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The effect of substitution on the cytotoxicity of molybdenum(II) and tungsten(II) compounds

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ABSTRACT

A series of allyl molybdenum $[(\eta^3\text{-}C_3H_5)Mo(CO)_2L_2Cl]$, $[(\eta^3\text{-}C_3H_4COOMe)Mo(CO)_2L_2Br]$, cyclopentadienyl molybdenum $[(\eta^5\text{-}C_5H_4R)Mo(CO)_2L_2][BF_4]$ (R = H, 4-$MeOC_6H_4CH_2$, 3,4,5-$(MeO)_3C_6H_2CH_2$), indenyl molybdenum $[(\eta^5\text{-}C_9H_6R)Mo(CO)_2L_2][BF_4]$ (R = H, 4-$MeOC_6H_4CH_2$) and cyclopentadienyl tungsten compounds $[(\eta^5\text{-}C_5H_5)W(CO)_2L_2][BF_4]$, where L_2 is *N,N′*-chelating ligand, were synthesized and characterized. The *in vitro* assay on human leukemia cells MOLT-4 has shown that the substitution in the π-ligand has lower effect of on cytotoxicity than exchange of the *N,N′*-chelating ligand. Nevertheless, even this modification can lead to considerable enhance of cytotoxicity as was evidenced on the series of the indenyl molybdenum(II) compounds.

1. Introduction

Cyclopentadienyl complexes of early transition metals have received great attention due to their biological properties [1–4]. The bis-cyclopentadienyl complexes $[(\eta^5\text{-}Cp)_2MCl_2]$ (Cp = C_5H_5; M = group IV, V, VI metal) and their congeners are under comprehensive scrutiny since the antitumor activity of $[(\eta^5\text{-}Cp)_2TiCl_2]$ was discovered in 1979 [5]. It is known that the bis-cyclopentadienyl compounds of Ti(IV) [6], V(IV) [7], Nb(IV) [8], Nb(V) [9], Mo(IV) [10] and Mo(VI) [9] are active toward Ehrlich ascites tumor. The complexes of other metals from group IV, V and VI are much less active or inactive [11]. Later studies on *cis*-platin resistant tumor cell lines have proved that the cytotoxicity could be enhanced through the substitution in the cyclopentadienyl ring. Promising results were obtained mainly for the aminoalkyl [12–14], methoxycarbonyl [15], and methoxybenzyl functionalized compounds [16,17].

In 2005, the molybdenum(II) compounds $[(\eta^3\text{-}C_3H_5)Mo(CO)_2L_2Br]$, $[(\eta^5\text{-}Cp)Mo(CO)_2L_2][BF_4]$ and $[(\eta^5\text{-}Ind)Mo(CO)_2L_2][BF_4]$ (Cp = C_5H_5; Ind = C_9H_7; L_2 = *N,N-*, *S,S-* and *P,P*-chelating ligands) were established as new class of the cytotoxic active compounds against several tumor cell lines [18]. Following studies have extended the series of cytotoxic active compounds and brought an early insight into the mechanism of the action [19–21].

The aim of this work is to describe effect of substitution on the cytotoxicity of the molybdenum(II) and tungsten(II) compounds. It covers several structural types, *N,N′*-chelating ligands and substituents in the allyl, cyclopentadienyl and indenyl ligands. The cytotoxicity of the compounds under study was established on human leukemia cells MOLT-4. This cell line is derived from human T-lymphoblastic leukemia and shows specific surface signs: $CD1^+$ (49%), $CD4^+$ (55%), $CD5^+$ (72%) and $CD7^+$ (77%). MOLT-4 contains wild type of protein p53, which is crucial in the cell response to cytostatic therapy and radiotherapy of p53wt tumors. Intact p53 pathway predicts them to be an excellent model for study of molecular mechanism responding mainly to DNA damage [22,23]. The current study follows our previous interest in chemistry of cyclopentadienyl compounds substituted in the cyclopentadienyl rings with functional groups [24,25].

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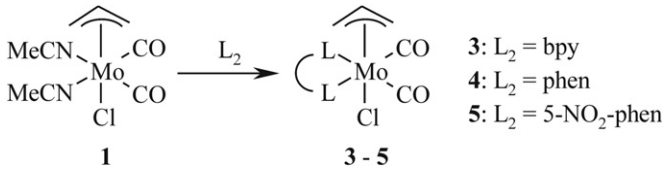


Scheme 1. Preparation of allyl complexes **3**–**5**.

2. Results and discussion

2.1. Synthesis of the allyl molybdenum complexes

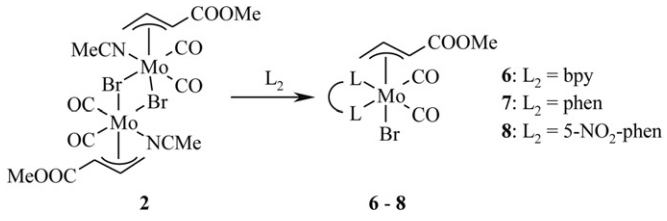
Literature procedure was used for the synthesis of the allyl molybdenum complexes [(η^3-C_3H_5)Mo(CO)$_2$L$_2$Cl] (**3**: L$_2$ = bpy, **4**: L$_2$ = phen) [26]. [(η^3-C_3H_5)Mo(CO)$_2$(5-NO$_2$-phen)Cl] (**5**) was prepared according to this procedure starting from [(η^3-C_3H_5)Mo(CO)$_2$(NCMe)$_2$Cl] and 5-nitrophenantroline (Scheme 1). ^{1}H NMR spectrum of compound **5** shows the signals of η^3-allyl ligand at 3.35 (1H), 3.29 (2H) and 1.37 ppm (2H). Coordinated 5-nitrophenathroline shows the signals at considerably lower field than the free ligand. The infrared spectrum of the compound **5** shows the bands in the region of terminal carbonyls stretching at 1930 (vs) and 1842 cm^{-1} (vs).

Methoxycarbonylallyl molybdenum compounds [(η^3-C_3H_4-COOMe)Mo(CO)$_2$L$_2$Br] (**6**: L$_2$ = bpy, **7**: L$_2$ = phen, **8**: L$_2$ = 5-NO$_2$-phen) were synthesized from [{(η^3-C_3H_4COOMe)Mo(CO)$_2$(NCMe)(μ-Br)}$_2$] (**2**) and appropriate *N*,*N*′-chelating ligand, see Scheme 2. The η^3-coordinated substituted allyl ligand gives characteristic pattern in the ^{1}H NMR spectra with one multiplet at ~3.9 ppm (1H), one singlet at ~3.5 ppm (3H), three doublets at ~3.3 (1H), ~2.1 (1H) and ~1.7 ppm (1H). Coordinated *N*,*N*′-chelating ligands give the signals in the range 9.4–7.5 ppm, see Tables 1 and 2. Spectrum of compound **7**·CH_2Cl_2 displays the singlet of uncoordinated dichloromethane at 5.45 ppm. Infrared spectra of the compounds **6**–**8** show characteristic C=O stretching of the ester group at 1695–1698 cm^{-1}. The stretching bands of the coordinated carbonyl ligands were found at considerably higher wavenumbers than in the case of the analogs with the unsubstituted allyl group (Table 3). It suggests a lower electron density at the metal that correlates with the electron-withdrawing properties of the substituent in the allyl ligand. Structures of the compounds **6**·0.5MeCN and **7**·CH_2Cl_2 were determined by single crystal X-ray diffraction analysis (Figs. 1 and 2).

2.2. Synthesis of the cyclopentadienyl molybdenum complexes

The complexes **12**–**17** were prepared from cationic acetonitrile complexes [(η^5-C_5H_4R)Mo(CO)$_2$(NCMe)$_2$][BF$_4$] (**9**: R = H, **10**: R = 4-MeOC$_6$H$_4$CH$_2$, **11**: R = 3,4,5-(MeO)$_3$C$_6$H$_2$CH$_2$) using reaction with the appropriate *N*,*N*-chelating ligand, see Scheme 3.

Starting cyclopentadienyl complex [(η^5-Cp)Mo(CO)$_2$(NCMe)$_2$][BF$_4$] (**9**) was prepared by literature procedure [27]. The ring-substituted analogs were synthesized using modified procedure (Scheme 4). The allyl complex [(η^3-C_3H_5)Mo(CO)$_2$(NCMe)$_2$Cl] (**1**) reacts with lithium cyclopentadienides to give allyl complexes [(η^3-C_3H_5)(η^5-C_5H_4R)Mo(CO)$_2$] (R = 4-MeOC$_6$H$_4$CH$_2$, 3,4,5-(MeO)$_3$C$_6$H$_2$CH$_2$). These intermediates were not isolated. They react with tetrafluoroboric acid in presence of acetonitrile to give cationic cyclopentadienyl complexes **10** and **11**, respectively.



Scheme 2. Preparation of methoxycarbonylallyl complexes **6**–**8**.

Table 1
^{1}H NMR data of coordinated bypiridine in molybdenum(II) compounds.[a]

	Doublet	Doublet	Multiplet	Multiplet
3	8.80	8.28	8.06	7.53
6	8.63, 8.52	8.31[b]	8.07	7.51
12	9.36	8.89	8.36	7.73
14	9.02	8.56	8.19	7.59
16	9.34	8.91	8.38	7.79
22	9.38	8.31	8.09	7.58
24	9.36, 9.26	8.33	8.11	7.61
28	9.25	8.61	8.21	7.56

[a] Chemical shifts are given in ppm.
[b] Multiplet.

^{1}H NMR spectra of the compounds **10** and **11** show two triplets of the cyclopentadienyl protons at ~5.5 and ~5.7 ppm, singlet of the coordinated acetonitrile at ~2.5 ppm and the signals of the substituents attached to the cyclopentadienyl ring. The infrared spectra show the C–H stretching band at ~3103 cm^{-1} that was assigned to the cyclopentadienyl ligand. Stretching bands of the carbonyl ligands were observed at 1977–1980 [ν_a(CO)] and 1886–1887 cm^{-1} [ν_s(CO)]. The coordinated acetonitrile ligands give two band of weak intensity at 2312–2322 [ν_a(CN)] and 2285–2289 cm^{-1} [ν_s(CN)]. The broad band of the B–F stretching at 1032 cm^{-1} proves the presence of the BF$_4$ anion.

