Mo(\eta^2\text{-}ClCH_2C{\equiv}CCH_2Cl)(CO)(O_2CCF_3)_2(1,10\text{-phenanthroline})]$

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Received January 25, 1994[●]

Summary: Reaction of $Ph_4P[MoCl(CO)_3L_2]$ with excess 1,4-dichlorobut-2-yne at room temperature gave high yields of the neutral complexes $[MoCl(CO)_2(\eta^3\text{-}CH_2C(COCl)C{=}CH_2)L_2]$ (L_2 = 2,2′-bipyridine, 1,10-phenanthroline), containing a 2-substituted η^3-bonded trans-butadienyl ligand, while analogous reactions carried out in the presence of methanol and tetrahydrofuran gave complexes of the type $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CO_2Me)CMe(OMe))L_2]$. Reactions of $[MoCl(CO)_2(\eta^3\text{-}CH_2C(COCl)C{=}CH_2)L_2]$ with primary or secondary amines or with methanol have been investigated. Reactions of $[Mo(CO)_2(\eta^3\text{-}CH_2C(COCl)C{=}CH_2)(1,10\text{-phenanthroline})]$ with excess sodium trifluoroacetate in the presence of silver ions yields either the carboxylate derivative containing the $\eta^3\text{-}CH_2C(CO_2COCF_3)C{=}CH_2$ ligand or, in the presence of excess 1,4-dichlorobut-2-yne, the complex $[Mo(\eta^2\text{-}ClCH_2C{\equiv}CCH_2Cl)(CO)(O_2CCF_3)_2(1,10\text{-phenanthroline})]$. The crystal structure of the latter complex has been determined by X-ray diffraction.

In an extension of previous investigations[1] into the reactivity of $Ph_4P[MoCl(CO)_3(2,2'\text{-bipyridine})]$ with 1,4-dichlorobut-2-yne, we described recently the formation of the complexes $[Mo(CO)_2(\eta^3\text{-}CH_2C(CONRR')C{=}CH_2)L_2X]$ (L_2 = 2,2′-bipyridine, 1,10-phenanthroline; X = Cl, $C_3F_7CO_2$) from analogous reactions carried out in the presence of an excess of either primary or secondary amines HNRR′.[2,3] X-ray structural analyses of two representative complexes revealed the stereochemistry of the functionalized η^3-bonded *trans*-butadienyl groups in these pseudooctahedral complexes.[1,2] We now report the isolation of an intermediate complex in these reactions and describe an initial investigation of its reactivity.

Treatment of $Ph_4P[MoCl(CO)_3L_2]$ with an excess of 1,4-dichlorobut-2-yne at room temperature yielded products of the general formula $[MoCl(CO)_2(\eta^3\text{-}CH_2C(COCl)C{=}CH_2)L_2]$ (L_2 = 2,2′-bipyridine (**1a**), 1,10-phenanthroline (**1b**)) in high yield.[4] Reaction of **1a** or **1b** with excess amine HNRR′ (R = H, R′ = (−)-CH(Me)(Ph); R = R′ = Et) or methanol in dichloromethane produced complexes of the type $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CONRR')C{=}CH_2)L_2]$ or $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CO_2Me)C{=}CH_2)L_2]$, respectively (Scheme 1). The IR and ^1H and ^{13}C NMR spectroscopic data recorded at ambient temperature for solutions of these complexes in CD_2Cl_2 were in accord with the presence of *trans*-η^3-butadienyl ligands and gave no evidence of more than one isomeric form or any rearrangement process found for some $[Mo(\eta^3\text{-allyl})(CO)_2L_2X]$ (L_2 = neutral bidentate ligand; X = halide, carboxylate) complexes.[5]

In the presence of a 2-fold molar excess of sodium trifluoroacetate, an acetone solution of 1 mol of pure **1b** reacted at room temperature with 2 mol of silver tetrafluoroborate to form an orange microcrystalline complex, which was identified by NMR and IR methods as $[Mo(CO)_2(\eta^3\text{-}CH_2C(CO_2COCF_3)C{=}CH_2)(1,10\text{-phenanthroline})(O_2CCF_3)]\cdot(\text{acetone})$[6] (**6b**). Under the same reaction conditions, but in the presence of an excess of 1,4-dichlorobut-2-yne, green crystals of $[Mo(\eta^2\text{-}ClCH_2C{\equiv}CCH_2Cl)(CO)(O_2CCF_3)_2(1,10\text{-phenanthroline})]$[7] (**7b**) were produced. The dichloro analogue of **7b** was formed on refluxing a solution of $Ph_4P[MoCl(CO)_3(1,10\text{-phenanthroline})]$ or **1b** in chloroform with an excess of 1,4-dichloro-2-butyne, indicating that the butadientyl complex **1b** was thermally unstable, and in the presence of the excess alkyne **1b** was converted to $[MoCl_2(\eta^2\text{-}ClCH_2C{\equiv}CCH_2Cl)(CO)(1,10\text{-phenanthroline})]$.

