Cyclopentadienyl molybdenum(II) compounds bearing carboxylic acid functional group

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Keywords: molybdenum; cyclopentadienyl; cytotoxicity; leukemia

Highlights:

Carboxylic acid functionalized cyclopentadienyl compounds were synthesized.

Characterization by spectroscopic methods and X-ray crystallography.

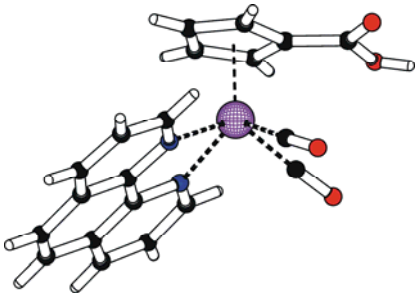
Cytotoxicity toward leukemia cells was established.

Abstract:

This work describes a procedure giving cyclopentadienyl molybdenum(II) compounds bearing carboxylic acid function group. It involves synthesis of carboxylic acid ester functionalized cyclopendienides, their coordination to molybdenum(II) precursor and saponification of ester function groups. The method is not limited only to compounds with the function group directly attached in the cyclopentadienyl ring but also to those functionalized in the side chain. The attempts to synthesize the indenyl analogues were only partially successful due to low stability in the saponification step. All reported structure types were elucidated from spectroscopic measurements and verified by X-ray crystallography. The second part of the work describes an effect of the

outer-coordination sphere on cytotoxicity of the cationic molybdenum(II) compounds bearing *N,N*-chelating ligands. The cytotoxicity of the modified species bearing phenanthroline ligand toward human leukemia cells MOLT-4 (IC_{50} = 10.5 ± 0.5 μmol l^{-1}) is higher than reported for cisplatin (IC_{50} = 15.8 ± 1.9 μmol l^{-1}).

Graphical Abstract: This work describes synthesis of the cyclopentadienyl molybdenum(II) compounds modified by carboxylic acid function group and effect of the functionalization of the cytotoxicity.



1. Introduction

Various transition metal complexes and organometallic compounds attract attention of biochemists and farmacochemists since cytostatic properties of cisplatin (*cis*-$[PtCl_2(NH_3)_2]$) were discovered by Rosenberg *et al.* [1, 2]. In past decades, a large variety of transition metal compounds was scrutinized and many structural patterns with promising cytostatic properties were recognized. Nevertheless, the quest for new species with enhanced activity toward cisplatin resistant tumor cells and reduced side-effects is still ongoing [3-20].

Our ongoing development of molybdenum-based cytostatic drug [21-24] follows the fundamental work of Romão *et al.*, who established cyclopentadienyl and indenyl molybdenum compounds $[(\eta^5\text{-Cp'})Mo(CO)_2L_2][BF_4]$ (Cp' = C_5H_5, C_9H_7, L_2 = neutral chelating ligand) as a new class of highly cytotoxic species active against several tumor cell lines [25]. In following studies, an early insight into mechanism of their action was reported [26, 27] and number of active compounds was extended with congeners bearing various substituents in the cyclopentadienyl ring and another bidentate ligands [21, 22, 28]. Enhanced *in vitro* cytotoxicity toward leukemia cells MOLT-4 was observed in case of water-soluble derivatives obtained by functionalization of cyclopentadienyl ring with amine function groups [24]. Another approach to reach water-soluble derivatives of $[(\eta^5\text{-Cp'})Mo(CO)_2L_2][BF_4]$ involves attachment of carboxylic acid group that is subject of present study.

The first notes about the modification of cyclopentadienyl ligand with carboxylic acid functional group are dated shortly after discovery ferrocene [29, 30]. Nevertheless, a quest for such modification has emerged much

later within a development of water soluble organometallic compounds designed for homogenous catalysis [31] and medicinal applications [32]. Strong hydrogen bond systems in the carboxylic acid functionalized organometallic compounds have been utilized for crystal engineering as well [33-35]. Nevertheless, the current research is focused mainly on the assembly of biomolecule conjugates suitable for target drug delivery [36-38], where acid functionalized cyclopentadienyl compounds form convenient building blocks.

Four distinct synthetic strategies are available for transition metal compounds bearing carboxylic acid functional group in the η^5-bonded cyclopentadienyl ligand. The direct coordination of Thiele's acid [$(C_5H_5COOH)_2$] is only described for technetium or rhenium carbonyls [39, 40]. More convenient pathway consists of metalation/carbonation procedure [30, 41, 42], which is commonly used for a direct functionalization of electron-rich middle and late transition metal compounds resistant to reduction under conditions of the metalation [*e.g.* (η^5-C_5H_5)$_2$Fe, (η^5-C_5H_5)Mn(CO)$_3$, (η^5-C_5H_5)(η^7-C_7H_7)V]. Carboxylic acid group could be also generated from ester group by hydrolysis [43]. Starting ester substituted derivatives are usually accessible from functionalized alkali metal cyclopentadienides [44, 45]. Such strategy has been successfully used for compounds with one or more functionalities in the cyclopentadienyl ring [43, 46] as well as in the side chain [37, 47]. Another approach covers oxidation of aldehyde (CHO), alcohol (CH_2OH), ketone (COR) and alkyne (CH≡CR) functionalities [48-50].

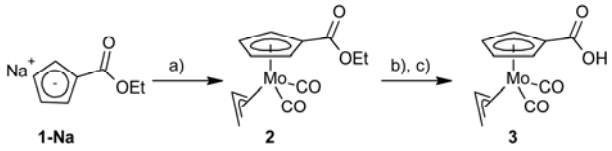
The aim of this study is to modify the outer coordination sphere of molybdenum(II) compounds with the carboxylic acid functionality in the attempt to improve their cytotoxic properties. As nature of ligand L_2 plays important role in a drug efficiency [21, 25], four *N,N*-chelators of different π-system size were chosen. Cytotoxic properties of these derivatives were examined *in vitro* on human leukemia cell line MOLT-4.

2. Results and discussion

2.1 Synthesis of allyl molybdenum precursors

The target molybdenum compounds [(η^5-Cp')Mo(CO)$_2$L$_2$][BF_4] are commonly synthesized from allyl precursors by protonation with strong acid followed with addition of appropriate chelating ligand. The starting derivative with carboxylic group directly attached in the cyclopentadienyl ring [(η^3-C_3H_5)(η^5-C_5H_4COOH)Mo(CO)$_2$] (**3**) was already reported [51, 52]. Nevertheless, we decided to develop alternative synthetic pathway, using hydrolysis of ester group, which could be further applicable for congeners bearing the carboxylic group in the side chain.

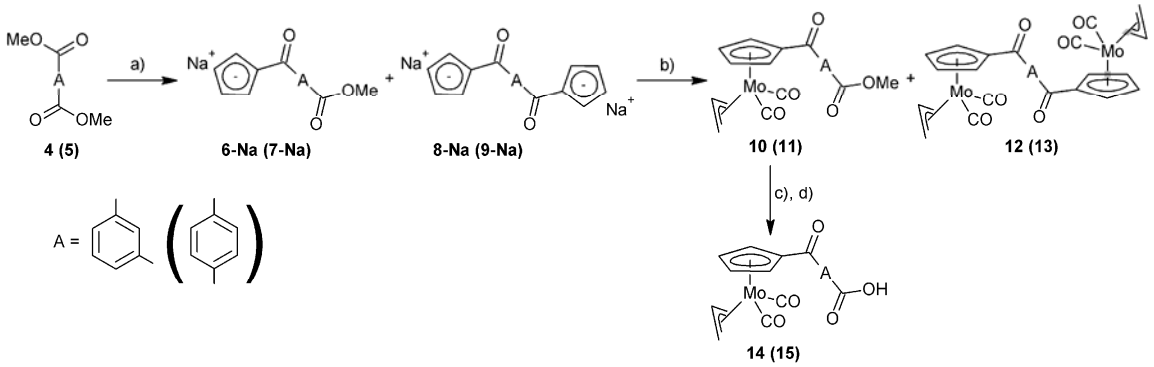
Ethyl ester functionalized compound [(η^3-C_3H_5)(η^5-C_5H_4COOEt)Mo(CO)$_2$] (**2**), readily available from Na[C_5H_4COOEt] (**1-Na**) and [(η^3-C_3H_5)Mo(CO)$_2$(NCMe)$_2$Cl], undergoes saponification of ester group in the mixture NaOH/MeOH/water. The desired species bearing carboxylic group (**3**) is then obtained in high yield after acidification (Scheme 1).



Scheme 1. Synthesis of molybdenum compound **3**. Reagents: a) [(η^3-C_3H_5)Mo(CO)$_2$(NCMe)$_2$Cl]/THF, b) NaOH/MeOH/water, c) HCl (aq.).