The ^{1}H NMR spectra of the compounds **12**–**17** show signals of the coordinated *N*,*N*-chelating ligands and the signals of the cyclopentadienyl ligand. The coordinated 2,2′-bipyridine gives two doublets at 9.02–9.36 (2H) and 8.56–8.91 ppm (2H) and two multiplets at 8.19–8.38 (2H) and 7.59–7.79 ppm (2H), see Table 1. In the case of the 1,10-phenathroline complexes one singlet at 8.18–8.40 ppm and doublets of doublets at 9.41–9.74, 8.75–9.01 and 7.91–8.18 ppm were observed (Table 2). The infrared spectra of the compounds **12**–**17** show the CO stretching bands at considerably lower wavenumbers [ν_a(CO): 1965–1975 cm^{-1}, ν_s(CO): 1884–1901 cm^{-1}] than the acetonitrile analogs (Table 3). The cationic character of the compounds **12**–**17** is evident from the B–F stretching of the BF$_4$ anion that was observed at ~1050 cm^{-1}. Structures of the complexes **14** and **16** were determined by X-ray diffraction analysis (Figs. 3 and 4).

2.3. Synthesis of the indenyl molybdenum complexes

Indenyl molybdenum compounds **22**–**25** were prepared similarly to their cyclopentadienyl analogs, see Scheme 5. The starting indenyl compound [(η^5-Ind)Mo(CO)$_2$(NCMe)$_2$][BF$_4$] (**18**) is available through the literature procedure [28].

Table 2
^{1}H NMR data of coordinated phenanthroline in molybdenum(II) compounds.[a]

	Multiplet	Multiplet	Singlet	Multiplet
4	9.18[b]	8.63[b]	8.06	7.87[b]
7·CH_2Cl_2	9.03, 8.89	8.63	8.10	7.85
13	9.43[b]	8.75[b]	8.18	7.91[b]
15	9.41[b]	8.77[b]	8.21	7.97[b]
17	9.74[c]	9.01[c]	8.40	8.18
23	9.74[b]	8.66[b]	8.08	7.95[b]
25	9.71, 9.64	8.68[c]	8.09	7.98
29	9.90[b]	8.98[b]	8.40	8.12[b]

[a] Chemical shifts are given in ppm.
[b] Doublet of doublet.
[c] Doublet.

Table 3
Summary of the infrared data.[a]

	ν_a(CO)	ν_s(CO)		ν_a(CO)	ν_s(CO)
3	1929	1835	**16**	1970	1890
4	1934	1848	**17**	1970	1890
5	1930	1842	**18**	1976	1886
6	1957	1867	**20**	1937	1863
7·CH_2Cl_2	1950	1865	**21**	1964	1895
8	1970	1873	**22**	1974	1978
9	1985	1888	**23**	1968	1874
10	1977	1887	**24**	1962	1885
11	1980	1886	**25**	1964	1886
12	1973	1901	**27**	2045	1959
13	1965	1884	**28**	2046	1973
14	1975	1888	**29**	2045	1969
15	1971	1888			

[a] Wavenumbers of the CO stretching bands are given in cm^{-1}.

Substituted indenyl compound [(η^3-C_3H_5)(η^5-$C_9H_6CH_2C_6H_4$-OMe)Mo(CO)$_2$] (**20**), necessary for the synthesis of [(η^5-$C_9H_6CH_2$-C_6H_4OMe)Mo(CO)$_2$(NCMe)$_2$][BF_4] (**21**), was prepared using the fulvene protocol (Scheme 6). Condensation of indene with 4-methoxybenzaldehyde in the presence of pyrrolidine gives benzofulvene **19**. Subsequent reaction with lithium triethylborohydride gives appropriate substituted lithium indenide that reacts with [(η^3-C_3H_5)Mo(CO)$_2$(NCMe)$_2$Cl] (**1**) to give ring-substituted indenyl molybdenum compound [(η^3-C_3H_5)(η^5-$C_9H_6CH_2C_6H_4$-OMe)Mo(CO)$_2$] (**20**). This intermediate was isolated. It forms mixture of *exo* and *endo* isomers in solution as was evidenced by NMR spectroscopy. At room temperature, the molar ratio between *exo* and *endo* isomers was found to be 3:1. Infrared spectrum of the solid sample shows two bands in the region of CO stretching at 1937 [ν_a(CO)] and 1863 cm^{-1} [ν_s(CO)]. The structure of the compound **20** obtained from X-ray diffraction analysis is shown in Fig. 5.

Protonation of [(η^3-C_3H_5)(η^5-$C_9H_6CH_2C_6H_4$OMe)Mo(CO)$_2$] (**20**) with tetrafluoroboric acid in presence of acetonitrile gives cationic complex [(η^5-$C_9H_6CH_2C_6H_4$OMe)Mo(CO)$_2$(NCMe)$_2$][BF_4] (**21**). The product was characterized with ^{1}H NMR and infrared spectroscopy.

The spectroscopic characterization of the indenyl complexes with the *N*,*N*-chelating ligands **22** and **23** was reported previously [18,29]. The complexes **24** and **25** give the ^{1}H NMR spectra with the pattern of the substituted indenyl ligand that has the signals of indenyl at ~7.1 (1H), ~6.8 (1H), ~6.6 (2H), ~6.4 (1H) and ~5.7 ppm (1H). The 4-methoxybenzyl group gives two doublets of the CH_2 group at 4.5 and 4.0 ppm, two doublets of benzene at 7.3 and 6.8 ppm and singlet of the methoxy group at 3.7 ppm. The coordinated 2,2′-bipyridine in the compound **24** gives multiplets at

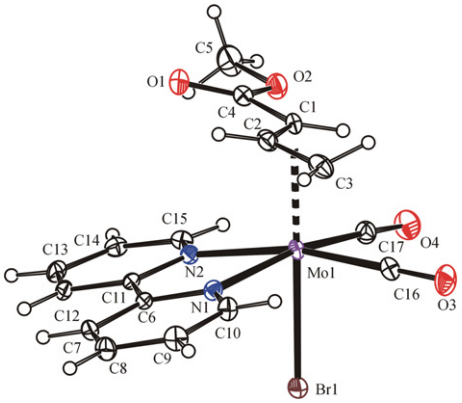


Fig. 1. ORTEP drawing of the molecule [(η^3-C_3H_4COOMe)Mo(CO)$_2$(bpy)Br] present in the crystal structure of **6**·0.5MeCN. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

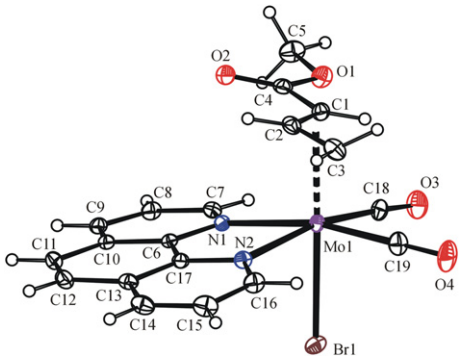


Fig. 2. ORTEP drawing of the molecule [(η^3-C_3H_4COOMe)Mo(CO)$_2$(phen)Br] present in the crystal structure of **7**·CH_2Cl_2. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

9.4 (1H), 3.3 (1H), 8.3 (2H), 8.1 (2H), 7.6 ppm (2H). Signals at 9.7 (1H), 9.6 (1H), 8.7 (2H), 8.1 (2H), 8.0 ppm (2H) were observed for the coordinated 1,10-phenanthroline in compound **25**. Infrared spectra of compounds **24** and **25** have the CO stretching band at 1962 and 1885 cm^{-1}.

2.4. Synthesis of the cyclopentadienyl tungsten complexes

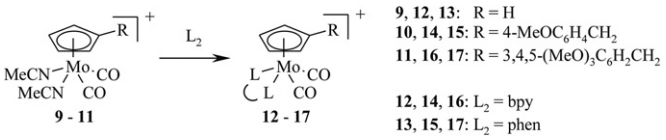
Cyclopentadienyl tungsten compounds [(η^5-Cp)W(CO)$_2$L$_2$][BF_4] (**28**: L_2 = bpy, **29**: L_2 = phen) were prepared from [(η^3-C_3H_5)(η^5-Cp)W(CO)$_2$] (**26**). Protonation with tetrafluoroboric acid in presence of acetonitrile gives [(η^5-Cp)W(CO)$_2$(NCMe)$_2$][BF_4] (**27**). Subsequent reaction with 2,2′-bipyridine and 1,10-phenanthroline gives [(η^5-Cp)W(CO)$_2$(bpy)][BF_4] (**28**) and [(η^5-Cp)W(CO)$_2$(phen)][BF_4] (**29**), respectively (Scheme 7).

^{1}H NMR spectra of the compounds **28** and **29** prove the presence of η^5-bonded cyclopentadienyl ligand and coordinated *N*,*N*-chelating ligand. The infrared spectra of these compounds have the CO stretching bands at considerably higher wavenumbers [ν_a(CO) ~2045; ν_s(CO) ~1970 cm^{-1}] than the molybdenum analogs **12** and **13** [ν_a(CO) ~1980; ν_s(CO) ~1886 cm^{-1}]. Structure of the compound **28** was determined by X-ray analysis (Fig. 6).

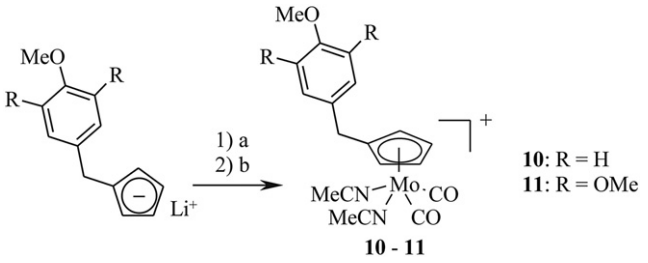
2.5. X-ray structures

Structures of the compounds **6**·0.5MeCN, **7**·CH_2Cl_2, **14**, **16**, **18**, **20**, **22**·CH_2Cl_2 and **28** were determined by single crystal X-ray diffraction analysis. Molecular structures of the complexes are shown in Figs. 1–8. Selected bond lengths and bond angles are listed in Tables 4 and 5. The unit cells of the compounds **6**·0.5MeCN, **14**, **18** and **22**·CH_2Cl_2 contain two crystallographically independent but essentially the same molecules of the complex. They are denoted **A** and **B**. In the structures of the following crystals, **14**, **18** and **22**·CH_2Cl_2, there are positionally disordered fluorine atoms in anionic parts (BF_4^- fragments). Attempts to treat these disorders were made but the results do not differ significantly from the starting structures.

The allyl complexes **6**·0.5MeCN and **7**·CH_2Cl_2 have distorted an octahedral structure around molybdenum(II). The η^3-bonded



Scheme 3. Preparation of cyclopentadienyl complexes **12**–**17**.



