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Stabilization of propene molybdenum and tungsten half–sandwich complexes by intramolecular coordination of a thioether function†

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This study reports the stabilizing effect of an intramolecularly coordinated thioether function in propene complexes of the general formula [{η^5:κ*S*-$C_5H_4(CH_2)_2SR$}M(CO)$_2$(η^2-C_2H_3Me)][BF_4] (M = Mo, W; R = Et, Ph). They are formed by protonation of allyl analogues [{η^5-$C_5H_4(CH_2)_2SR$}M(CO)$_2$(η^3-C_3H_5)] by tetrafluoroboric acid in non-coordinating solvents. In contrast to analogues with unsubstituted Cp ligands, these propene complexes are isolable in a pure form and characterized by NMR spectroscopy. The molybdenum compounds are stable at low temperature and the propene ligand can easily be exchanged by thioethers or acetonitrile. Several representatives of the reaction products were characterized by X-ray structure analysis. The stabilization effect in tungsten complexes [{η^5:κ*S*-$C_5H_4(CH_2)_2SR$}W(CO)$_2$(η^2-C_2H_3Me)][BF_4] (R = Et, Ph) was unusually high. The compounds are long-term stable at room temperature and do not undergo ligand exchange reactions even with strong chelators such as 1,10-phenanthroline. The molecular structure of the tungsten propene complex was confirmed by X-ray diffraction analysis on a single crystal.

Introduction

The ability of transition metals to form coordination compounds with alkenes was discovered almost two hundred years ago when W. C. Zeise[1] synthesized the first compound bearing π-bonded ethylene, K[$PtCl_3$(η^2-C_2H_4)]·H_2O, currently known as Zeise's salt.[1,2] After elucidation of the alkene coordination mode in the 1950s,[1,3] a variety of complexes with π-coordinated alkenes have been described, which was motivated by their key role in catalytic olefin oligomerization and polymerization reactions.[4–6] For example, the specific design of π-alkene intermediates permits the living polymerization catalysis of ethylene at unusually high temperatures to afford ultra-high molecular weight polyethylene with low dispersity.[7] The effects of supporting ligands on the stability of intermediate π-alkene species are further exemplified in recent studies dealing with ethylene oligomerization.[8,9]

Alkene intermediates are involved in metathesis reactions (*e.g.*, ring-closing metathesis, cross-metathesis, and metathesis polymerization).[10] These processes are commonly catalyzed by high-valent molybdenum and tungsten complexes[11] and by ruthenium compounds.[10,12] The potential of iron catalysts is currently under comprehensive investigation.[13–15] Gold(I)-ethylene complexes, stabilized with bulky phosphine ligands were investigated as catalysts for the hydroamination of ethylene.[16,17] Stereoregularity of transition metal catalyzed alkene hydroformylation is controlled upon transfer of hydride ligand to the coordinated alkene. Formed branched aldehydes serve as attractive synthetic precursors for pharmaceuticals.[18]

Alkene intermediates are formed upon C–H activation of hydrocarbons by cyclopentadienyl tungsten complexes [(η^5-Cp*)W(NO)(R)(η^3-allyl)] (Cp* = C_5Me_5; R = H, neopentyl), as documented on adducts bearing trapped carbon monoxide [(η^5-Cp*)W(NO)(CO)(η^2-alkene)] (Scheme 1, reaction A).[19,20]

Recently, we have proven formation of η^2-propene intermediates upon protonation of η^3-allyl molybdenum and tungsten compounds [(η^5-Ind′)M(CO)$_2$(η^3-allyl)] (Ind′ = substituted indenyl; M = Mo, W) by strong acid in non-coordinating solvents. The η^2-propene intermediates were stabilized by intramolecular coordination of 1-(quinol-8-yl)indenyl ligand. A tungsten complex, presented in Scheme 1 (reaction B), was found to be stable up to 0 °C.[21] This study further documented that the η^2-propene ligand, in this type of complex, can be easily

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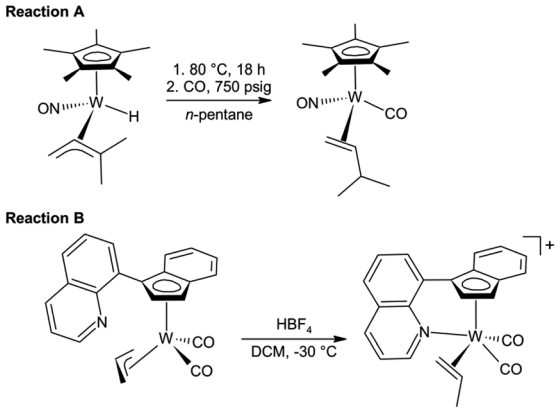


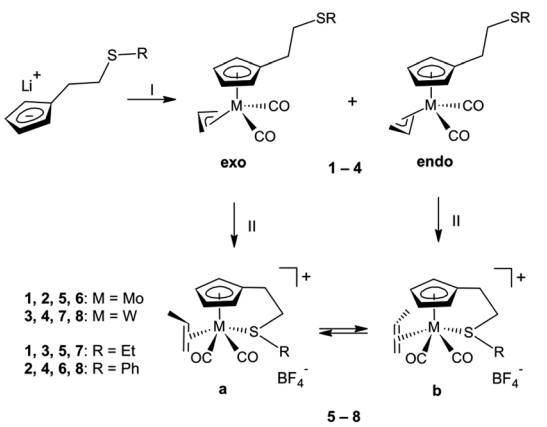
Scheme 1 Stabilization of η^2-alkene tungsten complexes by (a) CO coordination.[19] (b) Intramolecular coordination.[21]

exchanged by labile ligands (*e.g.*, dimethyl sulfide) while stronger ligands (*e.g.*, acetonitrile) induce η^3-to-η^5-indenyl ring slippage.[21]

The aim of this work is to describe stabilizing effects of the intramolecular coordination on cyclopentadienyl molybdenum and tungsten complexes without an annulated benzene ring. For this purpose, the thioether moiety in the side chain was chosen due to expected hemilabile coordination to the metal. Our secondary aim involves reactivity of η^2-propene complexes, prepared *in situ*, with thioethers and acetonitrile, as both ligands traditionally form labile complexes with early transition metals.

Results and discussion

The allyl(cyclopentadienyl) complexes **1–4** were prepared by the reaction of $[(\eta^3\text{-}C_3H_5)(MeCN)_2M(CO)_2Cl]$ (M = Mo, W) with lithium cyclopentadienides bearing a thioether group in the side chain $LiC_5H_4(CH_2)_2SR$ (R = Et, Ph), see Scheme 2. These precursors of propene complexes were isolated and characterized using ^{1}H NMR and IR spectroscopy.



Scheme 2 Synthesis of the precursors **1–4** and their protonation in a non-coordinating solvent: (I) $[(\eta^3\text{-}C_3H_5)(MeCN)_2M(CO)_2Cl]$ (M = Mo, W); (II) $HBF_4\cdot Et_2O$, CH_2Cl_2, −40 °C.