Deprotonation of **3** with sodium methanolate gives stable sodium salt Na[(η^3-C_3H_5)(η^5-C_5H_4COO)Mo(CO)$_2$] (**3-Na**) in high yield. Delocalization of the negative charge over both oxygen atoms of the carboxylate is evident from low wavenumber of the antisymmetric COO stretching mode (1584 cm^{-1}). Lower wavenumbers of the carbonyl stretching modes (ν_a = 1913 cm^{-1}, ν_s = 1839 cm^{-1}) reflect a higher electron density on molybdenum available for π-backbonding than observed for **3** (ν_a = 1927 cm^{-1}, ν_s = 1861 cm^{-1}).

Cyclopentadienides **6-Na** and **7-Na**, necessary for synthesis of molybdenum compounds with the carboxylic group in the side chain of the Cp ligand, were prepared by reaction of sodium cyclopentadienide with 1.5 equivalents of dimethyl isophthalate (**4**) and dimethyl terephthalate (**5**), respectively (Scheme 2). Although such stoichiometry leads to appearance of ~25% side products (**8-Na**, **9-Na**), it prevent contamination with starting diesters (**4**, **5**). We note that 1 : 1 stoichiometry does not give pure monocyclopentadienide (**6-Na**, **7-Na**) but a mixture with appropriate bis(cyclopentadienide) and unreacted diester. As both contaminants are hardly removable are by simple purification processes, we decided to use an excess of NaCp in order to prevent the contamination with diester and not separate the products in this reaction step but after coordination to molybdenum and saponification process (Scheme 2).



Scheme 2. Synthesis of molybdenum compounds with carboxylic group in the side chain of cyclopentadienyl. Reagents: a) NaCp/THF, b) $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2Cl]$, c) NaOH/MeOH/water, d) HCl (aq.).

Cyclopentadienides **6a** and **7a** react with $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2Cl]$ to give complexes with ester group in side chain **10** and **11**, respectively. After standard work up, these products contain about 25% of appropriate bridged compound (**12** and **13**) as evidenced by ^{1}H NMR spectroscopy. Such dinuclear complexes were isolated by long term stirring with sodium hydroxide solution in wet methanol. The mononuclear species are dissolved as the ester groups hydrolyze. Pure species **12** and **13** are then obtained after recrystallization from toluene. Infrared spectra of the compounds **12** and **13** show two CO stretching bands of the carbonyl ligand at ~1936 cm^{-1} (ν_a) and ~1845 cm^{-1} (ν_s). Stretching band of the keto group appears at ~1635 cm^{-1}. ^{1}H NMR spectra of the compounds **12** and **13** show two apparent triplets at ~5.8 and ~5.5 ppm ($^3J = {}^4J = 2.4$ Hz) typical for monosubstituted Cp ligand. Allyl ligands give signals at 3.89, 2.80 and 1.54 ppm. The dinuclear character of the species **12** and **13** is apparent from pattern of the bridge that is, in both cases, typical for symmetrical disubstituted benzene. 1,3-disubstituted ring of the compound **12** gives two triplets at 8.08 ppm (H^2) and 7.58 ppm (H^5) and doublet of doublets at 7.93 ppm ($H^{4,6}$). In case of **13**, four equivalent protons of 1,4-disubstituted benzene give one singlet at 7.80 ppm.

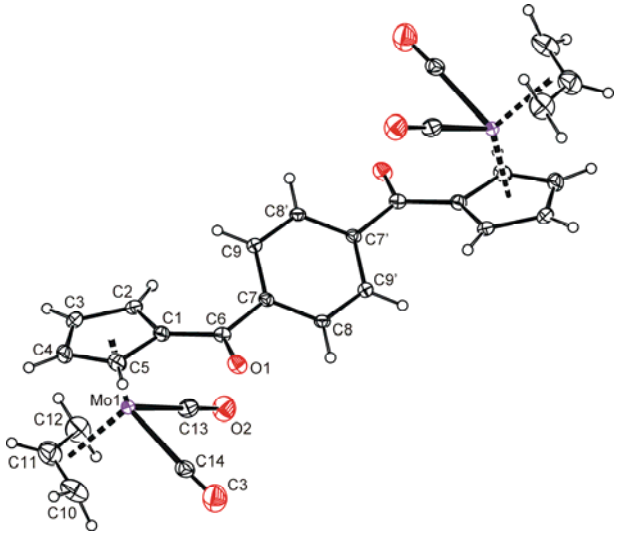


Figure 1. ORTEP drawing of [1,4-{(η^3-C_3H_5)Mo(CO)$_2$(η^5-C_5H_4CO)$_2$}$_2$$C_6H_4$] (**13**). The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level. One position of disordered atoms is omitted for clarity.

Single crystals of the compound **13**, suitable for X-ray analysis, were obtained by vacuum sublimation. The molecules consist of two [(η^3-C_3H_5)Mo(CO)$_2$] fragments connected via a bridging bis(cyclopentadienyl) ligand with rigorous overall C_i symmetry (Figure 1). The coordination sphere of both molybdenum atoms could be taken as pseudo-tetrahedral as centroids of η^3-allyl and η^5-cyclopentadienyl are considered to occupy one coordination site each. The geometric parameters, related with central metal, are given Table 1. Small dihedral angle between the Cp ring and a plane the ketone, defined by C1, C6, C7 and O1, [Pl_1–Pl_2 = 6.4(2)°] suggests more effective conjugation than between bridging benzene ring and the keto group [Pl_2–Pl_3 = 34.09(18)°]. The conjugation is also apparent from a shorter C1–C6 bond [1.471(5) Å] compared to neighboring C6–C7 bond [1.503(5) Å].

Table 1. Selected bond lengths (Å) and bond angles (°) of molybdenum complexes.

	13	**14**	**18**	**19**·0.5Et_2O
Mo–CO	1.961(5), 2.075(5)	1.948(2), 1.962(2)	1.945(3), 1.951(3)	1.965(4), 1.970(3)
Mo–N	–	–	–	2.187(3), 2.196(3)
Mo–Cg(C_5) [a]	2.0078(18)	2.0032(9)	2.0270(11)	1.9795(18)
Mo–Cg(C_3) [a]	1.997(7)	2.0057(2)	2.034(4)	–
OC–Mo–CO	77.48(19)	78.67(10)	78.46(11)	74.26(16)
Cg(C_3)–Mo–Cg(C_5) [a,b]	123.5(2)	125.53(10)	125.89(15)	–
N–Mo–N	–	–	–	73.77(10)

[a] Cg(C_5) is centroid of cyclopentadienyl ring.

[b] Cg(C_3) is centroid of allyl ligand.

The complexes with the carboxylic group in the side chain of the cyclopentadienyl ligand **14** and **15** were prepared by saponification of aforementioned crude compounds **10** and **11**, respectively (Scheme 2). Treatment with sodium hydroxide solution in aqueous methanol leads to selective hydrolysis of the ester groups to give sodium salts of desired products. The pure species with carboxylic group (**14** and **15**) are then precipitated upon acidification.

CO stretching bands of the carboxylic group were observed in the infrared spectra of the compounds **14** and **15** at 1688 cm^{-1} and 1683 cm^{-1}, respectively. ^1H NMR spectra show, beside the signals of allyl and cyclopentadienyl ligand, a typical pattern of unsymmetrical 1,3- and 1,4-disubstituted benzene, respectively. Crystal structure of the compound **14**, determined by X-ray diffraction analysis, proves a similar coordination sphere of molybdenum as aforementioned for compound **13**. A strong hydrogen bonding connects the carboxylic groups of a pair of molecules **14** to give a cyclic dimer as evident from short O2···O3' intermolecular distances [2.630(2) Å], see Figure 2.

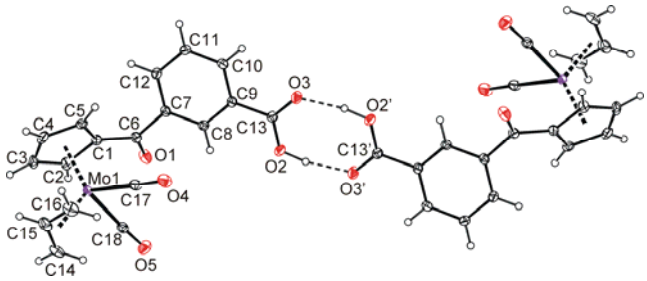
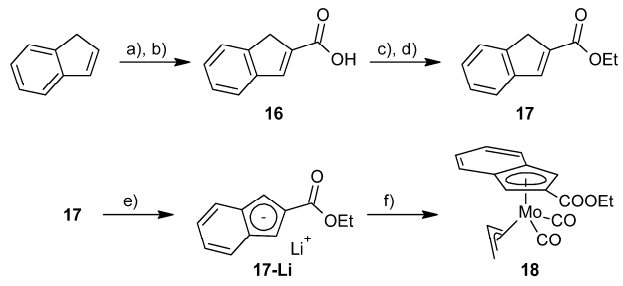


Figure 2. ORTEP drawing of [(η^3-C_3H_5)(η^5-$C_5H_4COC_6H_4COOH$-3)$Mo(CO)_2$] (**14**). The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

The assembly of the ester-functionalized indenyl molybdenum compound [(η^3-C_3H_5)(η^5-C_9H_6COOMe-2)$Mo(CO)_2$] (**18**) is summarized in the Scheme 3. In the first step, electrophilic substitution of $[BrCOCO]^+$ cation, generated from oxalyl bromide, on polarized double bond of indene gives indene-2-carbonyl bromide that readily hydrolyzes to appropriate carboxylic acid **16** [53]. X-ray diffraction analysis of **16** evidences the appearance of a cyclic dimer, in the solid state, with carboxylic groups connected through strong hydrogen bonds [O1···O3' = 2.612(2) Å)] (Figure 3).