Scheme 4. Preparation of starting cyclopentadienyl complexes **10** and **11**. a) $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2Cl]$ (**1**) in THF; b) HBF_4 in the mixture of CH_2Cl_2 and MeCN.

methoxycarbonylallyl and bromide occupy the axial positions while two terminal carbonyls and donor atoms of the *N*,*N*-chelating ligand are in the equatorial positions, see Figs. 1 and 2. In both structures, the allyl ligand adopts the usual conformation with the open side eclipsing the carbonyl ligands. This arrangement was previously observed in the solid-state structure of the analogs with the unsubstituted allyl ligand $[(\eta^3\text{-}C_3H_5)Mo(CO)_2L_2Br]$ (L_2 = bpy, phen) [30] as well as in the octahedral complexes containing *fac*-$[(\eta^3\text{-}C_3H_4COOMe)Mo(CO)_2]$ fragment [31]. The small angle between plane of the COO group (Pl_{C4O1O2}) and allyl (Pl_{C1C2C3}) [**6**·0.5MeCN **A**: 3.7(7) deg, **B**: 5.1(7) deg; **7**·CH_2Cl_2: 0.8(4) deg] suggests full conjugation of the ester group with η^3-allyl.

The cations of the compounds **14**, **16**, **18**, **22**·CH_2Cl_2 and **28** form a distorted square–pyramid around central metal. The *cis*-coordinated carbonyl groups and two nitrogen atoms form the basal plane. The apical position is occupied by the η^5-coordinated cyclopentadienyl (Figs. 4 and 5) or indenyl (Figs. 7 and 8). Both indenyl complexes (**18** and **22**·CH_2Cl_2) adopt similar conformation of the indenyl ligand with the benzene ring above the N–Mo–N

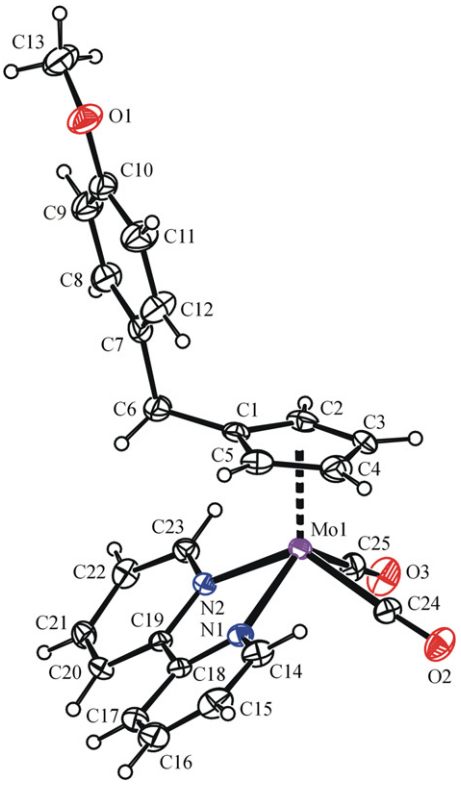


Fig. 3. ORTEP drawing of cation $[(\eta^5\text{-}C_5H_4CH_2C_6H_4OMe)Mo(CO)_2(bpy)]^+$ present in the crystal structure of **14**. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

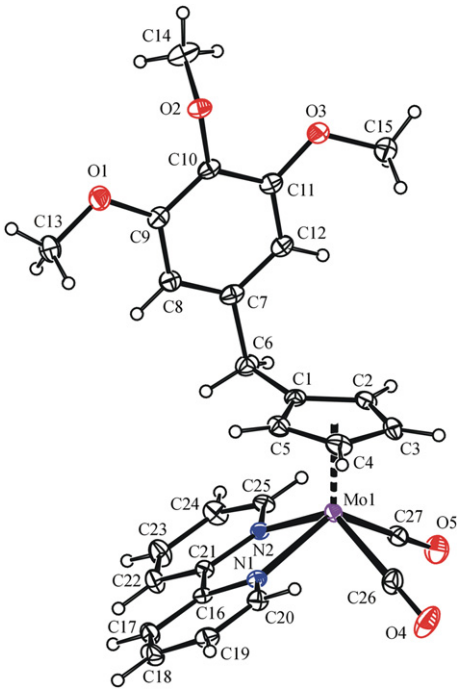


Fig. 4. ORTEP drawing of cation $[\{\eta^5\text{-}C_5H_4CH_2C_6H_2(OMe)_3\}Mo(CO)_2(bpy)]^+$ present in the crystal structure of **16**. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

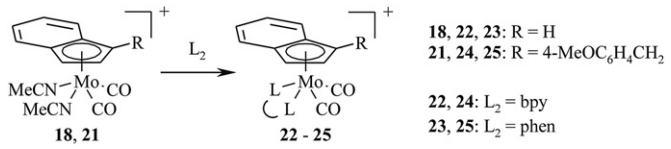
moiety. The bond distances Mo–N in the bipyridine complexes **14**, **16** and **22**·CH_2Cl_2 are systematically shorter [2.175(3)–2.189(4) Å] than in octahedral complexes containing bipyridine in equatorial position such as **6**·0.5MeCN [2.227(4)–2.343(4) Å] and $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(bpy)Br]$ [2.233(5) Å] [30]. This shortening is a result of weaker trans-effect of the carbonyl ligands in the square–pyramidal complexes [31,32].

The molecule of the compound **20** has pseudotetrahedral coordination around the molybdenum(II) with η^3-allyl, η^5-bonded substituted indenyl and two carbonyl ligands (Fig. 6). The allyl ligand is in *exo* orientation. The structural data of compound **20** [Mo–C(CO) = 1.938(2), 1.947(2) Å; Mo–Cg(allyl) = 2.043(2) Å; Mo–Cg(Cp) 2.026(1) Å; C(CO)–Mo–C(CO) = 80.5(1) deg; Cg(Cp)–Mo–Cg(allyl) 128.0(1) deg] are in line with those previously reported for several allyl–indenyl compounds $[(\eta^3\text{-}C_3H_5)(\eta^5\text{-}Ind')Mo(CO)_2]$ (Ind′ = substituted indenyl) [33–35].

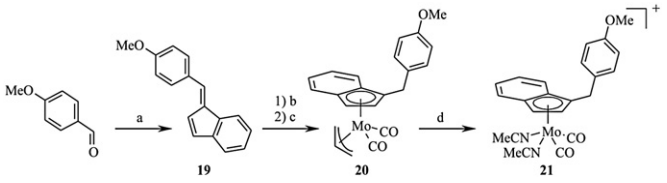
2.6. Cytotoxicity

The cytotoxic activity of the molybdenum(II) and tungsten(II) compounds was evaluated on human T-lymphocytic leukemia cells MOLT-4 in exponential grow phase, 24 h after the incubation with the drugs. The effect of the drug was examined by standard WST-1 viability assays [36].

It was observed that activity of the allyl complexes is strongly dependent on the coordinated *N*,*N*′-chelating ligand and the substituent in allyl ligand. The complexes containing 1,10-phenanthroline (**4** and **7**) show considerably higher cytotoxicity



Scheme 5. Preparation of indenyl complexes **22**–**25**.



Scheme 6. Preparation of starting indenyl complex **21**. a) indene, pyrrolidine b) Li[Et_3BH] in THF c) [(η^3-C_3H_5)Mo(CO)$_2$(NCMe)$_2$Cl] (**1**) in THF; d) HBF_4 in the mixture of CH_2Cl_2 and MeCN.

than 2,2′-bipyridine (**3** and **6**) and 5-nitro-1,10-phenanthroline complexes (**5** and **8**), see Table 6. The substitution with the methoxycarbonyl group has rather negative effect. The high activity was detected only for the 1,10-phenanthroline complex **7**·CH_2Cl_2. Even in this case, the IC_{50} value is about two times higher compared to the unsubstituted compound **4**.

The cyclopentadienyl and indenyl complexes of molybdenum and tungsten containing 2,2′-bipyridine ligand (**12**, **14**, **16**, **22**, **24** and **28**) display very low activity. Most of these compounds have the IC_{50} values higher than 130 μmol L^{-1}. Only the substituted indenyl complex **24** gives somewhat lower IC_{50} value (71.7 ± 19.0 μmol L^{-1}). Considerably higher cytotoxic effect (IC_{50} = 4.9–40 μmol L^{-1}) was observed in case of their 1,10-phenanthroline congeners **13**, **15**, **17**, **22**, **25** and **29**. The substitution in the cyclopentadienyl ring with 4-methoxybenzyl or 3,4,5-trimethoxybenzyl groups has only neglectable effect on the activity of molybdenum complexes. The substitution effect was much stronger in case of the indenyl compounds. Hence, the 4-methoxybenzyl substituted compounds **24** and **25** have about three times lower IC_{50} values compared to their unsubstituted counterparts **22** and **23**, respectively.

This study clearly shows that the combination of the *N*,*N*′-chelating ligand and substituent in the indenyl ligand can lead to very effective molybdenum cytotoxic agents. For example, the 1,10-phenanthroline complex with 4-methoxybenzyl substituted indenyl ligand (**25**) has IC_{50} value 4.9 ± 0.7 μmol L^{-1} (Fig. 9).

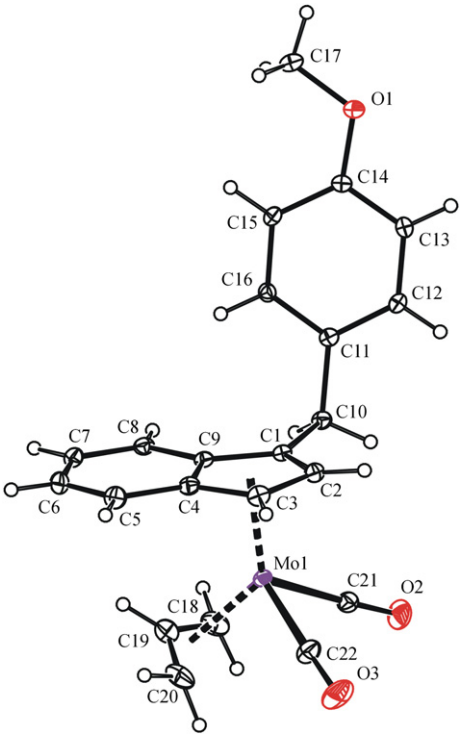


Fig. 5. ORTEP drawing of [(η^3-C_3H_5)(η^5-$C_9H_6CH_2C_6H_4OMe$)Mo(CO)$_2$] (**20**). The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

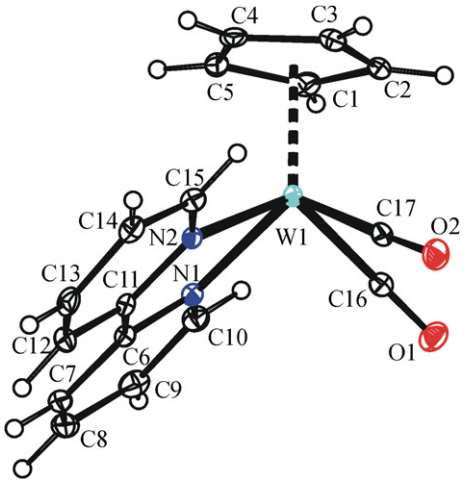
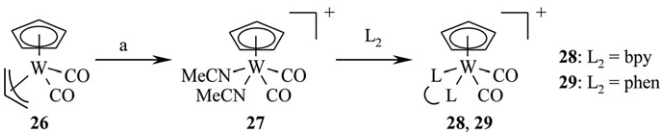


Fig. 6. ORTEP drawing of cation [(η^5-Cp)W(CO)$_2$(NCMe)$_2$]$^+$ present in the crystal structure of **28**. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.