The series of molybdenum and tungsten monocarbonyl alkyne complexes $M(CO)(RC{\equiv}CR)L_2X_2$ (L_2 = 2 PPh_3, 2 PEt_3, 2 pyridine, bis(diphenylphosphino)methane; X = Cl, Br) have been prepared by Templeton and co-workers,[8] and the structures of $Mo(CO)(\eta^2\text{-}PhC{\equiv}CH)(PEt_3)_2Br_2$ and $Mo(CO)(\eta^2\text{-}MeC{\equiv}CMe)(PMePh_2)_2Br_2$ have been established by X-ray analysis.[8,9] Analogous complexes with bidentate nitrogen donor ligands have been relatively

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[●] Abstract published in *Advance ACS Abstracts,* June 1, 1994.

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(4) Compound **1a**: ^1H NMR (270 MHz, 20 °C, CD_2Cl_2; ppm) 7.62–8.83 [8H, bpy], 6.38 [1H, *J* = 2.6Hz[, 5.72 [1H, *J* = 2.6 Hz], 3.56 [1H], 2.07 [1H]; IR (Nujol; cm^{-1}) 1990 (carbonyl), 1915 (carbonyl), 1708 (C=O). Anal. Calcd for $C_{17}H_{12}Cl_2MoN_2O_3$: C, 44.4; H, 2.61; N, 6.10. Found: C, 44.7; H, 2.97; N, 5.41. Compound **1b**: ^1H NMR (270 MHz, 20 °C, CD_2Cl_2; ppm) 7.91–9.14 [8H, phen], 6.40 [1H, *J* = 2.57 Hz], 5.81 [1H, *J* = 2.57 Hz], 3.73 [1H], 2.15 [1H]; IR (Nujol; cm^{-1}) 1982 (carbonyl), 1917 (carbonyl), 1711 (C=O). Anal. Calcd for $C_{19}H_{12}Cl_2MoN_2O_3$: C, 47.2; H, 2.48; N, 5.79. Found: C, 46.8; H, 2.48; N, 5.80.

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(6) Compound **6b**: ^1H NMR (270 MHz, 20 °C, CD_2Cl_2; ppm) 8.06–9.48 [8H, phen], 6.35 [1H, *J* = 2.2 Hz], 5.84 [1H, *J* = 2.2 Hz], 4.06 [1H], 1.95 [1H]; IR (Nujol; cm^{-1}) 1981 (carbonyl), 1896 (carbonyl), 1699, 1672 (C=O). Anal. Calcd for $C_{26}H_{18}F_6MoN_2O_8$: C, 44.8; H, 2.58; N, 4.82. Found: C, 44.6; H, 2.44; N, 4.85.

(7) Compound **7b**: ^1H NMR (270 MHz, 20 °C, CD_2Cl_2; ppm) 8.09–9.35 [8H, phen], 5.33 [4H, partially obscured by solvent]; IR (Nujol; cm^{-1}) 1961 (carbonyl), 1701 (C=O). Anal. Calcd for $C_{21}H_{12}Cl_2F_6MoN_2O_5$: C, 38.5; H, 1.84; N, 4.29. Found: C, 37.4; H, 1.97; N, 4.00.