^{1}H spectra of the complexes **1–4** contained two sets of signals for the allyl ligand, expected for complexes of the $[(\eta^5\text{-}Cp')M(CO)_2(\eta^3\text{-}C_3H_5)]$,[22] due to the presence of the *exo*/*endo* isomerism of the allyl ligand (Scheme 2). At room temperature, *exo*- and *endo*-conformers appear in molar ratio 7 : 2 for **1** and **2**, 5 : 2 for **3** and 2 : 1 for **4**. The assignment allyl resonances in **1–4** was aided by data from previously prepared analogues with unsubstituted cyclopentadienyl ligands.[23] The infrared spectra of **1–4** exhibit two absorption bands in the region of 2000–1800 cm^{-1}, assigned to the asymmetric and symmetric stretching modes of the terminal carbonyl ligands (Table 1).

Reaction of the complexes **1–4** with $HBF_4\cdot Et_2O$ in dichloromethane at −40 °C afforded the complexes bearing η^2-coordinated propene ligand $[\{\eta^5\text{:}\kappa S\text{-}C_5H_4(CH_2)_2SR\}M(CO)_2(\eta^2\text{-}CH_2CHCH_3)][BF_4]$ (Scheme 2).

The absence of coordinating solvents enabled isolation of molybdenum complexes **5** and **6** at low temperature. They were stored for days at −40 °C without signs of decomposition. We note that they were characterized by ^{1}H NMR spectroscopy only owing to their thermal instability.

The ^{1}H NMR spectra of complexes **5** and **6**, measured at room temperature, contained two sets of signals attributed to two isomeric species of $[\{\eta^5\text{:}\kappa S\text{-}C_5H_4(CH_2)_2SR\}Mo(CO)_2(\eta^2\text{-}C_2H_3Me)][BF_4]$ with different propene ligand orientations (Scheme 2). The origin of these two isomers is assumed to be correlated to whether the allyl ligand being protonated in **1** and **2** is in the *exo*- or *endo*-confirmation. Relative abundances of **a** and **b** isomers were determined from integration of well resolved doublets attributed to propene methyl groups (δ = 1.8–2.3 ppm). The resonance at higher field was assigned to **a** isomer due to the effect of proximity of carbonyl ligand.

In both cases (**5** and **6**), isomer **b** is formed as a major protonation product since the spectra measured immediately upon dissolution contain isomers **5a**/**5b** and **6a**/**6b** in molar ratio 4 : 5 and 3 : 5, respectively. The lower thermodynamic stability of the **b** isomers become evident from repeated

Table 1 Wavenumbers (in cm^{-1}) of characteristic infrared bands

Compound	ν_a(CO)	ν_s(CO)	ν(BF)
1	1935	1850	—
2	1936	1850	—
3	1929	1840	—
4	1929	1839	—
7	2025	1946	1034
8	2025	1915	1026
9	1975	1883	1019
10	1974	1882	1048
11	1986	1885	1026
12	1978	1890	1022
13	1975	1890	1022
14	1984	1901	1030
15	1982	1888	1029
16	1960	1898	1027
17	1981	1903	1049
18	1994	1886	1054
19	1989	1896	1054
20	1990	1882	—

measurements. After two hours at room temperature, the composition of the mixtures has changed considerably. The isomers **5a**/**5b** and **6a**/**6b** were observed in molar ratios 6 : 1 and 5 : 1, respectively. We note that the rearrangement of **a** to **b** is accompanied with slow decomposition of the propene complexes. After prolonged storage at room temperature, full decomposition was evidenced by disappearance of signals attributed to **a** and **b** and detection of free propene giving characteristic signal at 1.70 ppm (dt, $^{3}J(^{1}H,^{1}H)$ = 6.5 Hz, $^{4}J(^{1}H,^{1}H)$ = 1.5 Hz).

Conversion of **a** to **b**, was verified by NMR measurement with internal standard. Such experiments have shown the increase of **a** isomer concentration up to 130% and 160% of original concentration for **5a** and **6a**, respectively.

The tungsten complexes **7** and **8** are thermally stable. They were isolated at room temperature and can be long-term stored without signs of decomposition. The thermodynamic stability of tungsten-propene bond was further evidenced by their inertness toward coordinating solvents (*e.g.*, MeCN) and aromatic amines (*e.g.*, pyridine) including strong *N*,*N*-chelators (*e.g.*, 1,10-phenanthroline).

The complexes **7** and **8** were characterized by mass spectrometry, ^{1}H NMR, ^{13}C NMR and IR spectroscopy. In both cases, only one set of signals was observed in ^{1}H NMR spectra attributed to single isomer (presumably isomer **a**). The coordinated propene ligand gives three signals assigned to methyl group (doublet at ~2.1 ppm), methylidene group (**7**: 3.05 ppm; **8**: 2.64 ppm) and alkene CH group (**7**: 3.52 ppm; **8**: 3.22 ppm), with the use ^{1}H–^{1}H COSY technique. The ^{1}H NMR spectra also contained four signals of the cyclopentadienyl CH groups and four multiplets of ethylene chain, which implies intramolecular coordination of the thioether sulfur atom of the side chain. Low symmetry of the compounds **7** and **8** is also apparent from the ^{13}C NMR spectra. For instance, each of the two carbonyl ligands gives an independent signal (**7**: 213.3 and 214.3 ppm; **8**: 214.0 and 214.7 ppm). Detailed assignment of ^{13}C NMR spectra was done with use of ^{1}H–^{13}C HSQC technique.

The successful protonation of the allyl ligand is also evidenced in the IR spectra. The carbonyl stretching bands are shifted by ~90 cm^{-1} to higher wavenumbers compared to the precursor complexes **3** and **4** (Table 1).

Formation of the isomer **8a** was confirmed by X-ray diffraction analysis on a single crystal (Fig. 1). The coordination sphere of the tungsten atom adopts a distorted square pyramidal geometry. The apical position of the pyramid is occupied by the η^5-coordinated cyclopentadienyl ligand. The square base contains the two carbonyl ligands in *cis*-configuration, the intramolecularly coordinated sulfur atom of the thioether moiety and the C=C double bond of the propene ligand. Methyl group of propene ligand appears at *cis*-position with respect to neighboring carbonyl ligand C1O1 (isomer a in Scheme 2). Selected bond lengths and angles are presented in Table 2.

It is well established that the C=C double bond of the alkene ligand elongates upon coordination and that the substituents on the C=C carbon atoms bend away from the metal atom. This appears because of the sharing of electron density between the π-orbitals of the alkene and the orbitals of the metal center.[21] The dihedral angle defined by the metal atom, the C=C carbon atoms and carbon atom of the propene methyl group (α) can be used for quantifying distortion of the propene ligand. Its deviation from 90° express degree of its bending ($\alpha' = \alpha - 90$). Elongation of the C=C double bond in η^2-propene complexes

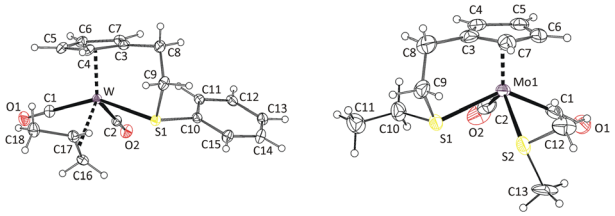


Fig. 1 X-ray structure of **8a** (left) and **9**-*cis* (right). Thermal ellipsoids set to 30% probability. Only one of the three crystallographically independent cations of **9**-*cis* is shown for clarity.