Scheme 7. Preparation of cyclopentadienyl complexes **28** and **29**. a) HBF_4 in the mixture of CH_2Cl_2 and MeCN.

3. Conclusion

The molybdenum(II) complexes are promising cytotoxic agents that deserve number of improvements. Their cytotoxic properties are tunable through the exchange of the *N*,*N*′-chelating ligand and through the substitution in the allyl, cyclopentadienyl or indenyl ligand.

The patent literature on various cell lines has shown that the proper chose of the *N*,*N*-chelating ligand is crucial for the design of

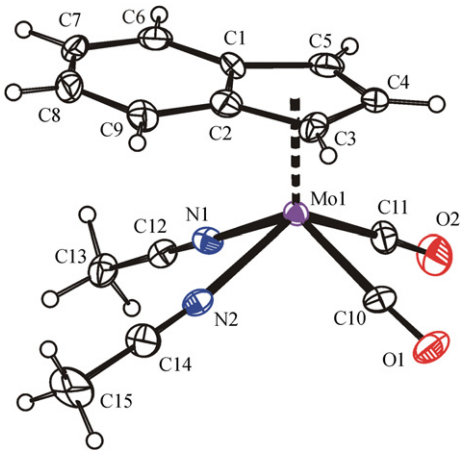


Fig. 7. ORTEP drawing of cation [(η^5-C_9H_7)Mo(CO)$_2$(NCMe)$_2$]$^+$ present in the crystal structure of **18**. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

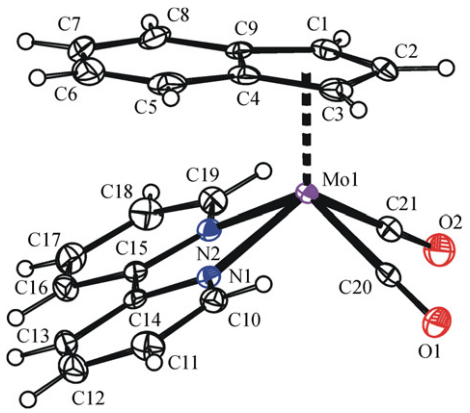


Fig. 8. ORTEP drawing of cation $[(\eta^5\text{-Ind})Mo(CO)_2(bpy)]^+$ present in the crystal structure of **22**·CH_2Cl_2. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

Table 4
Selected bond lengths (Å) and bond angles (deg) for the compounds **6**·0.5MeCN and **7**·CH_2Cl_2.

	6·0.5MeCN		**7**·CH_2Cl_2
	A	**B**	
Mo–C(CO)	1.963(5)	1.950(5)	1.956(3)
	1.970(5)	1.976(5)	1.968(3)
Mo–Cg(allyl)	2.054(5)	2.054(5)	2.060(3)
Mo–N	2.333(4)	2.227(4)	2.239(2)
	2.343(4)	2.240(4)	2.244(2)
Mo–Br	2.6353(6)	2.6267(6)	2.6339(4)
C(CO)–Mo–C(CO)	79.3(2)	80.7(2)	79.5(1)
Cg(allyl)–Mo–Br	176.7(2)	175.8(2)	177.8(1)
N–Mo–N	72.8(2)	73.2(2)	73.7(1)

the molybdenum-based drugs [18]. Our experiments on the leukemia cells MOLT-4 are supporting this theory. Hence, all the 1,10-phenanthrolines under the study exhibit considerably higher activity than complexes of 2,2′-bipyridine.

The attempt to enhance the cytotoxicity through the substitution in the π-ligands was only partially successful. Our desire to increase the cytotoxicity through the better cell uptake of more lipophilic compounds led us to prepare the cyclopentadienyl and indenyl compounds with methoxybenzyl groups. However, significant improvement was observed only in the case of indenyl compounds **24** and **25** that have about three times higher activity than the unsubstituted analog **22** and **23**, respectively. The cyclopentadienyl compounds show only neglectable substitution effect that strongly contrasts to metallocene compounds $[(\eta^5\text{-Cp}')_2MCl_2$; M = Ti, V, Mo], in which case modification with methoxybenzyl groups leads to dramatic increase of cytotoxicity toward various cell lines [16,17] including leukemia cells MOLT-4 [24]. This discrepancy could be caused with very different mechanism of the action on the molecular level.

In the near future, we are going to focus more on the allyl and indenyl complexes, extend the series of the *N*,*N*′-chelating ligands and to include the cytotoxicity assay toward *cis*-platin resistant leukemia cell lines.

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 [37]. Starting materials were available commercially or prepared according to literature procedures: $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2Cl]$ (**1**) [38], $[\{(\eta^3\text{-}C_3H_4COOMe)Mo(CO)_2(NCMe)(\mu\text{-}Br)\}_2]$ (**2**) [30], $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(bpy)Cl]$ (**3**) [26], $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(phen)Cl]$ (**4**) [26], $[(\eta^5\text{-Cp})Mo(CO)_2(NCMe)_2][BF_4]$ (**9**) [27], $[(\eta^5\text{-Ind})Mo(CO)_2(NCMe)_2][BF_4]$ (**18**) [28], $[(\eta^3\text{-}C_3H_5)(\eta^5\text{-Cp})W(CO)_2]$ (**26**) [39], 4-$MeOC_6H_4CH_2C_5H_4Li$ [40] and 3,4,5-$(MeO)_3C_6H_2CH_2$-C_5H_4Li [40].

4.2. Measurements

IR spectra were recorded in the 4000–400 cm^{-1} region on a Nicolet Magna 6700 FTIR spectrometer using diamond smart orbit ATR. ^1H NMR spectra were recorded on Bruker 400 and 500 MHz spectrometers at room temperature. $CDCl_3$ was distilled from CaH_2 and stored under nitrogen atmosphere. CD_3CN and d^6-acetone were used as obtained (Sigma–Aldrich) without further purification. Chemical shifts are given in ppm relative to TMS.

4.3. Synthesis of $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(5\text{-}NO_2\text{-phen})Cl]$ (**5**)

$[(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCMe)_2Cl]$ (**1**; 200 mg; 0.64 mmol) was dissolved in CH_2Cl_2 (50 mL) and treated with 5-nitro-1,10-phenanthroline (145 mg, 0.64 mmol). The solution was stirred for 30 min at room temperature. After that, the solvent was vacuum evaporated. The crude product was washed with ether and recrystallized from the mixture CH_2Cl_2/ether and vacuum dried. Yield: 270 mg (93%, 0.60 mmol). Anal. Calcd for $C_{17}H_{12}ClMoN_3O_4$: C, 45.00; H, 2.67; N, 9.26. Found: C, 45.12; H, 2.70; N, 9.23. ^1H NMR (d^6-acetone, 400 MHz, 25 °C, δ ppm): 9.45–9.40 (m, 2H,$C_{12}H_7N_2$), 9.24 (d, $J(^1H,^1H)$ = 8.2 Hz, 1H, $C_{12}H_7N_2$), 9.16 (s, 1H, $C_{12}H_7N_2$), 9.06 (d, $J(^1H,^1H)$ = 8.2 Hz,1H, $C_{12}H_7N_2$), 8.19 (s, 1H, $C_{12}H_7N_2$), 3.35 (m, 1H, C_3H_5), 3.29 (d, $J(^1H,^1H)$ = 6.2 Hz, 2H, C_3H_5), 1.37 (d, $J,(^1H,^1H)$ = 8.7 Hz, 2H, C_3H_5). FTIR (ATR, cm^{-1}): 1930 vs [ν_a(CO)], 1842 vs [ν_s(CO)], 1540 [ν_s(NO)], 1535 [ν_a(NO)].

Table 5
Selected bond lengths (Å) and bond angles (deg) for the compounds **14**, **16**, **18**, **22**·CH_2Cl_2 and **28**.

	14		**16**	**18**		**22**·CH_2Cl_2		**28**
	A	**B**		**A**	**B**	**A**	**B**	
M–C(CO)	1.968(4)	1.958(6)	1.968(5)	1.957(10)	1.975(9)	1.960(5)	1.948(6)	1.960(4)
	1.983(6)	1.983(6)	1.981(4)	1.968(10)	1.975(9)	1.963(6)	1.976(5)	1.967(3)
M–Cg(Cp)	1.987(2)	1.994(3)	1.991(2)	2.001(4)	1.987(4)	1.994(2)	2.000(2)	1.998(2)
M–N	2.182(4)	2.179(4)	2.175(3)	2.167(7)	2.167(7)	2.189(4)	2.189(4)	2.182(3)
	2.186(4)	2.189(4)	2.181(3)	2.172(8)	2.178(7)	2.189(4)	2.194(4)	2.168(3)
C(CO)–M–C(CO)	76.0(2)	75.4(2)	75.3(2)	74.2(4)	73.9(4)	75.9(2)	75.9(2)	74.9(2)
N–M–N	73.0(2)	72.8(2)	73.1(1)	76.8(3)	77.1(4)	72.9(2)	73.2(2)	72.5(1)

Table 6
IC_{50} (μmol L^{-1}) of the molybdenum(II) compounds against leukemic cells MOLT-4.[a]

	IC_{50}		IC_{50}		IC_{50}
3	17.3 ± 1.3	**12**	197 ± 33	**22**	172 ± 11
4	5.9 ± 0.5	**13**	19.9 ± 0.7	**23**	16.9 ± 0.7
5	32.0 ± 2.3	**14**	272 ± 9	**24**	71.7 ± 19.0
6	216 ± 12	**15**	18.7 ± 0.9	**25**	4.9 ± 0.7
7·CH_2Cl_2	11.3 ± 0.6	**16**	190 ± 24	**28**	135 ± 20
8	49.4 ± 5.1	**17**	12.3 ± 2.4	**29**	39.8 ± 0.9

[a] Exposure time: 24 h.

