Mendeleev Commun., 1991, **1(3)**, 103–104

Mendeleev Communications

First Example of the η^3-Prop-2-ynyl Ligand; Synthesis and Reactivity of Cationic (η^3-Prop-2-ynyl)arenedicarbonylmolybdenum Complexes; X-Ray Structure of $[Mo(CO)_2(\eta^6\text{-}C_6Me_5H)(\eta^3\text{-}HCCCH_2)]^+ BF_4^-$

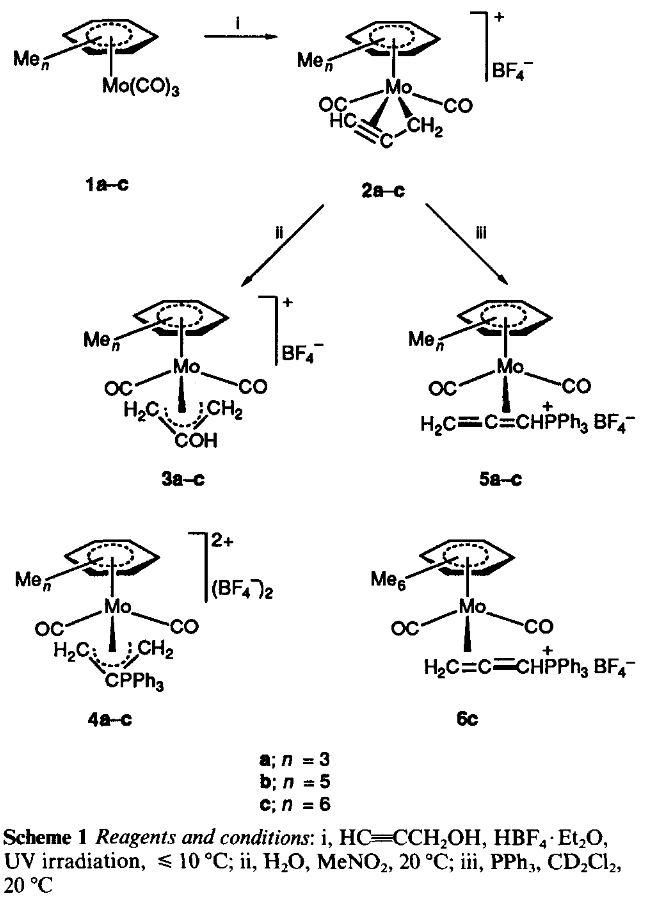
Vassily V. Krivykh,* Elena S. Taits, Pavel V. Petrovskii, Yuri T. Struchkov and Aleksandr I. Yanovskii

A N. Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences of the USSR, 117813 Moscow, USSR

A series of (η^3-prop-2-ynyl)arenedicarbonylmolybdenum complexes with a novel η^3-prop-2-ynyl ligand have been obtained, their structure has been established unambiguously by an X-ray diffraction study of a pentamethylbenzene derivative; the reactions of the η^3-prop-2-ynyl derivatives with H_2O and PPh_3 yield complexes with 2-hydroxyallyl, 2-triphenyl phosphonioallyl and 1-triphenylphosphoionallene ligands.

We have previously developed a simple one-pot synthesis of cationic allyl complexes of the transition metals of groups 16–18, which is based on the reaction of a metal carbonyl, allyl alcohol and strong protonic acid under UV irradiation.[1,2] Employing this technique using prop-2-yn-1-ol and arenetricarbonylchromium derivatives as reagents we have obtained cationic complexes containing the 2-hydroxyallyl ligand.[1] This ligand is evidently the result of the interaction of the initially generated prop-2-ynyl cation coordinated by the Cr atom with water.

In the present communication we report the first example of the stabilization of this cation in a mononuclear molybdenum complex. We have found that UV irradiation of tricarbonylarenemolybdenum complexes **1a–c** in the presence of prop-2-yn-1-ol and $HBF_4 \cdot Et_2O$ in diethyl ether solution yields stable complexes **2a–c** involving the previously unknown η^3–C_3H_3 ligand (Scheme 1). These complexes were characterized by their IR, ^1H and ^{13}C NMR spectroscopic data† and by single-crystal X-ray structure analysis,‡ which was carried out for the pentamethyl derivative **2b**. The molecular structure of **2b** is shown in Fig. 1.