Table 2 Selected bond lengths (Å) and angles (°) of molybdenum and tungsten complexes

	8a	**9**-*cis*[a]	**9**-*cis*[a]	**9**-*cis*[a]	**11**-*cis*	**12**-*cis*	**15**-*trans*	**16**-*cis*	**18**	**19a**
M–Cg(C$_5$)[b]	1.9877(15)	1.974(4)	1.984(4)	1.984(5)	1.9797(15)	1.9820(9)	2.0023(18)	1.9880(11)	1.9820(11)	1.9871(8)
M–C1	2.027(3)	1.99(1)	2.00(1)	2.01(1)	2.006(4)	2.000(2)	2.017(4)	1.975(2)	1.998(3)	1.984(2)
M–C2	1.983(3)	1.94(1)	1.95(1)	1.96(1)	1.964(3)	1.963(2)	1.959(4)	1.965(2)	1.951(2)	1.981(2)
M–L1[c]	2.5362(8)	2.509(2)	2.519(2)	2.516(2)	2.516(1)	2.5232(5)	2.505(1)	2.5416(5)	2.5120(7)	2.166(1)
M–L2[d]	2.210(2)	2.546(3)	2.530(2)	2.489(3)	2.5147(9)	2.5314(5)	2.490(1)	2.5395(6)	2.163(2)	2.168(1)
C1–M–Cg(C$_5$)	105.53(11)	117.9(3)	110.9(3)	113.5(4)	117.67(11)	113.30(6)	134.23(13)	114.69(8)	118.54(10)	116.30(5)
C2–M–Cg(C$_5$)	123.04(10)	122.4(4)	123.7(3)	126.6(3)	122.82(11)	125.97(6)	123.48(11)	115.15(7)	121.28(7)	117.91(5)
L1–M–Cg(C$_5$)[b,c]	104.41(5)	107.75(16)	106.60(14)	106.07(16)	107.42(5)	107.93(3)	105.68(7)	120.36(4)	107.20(4)	113.91(4)
L2–M–Cg(C$_5$)[b,d]	133.96(8)	118.14(17)	124.13(14)	123.37(16)	118.92(5)	120.98(3)	106.40(7)	121.60(4)	120.21(6)	116.86(4)
C1–M–L1[c]	149.8(1)	134.4(3)	142.0(3)	140.3(3)	134.7(1)	138.43(6)	147.85(3)	124.84(7)	134.17(9)	129.78(6)
C2–M–L2[d]	102.9(1)	119.4(3)	112.2(3)	109.8(3)	118.1(1)	113.03(6)	102.3(2)	123.23(6)	118.41(8)	125.23(6)
C1–M–C2	79.1(1)	74.3(5)	78.5(4)	77.7(4)	75.4(1)	76.74(8)	102.3(2)	75.66(9)	75.2(1)	74.85(7)
L1–M–L2[c,d]	77.53(7)	76.38(9)	75.53(8)	75.09(9)	74.61(3)	75.17(2)	147.85(3)	74.98(2)	75.15(5)	77.47(5)

[a] Three crystallographically independent molecules in the unit cell. [b] Cg(C$_5$) = center of the cyclopentadienyl ring. [c] L1 = sulfur atom of the pendant arm (**8a**, **9**-*cis*, **11**-*cis*, **12**-*cis* and **18**), sulfur atom of the monodentate thioether (**15**-*trans*, **16**-*cis*) or the nitrogen atom of the acetonitrile (**19a**). [d] L2 = center of the C=C double bond of propene (**8a**), sulfur atom of the monodentate thioether (**9**-*cis*, **11**-*cis*, **12**-*cis*, **15**-*trans*, **16**-*cis*) or the nitrogen atom of the acetonitrile (**18**, **19a**).

usually vary between 0.03–0.13 Å (ref. 24–27) compared to value determined for free propene molecule (1.341(2) Å) by the gas electron diffraction.[28] In the case of compound **8a**, the C=C bond elongates by 0.057 Å, which is comparable to data previously reported for indenyl tungsten(II) complex [{η^5:κ*N*-1-(C_9H_6N)C_9H_6}(η^2-C_2H_3Me)$W(CO)_2$][BF_4][21] (0.068 Å) and calixarene tungsten(IV) complex [{*p*-Bu^t-calix[4]-$(O)_4$}W(η^2-C_2H_3Me)], (0.058 Å).[25]

Complexes of electron rich metals such as Pt(II)[29,30] and Cu(I)[24] show low values of bending angle α′ not exceeding 15°. It implies a low effect of the coordination distortion on geometry of the propene ligand. The complexes of less electron rich metals, such as Ta(III),[27] Mo(II),[26] W(II)[21,31] and W(IV),[25] show higher α′ values. They vary between 21° and 30°, which documents a stronger effect of the coordination.

In our case (**8a**), the bending angle (21.9(3)°) fits into this range being close to value recently reported to structurally related indenyl tungsten(II) compound [{η^5:κ*N*-1-(C_9H_6N)C_9H_6}(η^2-C_2H_3Me)$W(CO)_2$][BF_4][21] (24.5(9)°).

To assess the stability of molybdenum(II)-to-alkene bond in **5** and **6**, protonation of their precursors (**1** and **2**) was done in presence of weak coordinating thioether ligands (Scheme 3). Infrared spectra of the isolated products **9–14** revealed shift of the carbonyl stretching bands by ∼40 cm^{-1} to higher wavenumbers compared to the precursors **1** and **2** (Table 1), which documents lower covalency of the Mo–CO bond in the cationic products due to reduced π-backbonding of the carbonyl ligands.

^{1}H NMR spectra of the compounds **9–14** contain four sharp signals at 5.0–6.5 ppm assigned to hydrogen atoms of the cyclopentadienyl ring. It indicates that the sulfur atom of the thioether side chain is intramolecularly coordinated. Additionally, the spectra of compounds **9**, **10** and **13** contained a second set of four signals in this region implying a presence of two isomeric species. They appear in molar ratios 5 : 1, 13 : 1 and 5 : 2 in solutions of **9**, **10** and **13**, respectively. The presence of two isomers is also evidenced in the ^{13}C NMR spectra of **9**, **10** and **13**. They contain two sets of signals for the carbon atoms of the carbonyl ligands. The ^{1}H and ^{13}C NMR spectra indicate low molecular symmetry of both isomers due to coordination of thioether side arm. The existence of two discrete isomeric species is also confirmed by the presence of two separate sets of signals for the ethylene spacers, observed in the ^{1}H NMR spectrum of **13**, which were assigned using the ^{1}H–^{1}H COSY technique. We note that signals of the ethylene spacer were not unambiguously assigned in the ^{1}H NMR spectra of **9** and **10** owing to the presence of other aliphatic functions.

Molecular structure of the compound **9**-*cis* was revealed by X-ray diffraction analysis on a single crystal (Fig. 1). The compound has the expected square-pyramidal structure with carbonyl ligands in expected *cis*-configuration. Such evidence together with similarities observed in NMR spectra led us to attribute the main product in spectra of **9–14** to the same isomer (see, *cis* in Scheme 3). The minor species, in the spectra of **9**, **10** and **13**, is ascribed to the isomer with the carbonyl ligands in the *trans*-configuration. Although this configuration is less common for compounds of general formula [Cp′$M(CO)_2L_2$], it was previously reported for derivatives bearing thioether ligands without intramolecular coordination.[32]

The formation of *cis*-isomers was evidenced by X-ray analysis also for compounds **11**-*cis* and **12**-*cis* (Fig. 2). They are isostructural with compound **9**-*cis* mentioned afore. Presence of simple thioether ligand in these structures enables to quantify effects of geometric constrain, caused by intramolecularly coordinated side arm. As evident from data given in Table 2, the intramolecular coordination causes only minor shortening of the Mo–S bond but the reduction of the bond angle Cg(C_5)–Mo–S is substantial (from ∼120 to ∼107°).