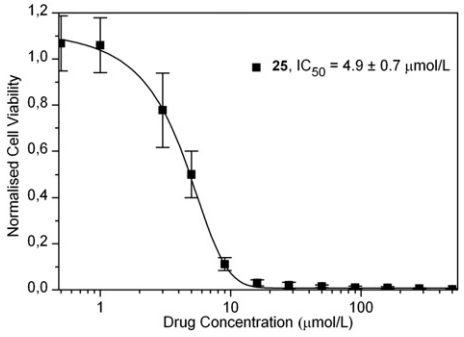


Fig. 9. Cytotoxicity curve showing the effect of the compound **25** on the viability of the leukemic cells MOLT-4.

4.4. Synthesis of [(η^3-C_3H_4COOMe)$Mo(CO)_2$(bpy)Br] (**6**)

The reaction was carried out as was described for compound **5** but with [{(η^3-C_3H_4COOMe)$Mo(CO)_2$(NCMe)(μ-Br)}$_2$] (**2**; 200 mg, 0.26 mmol) and 2,2′-bipyridine (81 mg, 0.52 mmol). Yield: 245 mg (97%, 0.50 mmol). Anal. Calcd for $C_{17}H_{15}BrMoN_2O_4$: C, 41.91; H, 3.10; N, 5.75. Found: C, 41.83; H, 3.01; N, 5.83. ^{1}H NMR (CD_3CN, 400 MHz, 25 °C, δ ppm): 8.63 (d, $J(^1H,^1H)$ = 5.0 Hz, 1H, $C_{10}H_8N_2$), 8.52 (d, $J(^1H,^1H)$ = 5.4 Hz, 1H, $C_{10}H_8N_2$), 8.31 (m, $J(^1H,^1H)$ = 8.8 Hz, 2H, $C_{10}H_8N_2$), 8.07 (m, 2H, $C_8H_8N_2$), 7.51 (m, 2H, $C_{10}H_8N_2$), 3.96 (m, 1H, C_3H_4), 3.46 (s, 3H, $COOCH_3$), 3.23 (dd, $J(^1H,^1H)$ = 6.7 Hz, $J(^1H,^1H)$ = 1.3 Hz, 1H, C_3H_4), 2.08 (d, $J(^1H,^1H)$ = 8.8 Hz, 1H, C_3H_4), 1.55 (d, $J(^1H,^1H)$ = 9.3 Hz, 1H, C_3H_4). FTIR (ATR, cm^{-1}): 1957 vs [ν_a(CO)], 1867 vs [ν_s(CO)], 1698 s [$\nu(CO)_{COOMe}$]. Single crystals of **6**·0.5MeCN suitable for X-ray diffraction analysis were prepared by overlayering of the acetonitrile solution with ether.

4.5. Synthesis of [(η^3-C_3H_4COOMe)$Mo(CO)_2$(phen)Br]·CH_2Cl_2 (**7**·CH_2Cl_2)

The reaction was carried out as was described for compound **5** but with [{(η^3-C_3H_4COOMe)$Mo(CO)_2$(NCMe)(μ-Br)}$_2$] (**2**; 200 mg, 0.26 mmol) and 1,10-phenanthroline (93 mg, 0.52 mmol). Yield: 251 mg (81%, 0.42 mmol). Anal. Calcd for $C_{20}H_{17}BrCl_2MoN_2O_4$: C, 40.30; H, 2.87; N, 4.70. Found: C, 40.22; H, 2.81; N, 4.67. ^{1}H NMR (CD_3CN, 400 MHz, 25 °C, δ ppm): 9.03 (d, $J(^1H,^1H)$ = 4.5 Hz, 1H, $C_{12}H_8N_2$), 8.89 (dd, $J(^1H,^1H)$ = 5.1 Hz, $J(^1H,^1H)$ = 1.5 Hz, 1H, $C_{12}H_8N_2$), 8.63 (m, 2H, $C_{12}H_8N_2$), 8.10 (s, 2H, $C_{12}H_8N_2$), 7.85 (m, 2H, $C_{12}H_8N_2$), 5.45 (s, 2H, CH_2Cl_2), 3.88 (m, 1H, C_3H_4), 3.48 (s, 3H, $COOCH_3$), 3.40 (dd, $J(^1H,^1H)$ = 6.8 Hz, $J(^1H,^1H)$ = 1.5 Hz, 1H, C_3H_4), 2.13 (d, $J(^1H,^1H)$ = 8.4 Hz, 1H, C_3H_4), 1.63 (dd, $J(^1H,^1H)$ = 9.1 Hz, $J(^1H,^1H)$ = 1.3 Hz, 1H, C_3H_4). FTIR (ATR, cm^{-1}): 1950 vs [ν_a(CO)], 1865 vs [ν_s(CO)], 1698 s [$\nu(CO)_{COOMe}$]. Single crystals of **7**·CH_2Cl_2 suitable for X-ray diffraction analysis were prepared by overlayering of the dichloromethane solution with hexane.

4.6. Synthesis of [(η^3-C_3H_4COOMe)$Mo(CO)_2$(5-NO_2-phen)Br] (**8**)

The reaction was carried out as was described for compound **5** but with [{(η^3-C_3H_4COOMe)$Mo(CO)_2$(NCMe)(μ-Br)}$_2$] (**2**; 200 mg, 0.26 mmol) and 5-nitro-1,10-phenanthroline (116 mg, 0.52 mmol). Yield: 251 mg (94%, 0.49 mmol). Anal. Calcd for $C_{19}H_{14}BrMoN_3O_6$: C, 41.03; H, 2.54; N, 7.56. Found: C, 41.11; H, 2.49; N, 7.69. ^{1}H NMR (d^6-acetone, 400 MHz, 25 °C, δ ppm): 9.37–9.19 (m, 3H,$C_{12}H_7N_2$), 9.07 (m, 2H,$C_{12}H_7N_2$), 8.19 (m, 2H,$C_{12}H_7N_2$), 4.04 (m, 1H, C_3H_4), 3.66 (d, $J(^1H,^1H)$ = 8.0 Hz, 1H, C_3H_4), 3.55 (s, 3H, $COOCH_3$), 1.18 (d, $J(^1H,^1H)$ = 8.9 Hz, 1H, C_3H_4), 1.68 (d, $J(^1H,^1H)$ = 8.8 Hz, 1H, C_3H_4). FTIR (ATR, cm^{-1}): 1970 vs [ν_a(CO)], 1873 vs [ν_s(CO)], 1695 s [$\nu(CO)_{COOMe}$].

4.7. Synthesis of [(η^5-$C_5H_4CH_2C_6H_4OMe$)$Mo(CO)_2(NCMe)_2$][BF_4] (**10**)

4-$MeOC_6H_4CH_2C_5H_4Li$ (619 mg, 3.22 mmol) was dissolved in THF, cooled at −80 °C and treated with [(η^3-C_3H_5)$Mo(CO)_2$(NC-Me)$_2$Cl] (**1**; 1.0 g, 3.22 mmol). The reaction mixture was stirred at room temperature overnight. After that, the volatiles were vacuum evaporated and the residuum was extracted with hot hexane. The extract was vacuum evaporated, dissolved in CH_2Cl_2 (30 mL), cooled at 0 °C and treated with acetonitrile (3 mL) and then with HBF_4·Et_2O (3.22 mmol). The reaction mixture was stirred for 1 h at room temperature. After that, the solvent was vacuum evaporated. The crude product was washed with ether and recrystallized from the mixture MeCN/ether and vacuum dried. Yield: 995 mg (61%, 1.97 mmol). Anal. Calcd for $C_{19}H_{19}BF_4MoN_2O_3$: C, 45.09; H, 3.78; N, 5.54. Found: C, 45.23; H, 3.59; N, 5.74. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C, δ ppm): 7.14 (d, $J(^1H,^1H)$ = 8.7 Hz, 2H, C_6H_4), 6.84 (d, $J(^1H,^1H)$ = 8.7 Hz, 2H, C_6H_4), 5.59 (t, $J(^1H,^1H)$ = 2.1 Hz, 2H, C_5H_4), 5.50 (t, $J(^1H,^1H)$ = 2.1 Hz, 2H, C_5H_4), 3.75 (s, 3H, OCH_3), 3.50 (s, 2H, CH_2), 2.50 (s, 6H, $NCCH_3$). FTIR (ATR, cm^{-1}): 3102 m [$\nu(CH_{Cp})$] 2312 w [ν_a(CN)], 2285 w [ν_s(CN)], 1977 vs [ν_a(CO)], 1887 vs [ν_s(CO)], 1067 vs-br [ν(BF)], 1032 vs-br [ν(BF)].

4.8. Synthesis of [{η^5-$C_5H_4CH_2C_6H_2(OMe)_3$}$Mo(CO)_2(NCMe)_2$][BF_4] (**11**)

The reaction was carried out as was described for compound **10** but with 3,4,5-$(MeO)_3C_6H_2CH_2C_5H_4Li$ (812 mg, 3.22 mmol). Yield: 1030 mg (56%, 1.82 mmol). Anal. Calcd for $C_{21}H_{23}BF_4MoN_2O_5$: C, 44.55; H, 4.09; N, 4.95. Found: C, 44.45; H, 4.13; N, 4.81. ^{1}H NMR (CD_3CN, 400 MHz, 25 °C, δ ppm): 6.59 (s, 2H, C_6H_2), 5.79 (t, $J(^1H,^1H)$ = 2.1 Hz, 2H, C_5H_4), 5.55 (t, $J(^1H,^1H)$ = 2.1 Hz, 2H, C_5H_4), 3.82 (s, 6H, OCH_3), 3.69 (s, 3H, OCH_3), 3.49 (s, 2H, CH_2), 2.45 (s, 6H, $NCCH_3$). FTIR (ATR, cm^{-1}): 3104 m [$\nu(CH_{Cp})$], 2322 w [ν_a(CN)], 2289 w [ν_s(CN)], 1980 vs [ν_a(CO)], 1886 vs [ν_s(CO)], 1063 vs-br [ν(BF)], 1033 vs-br [ν(BF)].