Scheme 3. Synthesis of indenyl molybdenum compound **20**. Reagents: a) $(COOBr)_2/CH_2Cl_2$, b) water, c) $SOCl_2/CH_2Cl_2$, d) EtOH, e) *n*-BuLi/THF, f) [(η^3-C_3H_5)$Mo(CO)_2(NCMe)_2Cl$].

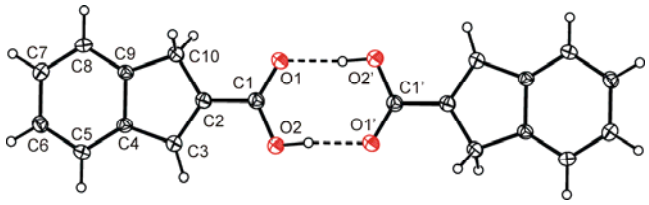


Figure 3. ORTEP drawing of C_9H_7COOH-2 (**16**). The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

Esterification followed by deprotonation and a reaction with $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2Cl]$ gives ester-substituted indenyl complex $[(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_9H_6COOEt\text{-}2)Mo(CO)_2]$ (**18**); see Scheme 3. ^{1}H NMR spectrum of the compound **18** reveals appearance of two isomers in solution generated by orientation of allyl ligand. The equimolar mixture of e*xo*- and *endo*-isomer, observed at room temperature, is rather unusual as *exo*-isomers of parent $[(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_9H_7)Mo(CO)_2]$ is about 1 kcal/mol more stable [54] and becomes predominant in $CDCl_3$ solution at room temperature ([*endo*]/[*exo*] = 2.55) [55]. The stabilization of *exo*-isomer has been also reported for various ring substituted congeners, including those with ester group in 1-position ([*endo*]/[*exo*] = 3–4) [56-58].

X-ray diffraction analysis verifies the proposed molecular structure of **18**. Figure 4 depicts the solid-state structure of the *exo*-isomer, in which carbon atoms of the allyl ligand are in eclipsing configuration with OC–Mo–CO moiety. The molecule reaches a conformation with benzene ring opposite to carbonyl ligands similarly as its unsubstituted parent [54].

Unfortunately, our attempts to hydrolyze the ester group selectively were unsuccessful due to lability of the bond between molybdenum and substituted indenyl ligand. Only intractable tarry solid was obtained at conditions necessary for saponification.

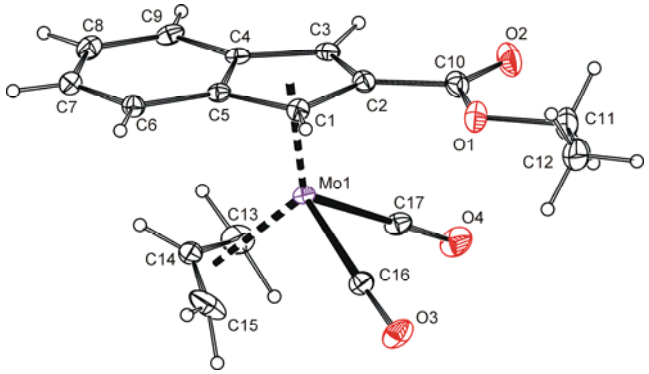
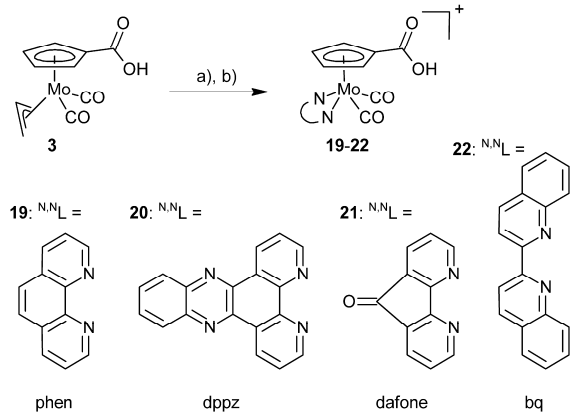


Figure 4. ORTEP drawing of $[(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_9H_6COOMe\text{-}2)Mo(CO)_2]$ (**18**). The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 20% probability level. One position of disordered atoms is omitted for clarity.

2.2 Synthesis of complexes with N,N-chelating ligands

Compounds **3**, **14** and **15** were used for synthesis of cationic compounds bearing chelating ligands. According to established procedure [21, 59], the complexes were treated with tetrafluoroboric acid in order to protonate allyl ligand and exchange it with *N,N*-chelators. Nevertheless, the desired cationic cyclopentadienyl compounds (**19**–**22**) were obtained only from precursor with the carboxylic group directly attached in the cyclopentadienyl ring (Scheme 4). In other cases (**14** and **15**), a more powerful electron-withdrawing character of the substituent led to protonation and subsequent exchange of the cyclopentadienyl ring to give trivial cationic allyl compounds of type $[(\eta^3\text{-}C_3H_5)Mo(CO)_2L_2(MeCN)][BF_4]$. Similar behavior was previously observed for some other ring-substituted congeners of $[(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)Mo(CO)_2]$ [60, 61].



Scheme 4. Synthesis of cationic molybdenum compounds bearing *N,N*-chelating ligands. Reagents: a) $HBF_4{\cdot}Et_2O/MeCN$, b) $^{N,N}L/CH_2Cl_2$. Abbreviations: 1,10-phenanthroline (phen), dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz), 4,5-diazafluoren-9-one (dafone) and 2,2'-biquinoline (bq).

The cyclopentadienyl complexes $[(\eta^5\text{-}C_5H_4COOH)Mo(CO)_2L_2][BF_4]$ (**19**: L_2 = phen, **20**: L_2 =dppz, **21**: L_2 = dafone, **22**: L_2 = bq) show characteristic CO stretching bands of carbonyl ligands at higher wavenumbers (ν_a: 1993–1974 cm^{-1}; ν_s: 1906–1863 cm^{-1}) than observed for starting complex **3**. In the cationic complexes, a lower electron density on molybdenum results in weaker back-donation into the π-antibonding orbitals of the carbonyl ligands. A strong band at 1723–1717 cm^{-1} was assigned to CO stretching of carboxylic group. In spectrum of compound **21**, keto-group of dafone ligand gives another CO stretching band at 1740 cm^{-1}.

^{1}H NMR spectra of the compounds **19**–**22** show a pattern consistent with expected C_s symmetry. The substituted cyclopentadienyl ligand gives two pseudo triplets at 5.85–6.65 ppm ($^3J = {}^4J = 2.4$ Hz). Low-fielded signals in region of 7.9–10.0 ppm prove coordination of given *N,N*-chelating ligands.

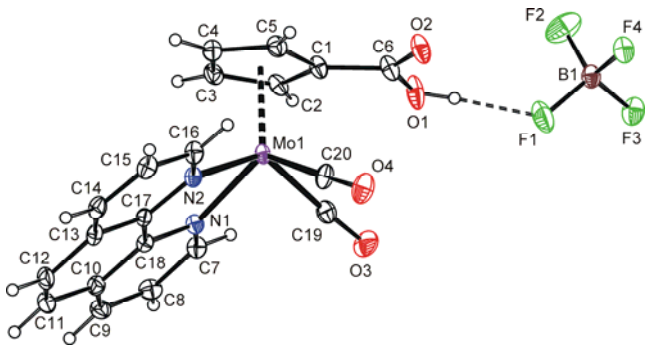


Figure 5. ORTEP drawing of [(η^5-C_5H_4COOH)$Mo(CO)_2$(phen)][BF_4] present in crystal structure of **19**·0.5Et_2O. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

The structure of phenanthroline complex **19** was determined by X-ray diffraction analysis (Figure 4). The compound crystalizes as a solvate **19**·0.5Et_2O. The coordination sphere of molybdenum forms a square pyramid with centroid of cyclopentadienyl ring in the apical position. The basal plane is occupied with *cis*-coordinated carbonyl ligands and nitrogen atoms of the phenanthroline. The solid-state structure is stabilized with strong hydrogen bond between carboxylic group of the cyclopentadienyl ligand and tetrafluoroborate anion [O1···F1 = 2.685(4) Å].