Scheme 1 *Reagents and conditions*: i, $HC{\equiv}CCH_2OH$, $HBF_4 \cdot Et_2O$, UV irradiation, ≤ 10 °C; ii, H_2O, $MeNO_2$, 20 °C; iii, PPh_3, CD_2Cl_2, 20 °C

---

† *Spectroscopic data* for $[Mo(CO)_2(\eta^3\text{-}C_3H_3)(C_6Me_6)]^+ BF_4^-$ **2c**: IR ν_{CO}/cm^{-1} ($MeNO_2$) 1989vs, 1917vs; ^1H NMR (CD_3NO_2) δ 5.54 (dd, $^4J_{av}$ 2.34 Hz, HC≡), 4.02 (dd, ^4J 2.22, ^2J 10.82 Hz, C*H*H), 3.27 (dd, ^4J 2.47, ^2J 10.82 Hz, CH$\underline{H}$), 2.41 (s, 18H, CH_3); ^{13}C NMR (CH_3NO_2) δ 237.32, 230.91, (s, CO), 123.70 (s, C_{ipso}), 74.53 (d, $^1J_{C-H}$ 242.8 Hz, ≡CH), 69.90 (d, $^2J_{^{13}C-^1H}$ 28.6 Hz, ≡C—), 39.56 (t, $^1J_{^{13}C-^1H}$ 166.6 Hz, CH_2), 17.54 (q, $^1J_{^{13}C-^1H}$ 130.1 Hz, CH_3).

For $[Mo(CO)_2[\eta^3\text{-}CH_2C(PPh_3)CH_2](\eta^6\text{-}C_6Me_6)]^{2+}(BF_4^-)_2$ **4c**: IR ν_{CO}/cm^{-1} ($MeNO_2$) 2033vs, 1987vs; ^1H NMR (CD_3NO_2) *δ* 8.06–7.72 (m, 15H, 3Ph), 3.70 (d, $^3J_{^{31}P-^1H}$ 9.9 Hz, $2H_{syn}$), 2.39 (s, 18H, 6Me), 1.96 (d, $^3J_{^{31}P-^1H}$ 17.2 Hz, $2H_{anti}$); ^{13}C NMR δ 222.39 (s, 2CO), 122.40 (s, C_{ipso}), 87.05 (d, $^1J_{^{31}P-^{13}C}$ 77.6 Hz, C—P), 50.21 (t, $^1J_{^{13}C-^1H}$ 164.8 Hz, CH_2), 17, 10 (q, $^1J_{^{13}C-^1H}$ 130.8 Hz, Me).

For $[Mo(CO)_2(\eta^2\text{-}CH(PPh_3){=}C{=}CH_2)(C_6Me_6)]^+ BF_4^-$ **5c**: IR ν_{CO}/cm^{-1} ($MeNO_2$) 1938vs, 1870vs; ^1H NMR δ 7.85–7.47 (m, 15H, 3Ph), 6.17 (m, =C*H*H), 5.64 (m, =CH*H*), 2.24 (s, 18H, 6Me), 1.46 (dt, $^4J_{^1H-^1H}$ 2.9, $^2J_{^{31}P-^1H}$ 5.9 Hz, =CHP).

For $[Mo(CO)_2(\eta^2\text{-}CH(PPh_3){=}C{=}CH_2)(C_6Me_6)]^+ BF_4^-$ **6c**: ^1H NMR δ 7.9–7.5 (m, 15H, 3Ph), 6.39 (dt, $^4J_{^1H-^1H}$ 2.25, $^2J_{^{31}P-^1H}$ 33.9 Hz, =CHP), 2.21 (s, 18H, 6Me), 0.70 (dd, $^4J_{^1H-^1H}$ 2.29, $^4J_{^{31}P-^1H}$ 3.88 Hz, =CH_2).