4.9. Synthesis of [(η^5-Cp)$Mo(CO)_2$(bpy)][BF_4] (**12**)

(η^5-Cp)$Mo(CO)_2(NCMe)_2$][BF_4] (**9**; 100 mg; 0.26 mmol) was dissolved in CH_2Cl_2 (50 mL) and treated with 2,2′-bipyridine (41 mg, 0.26 mmol). The solution was stirred for 18 h at room temperature. After then, the solvent was vacuum evaporated. The crude product was washed with ether and recrystallized from the mixture CH_2Cl_2/ether and vacuum dried. Yield: 112 mg (94%, 0.24 mmol). Anal. Calcd for $C_{17}H_{13}BF_4MoN_2O_2$: C, 44.38; H, 2.85; N, 6.09. Found: C, 44.19; H, 2.86; N, 6.28. ^{1}H NMR (d^6-acetone, 400 MHz, 25 °C, δ ppm): 9.36 (d, $J(^1H,^1H)$ = 5.4 Hz, 2H, $C_{10}H_8N_2$), 8.89 (d, $J(^1H,^1H)$ = 8.0 Hz, 2H, $C_{10}H_8N_2$), 8.36 (m, 2H, $C_{10}H_8N_2$), 7.73 (m, 2H, $C_{10}H_8N_2$), 6.10 (s, 5H, C_5H_5). FTIR (ATR, cm^{-1}): 1973 vs [ν_a(CO)], 1901 vs [ν_s(CO)], 1043 vs-br [ν(BF)].

Table 7
Crystallographic data for **6**·0.5MeCN, **7**·CH_2Cl_2, **14**, **16**, **18**, **20**, **22**·CH_2Cl_2 and **28**.

Compound	**6**·0.5MeCN	**7**·CH_2Cl_2	**14**	**16**	**18**	**20**	**22**·CH_2Cl_2	**28**
Formula	$2(C_{17}H_{15}BrMoN_2O_4)$, C_2H_3N	$C_{19}H_{15}BrMoN_2O_4$, CH_2Cl_2	$C_{25}H_{21}MoN_2O_3$, BF_4	$C_{27}H_{25}MoN_2O_5$, BF_4	$C_{15}H_{13}MoN_2O_2$, BF_4	$C_{22}H_{20}MoO_3$	$C_{21}H_{15}MoN_2O_2$, B F_4, CH_2Cl_2	$C_{17}H_{13}N_2O_2W$, BF_4
Cryst. syst.	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [Å]	12.7340(8)	7.2330(4)	20.1841(14)	9.9180(8)	14.2299(10)	8.2500(4)	19.8980(12)	9.1340(4)
b [Å]	13.4059(6)	10.4111(6)	14.2470(14)	15.1771(11)	14.0300(10)	10.5171(4)	13.3840(15)	9.2370(4)
c [Å]	13.5950(8)	15.4780(7)	18.8270(5)	19.6730(7)	17.0281(7)	11.0289(3)	18.6891(15)	10.5881(4)
α [deg]	60.767(5)	101.258(4)	90	90	90	103.126(3)	90	92.959(4)
β [deg]	69.409(5)	99.237(5)	117.105(3)	114.554(5)	90.630(7)	91.615(4)	111.208(5)	92.846(4)
γ [deg]	78.155(4)	105.815(4)	90	90	90	100.286(4)	90	112.825(4)
Z	2	2	8	4	8	2	8	2
μ [mm^{-1}]	2.829	2.757	0.606	0.555	0.823	0.735	0.851	7.103
D_x [g cm^{-3}]	1.780	1.848	1.599	1.579	1.704	1.555	1.704	2.220
Cryst size [mm]	0.29 × 0.26 × 0.18	0.35 × 0.21 × 0.11	0.43 × 0.42 × 0.13	0.32 × 0.25 × 0.03	0.40 × 0.26 × 0.23	0.49 × 0.29 × 0.09	0.38 × 0.27 × 0.15	0.26 × 0.25 × 0.13
Cryst color	Red	Red	Red	Red	Red	Orange	Red	Red
Cryst shape	Block	Block	Plate	Plate	Block	Plate	Block	Block
θ range [deg]	1.71–27.50	2.10–27.50	1.82–27.38	1.76–27.50	1.43–27.50	2.43–27.50	1.88–27.50	1.93–27.49
h k l range	−16/16, −17/17, −17/17	−9/9, −13/13, −20/20	−26/26, −17/18, −24/23	−12/12, −19/18, −25/24	−14/18, −18/16, −22/22	−10/10, −13/13, −14/14	−25/23, −17/17, −23/24	−11/11, −11/11, −13/13
No. of reflns measd	34,071	19,187	37,316	27,606	27,388	17,591	42,365	15,343
No. of unique reflns; R_{int}[a]	8659, 0.056	4881, 0.038	10,729, 0.054	6151, 0.076	7717, 0.121	4180, 0.031	10,474, 0.084	3732, 0.045
No. of obsd reflns [$I > 2\sigma(I)$]	6684	4259	7619	4376	3043	3957	7351	3528
No. of params	478	271	649	361	451	235	613	244
S[b] all data	1.149	1.107	1.150	1.100	1.011	1.073	1.104	1.113
R,[c] wR[c]	0.0665, 0.0830	0.0358, 0.0569	0.0934, 0.1190	0.0839, 0.0868	0.1975, 0.1242	0.0259, 0.0593	0.0949, 0.1248	0.0238, 0.0518
$\Delta\rho$, max., min. [e $Å^{-3}$]	0.701, −0.754	0.860, −0.748	1.426, −1.252	0.485, −0.648	0.736, −0.760	1.304, −0.610	1.401, −0.983	1.202, −1.814

[a] $R_{int} = \sum|F_o^2 - F_o, \text{mean}^2|/\sum F_o^2$.
[b] $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})^{1/2}]$ for all data.
[c] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)^{1/2}]$ for all data.

4.10. Synthesis of [(η^5-Cp)Mo(CO)$_2$(phen)][BF$_4$] (**13**)

The reaction was carried out as was described for compound **12** but with 1,10-phenanthroline (47 mg, 0.26 mmol). Yield: 105 mg (83%, 0.22 mmol). Anal. Calcd for $C_{19}H_{13}BF_4MoN_2O_2$: C, 47.14; H, 2.71; N, 5.79. Found: C, 47.19; H, 2.92; N, 5.65. ^{1}H NMR (CD_3CN, 400 MHz, 25 °C, δ ppm): 9.43 (dd, $J(^1H,^1H)$ = 5.5 Hz, $J(^1H,^1H)$ = 1.2 Hz, 2H, $C_{12}H_8N_2$), 8.75 (dd, 2H, $J(^1H,^1H)$ = 8.4 Hz, $J(^1H,^1H)$ = 1.2 Hz, $C_{12}H_8N_2$), 8.18 (s, 2H, $C_{12}H_8N_2$), 7.91 (dd, $J(^1H,^1H)$ = 8.4 Hz, $J(^1H,^1H)$ = 5.6 Hz, 2H, $C_{12}H_8N_2$), 5.80 (s, 5H, C_5H_5). FTIR (ATR, cm^{-1}): 1965 vs [ν_a(CO)], 1884 vs [ν_s(CO)], 1051 vs-br [ν(BF)].

4.11. Synthesis of [(η^5-C$_5$H$_4$CH$_2$C$_6$H$_4$OMe)Mo(CO)$_2$(bpy)][BF$_4$] (**14**)

The reaction was carried out as was described for compound **12** but with [(η^5-C$_5$H$_4$CH$_2$C$_6$H$_4$OMe)Mo(CO)$_2$(NCMe)$_2$][BF$_4$] (**10**; 100 mg, 0.20 mmol) and 2,2′-bipyridine (31 mg, 0.2 mmol).

Yield: 103 mg (89%, 0.18 mmol). Anal. Calcd for $C_{25}H_{21}BF_4MoN_2O_3$: C, 51.75; H, 3.65; N, 4.83. Found: C, 51.58; H, 3.62; N, 4.95. ^{1}H NMR (CD_3CN, 400 MHz, 25 °C, δ ppm): 9.02 (d, $J(^1H,^1H)$ = 5.6 Hz, 2H, $C_{10}H_8N_2$), 8.56 (d, $J(^1H,^1H)$ = 8.0 Hz, 2H, $C_{10}H_8N_2$), 8.19 (m, 2H, $C_{10}H_8N_2$), 7.59 (m, 2H, $C_{10}H_8N_2$), 6.88 (d, $J(^1H,^1H)$ = 8.4 Hz, 2H, C_6H_4), 6.76 (d, $J(^1H,^1H)$ = 8.4 Hz, 2H, C_6H_4), 5.73 (t, $J(^1H,^1H)$ = 2.1 Hz, 2H, C_5H_4), 5.63 (t, $J(^1H,^1H)$ = 2.1 Hz, 2H, C_5H_4), 3.71 (s, 3H, OCH_3), 3.00 (s, 2H, CH_2). FTIR (ATR, cm^{-1}): 1975 vs [ν_a(CO)], 1888 vs [ν_s(CO)], 1055 vs-br [ν(BF)]. Single crystals suitable for X-ray diffraction analysis were prepared by overlayering of the dichloromethane solution with hexane.

4.12. Synthesis of [(η^5-C$_5$H$_4$CH$_2$C$_6$H$_4$OMe)Mo(CO)$_2$(phen)][BF$_4$] (**15**)

The reaction was carried out as was described for compound **12** but with [(η^5-C$_5$H$_4$CH$_2$C$_6$H$_4$OMe)Mo(CO)$_2$(NCMe)$_2$][BF$_4$] (**10**; 100 mg, 0.20 mmol) and 1,10-phenanthroline (36 mg, 0.20 mmol). Yield: 115 mg (95%, 0.19 mmol). Anal. Calcd for $C_{27}H_{21}BF_4MoN_2O_3$: C, 53.67; H, 3.50; N, 4.64. Found: C, 53.71; H, 3.52; N, 4.69. ^{1}H NMR (CD_3CN, 400 MHz, 25 °C, δ ppm): 9.41 (dd, 2H, $J(^1H,^1H)$ = 5.6 Hz, $J(^1H,^1H)$ = 1.0 Hz, $C_{12}H_8N_2$), 8.77 (dd, 2H, $J(^1H,^1H)$ = 8.2 Hz, $J(^1H,^1H)$ = 1.2 Hz, $C_{12}H_8N_2$), 8.21 (s, 2H, $C_{12}H_8N_2$), 7.97 (dd, $J(^1H,^1H)$ = 8.2 Hz, $J(^1H,^1H)$ = 5.6 Hz, 2H, $C_{12}H_8N_2$), 6.73 (d, $J(^1H,^1H)$ = 8.4 Hz, 2H, C_6H_4), 6.61 (d, $J(^1H,^1H)$ = 8.4 Hz, 2H, C_6H_4), 5.76 (t, $J(^1H,^1H)$ = 2.0 Hz, 2H, C_5H_4), 5.68 (t, $J(^1H,^1H)$ = 2.0 Hz, 2H, C_5H_4), 3.67 (s, 3H, OCH_3), 2.92 (s, 2H, CH_2). FTIR (ATR, cm^{-1}): 1971 vs [ν_a(CO)], 1888 vs [ν_s(CO)], 1056 vs-br [ν(BF)].