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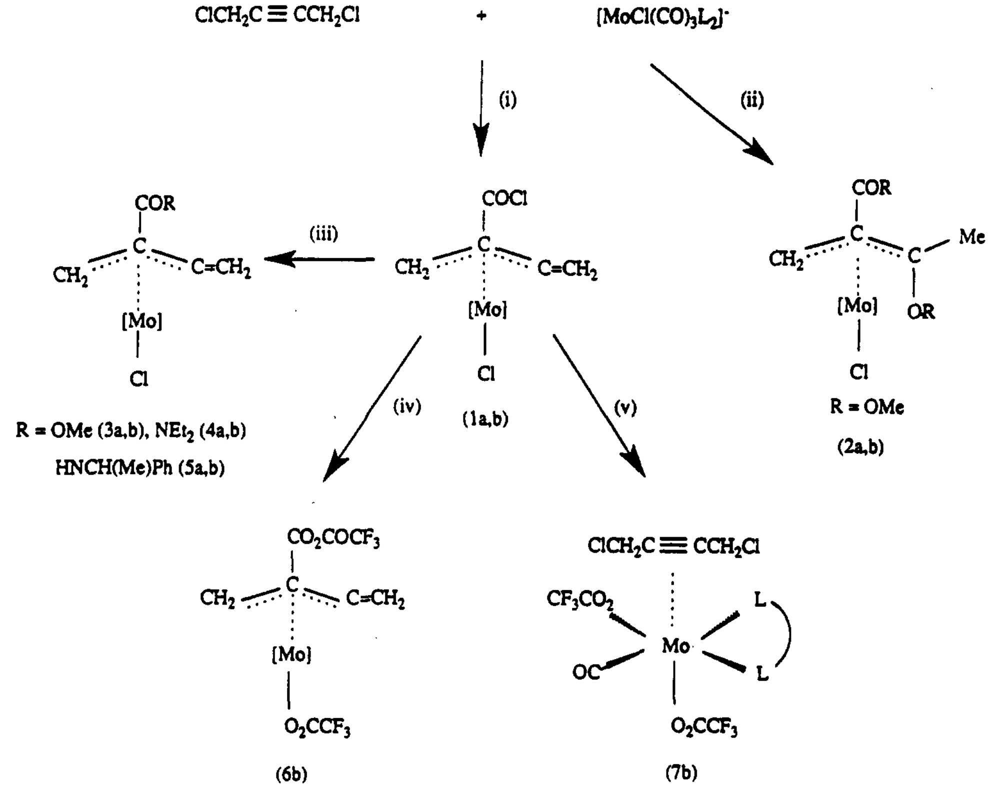
Scheme 1[a]



[a] Abbreviations: [Mo] = $Mo(CO)_2L_2$; L_2 = 2,2′-bipyridine (*a*), 1,10-phenanthroline (*b*). Conditions: (i) $CHCl_3$, 20 °C; (ii) MeOH/THF; (iii) MeOH, $HNEt_2$, or HNCH(Me)Ph; (iv) $AgBF_4/NaO_2CCF_3$/acetone, 20 °C; (v) as in (iv) with excess $ClCH_2C{\equiv}CCH_2Cl$.

neglected,[10] and we report herein the first structure of such a complex to be accessed via an η^3-butadienyl derivative.

Complex **7b** was soluble in chlorinated solvents and formed crystals suitable for X-ray crystallography from a CH_2Cl_2/petroleum ether mixture.[11] Figure 1 shows an ORTEP view of this molecule and the atomic numbering scheme used. The molybdenum coordination sphere can be described as heptacoordinate, with normal bond distances between the metal atom and donor atoms of the bidentate 1,10-phenanthroline, carbonyl, and two monodentate carboxylate ligands. The alkyne multiple carbon–carbon bond length and bent *cis*-alkyne geometry are in accord with observations for η^2-alkyne moieties in complexes of the type $[Mo(CO)(\eta^2\text{-alkyne})(PR_3)_2X_2]$.[8,9] Metal–alkyne carbon distances have been shown to reflect the extent of electron donation from alkyne to the metal, and the average distance of 2.02(1) Å in **7b** is in keeping with

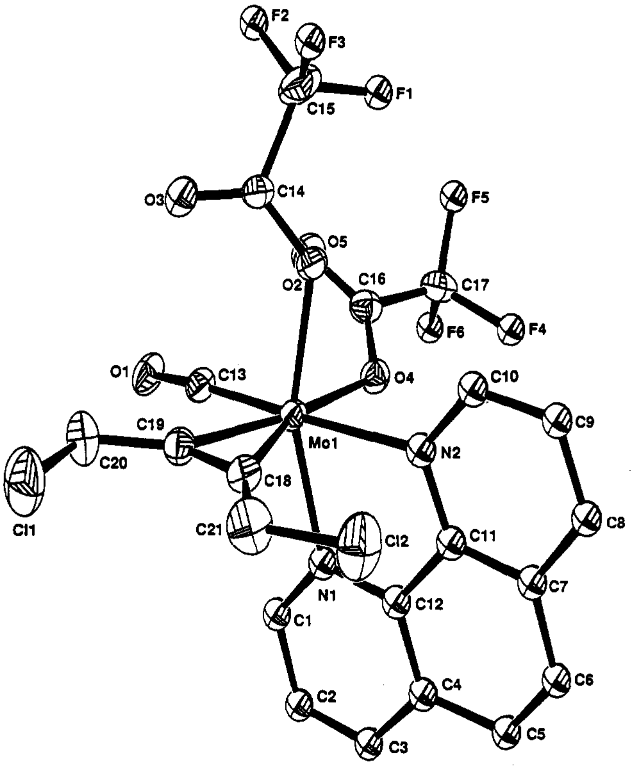


Figure 1. ORTEP view of the molecular structure of **7b** (hydrogen atoms omitted). Selected bond lengths (Å) and bond angles (deg): Mo–C(13) = 1.993(11), Mo–C(18) = 2.014(8), Mo–C(19) = 2.024(8), Mo–N(1)– =2.196(6), Mo–N(2) = 2.223(8), C(18)–C(19) = 1.330(16); C(18)–Mo–C(19) = 38.5(5), C(13)–Mo–C(19) = 109.3(4), N(1)–Mo–N(2) = 75.6(3).

four-electron donation from the butyne group. The bidentate alkyne and the carbonyl group are in a parallel

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[10] Andreas, M.; McDermott, G. A.; Dorries, A. M.; van Engen, D. *Organometallics* **1987**, *6*, 1503.