‡ *Crystal data* for **2c**: $C_{16}H_{19}BO_2F_4Mo$, $M_r = 426.1$, triclinic, space group $P\bar{1}$, $a = 7.900(2)$, $b = 9.121(2)$, $c = 12.525(3)$ Å, $\alpha = 97{,}19(3)$, $\beta = 102.21(3)$, $\gamma = 95.65(3)°$, $V = 867.9(4)$ Å^3, $D_c = 1.630$ g cm^{-3} for $Z = 2$, μ(Mo-Kα) = 7.8 cm^{-1}. 4929 Independent reflections were measured at 173 K on a Siemens P3/PC automatic diffractometer using Mo-K*a*-radiation ($\lambda = 0.71069$ Å, graphite monochromator). The structure was solved by the heavy-atom technique and refined by full-matrix least-squares in the anisotropic approximation. For each of the F atoms of the disordered BF_4^- anion two alternative positions were refined. All H atoms were located in a difference Fourier synthesis and included in the final refinement in the isotropic approximation. The refinement of 329 variables against 3693 reflections with $F^2 > 4\sigma$ converged to $R = 0.0250$, $R_w = 0.0304$. All calculations were carried out on an IBM AT PC by means of the SHELXTL PC program package. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, Issue No. 1.

Mendeleev Commun., 1991, 1(3), 103–104

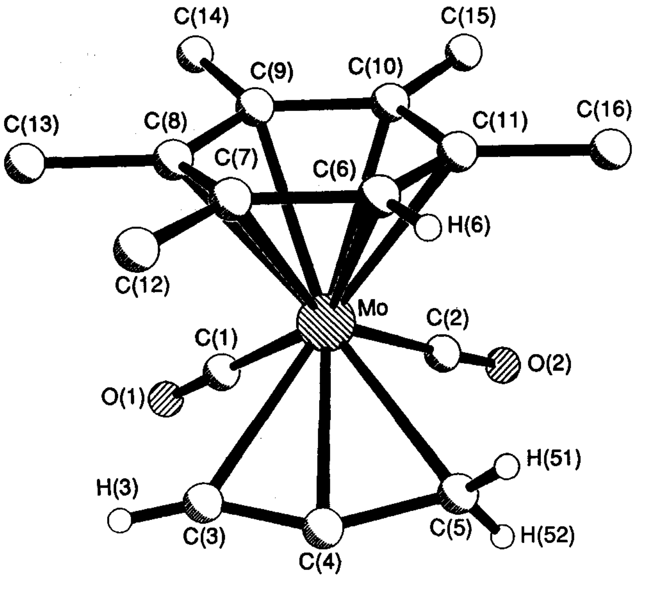
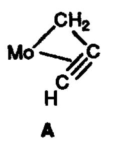
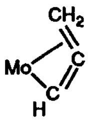


Fig. 1 Molecular structure of **2c**. All H atoms of the Me groups are omitted for clarity. Main bond lengths (Å) and angles (°): Mo—C(3) 2.319(3), Mo—C(4) 2.282(3), Mo—C(5) 2.340(3), C(3)—C(4) 1.236(4), C(4)—C(5) 1.380(4), Mo—C(1) 1.968(2), Mo—C(2) 1.962(2), C(1)—O(1) 1.146(3), C(2)—O(2) 1.150(3), Mo—C(arene) 2.359–2.450; C(3)C(4)C(5) 150.9(3)