Observation of the rather unusual *trans*-isomers in solutions of **10**, **12** and **13** let us to investigate protonation of parent allyl complex [(η^5-C_5H_5)$Mo(CO)_2$(η^3-C_3H_5)] in the presence of simple thioethers (Scheme 4). Infrared spectra of reaction products **15–17** show carbonyl stretching bands at similar wavenumbers as the compounds with intramolecular coordination (Table 1). ^{1}H NMR spectra contain one singlet at 5.7 ppm assigned to

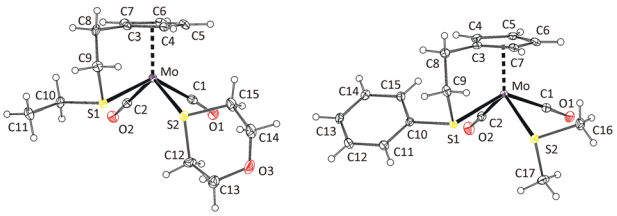
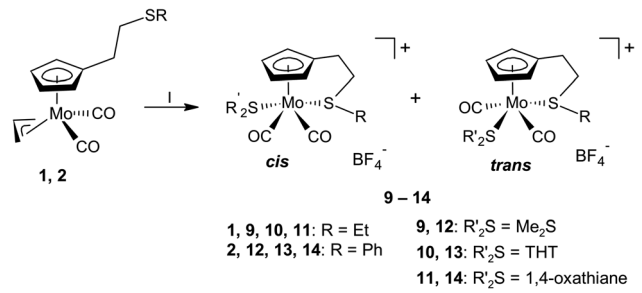
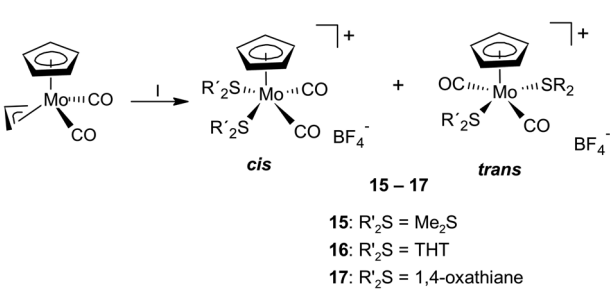


Fig. 2 X-ray structure of **11**-*cis* (left) and **12**-*cis* (right). Thermal ellipsoids set to 30% probability.



Scheme 3 Protonation of **1** and **2** in the presence of thioethers: (I) $HBF_4 \cdot Et_2O$, CH_2Cl_2, 1.1 equiv. SR'_2, 0 °C.



Scheme 4 Synthesis of the thioether complexes **15–17**: (I) $HBF_4 \cdot Et_2O$, CH_2Cl_2, 2.2 equiv. SR'_2, 0 °C.

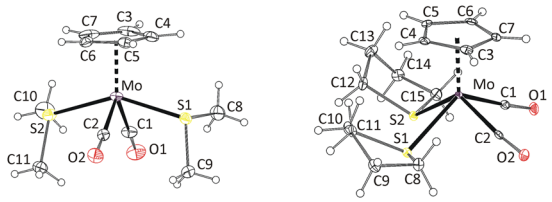
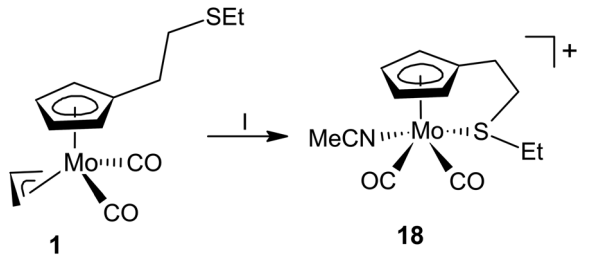


Fig. 3 X-ray structure of **15**-*trans* (left) and **16**-*cis* (right). Thermal ellipsoids set to 30% probability.



Scheme 5 Synthesis of acetonitrile complex **18**: (I) $HBF_4 \cdot Et_2O$, acetonitrile, 0 °C.

cyclopentadienyl hydrogens, and one set of signals of given coordinated thioether. The integral intensities of the signals prove that two thioether ligands are coordinated. ^{13}C NMR spectra of **15–17** contain a sole signal in the region of carbonyl ligands at ~244 ppm, which is in line with expected C_s molecular symmetry. Unfortunately, our NMR experiments are not conclusive about configuration of carbonyl ligands. They imply formation of a single isomer or a fast equilibrium between the *cis*- and *trans*-isomers. The later interpretation in more convenient, as representatives of both isomers (**15**-*trans* and **16**-*cis*) were evidenced by X-ray crystallography (Fig. 3).

Complex cations in **15**-*trans* and **16**-*cis* adopt expected distorted square pyramidal structures with cyclopentadienyl ligand in the apical position. Two carbonyl ligands and sulfur atoms of thioethers occupy the basal plane. The *trans*-configuration of the carbonyl ligands in **15**-*trans* causes a greater distortion of the square pyramidal geometry than is observable for the cationic complexes in *cis*-configuration. This is evident from the values of the C1–Mo–C2 (102.3(2)°) and S1–Mo–S2 (147.85(3)°) angles. They differ by ~45°, which contrasts with the structures of the other two complexes with unsubstituted cyclopentadienyl ligands (Fig. 3 and 4). The difference between C1–M–L1 and C2–M–L2 is only 1.61° and 4.55° in structures **16**-*cis* and **19a**, respectively (Table 2). Despite this difference in bond angles, there is only a negligible difference in corresponding Mo–S and Mo–C bond lengths in **15**-*trans* and **16**-*cis*.

The protonation of the allyl molybdenum complex **1** was further studied in the presence of acetonitrile. Such ligand is usually coordinated to molybdenum(II) stronger than thioethers[21] but the coordination is weak enough to undergo of ligand exchange reactions. Hence, acetonitrile complexes are known as stable precursors for the assembly variety of structural motifs including bis(cyclopentadienyl) compounds[33] or complexes bearing *N*,*N*-bidentate ligands.[34]

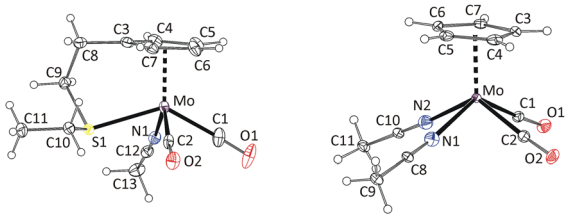


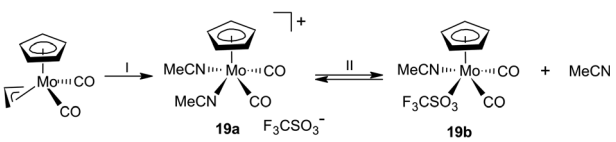
Fig. 4 X-ray structure of **18** (left) and **20a** (right). Thermal ellipsoids set to 30% probability.

Compounds **1** reacts with $HBF_4 \cdot Et_2O$ in acetonitrile to give cationic complex **18** (Scheme 5). The carbonyl stretching bands in the IR spectrum of **18** are shifted by about 40 cm^{-1} to higher energy compared to the precursor complex **1**, which resembles behavior of the thioether complexes (Table 1).