[11] Crystallographic data for **7b**: $C_{21}H_{12}O_5N_2Cl_2F_6Mo$, M_r = 653.2, triclinic, space group $P\bar{1}$, a = 11.086(6) Å, b = 12.422(3) Å, c = 12.619(1) Å, α = 62.50(2)°, β = 86.74(3)°, γ = 67.41(3)°, V = 1407.6 Å^3, Z = 2, d_{calc} = 1.54 g cm^{-3}, $\lambda(Mo\ K_\alpha)$ = 0.709 30 Å, $\mu(Mo\ K\alpha)$ = 6.46 cm^{-1}, $F(000)$ = 644. Data were measured at room temperature on a CAD4 automatic four-circle diffractometer in the range $2 \le \theta \le 24°$. Of the 4667 reflections collected, 3567 were unique with $I \ge 3\sigma(I)$. Data were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by Patterson methods, using the SHELX76 and SHELX86 suite of programs (GM Sheldrick, Computer programs for crystal structure determinations and refinements, Universities of Cambridge and Göttingen). In the final least-squares cycles the Mo, Cl, and O atoms, along with the C(11)–C(20), were allowed to vibrate anisotropically. All other atoms were treated isotropically. Hydrogen atoms were included at calculated positions. Final residuals after 18 cycles of blocked-matrix least squares were R = 0.0712 and R_w = 0.0782 for a weighting scheme of $w = 5.9034/[\sigma^2(F) + 0.00079(F)^2]$. The maximum final shift/esd was 0.530. The maximum and minimum residual densities were +0.58 and −0.35 Å^{-3}, respectively.

configuration, which arises from optimization of the π-donor and π-acceptor capabilities of the alkyne. The *cis*-Mo(CO)(alkyne) unit occupies two sites in the girdle plane of a distorted pentagonal bipyramid, with one oxygen of the monodentate carboxylate O(4) and one nitrogen of the phenanthroline ligand N(2) completing the pentagonal plane (±0.016 Å from the least-squares plane). The second carboxylate oxygen O(2) and nitrogen of phenanthroline N(1) occupy mutually trans axial positions, at an angle of 158.6(2)° relative to the metal atom. Bond lengths and angles within the bidentate phenanthroline and two monodentate trifluoroacetate ligands (despite some disorder of the fluorine atoms therein) are in the main unexceptional. Some additional disorder was present in the Cl(2) position on the alkyne, and the chlorine position illustrated in Figure 1 had 80% occupancy. The Mo–O(4) bond trans to the strongly bonded alkyne is 2.160(5) Å, longer than the Mo–O(2) bond of 2.087(5) Å, which is trans to one nitrogen atom of the 1,10-phenanthroline ligand. Of interest are the bonding distances between the metal center and the two nitrogen atoms of the phenanthroline ligand. The atom N(1) is trans to the oxygen atom O(2) of one trifluoroacetate group and is at a distance of 2.196(6) Å from the metal. By comparison, the Mo–N(2) distance at 2.223(8) Å is longer, reflecting both the trans influence of the strongly bonded carbonyl ligand and the proximity of the π system associated with N(2) to an empty metal d orbital.

No evidence was found for the double addition of alcohols or amines to preformed **1a** or **1b** leading to a η^3-$CH_2C(CO_2Me)CMe(OMe)$ or η^3-$CH_2C(CONRR')CMe(NRR')$ ligand containing complex. However, reaction of $Ph_4P[MoCl(CO)_3L_2]$ with 1,4-dichlorobut-2-yne in a methanol/tetrahydrofuran mixture yielded the complexes $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CO_2Me)CMe(OMe))L_2]$ (L_2 = 2,2′-bipyridine, 1,10-phenanthroline) as the only major metal-containing product (Scheme 1). In view of the evident importance of solvent type and reaction conditions in controlling the nature of the products formed in these reactions, and the known synthetic utility of other allyl and butadienyl molybdenum complexes,[12] we are currently investigating the potential of these complexes to serve as organic synthons.

Supplementary Material Available: Tables of bond lengths and angles (6 pages). Ordering information is given on any current masthead page.

OM940068L

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