2.3 Cytotoxicity study

Cytotoxic activity of the cationic compounds **19**–**22** was evaluated on human T-lymphocytic leukemia cells MOLT-4 in exponential grow phase using standard WST-1 viability assays. The effect of the molybdenum compounds was estimated after 24 h exposition as half-maximal inhibitory concentration (IC_{50}) calculated from cytotoxicity curves; Table 2. The modification of the cationic compounds with the carboxylic acid group have only a minor effect on solubility in water that led us to use previously described protocol involving predissolution of the compounds in dimethyl sulfoxide [62].

The obtained IC_{50} values suggest rather minor effect of carboxylic acid function group on cytotoxicity of the molybdenum(II) compounds. The considerably improvement was observed only in case of phenanthroline complex **19** (IC_{50} = 10.5 ± 0.5 μmol l^{-1}) when comparing its performance with the parent cyclopentadienyl analogue [(η^5-C_5H_5)$Mo(CO)_2$(phen)][BF_4] (IC_{50} = 19.9 ± 0.7 μmol l^{-1}) or cisplatin (IC_{50} = 15.8 ± 1.9 μmol l^{-1}) under the same cultivation conditions [21]. Unfortunately, further modification of the active species by another chelating ligand such as dipyrido[3,2-*a*:2',3'-c]phenazine (dppz), 4,5-diazafluoren-9-one (dafone) and 2,2'-biquinoline (bq) did not bring expected improvement probably due to lower solubility in the cultivation media.

Table 2. Cytotoxicity of the molybdenum compounds.[a]

	19	**20**	**21**	**22**
IC_{50} [a]	10.5 ± 0.5	27.6 ± 2.6	> 50	> 50

[a] The values given in μmol l^{-1}; Exposure time is 24 h.

3. Conclusion

This study has clearly demonstrated that carboxylic acid functionalized molybdenum(II) compounds of the formula $[(\eta^3\text{-}C_3H_5)(\eta^5\text{-Cp'})Mo(CO)_2]$ can be easily synthesized by saponification of appropriate ester substituted analogues. This procedure is suitable for derivative with function group directly attached in the cyclopentadienyl ring as well as to those with ester group in the side chain. The given substitution pattern does not reduce stability of the compounds. Hence, the allyl ligand is not protonated by carboxylic acid function as observed in case of stronger mineral acids *e.g.* HCl or HBF_4 [58, 60]. We note that the saponification protocol is not appropriate for compounds with labile Cp'–Mo bond, such as the indenyl analogue, which may undergo decomposition in basic aqueous solutions.

Our experiments have further shown that carboxylic acid functionalized compounds of the general formula $[(\eta^3\text{-}C_3H_5)(\eta^5\text{-Cp'})Mo(CO)_2]$ (**3**, **14** and **15**) are not water-soluble themselves but only in form of sodium salts. The dependence of solubility on pH value was successfully utilized for purification purposes since the ionic species were found to be enough stable under inert atmosphere.

In the next step, the compound **3** was used for the assembly of the cationic species of the formula $[(\eta^5\text{-}C_5H_4COOH)Mo(CO)_2(L_2)][BF_4]$ those were submitted to cytotoxicity assays on leukemia cells MOLT-4. Unfortunately, the modification in the cyclopentadienyl ring has rather minor effect on activity probably owing to negligible effect on water-solubility. Strong cytotoxic effect was observed only in case of phenanthroline complex **19**, which activity toward human leukemia cells MOLT-4 exceeds cisplatin.

4. Experimental section

4.1 Methods and materials

All operations were performed under nitrogen using conventional Schlenk-line techniques. The solvents were purified and dried by standard methods [63]. Starting materials were available commercially or prepared

according to literature procedures: [(η^3-C_3H_5)Mo(CO)$_2$(NCMe)$_2$Cl] [55], Na[C_5H_4COOEt] (**1-Na**) [64], dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz) [65, 66], 4,5-diazafluoren-9-one (dafone) [67].

4.2 Measurements

Infrared spectra were recorded in the 4000–400 cm^{-1} region with a Nicolet iS50 FTIR spectrometer using a diamond smart orbit ATR. ^{1}H NMR spectra were measured at 300 K on a Bruker 400 Avance spectrometer. Chemical shifts are given in ppm relative to the external standard (TMS). Deuterated solvents were used as obtained (Acros Organics) without further purification.

*4.3 Synthesis of [(η^3-C_3H_5)(η^5-C_5H_4COOEt)Mo(CO)$_2$] (**2**)*

Na[C_5H_4COOEt] (**1-Na**; 1.54 g, 9.62 mmol) was dissolved in THF (20 ml), cooled to –80°C and then added dropwise to a solution of [(η^3-C_3H_5)Mo(CO)$_2$(NCMe)$_2$Cl] (3.00 g, 9.66 mmol) in THF (20 ml) precooled to –80°C. The reaction mixture was stirred at room temperature overnight and then vacuum evaporated to dryness. The crude product was extracted with hot hexane (3 × 50 ml). The volatiles were vacuum evaporated and the final product was washed with cold hexane (5 ml) and vacuum dried. Yield: 2.07 g (6.27 mmol, 65%). Calcd for $C_{13}H_{14}MoO_4$: C, 47.29; H, 4.27. Found: C, 47.55; H, 4.01. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 5.72 (t, $^3J(^1H,^1H) = {}^4J(^1H,^1H)$ = 2.2 Hz, 2H, C_5H_4), 5.37 (t, $^3J(^1H,^1H) = {}^4J(^1H,^1H)$ = 2.2 Hz, 2H, C_5H_4), 4.27 (q, $^3J(^1H,^1H)$ = 7.1 Hz, 2H, CH_2CH_3), 3.85 (s-br, 1H, C_3H_5), 2.80 (s-br, 2H, C_3H_5), 1.34 (t, $^3J(^1H,^1H)$ = 7.1Hz, 3H, CH_2CH_3), 1.00 (s-br, 2H, C_3H_5). FTIR (ATR, cm^{-1}): 1944 vs [ν_a(C≡O)], 1863 vs [ν_s(C≡O)], 1712 s [ν(C=O)].

*4.4 Synthesis of [(η^3-C_3H_5)(η^5-C_5H_4COOH)Mo(CO)$_2$] (**3**)*

[(η^3-C_3H_5)(η^5-C_5H_4COOEt)Mo(CO)$_2$] (**2**; 1.80 g, 5.45 mmol) was dissolved in solution of NaOMe (0.5 mol/l in MeOH, 60 ml, 30 mmol) and stirred for 2h. The reaction mixture was treated with water (5 ml) and stirred overnight. After that, the mixture was diluted with water (50 ml) and washed with CH_2Cl_2 (3 × 50 ml). The aqueous phase was treated with aqueous HCl (w = 35%) dropwise until the pH is acidic. Upon acidification yellow solid precipitates. The product was extracted with CH_2Cl_2 (50 ml), separated from aqueous phase and dried with magnesium sulfate. The volatiles were vacuum evaporated and the final product was washed with hexane (20 ml) and vacuum dried. Yield 1.47 g (4.78 mmol, 89%). Calcd for $C_{11}H_{10}MoO_4$: C, 43.73; H, 3.34. Found: 43.49; H, 3.61. ^{1}H NMR (CD_3COCD_3, 500 MHz, δ ppm; 4:1 mixture of isomer **a** (*exo*-C_3H_5) and **b** (*endo*-C_3H_5)): 5.91 (s-br, 2H of **a** and 2H of **b**, C_5H_4), 5.56 (s-br, 2H of **a** and 2H of **b**, C_5H_4), 4.18 (s-br, 1H of **a**,

H^{meso}, C_3H_5), 3.78 (s-br, 2H of **a**, H^{syn}, C_3H_5), 3.73 (s-br, 2H of **b**, H^{syn}, C_3H_5), 1.79 (s-br, 2H of **b**, H^{anti}, C_3H_5), 0.98 (s-br, 2H of **a**, H^{anti}, C_3H_5). FTIR (ATR, cm^{-1}): 1927vs [ν_a(C≡O)], 1861 vs [ν_s(C≡O)], 1678 s [ν(C=O)].