The ^1H NMR spectrum of compound **18** contains four sharp signals in the region 5.0–6.5 ppm, those were assigned to the hydrogen atoms of the cyclopentadienyl ring. It further contains four multiplets (2.62, 2.96, 3.68 and 4.08 ppm) attributed to the hydrogen atoms of the methylene spacers and signals for the ethyl group (1.39 and 2.88 ppm). Such pattern is very similar to analogues **9–11** mentioned afore, which implies appearance of the same structural motif. Signal of acetonitrile ligand appears at 2.54 ppm. Its integral intensity proves that only one molecule of the ligand is coordinated.

The structure of **18** was confirmed by X-ray diffraction analysis (Fig. 4). The coordination sphere adopts a distorted square pyramidal geometry resembling other cationic complexes under the study. The carbonyl ligands are in expected *cis*-configuration. The geometrical constrain induced by the intramolecular coordination of thioether function Cg(C_5)–Mo–S angle (107.20(4)°) is comparable to that in crystal structures of **8**, **9**-*cis*, **11**-*cis* and **12**-*cis* (Table 2).

As protonation of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ by $HBF_4 \cdot Et_2O$ in presence of acetonitrile is well described in literature,[35,36] we decided to study the protonation with another strong acid CF_3SO_3H. The reaction was done in acetonitrile at 0 °C. ^1H NMR spectrum in CD_2Cl_2 revealed a formation of two molybdenum complexes **19a** and **19b** in solution (Scheme 6). They give two sets of signals assigned to cyclopentadienyl (5.74 ppm for **b** and 5.75 ppm for **a**) and the coordinated acetonitrile ligands (2.50 ppm for **b** and 2.54 ppm for **a**). The spectrum further contains a singlet at 1.97 ppm which originates from free acetonitrile. It implies that recrystallization from acetonitrile produces $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(MeCN)_2](CF_3SO_3)$ (**19a**) in a pure form and dissolution in CD_2Cl_2 leads to



Scheme 6 Synthesis of **19a** and its transformation to **19b**: (I) CF_3SO_3H, MeCN, 0 °C (II) CD_2Cl_2.

partial exchange of acetonitrile ligand with triflate. Such interpretation well correlates with formation equimolar amounts of **19b** and free acetonitrile, evidenced by the ^{1}H NMR technique.

Single crystal of **19a**, prepared by a slow diffusion of diethyl ether into an acetonitrile solution, enabled to verify its solid-state structure (Fig. 4). We note that geometric parameters describing coordination sphere of molybdenum (Table 2) are in line with those reported previously for $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(\text{-}NCMe)_2][BF_4]$.[35]

Conclusions

This study describes protonation of allyl ligand in molybdenum and tungsten complexes $[(\eta^5\text{-}Cp')(\eta^3\text{-allyl})M(CO)_2]$ (M = Mo, W) bearing cyclopentadienyl ligand decorated with a thioether function in the side chain. After allyl ligand protonation, the thioether moiety coordinates intramolecularly to the central metal and stabilizes the η^2-bond of appeared propene ligand.

Molybdenum complexes $[\{\eta^5{:}\kappa S\text{-}C_5H_4(CH_2)_2SR\}Mo(CO)_2(\eta^2\text{-}C_2H_3Me)][BF_4]$ (R = Et, Ph), formed by this pathway, are isolable at low temperature while tungsten analogues are long-term stable at room temperature. Unusually high thermodynamic stability of tungsten complexes is documented by inertness toward coordinating solvents (*e.g.*, acetonitrile) and strong chelators (*e.g.*, 1,10-phenanthroline). In the case of less stable molybdenum compounds, η^2-propene ligand can be easily exchanged even by labile ligands (*e.g.*, thioethers). The products of ligand exchange $[\{\eta^5{:}\kappa S\text{-}C_5H_4(CH_2)_2SR\}Mo(CO)_2(SR'_2)][BF_4]$ form both *cis*- and *trans*-isomers in solution, though structure of *cis*-isomers were resolved by X-ray crystallography. Rather unusual *trans*-isomer was structurally characterized in the case of analoque without intramolecular coordination $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(SMe_2)_2][BF_4]$ formed by protonation of cyclopentadienyl complex $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ in the presence of dimethyl sulfide.

Experimental

Materials

Synthesis of the organometallic compounds was done under an argon atmosphere using conventional Schlenk-line techniques. The products were stored under argon atmosphere at −20 °C. The solvents were dried using standard methods.[37] The reagents were purchased from comercial sources (Sigma-Aldrich, Acros Organics and Penta) or prepared according to literature procedures: $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$;[38] $[(\eta^3\text{-}C_3H_5)(MeCN)_2\text{-}Mo(CO)_2Cl]$;[39] $[(\eta^3\text{-}C_3H_5)(EtCN)_2W(CO)_2Cl]$.[40]

Methods

^{1}H, ^{13}C{^{1}H}, ^{13}C-APT, ^{1}H–^{1}H COSY and ^{1}H–^{13}C HSQC NMR spectra were measured on the Bruker Avance 500 MHz and Bruker Avance 400 MHz spectrometers. The spectra were calibrated to the residual signal of the solvent relative to Me_4Si. Poly(dimethylsiloxane) was used as internal standard in stability studies. Infrared spectra were recorded on a Nicolet iS50 FTIR spectrometer using a diamond Smart Orbit ATR in the region 4000–400 cm^{-1}. Mass spectra were collected on a quadruple mass spectrometer LCMS 2010 (Shimadzu, Japan). The samples were dissolved in acetone and injected into the mass spectrometer with an infusion mode at a constant flow rate of 10 μL min^{-1}. Electrospray ionization-mass spectrometry (ESI-MS) was used for the identification of the analyzed samples.

X-ray crystallography

Data for **9**-*cis*, **11**-*cis*, **12**-*cis*, **16**-*cis* and **19a** was collected on the Rigaku XtaLAB Synergy S diffractometer equipped with micro-focus CuKα/MoKα radiation and a Hybrid Pixel Array Detector (HyPix-6000HE). An Oxford Cryosystems (Cryostream 800) cooling device was used for data collection and the crystals were kept at 100 K during data collection. CrysAlisPro software[41] was used for data collection, cell refinement and data reduction. Data were corrected for absorption effects using empirical absorption correction (spherical harmonics), implemented in SCALE3 ABSPACK scaling algorithm and numerical absorption correction based on gaussian integration over a multifaceted crystal model. Using Olex2,[42] the structures were solved with the SHELXT[43] and SHELXS[44] structure solution program using intrinsic phasing (**9**-*cis*, **12**-*cis*, **16**-*cis* and **19a**) and direct methods (**11**-*cis*) and refined with the SHELXL[45] refinement package using least squares minimization. Hydrogen atoms of all molecules were placed in calculated positions. The diffraction experiments for **8a**, **15**-*trans* and **18** were performed on Bruker D8 VENTURE Kappa Duo PHOTONIII by IμS micro-focus sealed tube CuKα (λ = 1.54178) radiation at low temperature. The structures were solved by direct methods (SHELXS)[42] and refined by full matrix least squares based on F^2 (SHELXL2018).[44] The hydrogen atoms on carbon were fixed into idealized positions (riding model) and assigned atomic displacement parameters either $U_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or $U_{iso}(H) = 1.5\ U_{eq}$ (pivot atom) for methyl moiety.