4.13. Synthesis of [{η^5-C$_5$H$_4$CH$_2$C$_6$H$_2$(OMe)$_3$}Mo(CO)$_2$(bpy)][BF$_4$] (**16**)

The reaction was carried out as was described for compound **12** but with [{η^5-C$_5$H$_4$CH$_2$C$_6$H$_2$(OMe)$_3$}Mo(CO)$_2$(NCMe)$_2$][BF$_4$] (**11**; 100 mg, 0.18 mmol) and 2,2′-bipyridine (28 mg, 0.18 mmol). Yield: 107 mg (93%, 0.17 mmol). Anal. Calcd for $C_{27}H_{25}BF_4MoN_2O_5$: C, 50.65; H, 3.94; N, 4.38. Found: C, 50.44; H, 3.98; N, 4.33. ^{1}H NMR (d^6-acetone, 500 MHz, 25 °C, δ ppm): 9.34 (d, $J(^1H,^1H)$ = 5.6 Hz, 2H, $C_{10}H_8N_2$), 8.91 (d, $J(^1H,^1H)$ = 8.2 Hz, 2H, $C_{10}H_8N_2$), 8.38 (m, 2H, $C_{10}H_8N_2$), 7.79 (m, 2H, $C_{10}H_8N_2$), 6.45 (s, 2H, C_6H_2), 6.14 (t, $J(^1H,^1H)$ = 2.1 Hz, 2H, C_5H_4), 5.91 (t, $J(^1H,^1H)$ = 2.1 Hz, 2H, C_5H_4), 3.72 (s, 6H, OCH_3), 3.65 (s, 3H, OCH_3), 3.19 (s, 2H, CH_2). FTIR (ATR, cm^{-1}): 1970 vs [ν_a(CO)], 1890 vs [ν_s(CO)], 1047 vs-br [ν(BF)]. Single crystals suitable for X-ray diffraction analysis were prepared by overlayering of the dichloromethane solution with hexane.

4.14. Synthesis of [{η^5-C$_5$H$_4$CH$_2$C$_6$H$_2$(OMe)$_3$}Mo(CO)$_2$(phen)][BF$_4$] (**17**)

The reaction was carried out as was described for compound **12** but with [{η^5-C$_5$H$_4$CH$_2$C$_6$H$_2$(OMe)$_3$}Mo(CO)$_2$(NCMe)$_2$][BF$_4$] (**11**; 100 mg, 0.18 mmol) and 1,10-phenanthroline (33 mg, 0.18 mmol). Yield: 99 mg (82%, 0.15 mmol). Anal. Calcd for $C_{29}H_{25}BF_4MoN_2O_5$: C, 52.44; H, 3.79; N, 4.22. Found: C, 52.36; H, 3.83; N, 4.25. ^{1}H NMR (d^6-acetone, 500 MHz, 25 °C, δ ppm): 9.74 (d, $J(^1H,^1H)$ = 5.3 Hz, 2H, $C_{12}H_8N_2$), 9.01 (d, $J(^1H,^1H)$ = 7.5 Hz, 2H, $C_{12}H_8N_2$), 8.40 (s, 2H, $C_{12}H_8N_2$), 8.18 (m, 2H, $C_{12}H_8N_2$), 6.38 (s, 2H, C_6H_2), 6.16 (s-br, 2H, C_5H_4), 5.96 (s-br, 2H, C_5H_4), 3.67 (s, 6H, OCH_3), 3.62 (s, 3H, OCH_3), 3.09 (s, 2H, CH_2). FTIR (ATR, cm^{-1}): 1970 vs [ν_a(CO)], 1890 vs [ν_s(CO)], 1058 vs-br [ν(BF)].

4.15. X-ray of [(η^5-Ind)Mo(CO)$_2$(NCMe)$_2$][BF$_4$] (**18**)

Single crystals suitable for X-ray diffraction analysis were prepared by overlayering of the acetonitrile solution with ether.

4.16. Synthesis of 4-MeOC$_6$H$_4$CHC$_9$H$_6$ (**19**)

Pyrrolidine (7.1 g, 0.1 mol) was added dropwise to the mixture of indene (11.6 g, 0.1 mol) and 4-methoxybenzaldehyde (13.6 g, 0.1 mol) in 100 mL of methanol. When the addition was complete, the solution was heated at 50 °C and stirred for 60 min. The reaction mixture was cooled at room temperature. Crude product was precipitated after addition of acetic acid (6.6 g, 0.11 mol). Suspension was diluted with 500 mL of water and yellow precipitate was filtered on the glass frit and washed several times with water and then with ether. Product was purified by Soxhlet extraction with hexane and vacuum dried. Yield: 16.9 g (72%, 72 mmol). Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.94; H, 6.10. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C, δ ppm): 7.58 (dd, 1H, C_9H_6), 7.68 (d, 2H, C_6H_4), 7.33 (s, 1H, $C_9H_6CHC_6H_4$), 7.22 (dd, 1H, C_9H_6), 7.16–7.09 (m, 2H, C_9H_6), 6.96 (d, 1H, C_9H_6), 6.90 (d, 1H, C_9H_6), 6.84 (d, 2H, C_6H_4), 3.72 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, 101 MHz, 25 °C, δ ppm): 160.2, 142.0, 138.3, 137.9, 129.8 (5C$_{ipso}$, C_9H_6 and C_6H_4), 134.0, 128.8, 127.3, 126.1, 125.1, 121.1, 119.1 (7C, C_9H_6 and $C_9H_6CHC_6H_4$), 132.0, 114.4 (2 × 2C, C_6H_4), 55.5 (OCH$_3$).

4.17. Synthesis of [(η^3-C$_3$H$_5$)(η^5-C$_9$H$_6$CH$_2$C$_6$H$_4$OMe)Mo(CO)$_2$] (**20**)

4-MeOC$_6$H$_4$CHC$_9$H$_6$ (**19**; 754 mg, 3.22 mmol) was dissolved in THF and treated with Li[BEt$_3$H] (3.22 mL of 1 M solution in THF). The reaction mixture was heated for reflux for 2 h, cooled at −80 °C and treated with [(η^3-C$_3$H$_5$)Mo(CO)$_2$(NCMe)$_2$Cl] (**1**; 1.0 g, 3.22 mmol). The reaction mixture was stirred at room temperature overnight. After that, the volatiles were vacuum evaporated and the residuum was extracted with hot hexane. The crude product was vacuum sublimed at 130 °C (10 Pa). Yield: 925 mg (67%, 2.16 mmol). Anal. Calcd for $C_{22}H_{20}MoO_3$: C, 61.69; H, 4.71. Found: C, 61.47; H, 4.93. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C, δ ppm), 3:1 mixture of **20a** (*exo*-C$_3$H$_5$) and **20b** (*endo*-C$_3$H$_5$): 7.17–6.89 (m, 6H of **a** and 6H of **b**), 6.81–6.75 (m, 2H of **a** and 2H of **b**), 5.87 (d, $J(^1H,^1H)$ = 2.8 Hz, 1H of **a**, C_9H_6), 5.80 (d, $J(^1H,^1H)$ = 2.8 Hz, 1H of **b**, C_9H_6), 5.67 (d, $J(^1H,^1H)$ = 2.8 Hz, 1H of **a**, C_9H_6), 5.61 (d, $J(^1H,^1H)$ = 2.8 Hz, 1H of **b**, C_9H_6), 4.26–4.02 (m, 2H of **a** and 2H of **b**, CH_2), 3.74 (s, 3H of **b**, OCH_3), 3.73 (s, 3H of **a**, OCH_3), 3.40 (m, 2H of **b**, *syn* of C$_3$H$_3$), 3.33 (m, 1H of **b**, *meso* of C$_3$H$_3$), 2.25 (m, 2H of **a**, *syn* of C$_3$H$_3$), 0.97 (d, $J(^1H,^1H)$ = 11.1 Hz, 1H of **a**, *anti* of C$_3$H$_3$), 0.87 (d, $J(^1H,^1H)$ = 11.1 Hz, 1H of **a**, *anti* of C$_3$H$_3$), 0.16 (tt, $J(^1H,^1H)$ = 11.1 Hz, $J(^1H,^1H)$ = 7.4 Hz, 1H of **a**, *meso* of C$_3$H$_3$), −0.81 (m, 2H of **b**, *anti* of C$_3$H$_3$). FTIR (ATR, cm^{-1}): 1937 vs [ν_a(CO)], 1863 vs [ν_s(CO)]. Single crystals suitable for X-ray diffraction analysis were prepared slow cooling of the hexane solution from 60 to 25 °C.

4.18. Synthesis of [(η^5-$C_9H_6CH_2C_6H_4OMe$)Mo(CO)$_2$(NCMe)$_2$][BF_4] (**21**)

[(η^3-C_3H_5)(η^5-$C_9H_6CH_2C_6H_4OMe$)Mo(CO)$_2$] (**20**; 800 mg, 1.87 mmol) was dissolved in CH_2Cl_2 (30 mL), cooled at 0 °C and treated with acetonitrile (3 mL) and then with $HBF_4 \cdot Et_2O$ (1.87 mmol). The reaction mixture was stirred for 1 h at room temperature. After that, the solvent was vacuum evaporated. The crude product was washed with ether and recrystallized from the mixture MeCN/ether and vacuum dried. Yield: 915 mg (88%, 1.65 mmol). Anal. Calcd for $C_{23}H_{21}BF_4MoN_2O_3$: C, 49.67; H, 3.81; N, 5.04. Found: C, 49.56; H, 3.75; N, 5.1 5. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C, δ ppm): 7.99 (m, 1H, C_9H_6), 7.80 (m, 1H, C_9H_6), 7.58 (m, 2H, C_9H_6), 7.37 (m, 2H, C_6H_4), 7.37 (m, 2H, C_6H_4), 6.87 (m, 2H, C_6H_4), 6.28 (m, 1H, C_9H_6), 5.60 (m, 1H, C_9H_6), 4.43 (m, 1H, CH_2), 3.83 (m, 1H, CH_2), 3.74 (s, 3H, OCH_3), 2.64, 2.60, 2.57 (3 × s-br, 6H, CH_3CN). FTIR (ATR, cm^{-1}): 2321 w [ν_a(CN)], 2289 w [ν_s(CN)], 1964 vs [ν_a(CO)], 1895 vs [ν_s(CO)], 1052 vs-br [ν(BF)], 1030 vs-br [ν(BF)].