*4.5 Synthesis of Na[(η^3-C_3H_5)(η^5-C_5H_4COO)Mo(CO)$_2$] (**3-Na**)*

[(η^3-C_3H_5)(η^5-C_5H_4COOH)Mo(CO)$_2$] (**3**; 50 mg; 0.17 mmol) was dissolved in methanol (5 ml) and treated with methanolic solution of NaOMe (c = 0.5 mol/l; 0.33 ml, 0.17 mmol) and stirred for 10 min. The solvent was vacuum evaporated and the product was washed with Et_2O and vacuum dried. Yield: 52 mg (0.16 mmol, 97%). Calcd for $C_{11}H_9MoNaO_4$: C, 40.76; H, 2.80. Found: C, 40.46; H, 2.54. ^{1}H NMR (CD_3COCD_3, 500 MHz, δ ppm; 4:1 mixture of isomer **a** (*exo*-C_3H_5) and **b** (*endo*-C_3H_5)): 5.51 (t, $^3J(^1H,^1H) = {}^4J(^1H,^1H)$ = 2.2 Hz, 2H of **a** and 2H of **b**, C_5H_4), 5.29 (t, $^3J(^1H,^1H) = {}^4J(^1H,^1H)$ = 2.2 Hz, 2H of **a** and 2H of **b**, C_5H_4), 3.85 (tt, $^3J(^1H,^1H)$ = 10.8 Hz, $^3J(^1H,^1H)$ = 7.0 Hz, 1H of **a**, H^{meso}, C_3H_5), 3.48 (s-br, 1H of **b**, H^{meso}, C_3H_5), 2.78 (d, $^3J(^1H,^1H)$ = 5.6 Hz, 2H of **b**, H^{syn}, C_3H_5), 2.68 (d, $^3J(^1H,^1H)$ = 7.0 Hz, 2H of **a**, H^{syn}, C_3H_5), 1.52 (d, $^3J(^1H,^1H)$ = 10.0 Hz, 2H of **b**, H^{anti}, C_3H_5), 0.77 (d, $^3J(^1H,^1H)$ = 10.8 Hz, 2H of **a**, H^{anti}, C_3H_5). FTIR (ATR, cm^{-1}): 1913 vs [ν_a(C≡O)], 1839 vs [ν_s(C≡O)], 1584 s [ν_a(COO)].

*4.6 Synthesis of [1,3-{(η^3-C_3H_5)Mo(CO)$_2$(η^5-C_5H_4CO)$_2$}$_2$$C_6H_4$] (**12**) and [($\eta^3$-$C_3H_5$)($\eta^5$-$C_5H_4COC_6H_4COOH$-3)Mo(CO)$_2$] (**14**)*

Solution of sodium cyclopentadienide (2.1 g, 24 mmol) in THF (50 ml) was treated dimethyl isophthalate (**4**; 3.1 g, 16 mmol) and heated under reflux overnight. After cooling to room temperature, volatiles were vacuum evaporated and crude product was washed with Et_2O and vacuum dried to give 3.2 g of yellow powder. FTIR (ATR, cm^{-1}): 1705 vs [ν(C=O)], 1511 br [ν(C=O)]. 0.8 g of this intermediate was dissolved in THF (20 ml), cooled to –80°C and then added dropwise to a solution of [(η^3-C_3H_5)Mo(CO)$_2$(NCMe)$_2$Cl] (1.6 g; 5.15 mmol) in THF (20 ml) precooled to –80°C. The reaction mixture was stirred at room temperature overnight and then vacuum evaporated to dryness. The crude product was extracted with hot hexane (3 × 50 ml). The volatiles were vacuum evaporated and the final product was washed with cold hexane and vacuum dried. Appearance of **10** and **12** in molar ratio 3:1 mixture was confirmed by ^{1}H NMR spectroscopy. This mixture was dissolved in solution of NaOMe (0.5 mol/l in MeOH, 40 ml, 20 mmol) and stirred for 2h. The reaction mixture was treated with water (3 ml) and stirred overnight. After that, the mixture was diluted with water (50 ml) and washed with toluene (3 × 50 ml). The collected organic phases were dried with magnesium sulfate and volatiles were vacuum evaporated. Pure compound **12** was obtained after washing with cold hexane (5 ml) and vacuum drying. **12:** Yield: 0.47 g

(0.73 mmol, 18% based on dimethyl isophthalate). Yellow powder. Calcd for $C_{28}H_{22}Mo_2O_6$: C, 52.03; H, 3.43. Found: C, 52.20; H, 3.56. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.08 (t, $^4J(^1H,^1H)$ = 0.8 Hz, 1H, H^2, C_6H_4), 7.93 (dd, $^3J(^1H,^1H)$ = 7.8 Hz, $^4J(^1H,^1H)$ = 0.8 Hz, 2H, $H^{4,6}$ C_6H_4), 7.58 (t, $^3J(^1H,^1H)$ = 7.8 Hz, 1H, H^5, C_6H_4), 5.76 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.4 Hz, 4H, C_5H_4), 5.52 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.4 Hz, 4H, C_5H_4), 3.89 (s-br, 2H, C_3H_5), 2.80 (s-br, 4H, C_3H_5), 1.54 (s-br, 4H, C_3H_5). FTIR (ATR, cm^{-1}): 1936 vs [ν_a(C≡O)], 1846 vs [ν_s(C≡O)], 1637 s [ν(C=O)]. The aqueous phase was treated with aqueous HCl (w = 35%) dropwise until the pH is acidic. Upon acidification yellow solid precipitates. The product was extracted with CH_2Cl_2 (50 ml), separated from aqueous phase and dried with magnesium sulfate. The volatiles were vacuum evaporated and the final product was washed with hexane (20 ml) and vacuum dried. **14:** Yield: 0.73 g (1.80 mmol, 45% based on dimethyl isophthalate). Yellow powder. Calcd for $C_{18}H_{14}MoO_5$: C, 53.22; H, 3.47. Found: C, 53.54; H, 3.57. ^{1}H NMR (CD_3OD, 400 MHz, δ ppm): 8.40 (s, 1H, H^2, C_6H_4), 8.26 (d, $^3J(^1H,^1H)$ = 7.7 Hz, 1H, $H^{4,6}$, C_6H_4), 8.00 (d, $^3J(^1H,^1H)$ = 7.7 Hz, 1H, $H^{4,6}$, C_6H_4), 7.65 (t, $^3J(^1H,^1H)$ = 7.7 Hz, 1H, H^5,C_6H_4), 5.92 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.3 Hz, 2H, C_5H_4), 5.63 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.3 Hz, 2H, C_5H_4), 4.10 (s-br, 1H, C_3H_5), 2.82 (d, $^3J(^1H,^1H)$ = 6.3 Hz, 2H, C_3H_5), 1.02 (s-br, 2H, C_3H_5). FTIR (ATR, cm^{-1}): 1937 vs [ν_a(C≡O)], 1850 vs [ν_s(C≡O)], 1688 s [ν(C=O)], 1628s [ν(C=O)]. Single crystals suitable for X-ray diffraction analysis were prepared by slow evaporation methanolic solution under inert atmosphere.

*4.7 Synthesis of [1,4-{(η^3-C_3H_5)Mo(CO)$_2$(η^5-$C_5H_4CO)_2$}$_2$$C_6H_4$] (**13**) and [($\eta^3$-$C_3H_5$)($\eta^5$-$C_5H_4COC_6H_4COOH$-4)Mo(CO)$_2$] (**15**)*

The reaction was carried out as was described for compounds **12** and **14**, but with dimethyl terephthalate (2.4 g, 15 mmol). **13:** Yield: 0.38 g (0.59 mmol, 15% based on dimethyl terephthalate). Yellow powder. Calcd for $C_{28}H_{22}Mo_2O_6$: C, 52.03; H, 3.43. Found: C, 52.28; H, 3.65. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.80 (s, 4H, C_6H_4), 5.75 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.4 Hz, 4H, C_5H_4), 5.53 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.4 Hz, 4H, C_5H_4), 3.89 (s-br, 2H, C_3H_5), 2.80 (s-br, 4H, C_3H_5), 1.54 (s-br, 4H, C_3H_5). FTIR (ATR, cm^{-1}): 1937 vs [ν_a(C≡O)], 1850 vs [ν_s(C≡O)], 1628 s [ν(C=O)]. Single crystals suitable for X-ray diffraction analysis were prepared by sublimation in a flame sealed ampoule at 100°C (p = 0.01 Pa). **15:** Yield: 0.71 g (1.75 mmol, 44% based on dimethyl terephthalate). Yellow powder. Calcd for $C_{18}H_{14}MoO_5$: C, 53.22; H, 3.47. Found: C, 53.49; H, 3.62. ^{1}H NMR (CD_3OD), 400 MHz, δ ppm): 8.16 (d, $^3J(^1H,^1H)$ = 8.3 Hz, 2H, C_6H_4), 7.85 (d, $^3J(^1H,^1H)$ = 8.3 Hz, 2H, C_6H_4), 5.93 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.3 Hz, 2H, C_5H_4), 5.61 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.3 Hz, 2H, C_5H_4),

4.09 (s-br, 1H, C_3H_5), 2.81 (d, $^3J(^1H,^1H)$ = 6.5 Hz, 2H, C_3H_5), 1.02 (s-br, 2H, C_3H_5). FTIR (ATR, cm^{-1}): 1934 vs [ν_a(C≡O)], 1837 vs [ν_s(C≡O)], 1683 s [ν(C=O)], 1626 s [ν(C=O)].