Synthesis of $C_5H_5(CH_2)_2SEt$

The substituted cyclopentadiene was prepare using modification of the previously described procedures.[46,47]

Freshly monomerized cyclopentadiene (5.2 mL, 62 mmol) was added dropwise to a suspension of sodium sand (1.6 g, 70 mmol) in 30 mL of THF. The mixture was stirred at room temperature for 16 h and then it was filtered from excess of sodium using a Schlenk frit. The sodium cyclopentadienide solution was precooled to −40 °C, treated with $Cl(CH_2)_2SEt$ (7.0 g, 56 mmol) dropwise and the reaction mixture was stirred at room temperature for 16 h. The reaction was quenched with a ice/water mixture and the crude product was extracted with diethyl ether (2 × 10 mL). The volatiles were removed on a rotavapor and the product purified by vacuum distillation (bp = 110 °C at 67 Pa). Yield: 3.9 g (19 mmol, 34%). Yellow liquid. ^{1}H NMR [400 MHz, $CDCl_3$, 1 : 1 mixture of 1- and 2-isomers (**a** : **b**)]: δ = 1.27 (t, $^3J(^1H,^1H)$ = 7.4 Hz, 3H, SCH_2CH_3); 2.57 (q, $^3J(^1H,^1H)$ = 7.4 Hz, 2H, SCH_2CH_3); 2.63–2.76 (m, 4H of **a** and 4H **b**, $C_5H_5CH_2CH_2S$); 2.93 (q, $^3J(^1H,^1H)$ = 1.4 Hz, 2H, $H^{5,5}$ of **a**, C_5H_5); 2.96–2.98 (m, 2H, $H^{5,5}$ of **b**, C_5H_5); 6.06–6.09 (m, H^4 of **a**,

C_5H_5); 6.22 (s, H^4 of **b**, C_5H_5); 6.28 (dq, $^3J(^1H,^1H)$ = 5.4 Hz, $^4J(^1H,^1H)$ = 1.5 Hz, H^3 of **b**, C_5H_5); 6.41–6.47 (m, 3H, $H^{3,2}$ of **a**, H^1 of **b**, C_5H_5).

Synthesis of $C_5H_5(CH_2)_2SPh$

The steps of synthesis followed the procedure for $C_5H_5(CH_2)_2$-SEt, but with 4.88 mL (58.0 mmol) of freshly monomerized cyclopentadiene, 1.47 g (63.9 mmol) of elemental sodium and 9.56 g (55.4 mmol) of $Cl(CH_2)_2SPh$. The desired product came over as the second fraction (100 °C, 13 mm Hg). Yield: 2.59 g (12.8 mmol, 23%). Yellow liquid. ^1H NMR [400 MHz, $CDCl_3$, 1 : 1 mixture of 1- and 2-isomers (**a** : **b**)] 2.80–2.89 (m, 2H of **a** and 2H of **b**, $C_5H_5CH_2CH_2S$); 3.03 (s, 2H, $H^{5,5}$ of **a**, C_5H_5); 3.09 (s, 2H, $H^{5,5}$ of **b**, C_5H_5); 3.20–3.28 (m, 2H of **a** and 2H of **b**, $C_5H_5CH_2$-CH_2S); 6.22 (s, 1H, H^4 of **a**, C_5H_5); 6.37 (s, 1H, H^4 of **b**, C_5H_5); 6.41 (d, $^3J(^1H,^1H)$ = 5.3 Hz, 1H, H^3 of **b**, C_5H_5); 6.57 (s, 3H, $H^{2,3}$ of **a**, H^1 of **b**, C_5H_5); 7.29 (t, $^3J(^1H,^1H)$ = 7.2 Hz, 2H of **a** and 2H of **b**, $H^{2,6}$ C_6H_5); 7.40 (t, $^3J(^1H,^1H)$ = 7.5 Hz, 2H of **a** and 2H of **b**, $H^{3,5}$ C_6H_5); 7.47 (d, $^3J(^1H,^1H)$ = 7.5 Hz, 1H of **a** and 1H of **b**, H^4 C_6H_5).

Synthesis of [{η⁵-$C_5H_4(CH_2)_2SEt$}$Mo(CO)_2(η^3$-$C_3H_5)$] (1)

$C_5H_5(CH_2)_2SEt$ (469 mg, 3.04 mmol) was dissolved in 15 mL of THF, cooled to −60 °C and treated dropwise with a solution of butyllithium (1.6 M in hexanes, 1.9 mL, 3.04 mmol). The reaction mixture was stirred for 1 h and then added dropwise to a solution of $[(\eta^3\text{-}C_3H_5)(MeCN)_2Mo(CO)_2Cl]$ (922 mg, 2.97 mmol) in 10 mL of THF. The reaction mixture was stirred 16 h at room temperature. The volatiles were vacuum evaporated, the crude product extracted with hexane (3 × 25 mL, 60 °C). The volume of the extract was halved by vacuum evaporation and the product was precipitated as a yellow powder by cooling the mixture to −80 °C. The leftover solvent was decanted off and the product was dried in vacuum. Yield: 766 mg (2.21 mmol, 75%). Yellow powder. Anal. calc. for $C_{14}H_{18}SO_2Mo$: C: 48.56; H: 5.24; S: 9.26. Found: C: 48.44; H: 5.10; S: 9.05. ^1H NMR [500 MHz, CD_2Cl_2, 7 : 2 mixture of isomers *exo* : *endo*]: δ = 0.91 (d, $^3J(^1H,^1H)$ = 10,8 Hz, 2H, H^{anti} of *exo*, C_3H_5); 1.22 (t, $^3J(^1H,^1H)$ = 7.3 Hz, 3H, SCH_2CH_3); 1.65 (d, $^3J(^1H,^1H)$ = 10.5 Hz, 2H, H^{anti} of *endo*, C_3H_5); 2.47 (t, $^3J(^1H,^1H)$ = 7.4 Hz, 2H, $C_5H_4CH_2CH_2S$); 2.52 (q, $^3J(^1H,^1H)$ = 7.3 Hz, 2H, SCH_2CH_3); 2.64 (t, $^3J(^1H,^1H)$ = 7.4 Hz, 2H, $C_5H_4CH_2CH_2S$); 2.74 (d, $^3J(^1H,^1H)$ = 7.0 Hz, 2H, H^{syn} of *exo*, C_3H_5); 2.78–2.83 (m, 2H, H^{syn} of *endo*, C_3H_5); 3.59–3.69 (m, 1H, H^{meso} of *endo*, C_3H_5); 3.92 (tt, $^3J(^1H,^1H)$ = 10.8 Hz, $^4J(^1H,^1H)$ = 7.0 Hz, 1H, H^{meso} of *exo*, C_3H_5); 5.17 (s, 2H, C_5H_4); 5.22 (s, 2H, C_5H_4). IR (ATR, cm^{-1}): 1935 *vs.* [ν_a(CO)], 1850 *vs.* [ν_s(CO)].