4.19. Synthesis of [(η^5-Ind)Mo(CO)$_2$(bpy)][BF_4]·CH_2Cl_2 (**22**)

The reaction was carried out as was described for compound **12** but with [(η^5-Ind)Mo(CO)$_2$(NCMe)$_2$][BF_4] (**18**; 100 mg, 0.23 mmol) and 2,2′-bipyridine (36 mg, 0.23 mmol). Yield: 110 mg (93%, 0.21 mmol). Analytical and spectroscopic data are in the line with those reported elsewhere [29]. Single crystals of **22**·CH_2Cl_2 suitable for X-ray diffraction analysis were prepared by overlayering of the dichloromethane solution with hexane.

4.20. Synthesis of [(η^5-Ind)Mo(CO)$_2$(phen)][BF_4] (**23**)

The reaction was carried out as was described for compound **12** but with [(η^5-Ind)Mo(CO)$_2$(NCMe)$_2$][BF_4] (**18**; 100 mg, 0.23 mmol) and 1,10-phenanthroline (42 mg, 0.23 mmol). Yield: 105 mg (85%, 0.20 mmol). Analytical and spectroscopic data are in the line with those reported elsewhere [18].

4.21. Synthesis of [(η^5-$C_9H_6CH_2C_6H_4OMe$)Mo(CO)$_2$(bpy)][BF_4] (**24**)

The reaction was carried out as was described for compound **12** but with [(η^5-$C_9H_6CH_2C_6H_4OMe$)Mo(CO)$_2$(NCMe)$_2$][BF_4] (**21**; 100 mg, 0.18 mmol) and 2,2′-bipyridine (28 mg, 0.18 mmol). Yield: 110 mg (97%, 0.17 mmol). Anal. Calcd for $C_{29}H_{23}BF_4MoN_2O_3$: C, 55.27; H, 3.68; N, 4.44. Found: C, 55.32; H, 3.73; N, 4.28. ^{1}H NMR (CD_3CN, 400 MHz, 25 °C, δ ppm): 9.36 (dq, $J(^1H,^1H)$ = 5.8 Hz, $J(^1H,^1H)$ = 0.8 Hz, 1H, $C_{10}H_8N_2$), 9.26 (dq, $J(^1H,^1H)$ = 5.8 Hz, $J(^1H,^1H)$ = 0.7 Hz, 1H, $C_{10}H_8N_2$), 8.33 (d, $J(^1H,^1H)$ = 8.3 Hz, 2H, $C_{10}H_8N_2$), 8.11 (t, $J(^1H,^1H)$ = 7.9 Hz, 2H, $C_{10}H_8N_2$), 7.61 (m, 2H, $C_{10}H_8N_2$), 7.27 (d, $J(^1H,^1H)$ = 8.8 Hz, 2H, C_6H_4), 7.12 (m, 1H, C_9H_6), 6.84 (d, $J(^1H,^1H)$ = 8.8 Hz, 2H, C_6H_4), 6.83 (m, 1H, C_9H_6), 6.69 (m, 2H, C_9H_6), 6.45 (d, $J(^1H,^1H)$ = 2.8 Hz, 1H, C_9H_6), 5.64 (d, $J(^1H,^1H)$ = 2.8 Hz, 1H, C_9H_6), 4.47 (d, $J(^1H,^1H)$ = 15.1 Hz, 1H, CH_2), 3.92 (d, $J(^1H,^1H)$ = 15.1 Hz, 1H, CH_2), 3.72 (s, 3H, OCH_3). FTIR (ATR, cm^{-1}): 1962 vs [ν_a(CO)], 1885 vs [ν_s(CO)], 1054 vs-br [ν(BF)], 1032 vs-br [ν(BF)].

4.22. Synthesis of [(η^5-$C_9H_6CH_2C_6H_4OMe$)Mo(CO)$_2$(phen)][BF_4] (**25**)

The reaction was carried out as was described for compound **12** but with [(η^5-$C_9H_6CH_2C_6H_4OMe$)Mo(CO)$_2$(NCMe)$_2$][BF_4] (**21**; 100 mg, 0.18 mmol) and 1,10-phenanthroline (33 mg, 0.18 mmol). Yield: 108 mg (92%, 0.17 mmol). Anal. Calcd for $C_{31}H_{23}BF_4MoN_2O_3$: C, 56.91; H, 3.54; N, 4.28. Found: C, 56.98; H, 3.45; N, 4.30. ^{1}H NMR (CD_3CN, 400 MHz, 25 °C, δ ppm): 9.71 (s-br, 1H, $C_{12}H_8N_2$), 9.64 (s-br, 1H, $C_{12}H_8N_2$), 8.68 (d, $J(^1H,^1H)$ = 8.2 Hz, 2H, $C_{12}H_8N_2$), 8.09 (s, 2H, $C_{12}H_8N_2$), 7.98 (m, 2H, $C_{12}H_8N_2$), 7.29 (d, $J(^1H,^1H)$ = 8.3 Hz, 2H, C_6H_4), 7.03 (d, $J(^1H,^1H)$ = 8.6 Hz, 1H, C_9H_6), 6.84 (d, $J(^1H,^1H)$ = 8.3 Hz, 2H, C_6H_4), 6.73 (d, $J(^1H,^1H)$ = 8.6 Hz, 1H, C_9H_6), 6.55 (s-br, 1H, C_9H_6), 6.29 (m, 2H, C_9H_6), 5.70 (s-br, 1H, C_9H_6), 4.56 (d, $J(^1H,^1H)$ = 15.0 Hz, 1H, CH_2), 4.00 (d, $J(^1H,^1H)$ = 15.0 Hz, 1H, CH_2), 3.72 (s, 3H, OCH_3). FTIR (ATR, cm^{-1}): 1964 vs [ν_a(CO)], 1886 vs [ν_s(CO)], 1055 vs-br [ν(BF)], 1032 vs-br [ν(BF)].

4.23. Synthesis of [(η^5-Cp)W(CO)$_2$(NCMe)$_2$][BF_4] (**27**)

The reaction was carried out as was described for compound **21** but with [(η^3-C_3H_5)(η^5-Cp)W(CO)$_2$] (**26**; 647 mg, 1.87 mmol). Yield: 788 mg (89%, 1.66 mmol). Anal. Calcd for $C_{11}H_{11}BF_4N_2O_2W$: C, 27.88; H, 2.34; N, 5.91. Found: C, 27.74; H, 2.38; N, 5.84. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C, δ ppm): 5.73 (s, 5H, C_5H_5), 2.47 (s, 3H, $NCCH_3$), 2.10 (s, 3H, $NCCH_3$). FTIR (ATR, cm^{-1}): 3104 m [$\nu(CH_{Cp})$], 2316 w [ν_a(CN)], 2288 w [ν_s(CN)], 2045 vs [ν_a(CO)], 1959 vs [ν_s(CO)], 1055 vs-br [ν(BF)].

4.24. Synthesis of [(η^5-Cp)W(CO)$_2$(bpy)][BF_4] (**28**)

The reaction was carried out as was described for compound **12** but with [(η^5-Cp)W(CO)$_2$(NCMe)$_2$][BF_4] (**27**; 100 mg, 0.21 mmol) and 2,2′-bipyridine (33 mg, 0.21 mmol). Yield: 105 mg (91%, 0.19 mmol). Anal. Calcd for $C_{17}H_{13}BF_4N_2O_2W$: C, 37.26; H, 2.39; N, 5.11. Found: C, 37.28; H, 2.46; N, 5.09. ^{1}H NMR (CD_3CN, 400 MHz, 25 °C, δ ppm): 9.25 (d, $J(^1H,^1H)$ = 5.6 Hz, 2H, $C_{10}H_8N_2$), 8.61 (d, $J(^1H,^1H)$ = 8.4 Hz, 2H, $C_{10}H_8N_2$), 8.21 (m, 2H, $C_{10}H_8N_2$), 7.56 (m, 2H, $C_{10}H_8N_2$), 5.56 (s, 5H, C_5H_5). FTIR (ATR, cm^{-1}): 2046 vs [ν_a(CO)], 1973 vs [ν_s(CO)], 1056 vs-br [ν(BF)]. Single crystals suitable for X-ray diffraction analysis were prepared by overlayering of the dichloromethane solution with hexane.

4.25. Synthesis of [(η^5-Cp)W(CO)$_2$(phen)][BF_4] (**29**)

The reaction was carried out as was described for compound **12** but with [(η^5-Cp)W(CO)$_2$(NCMe)$_2$][BF_4] (**27**; 100 mg, 0.21 mmol) and 1,10-phenanthroline (38 mg, 0.21 mmol). Yield: 114 mg (95%, 0.20 mmol). Anal. Calcd for $C_{19}H_{13}BF_4N_2O_2W$: C, 39.90; H, 2.29; N, 4.90. Found: C, 39.95; H, 2.18; N, 4.87. ^{1}H NMR (d^6-acetone, 400 MHz, 25 °C, δ ppm): 9.90 (dd, $J(^1H,^1H)$ = 5.2 Hz, $J(^1H,^1H)$ = 1.2 Hz, 2H, $C_{12}H_8N_2$), 8.98 (dd, 2H, $J(^1H,^1H)$ = 8.0 Hz, $J(^1H,^1H)$ = 1.2 Hz, $C_{12}H_8N_2$), 8.40 (s, 2H, $C_{12}H_8N_2$), 8.12 (dd, $J(^1H,^1H)$ = 8.0 Hz, $J(^1H,^1H)$ = 5.6 Hz, 2H, $C_{12}H_8N_2$), 6.05 (s, 5H, C_5H_5). FTIR (ATR, cm^{-1}): 2045 vs [ν_a(CO)], 1969 vs [ν_s(CO)], 1056 vs-br [ν(BF)].

4.26. Crystallography

The X-ray data for crystals of **6**·0.5MeCN, **7**·CH_2Cl_2, **14**, **16**, **18**, **20**, **22**·CH_2Cl_2 and **28** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo Kα radiation (λ = 0.71073 Å), a graphite monochromator, and the φ and χ scan mode. Data reductions were performed with DENZO-SMN [41]. The absorption was corrected by integration methods [42]. Structures were solved by direct methods (Sir92) [43] and refined by full matrix least-square based on F^2 (SHELXL97) [44]. Crystallographic data are summarized in Table 7.

Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$ (pivot atom) or of $1.5U_{eq}$ for the methyl moiety with C–H = 0.96, 0.97, and 0.93 Å for methyl, methylene and hydrogen atoms in Cp ring, respectively.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos.

CCDC 881621–881628. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

4.27. Cytotoxicity studies

The studies were performed on the human T-lymphocytic leukemia cells MOLT-4 obtained from the American Type Culture Collection (USA). The cells were cultured in Iscove's modified Dulbecco's medium 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 [24]. Briefly, the MOLT-4 cells were seeded in 96-wells plate, incubated in 0–1000 μmol/L 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).

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Appendix A. Supplementary material

CCDC 881621–881628 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.jorganchem.2012.07.011.

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