*4.8 Synthesis of C_9H_7COOH-2 (**16**)*

Indene (27.0 g, 232 mmol) was treated with oxalyl bromide (25.0 g, 116 mmol) dropwise and then heated to reflux for 4 h. After cooling to room temperature, reaction was quenched with ice/water mixture and neutralized with aqueous solution of sodium carbonate (w = 10%). The aqueous phase was washed with Et_2O (2 × 100 ml) and treated with aqueous HCl (w = 35%) dropwise until the pH is acidic. Upon acidification white solid precipitates. The product was extracted with Et_2O (3 × 100 ml). The combined organic phases were dried with magnesium sulfate and volatiles were vacuum evaporated. Final product was vacuum dried. Yield: 8.9 g (56 mmol, 48%). Analytical and spectroscopic data are in line with those published elsewhere [68]. FTIR (ATR, cm^{-1}): 1663 vs [ν(C=O)]. Single crystals suitable for X-ray diffraction analysis were prepared by slow Et_2O solution under inert atmosphere.

*4.9 Synthesis of C_9H_7COOEt-2 (**17**)*

C_9H_7COOH-2 (**16**; 1.00 g, 6.24 mmol) was dissolved in $SOCl_2$ (6 ml) and stirred at room temperature for 1 h. After that, the volatiles were vacuum evaporated. Resulting solid was treated with ethanol (6.3 ml) and stirred at room temperature for 2 h. After dilution with Et_2O, the reaction was quenched with addition of water (10 ml). The mixture was neutralized with aqueous solution of sodium carbonate (w = 10%). The combined organic phases were dried with magnesium sulfate and volatiles were vacuum evaporated. Final product was vacuum dried. Yield: 0.95 g (5.05 mmol, 81%). Analytical and spectroscopic data are in line with those published elsewhere [69]. FTIR (ATR, cm^{-1}): 1699 vs [ν(C=O)].

*4.10 Synthesis of [(η^3-C_3H_5)(η^5-C_9H_6COOEt-2)Mo(CO)$_2$] (**18**)*

A solution of C_9H_7COOEt-2 (**17**; 0.45 g, 2.39 mmol) in THF (30 ml) was cooled to 0°C and treated with *n*-BuLi (1.6 mol/l in hexane; 1.50 ml, 2.40 mmol) dropwise and then stirred at room temperature for 1 h. The reaction mixture was cooled to –80°C and then added dropwise to a solution of [(η^3-C_3H_5)Mo(CO)$_2$(NCMe)$_2$Cl] (0.75 g, 2.41 mmol) in THF (20 ml) precooled to –80°C. The reaction mixture was stirred at room temperature overnight and then vacuum evaporated to dryness. The crude product was extracted with hot hexane (3 × 30 ml). The volatiles were vacuum evaporated and the final product was washed with cold hexane (5 ml) and vacuum

dried. Yield: 0.60 g (1.58 mmol, 66%). Yellow powder. Calcd for $C_{17}H_{16}MoO_4$: C, 53.70; H, 4.24. Found: C, 53.98; H, 4.05. ^{1}H NMR ($CDCl_3$, 500 MHz, δ ppm; 1:1 mixture of isomer **a** (*exo*-C_3H_5) and **b** (*endo*-C_3H_5)): 7.11–6.97 (m, 4H of **a** and 4H of **b**, $H^{4–7}$, C_9H_6), 6.53, 6.44 (2 × s, 2H of **a** and 2H of **b**, $H^{1,3}$, C_9H_6), 4.37, 4.27 (2 × q, ^3J = 7.1 Hz, 2H of **a** and 2H of **b**, CH_2CH_3), 3.50 (d, ^3J = 6.5 Hz, 2H of **b**, H^{syn}, C_3H_5), 3.37 (tt, ^3J = 11.0 Hz, ^3J = 6.5 Hz, 1H of **b**, H^{meso}, C_3H_5), 2.37 (d, ^3J = 7.4 Hz, 2H of **a**, H^{syn}, C_3H_5), 1.40, 1.30 (2 × q, ^3J = 7.1 Hz, 3H of **a** and 3H of **b**, CH_2CH_3), 1.03 (d, ^3J = 11.2 Hz, 2H of **a**, H^{anti}, C_3H_5), –0.05 (tt, ^3J = 11.2 Hz, ^3J = 7.4 Hz, 1H of **a**, H^{meso}, C_3H_5), –0.77 (d, ^3J = 11.0 Hz, 2H of **b**, H^{anti}, C_3H_5). FTIR (ATR, cm^{-1}): 1962 vs [ν_a(C≡O)], 1883 vs [ν_s(C≡O)], 1705 s [ν(C=O)]. Single crystals suitable for X-ray diffraction analysis were prepared by sublimation in a flame sealed ampoule at 100°C (p = 0.01 Pa).

*4.11 Synthesis of [(η^5-C_5H_4COOH)Mo(CO)$_2$(phen)][BF_4] (**19**)*

[(η^3-C_3H_5)(η^5-C_5H_4COOH)Mo(CO)$_2$] (**3**; 0.80 g, 2.65 mmol) was dissolved in CH_2Cl_2 (10 ml), cooled at 0°C, treated with acetonitrile (1 ml) and then with HBF_4·Et_2O (0.36 ml, 2.65 mmol). The reaction mixture was stirred at room temperature overnight and then volatiles were vacuum evaporated. The intermediate was washed with Et_2O, recrystallized from a mixture CH_2Cl_2/Et_2O dissolved in acetone (20 ml) and treated with 1,10-phenanthroline (0.48 g, 2.66 mmol). The reaction mixture was stirred at room temperature overnight. The crude product was washed with Et_2O, recrystallized from CH_2Cl_2/Et_2O and vacuum dried. Yield: 1.15 g (2.18 mmol, 82%). Orange powder. Calcd for $C_{20}H_{13}BF_4MoN_2O_4$: C, 45.49; H, 2.48; N, 5.30. Found: C, 45.26; H, 2.40; N, 5.57. ^{1}H NMR (CD_3COCD_3, 400 MHz, δ ppm): 9.42 (dd, $^3J(^1H,^1H)$ = 5.5 Hz, $^4J(^1H,^1H)$ = 1.3 Hz, 2H, $H^{2,9}$, $C_{12}H_8N_2$), 8.80 (dd, $^3J(^1H,^1H)$ = 8.2 Hz, $^4J(^1H,^1H)$ = 1.3 Hz, 2H, $H^{4,8}$, $C_{12}H_8N_2$), 8.21 (s, 2H, $H^{5,6}$, $C_{12}H_8N_2$), 7.96 (dd, $^3J(^1H,^1H)$ = 8.2 Hz, $^3J(^1H,^1H)$ = 5.5 Hz, 2H, $H^{3,8}$, $C_{12}H_8N_2$), 6.28 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.4 Hz, 2H, C_5H_4), 5.85 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.4 Hz, 2H, C_5H_4). FTIR (ATR, cm^{-1}): 1975 vs [ν_a(C≡O)], 1898 vs [ν_s(C≡O)], 1717 s [ν(C=O)], 1030 vs-br [ν_a(BF)]. Single crystals of **19**·0.5Et_2O suitable for X-ray diffraction analysis were prepared by slow diffusion of Et_2O into acetonitrile solution.

*4.12 Synthesis of [(η^5-C_5H_4COOH)Mo(CO)$_2$(dppz)][BF_4] (**20**)*

The reaction was carried out as was described for compound **19**, but with dipyrido[3,2-*a*:2',3'-c]phenazine (0.75 g, 2.66 mmol). Yield: 1.28 g (2.03 mmol, 77%). Red powder. Calcd for $C_{26}H_{15}BF_4MoN_4O_4$: C, 45.55; H, 2.40; N, 8.89. Found: C, 45.24; H, 2.12; N, 9.05. ^{1}H NMR (CD_3COCD_3, 400 MHz, δ ppm): 9.97 (dd, $^3J(^1H,^1H)$ = 8.1 Hz, $^4J(^1H,^1H)$ = 1.3 Hz, 2H, $H^{1,8}$, $C_{18}H_{10}N_4$), 9.83 (dd, $^3J(^1H,^1H)$ = 5.6 Hz, $^4J(^1H,^1H)$ = 1.3 Hz, 2H, $H^{3,6}$,

$C_{18}H_{10}N_4$), 8.53 (dd, $^3J(^1H,^1H)$ = 6.6 Hz, $^4J(^1H,^1H)$ = 3.5 Hz, 2H, $H^{10–13}$, $C_{18}H_{10}N_4$), 8.33 (dd, $^3J(^1H,^1H)$ = 8.1 Hz, $^3J(^1H,^1H)$ = 5.6 Hz, $H^{2,7}$, 2H, $C_{18}H_{10}N_4$), 8.22 (dd, $^3J(^1H,^1H)$ = 6.6 Hz, $^4J(^1H,^1H)$ = 3.5 Hz, 2H, $H^{10–13}$, $C_{18}H_{10}N_4$), 6.65 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.4 Hz, 2H, C_5H_4), 6.25 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.4 Hz, 2H, C_5H_4). FTIR (ATR, cm^{-1}): 1975 vs [ν_a(C≡O)], 1895 vs [ν_s(C≡O)], 1723 s [ν(C=O)], 1030 vs-br [ν_a(BF)].