Synthesis of [(η⁵-$C_5H_4(CH_2)_2SPh$)$Mo(CO)_2(η^3$-$C_3H_5)$] (2)

The steps of the synthesis followed the procedure for **1**, but with $C_5H_5(CH_2)_2SPh$ (616 mg, 3.05 mmol), butyllithium (1.6 M in hexanes, 1.99 mL, 3.18 mmol) and $[(\eta^3\text{-}C_3H_5)(MeCN)_2$-$Mo(CO)_2Cl]$ (925 mg, 2.98 mmol). Yield: 805 mg (2.10 mmol, 68%). Pale yellow powder. Anal. calc. for $C_{18}H_{18}SO_2Mo$: C: 54.82; H: 4.60; S: 8.13. Found: C, 54.63; H, 4.48; S: 8.03. ^1H NMR [500 MHz, CD_2Cl_2; 7 : 2 mixture of isomers *exo* : *endo*]: δ = 0.91 (d, $^3J(^1H,^1H)$ = 10.8 Hz, 2H, H^{anti} of *exo*, C_3H_5); 1.63 (d, $^3J(^1H,^1H)$ = 10.4 Hz, 2H, H^{anti} of *endo*, C_3H_5); 2.54 (t, $^3J(^1H,^1H)$ = 7.5 Hz, 2H, $C_5H_5CH_2CH_2SPh$); 2.73 (d, $^3J(^1H,^1H)$ = 6.9 Hz, 2H, H^{syn} of *exo*, C_3H_5); 2.80 (d, $^3J(^1H,^1H)$ = 5.3 Hz, 2H, H^{syn} of *endo*, C_3H_5); 3.01 (t, $^3J(^1H,^1H)$ = 7.5 Hz, 2H, $C_5H_5CH_2CH_2SPh$); 3.59–3.67 (m, 1H, H^{meso} of *endo*, C_3H_5); 3.90 (tt, $^3J(^1H,^1H)$ = 10.7 Hz, $^3J(^1H,^1H)$ = 7.1 Hz, 1H, H^{meso} of *exo*, C_3H_5); 5.18 (s, 2H, C_5H_4); 5.22 (s, 2H, C_5H_4); 7.20 (t, $^3J(^1H,^1H)$ = 7.1 Hz, 1H, C_6H_5); 7.28–7.34 (m, 4H, C_6H_5). IR (ATR; cm^{-1}): 1936 *vs.* [ν_a(CO)], 1850 *vs.* [ν_s(CO)].

Synthesis of [{η⁵-$C_5H_4(CH_2)_2SEt$}$W(CO)_2(η^3$-$C_3H_5)$] (3)

The steps of synthesis followed the procedure for compound **1**, but with $C_5H_5(CH_2)_2SEt$ (936 mg, 6.07 mmol), butyllithium (1.6 M in hexanes, 3.8 mL, 6.08 mmol) and $[(\eta^3\text{-}C_3H_5)(EtCN)_2$-$W(CO)_2Cl]$ (2.25 g, 5.65 mmol). Yield: 2.35 g (5.41 mmol, 96%). Orange liquid. Anal. calc. for $C_{14}H_{18}SO_2W$: C:38.73; H: 4.18; S: 7.38. Found: C: 38.57; H: 3.94; S: 7.11. ^1H NMR [400 MHz, C_6D_6, 5 : 2 mixture of isomers *exo* : *endo*]: δ = 1.03 (t, $^3J(^1H,^1H)$ = 7.4 Hz, 3H, SCH_2CH_3); 1.08–1.15 (m, 2H, H^{anti} of *exo* and *endo*, C_3H_5); 2.12 (t, $^3J(^1H,^1H)$ = 7.1 Hz, 2H, $C_5H_4CH_2CH_2S$); 2.19 (q, $^3J(^1H,^1H)$ = 7.3 Hz, 2H, SCH_2CH_3); 2.26 (t, $^3J(^1H,^1H)$ = 6.8 Hz, 2H, $C_5H_4CH_2CH_2S$); 2.38 (d, $^3J(^1H,^1H)$ = 6.1 Hz, 2H, H^{syn} of *exo*, C_3H_5); 2.61–2.67 (m, 2H, H^{syn} of *endo*, C_3H_5); 2.84–2.95 (m, $1H^{meso}$ of *exo*, C_3H_5); 3.51–3.62 (m, $1H^{meso}$ of *endo*, C_3H_5); 4.50 (s, 2H, C_5H_4); 4.57 (s, 2H, C_5H_4). IR (ATR, cm^{-1}): 1929 *vs.* [ν_a(CO)], 1840 *vs.* [ν_s(CO)].

Synthesis of [{η⁵-$C_5H_4(CH_2)_2SPh$}$W(CO)_2(η^3$-$C_3H_5)$] (4)

The steps of synthesis followed the procedure for compound **1**, but with $C_5H_5(CH_2)_2SPh$ (297 mg, 1.47 mmol), butyllithium (1.6 M in hexanes, 1.0 mL, 1.6 mmol) and $[(\eta^3\text{-}C_3H_5)(EtCN)_2$-$W(CO)_2Cl]$ (545 mg, 1.37 mmol). Yield: 498 mg (1.15 mmol, 82%). Orange liquid. Anal. calc. for $C_{18}H_{18}SO_2W$: C: 44.83; H: 3.76; S: 6.65. Found: C: 44.55; H: 3.59; S: 6.37. ^1H NMR [400 MHz, $CDCl_3$, 2 : 1 mixture of isomers *exo* : *endo*]: δ = 1.19 (d, $^3J(^1H,^1H)$ = 9.9 Hz, 2H, H^{anti} of *exo*, C_3H_5); 1.32–1.39 (m, 2H, H^{anti} of *endo*, C_3H_5); 2.66 (t, $^3J(^1H,^1H)$ = 7.5 Hz, 2H, $C_5H_4CH_2$-CH_2S); 2.72 (d, $^3J(^1H,^1H)$ = 5.9 Hz, 2H, H^{syn} of *exo*, C_3H_5); 2.79–2.85 (m, 2H, H^{syn} of *endo*, C_3H_5); 3.13 (t, $^3J(^1H,^1H)$ = 7.4 Hz, 2H, $C_5H_4CH_2CH_2S$); 3.46–3.56 (m, 1H, H^{meso} of *exo*, C_3H_5); 3.74–3.82 (m, 1H, H^{meso} of *endo*, C_3H_5); 5.25–5.38 (m, 4H, C_5H_4); 7.32–7.43 (m, 5H, C_6H_5). IR (ATR, cm^{-1}): 1929 *vs.* [ν_a(CO)], 1839 *vs.* [ν_s(CO)].

Synthesis of [{η⁵:κ*S*-$C_5H_4(CH_2)_2SEt$}$Mo(CO)_2(η^2$-$C_2H_3Me)$][BF_4] (5)

Compound **1** (252 mg, 0.73 mmol) was dissolved in 10 mL of dichloromethane, the solution was cooled to −40 °C and treated with $HBF_4 \cdot Et_2O$ (98 μL, 0.73 mmol) dropwise. The solution was stirred at −40 °C for 16 h, the solvent was vacuum evaporated, and the crude product was purified by dissolution in a small amount of dichloromethane (~0.5 mL) and subsequent precipitation by the addition of diethyl ether (10 mL), the solvents were decanted and the solid was vacuum dried. This process was repeated up to three times. Care was taken to keep the reaction mixture at or below −40 °C and to measure the ^1H NMR spectra directly after isolation. Yield: 316 mg (0.60 mmol,

82%). Orange solid. ^{1}H NMR [500 MHz, CD_2Cl_2, 4 : 5 mixture of isomers **a** : **b**]: δ = 1.27 (t, $^3J(^1H,^1H)$ = 7.4 Hz, 3H of **b**, SCH_2CH_3); 1.31 (t, $^3J(^1H,^1H)$ = 7.4 Hz, 3H of **a**, SCH_2CH_3); 1.88 (d, $^3J(^1H,^1H)$ = 5.5 Hz, 3H of **a**, CH_2CHCH_3); 2.21 (d, $^3J(^1H,^1H)$ = 6.0 Hz, 3H of **b**, CH_2CHCH_3); 4.90 (s, 1H of **b**, C_5H_4); 4.95 (s, 1H of **a**, C_5H_4); 5.35 (s, 1H of **b**, C_5H_4); 6.08 (s, 1H of **a**, C_5H_4); 6.10 (s, 1H of **b**, C_5H_4); 6.25 (s, 1H of **a**, C_5H_4); 6.35 (s, 1H of **b**, C_5H_4).