In molecule **2b**, as in the π-allyl Mo complexes [*e.g.* in the structures of $(\eta^3\text{-MeC}_3\text{H}_4)\text{Mo(Cp)(CO)}_2$[3] or $(\eta^3\text{-C}_3\text{H}_5)\text{Mo(Cp)Cl}_2\text{(CO)}$[4]] three carbon atoms are at bonding distances from the Mo atom (2.282–2.340 Å). However, in contrast to the allyl derivatives wherein the central C atom is considerably (*ca.* 0.7 Å) displaced from the plane passing through the metal atom and the peripheral atoms of the allyl ligand, the MoC(3)C(4)C(5) group in complex **2b** is in fact planar to within 0.014 Å. It is noteworthy that the C(3)≡C(4) distance in **2b** is somewhat shorter than that in most transition metal complexes with coordinated alkynes {1.269 Å in $\text{Cp}_2\text{Mo(PhC}{\equiv}\text{CPh)}$,[5] 1.277 Å in $[\text{CpMo(CO)(MeC}{\equiv}\text{CMe)}_2]\text{BF}_4$[6]}. The C(3)≡C(4) triple bond character is in good agreement with the relatively small decrease [to 150.9(3)°] of the C(3)C(4)C(5) angle upon coordination and the ^{13}C NMR data for **2**, exhibiting rather large values of $J_{^{13}\text{C}(3)-^{1}\text{H}}$ 243–246 Hz and typical for coordinated alkyne chemical shifts of $\delta_{\text{C}(3)}$ 70–75 and $\delta_{\text{C}(4)}$ 67–70. Thus one can interpret the bonding in complexes **2** in terms of two resonance structures **A** and **B**, one of which (the prop-2-ynyl form *A*) contributes considerably more than the other.



A



B

Complexes **2** exhibit quite unusual reactivity towards nucleophiles such as H_2O or PPh_3. They react with water only very slowly, yielding 2-hydroxyallyl derivatives **3**. Signals indicating the presence of **3** appeared in the solution of **2c** in CD_3NO_2, containing ~ 5% H_2O (50-fold excess) only after it was left to stand for 5 days in the NMR tube. The content of **3c** amounted to ~ 3% relative to **2c**. If the reaction of **1** with prop-2-yn-1-ol under UV irradiation is carried out in the presence of 50% aqueous HBF_4 (50-fold excess) a mixture of **2c** and **3c** in a ratio of 73 : 27 is formed. The presence of PPh_3 in the reaction mixture leads to the formation of equal amounts of complexes **2** and **4**. Reaction of the isolated individual complexes **2** with PPh_3 yields two products, one of which is the 2-phosphonioallyl complex **4** and the other the phosphonioallene derivative **5** with the allene ligand coordinated *via* the substituted double bond. We have managed to obtain only ^{1}H NMR evidence for the presence of the second isomer of the phosphonioallene complex **6c** during the course of the reaction which was carried out in the NMR tube. Thus after addition of an equimolecular amount of PPh_3 to **2c** in CD_2Cl_2 the starting compound quickly disappears giving way to a mixture of three products **4c**, **5c** and **6c**. 10 min after the addition of PPh_3 their relative proportions are 1 : 1.6 : 0.3 and, just as for the chromium derivatives[7] analogous to **5** and **6**, complex **6c** is slowly and irreversibly converted into **5c**. Almost complete conversion of **6c** is achieved after 12 days, the relative proportions of **4c** and **5c** in the reaction mixture becoming *ca.* 1 : 2.

The peculiar feature of the above-mentioned reactions is the site of the nucleophilic attack, which is directed not only at the terminal C atoms, which is the case with most open π-ligands,[8] but also to a considerable degree and sometimes even exclusively at the central atom of the C_3H_3 ligand.

Received in USSR, 10th December 1990
Received in UK, 15th March 1991; *Com. 0/05583B*

References

1 A. N. Nesmeyanov, V. V. Krivykh, E. S. Il'minskaya and M. I. Rybinskaya, *J. Organomet. Chem.*, 1981, **209**, 309.

2 V. V. Krivykh, O. V. Gusev and M. I. Rybinskaya, *J. Organomet. Chem.*, 1989, **362**, 351 and references therein.

3 N. W. Murrall and A. J. Welch, *Acta Crystallogr., Sect C*, 1984, **40**, 401.

4 J. L. Davidson and G. Vasopollo, *J. Organomet. Chem.*, 1985, **291**, 43.

5 A. De Cian, J. Colin, M. Schappacher, L. Ricard and R. Weiss, *J. Am. Chem. Soc.*, 1981, **103**, 1850.

6 K. A. Mead, H. Morgan and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 271.

7 V. V. Krivykh, E. S. Taits and M. I. Rybinskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2866.

8 S. G. Davies, M. L. H. Green and D. M. P. Mingos, *Tetrahedron*, 1978, **34**, 3047.