*4.13 Synthesis of [(η^5-C_5H_4COOH)Mo(CO)$_2$(dafone)][BF_4] (**21**)*

The reaction was carried out as was described for compound **19**, but with 4,5-diazafluoren-9-one (0.485 g, 2.66 mmol). Yield: 1.05 g (1.98 mmol, 75%). Red powder. Calcd for $C_{19}H_{11}BF_4MoN_2O_5$: C, 43.05; H, 2.09; N, 5.29. Found: C, 43.35; H, 2.24; N, 5.42. ^{1}H NMR (CD_3COCD_3, 400 MHz, δ ppm): 9.24 (dd, $^3J(^1H,^1H)$ = 5.8 Hz, $^4J(^1H,^1H)$ = 0.8 Hz, 2H, $H^{3,6}$, $C_{11}H_6N_2O$), 8.43 (dd, $^3J(^1H,^1H)$ = 7.5 Hz, $^4J(^1H,^1H)$ = 0.8 Hz, 2H, $H^{1,8}$, $C_{11}H_6N_2O$), 7.93 (dd, $^3J(^1H,^1H)$ = 7.5 Hz, $^3J(^1H,^1H)$ = 5.8 Hz, 2H, $H^{2,7}$, $C_{11}H_6N_2O$), 6.50 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.4 Hz, 2H, C_5H_4), 6.24 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.4 Hz, 2H, C_5H_4). FTIR (ATR, cm^{-1}): 1993 vs [ν_a(C≡O)], 1906 vs [ν_s(C≡O)], 1740 s [ν(C=O)], 1717 s [ν(C=O)], 1030 vs-br [ν_a(BF)].

*4.14 Synthesis of [(η^5-C_5H_4COOH)Mo(CO)$_2$(bq)][BF_4] (**22**)*

The reaction was carried out as was described for compound **19**, but with 2,2'-biquinoline (0.68 g, 2.65 mmol). Yield: 1.10 g (1.82 mmol, 69%). Red powder. Calcd for $C_{26}H_{17}BF_4MoN_2O_4$: C, 51.69; H, 2.84; N, 4.64. Found: C, 51.36; H, 2.95; N, 4.35. ^{1}H NMR (CD_3CN, 400 MHz, δ ppm): 8.99 (d, $^3J(^1H,^1H)$ = 8.7 Hz, 2H, $H^{4,4'}$, $C_{18}H_{12}N_2$), 8.67 (d, $^3J(^1H,^1H)$ = 8.7 Hz, 2H, $H^{3,3'}$, $C_{18}H_{12}N_2$), 8.52 (d, $^3J(^1H,^1H)$ = 8.7 Hz, 2H, $H^{8,8'}$, $C_{18}H_{12}N_2$), 8.25 (d, $^3J(^1H,^1H)$ = 8.3 Hz, 2H, $H^{5,5'}$, $C_{18}H_{12}N_2$), 8.12 (ddd, $^3J(^1H,^1H)$ = 8.7 Hz, $^3J(^1H,^1H)$ = 7.0 Hz, $^4J(^1H,^1H)$ = 1.3 Hz, 2H, $H^{7,7'}$, $C_{18}H_{12}N_2$), 7.92 (ddd, $^3J(^1H,^1H)$ = 8.3 Hz, ^{3}J(^{1}H,^{1}H) = 7.0 Hz, $^4J(^1H,^1H)$ = 1.0 Hz, 2H, $H^{6,6'}$, $C_{18}H_{12}N_2$), 6.14 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.3 Hz, 2H, C_5H_4), 5.96 (t, $^3J(^1H,^1H)$ = $^4J(^1H,^1H)$ = 2.3 Hz, 2H, C_5H_4). FTIR (ATR, cm^{-1}): 1975 vs [ν_a(C≡O)], 1895 vs [ν_s(C≡O)], 1723 s [ν(C=O)], 1030 vs-br [ν_a(BF)].

4.15 X-ray crystallography

The X-ray data for the crystals of the compounds **13**, **14**, **16** and **19**·0.5Et_2O were obtained at 150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Data reductions were performed with DENZO-SMN [70]. The absorption was corrected by integration methods [71]. Structures were solved by direct methods (Sir92) [72] and refined by full-matrix least squares based on F^2 (SHELXL97) [73]. Hydrogen atoms were mostly localized on a

difference Fourier map. However, to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $U_{iso}(H) = 1.2[U_{eq}$(pivot atom)] or $1.5U_{eq}$ for the methyl moiety with C−H = 0.96, 0.97, and 0.93 Å for methyl, methylene, and hydrogen atoms in aromatic rings or the allyl moiety, respectively. The structure of **13** contains a positional disorder of allyl group at one of the carbon atoms (C11) and was split into two positions with equal occupancy, this disorder was treated with SHELXL software [73].

Crystallographic data for **18** were collected on Nonius KappaCCD diffractometer equipped with Bruker APEX-II CCD detector by monochromatized MoKα radiation (λ = 0.71073 Å) at a temperature of 150(2) K. The structure was solved by direct methods (XT) [74] and refined by full matrix least squares based on F^2 (SHELXL2014) [75]. The absorption correction was carried on using numerical method. The hydrogen atoms were found on difference Fourier map and were recalculated into idealized positions. All hydrogen atoms were refined as fixed (riding model) with assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or $1.5\ U_{eq}$ for methyl moiety.

CCDC 1569911 (for **14**), 1569912 (for **16**), 1569913 (for **19**·0.5Et_2O), 1569914 (for **13**) and 1584976 (for **18**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.16 Biological studies

The studies were performed on the human T-lymphocytic leukemia cells MOLT-4 obtained from the American Type Culture Collection (USA) obtained from the European Collection of Cell Cultures (Porton Down, Salisbury, Great Britain). The cells were cultured in Iscove's modified Dulbecco's medium (IMDM) supplemented with a 20% fetal calf serum and 0.05% L-glutamine (all Sigma-Aldrich, USA) in a humidified incubator at 37 °C and a controlled 5% CO_2 atmosphere. The cell lines in the maximal range of up to 20 passages have been used for this study. Cytotoxicity of the compounds was evaluated by the WST-1 cell viability test (Roche, Germany) according to manufacturer's instructions as described previously [62]. Briefly, the leukemia cells were seeded in 96-wells plate, incubated in solutions of the compounds for 24 h, then washed and incubated for 180 min in WST-1 solution. The absorbance at 440 nm corresponding to cell viability was measured using multiplate reader (Tecan Infinite 200). The inhibitory effect of the compounds were analyzed through measurement of cell proliferation and viability using propidium iodide (Sigma-Aldrich, USA) and a flow cytometer with Coulter volume.

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References

[1] B. Rosenberg, L. van Camp, T. Krigas, Nature 205 (1965) 698–699.
[2] B. Rosenberg, L. van Camp, J. E. Trosko, V. H. Mansour, Nature 222 (1969) 385–386.
[3] K. D. Mjos, C. Orvig, Chem. Rev. 114 (2014) 4540–4563.
[4] Z. Liu, P. J. Sadler, Acc. Chem. Res. 47 (2014) 1174–1185.
[5] G. Süss-Fink, Dalton Trans. 39 (2009) 1673–1688.
[6] W. Liu, R. Gust, Chem. Soc. Rev. 42 (2013) 755–773.
[7] C. Santini, M. Pellei, V. Gandin, M. Porchia, F. Tisato, C. Marzano, Chem. Rev. 114 (2014) 815–862.
[8] K. Strohfeldt, M. Tacke, Chem. Soc. Rev. 37 (2008) 1174–1187.
[9] H. K. Liu, P. J. Sadler, Acc. Chem. Res. 44 (2011) 349–359.
[10] A. Gautier, F. Cisnetti, Metallomics 4 (2012) 23–32.
[11] N. P. E. Barry, P. J. Sadler, Chem. Soc. Rev. 41 (2012) 3264–3279.
[12] A. F. A. Peacock, P. J. Sadler, Chem. Asian J. 3 (2008) 1890–1899.
[13] O. J. Stacey, S. J. A. Pope, RSC Adv. 3 (2013) 25550–25564.
[14] S. K. Singh, D. S. Pandey, RSC Adv. 4 (2014) 1819-1840.
[15] N. Cutillas, G. S. Yellol, C. de Haro, C. Vicente, V. Rodríguez, J. Ruiz, Coord. Chem. Rev. 257 (2013) 2784–2797.
[16] J. S. Butler, P. J. Sadler, Curr. Opin. Chem. Biol. 17 (2013) 175–188.
[17] N. Muhammad, Z. Guo, Curr. Opin. Chem. Biol. 19 (2014) 144–153.
[18] S. H. van Rijt, P. J. Sadler, Drug Discov. Today 14 (2009) 1089–1097.
[19] J. Honzíček, J. Vinklárek, Inorg. Chim. Acta 437 (2015) 87–94.
[20] I. Honzíčková, J. Honzíček, J. Vinklárek, Z. Padělková, M. Řezáčová, L. Šebestová, Appl. Organomet. Chem. 28 (2014) 252–258.
[21] J. Honzíček, J. Vinklárek, Z. Padělková, L. Šebestová, K. Foltánová, M. Řezáčová, J. Organomet. Chem. 716 (2012) 258–268.
[22] J. Honzíček, J. Vinklárek, M. Erben, Z. Padělková, L. Šebestová, M. Řezáčová, J. Organomet. Chem. 749 (2014) 387–393.
[23] L. Šebestová, R. Havelek, M. Řezáčová, J. Honzíček, Z. Kročová, J. Vinklárek, Chem. Biol. Interact. 242 (2015) 61–70.
[24] O. Mrózek, L. Šebestová, J. Vinklárek, M. Řezáčová, A. Eisner, Z. Růžičková, J. Honzíček, Eur. J. Inorg. Chem. (2016) 519–529.
[25] M. R. P. Norton de Matos, C. C. Romão, C. C. L. Pereira, S. S. Rodrigues, M. Mora, M. J. P. Silva, P. M. Alves, C. A. Reis, International Patent WO/2005/087783.
[26] D. Bandarra, M. Lopes, T. Lopes, J. Almeida, M. S. Saraiva, M. Vasconcellos-Dias, C. D. Nunes, V. Félix, P. Brandão, P. D. Vaz, M. Meireles, M. J. Calhorda, J. Inorg. Biochem. 104 (2010) 1171–1177.
[27] T. Turki, T. Guerfel, F. Bouachir, Polyhedron 28 (2009) 569–573.
[28] M. S. Saraiva, S. Quintal, F. M. C. Portugal, T. A. Lopes, V. Félix, J. M. F. Nogueira, M. Meireles, M. G. B. Drew, M. J. Calhorda, J. Organomet. Chem. 693 (2008) 3411–3418.
[29] R. B. Woodward, M. Rosenblum, M. C. Whiting, J. Am. Chem. Soc. 74 (1952) 3458–3459.
[30] R. A. Benkeser, D. Goggin, G. Schroll, J. Am. Chem. Soc. 76 (1954) 4025–4026.
[31] F. Shafiq, D. J. Szalda, C. Creutz, R. M. Bullock, Organometallics 19 (2000) 824–833.
[32] L. S. Micallef, B. T. Loughrey, P. C. Healy, P. G. Parsons, M. L. Williams, Organometallics 29 (2010) 6237–6244.
[33] D. Braga, L. Maini, F. Grepioni, Angew. Chem. Int. Ed. 37 (1998) 2240–2242.
[34] D. Braga, M. Polito, D. D'Addario, Cryst. Growth Des. 4 (2004) 1109–1112.
[35] D. Braga, M. Polito, S. L. Giaffreda, F. Grepioni, Dalton Trans. (2005) 2766–2773.
[36] B. Albada, N. Metzler-Nolte, Chem. Rev. 116 (2016) 11797–11839.
[37] T. Uehara, T. Uemura, S. Hirabayashi, S. Adachi, K. Odaka, H. Akizawa, Y. Magata, T. Irie, Y. Arano, J. Med. Chem. 50 (2007) 543–549.
[38] Q. Nadeem, D. Can, Y. Shen, M. Felber, Z. Mahmood, R. Alberto, Org. Biomol. Chem. 12 (2014) 1966–1974.

[39] Y. Liu, B. Spingler, P. Schmutz, R. Alberto, J. Am. Chem. Soc. 130 (2008) 1554–1555.
[40] S. Top, J. S. Lehn, P. Morel, G. Jaouen, J. Organomet. Chem. 583 (1999) 63–68.
[41] C. Elschenbroich, O. Schiemann, O. Burghaus, K. Harms, J. Am. Chem. Soc. 119 (1997) 7452–7457.
[42] A. B. Ilyukhin, P. S. Koroteev, M. A. Kiskin, Z. V. Dobrokhotova, V. M. Novotortsev, J. Mol. Struct. 1033 (2013) 187–199.
[43] A. R. Petrov, K. Jess, M. Freytag, P. G. Jones, M. Tamm, Organometallics 32 (2013) 5946–5954.
[44] W. P. Hart, D. W. Macomber, M. D. Rausch, J. Am. Chem. Soc. 102 (1980) 1196–1198.
[45] L. Busetto, C. Cassani, V. Zanotti, V. G. Albano, P. Sabatino, Organometallics 20 (2001) 282–288.
[46] S. Ursillo, D. Can, H. W. P. N'Dongo, P. Schmutz, B. Spingler, R. Alberto, Organometallics 33 (2014) 6945–6952.
[47] k. Splith, n. Neundorf, W. Hu, H. W. Peindy N'Dongo, V. Vasylyeva, K. Merz, U. Schatzschneider, Dalton Trans. 39 (2010) 2536–2545.
[48] G. Schmitt, S. Özman, J. Org. Chem. 41 (1976) 3331–3332.
[49] P. C. Reeves, Org. Synth., Coll. Vol. 6 (1988) 625–628.
[50] S. Vanicek, H. Kopacka, K. Wurst, T. Müller, H. Schottenberger, B. Bildstein, Organometallics 33 (2014) 1152–1156.
[51] D. R. van Staveren, T. Weyhermüller, N. Metzler-Nolte, Organometallics 19 (2000) 3730–3735.
[52] S. S. Braga, V. Mokal, F. A. A. Paz, M. Pillinger, A. F. Branco, V. A. Sardão, C. V. Diogo, P. J. Oliveira, M. P. M. Marques, C. C. Romão, I. S. Gonçalves, Eur. J. Inorg. Chem. (2014) 5034–5045.
[53] W. Treibs, H. Orttmann, Chem. Berichte 93 (1960) 545–551.
[54] I. S. Gonçalves, L. F. Veiros, C. A. Gamelas, C. Cabrita, M. J. Calhorda, C. F. G. C. Geraldes, J. Green, E. Packham, M. G. B. Drew, V. Félix, A. G. Santos, C. C. Romão, J. Organomet. Chem. 792 (2015) 154–166.
[55] J. W. Faller, C. C. Chen, M. J. Mattina, A. Jakubowski, J. Organomet. Chem. 52 (1973) 361–386.
[56] J. Honzíček, C. C. Romão, M. J. Calhorda, A. Mukhopadhyay, J. Vinklárek, Z. Padělková, Organometallics 30 (2011) 717–725.
[57] I. Honzíčková, J. Vinklárek, C. C. Romão, Z. Růžičková, J. Honzíček, New J. Chem. 40 (2016) 245–256.
[58] J. Honzíček, J. Vinklárek, M. Erben, J. Lodinský, L. Dostál, Z. Padělková, Organometallics 32 (2013) 3502–3511.
[59] C. C. L. Pereira, S. S. Braga, F. A. A. Paz, M. Pillinger, J. Klinowski, I. S. Gonçalves, Eur. J. Inorg. Chem. (2006) 4278–4288.
[60] J. Honzíček, P. Kratochvíl, J. Vinklárek, A. Eisner, Z. Padělková, Organometallics 31 (2012) 2193–2202.
[61] J. Schejbal, J. Honzíček, J. Vinklárek, M. Erben, Z. Růžičková, Eur. J. Inorg. Chem. (2014) 5895–5907.
[62] J. Honzíček, I. Klepalová, J. Vinklárek, Z. Padělková, I. Císařová, P. Šiman, M. Řezáčová, Inorg. Chim. Acta 373 (2011) 1–7.
[63] W. L. F. Armarego, D. D. Perrin, in *Purification of Laboratory Chemicals*, Butterworth-Heinemann, Oxford, 1996.
[64] W. P. Hart, D. Shihua, M. D. Rausch, J. Organomet. Chem. 282 (1985) 111–121.
[65] W. Paw, R. Eisenberg, Inorg. Chem. 36 (1997) 2287–2293.
[66] M. J. Edelmann, J. M. Raimundo, N. F. Utesch, F. Diederich, C. Boudon, J. P. Gisselbrecht, M. Gross, Helv. Chim. Acta 85 (2002) 2195–2213.
[67] T.-S. Wong, R.-T. Chen , F.-C. Fang, C.-C. Wu, Y.-T. Lin, Org. Lett. 7 (2005) 1979–1982.
[68] T. Mita, K. Suga, K. Sato, Y. Sato, Org. Lett. 17 (2015) 5276–5279.
[69] B. G. Das, A. Chirila, M. Tromp, J. N. H. Reek, B. de Bruin, J. Am. Chem. Soc. 138 (2016) 8968–8975.
[70] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307–326.
[71] P. Coppens, in *Crystallographic Computing* (Eds.: F. R. Ahmed, S. R. Hall, C. P. Huber), Munksgaard, Copenhagen, **1970**, pp. 255–270.
[72] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, J. Appl. Cryst. 27 (1994) 435–436.
[73] G. M. Sheldrick, SHELXL97, University of Göttingen, Germany (2008).
[74] G. M. Sheldrick, Acta Cryst. A71 (2015) 3–8.
[75] G. M. Sheldrick, Acta Cryst. C71 (2015) 3–8.