Synthesis of [{η^5:κ*S*-$C_5H_4(CH_2)_2SPh$}Mo(CO)$_2$(η^2-C_2H_3Me)][BF_4] (6)

The steps of synthesis followed the procedure for compound **5**, but with **2** (105 mg, 0.27 mmol), $HBF_4 \cdot Et_2O$ (38 μL, 0.28 mmol). Yield: 101 mg (0.21 mmol, 79%). Orange solid. ^{1}H NMR [500 MHz, CD_2Cl_2, 3 : 5 mixture of isomers **a** : **b**]: δ = 1.98 (d, $^3J(^1H,^1H)$ = 5.7 Hz, 3H of **a**, CH_2CHCH_3); 2.24 (d, $^3J(^1H,^1H)$ = 6.0 Hz, 3H of **b**, CH_2CHCH_3); 4.96 (s, 1H of **b**, C_5H_4); 5.10 (s, 2H of **a**, C_5H_4); 5.36 (s, 1H of **b**, C_5H_4); 5.37 (s, 1H of **b**, C_5H_4); 6.33 (s, 1H of **a**, C_5H_4); 6.35 (s, 1H of **a**, C_5H_4); 6.43 (s, 1H of **b**, C_5H_4).

Synthesis of [{η^5:κ*S*-$C_5H_4(CH_2)_2SEt$}W(CO)$_2$(η^2-C_2H_3Me)][BF_4] (7)

Compound **3** (731 mg, 1.68 mmol) was dissolved in 10 mL of acetonitrile, the solution was cooled to 0 °C and treated with $HBF_4 \cdot Et_2O$ (250 μL, 1.85 mmol) dropwise. The solution was stirred at room temperature for 17 h, the solvent was vacuum evaporated, and the crude product was purified by dissolution in a small amount of dichloromethane (~0.5 mL), the solution was cooled to −40 °C and subsequently the product was precipitated by the addition of diethyl ether (10 mL), the solvents were decanted and the solid was dried *in vacuo*. This process was repeated up to three times. Yield: 537 mg (1.03 mmol, 61%). Yellow solid. Anal. calc. for $C_{14}H_{19}SO_2WBF_4$: C: 32.21; H: 3.67; S: 6.14. Found: C: 32.01; H: 3.43; S: 5.90. Positive-ion MS (acetone): *m*/*z* (%) = 393 (100) $[M - C_3H_6]^+$. ^{1}H NMR [500 MHz, CD_2Cl_2]: δ = 1.22 (t, $^3J(^1H,^1H)$ = 7.4 Hz, 3H, SCH_2CH_3); 2.09 (d, $^3J(^1H,^1H)$ = 5.2 Hz, 3H, CH_2CHCH_3); 2.64 (d, $^3J(^1H,^1H)$ = 10.0 Hz, 2H, CH_2CHCH_3); 2.75–2.80 (m, 1H, SCH_2CH_3); 2.82–2.89 (m, 1H, $C_5H_4CH_2CH_2S$); 2.92–3.00 (m, 1H, SCH_2CH_3); 3,12 (ddd, $^3J(^1H,^1H)$ = 14.6 Hz, $^4J(^1H,^1H)$ = 5.4 Hz, $^5J(^1H,^1H)$ = 2.2 Hz, 1H, $C_5H_4CH_2CH_2S$); 3.18–3.26 (m, 1H, CH_2CHCH_3); 3.77 (td, $^3J(^1H,^1H)$ = 13.7 Hz, $^4J(^1H,^1H)$ = 5.5 Hz, 1H, $C_5H_4CH_2CH_2S$); 3.89 (ddd, $^3J(^1H,^1H)$ = 10.9 Hz, $^4J(^1H,^1H)$ = 4.7 Hz, $^5J(^1H,^1H)$ = 2.8 Hz, 1H, $C_5H_4CH_2CH_2S$); 5.01 (m, 1H, C_5H_4); 5.08 (s, 1H, C_5H_4); 6.24 (m, 1H, C_5H_4); 6.37 (s, 1H, C_5H_4). ^{13}C NMR [126 MHz, CD_2Cl_2]: δ = 13.6 (SCH_2CH_3); 25.9 (CH_2CHCH_3); 26.5 ($C_5H_4CH_2CH_2S$); 34.8 (SCH_2CH_3); 45.0 (CH_2CHCH_3); 51.4 ($C_5H_4CH_2CH_2S$); 51.8 (CH_2CHCH_3); 76.1 (C_5H_4); 85.1 (C_5H_4); 88.0 (C_5H_4); 94.0 (C_5H_4); 139.8 (C_5H_4); 214.0 (CO); 214.7 (CO). IR (ATR, cm^{-1}): 2025 *vs.* [ν_a(CO)], 1946 *vs.* [ν_s(CO)], 1034 *vs.* [ν(BF)].

Synthesis of [{η^5:κ*S*-$C_5H_4(CH_2)_2SPh$}W(CO)$_2$(η^2-C_2H_3Me)][BF_4] (8)

The steps of synthesis followed the procedure for compound **7**, but with **4** (135 mg, 0.28 mmol) and $HBF_4 \cdot Et_2O$ (40 μL, 0.30 mmol). Yield: 102 mg (0.18 mmol, 64%). Yellow solid. Anal. calc. for $C_{18}H_{19}SO_2WBF_4$: C: 37.93; H: 3.36; S: 5.62. Found: C: 37.60; H: 3.14; S: 5.35. Positive-ion MS (acetone): *m*/*z* (%) = 441 (100) $[M - C_3H_6]^+$. ^{1}H NMR [500 MHz, CD_2Cl_2]: δ = 2.14 (d, $^3J(^1H,^1H)$ = 4.7 Hz, 3H, CH_2CHCH_3); 2.45–2.57 (m, 1H, $C_5H_4CH_2CH_2S$); 2.66 (dd, $^2J(^1H,^1H)$ = 11.8 Hz, $^3J(^1H,^1H)$ = 5.3 Hz, 1H, $C_5H_4CH_2CH_2S$); 2.99–3.11 (m, 2H, CH_2CHCH_3); 3.52 (s, 1H, CH_2CHCH_3); 3.97–4.04 (m, 1H, $C_5H_4CH_2CH_2S$); 4.12–4.19 (m, 1H, $C_5H_4CH_2CH_2S$); 5.07 (s, 1H, C_5H_4); 5.16 (s, 1H, C_5H_4); 6.45 (s, 1H, C_5H_4); 6.53 (s, 1H, C_5H_4); 7.51 (5H, C_6H_5). ^{13}C NMR [126 MHz, CD_2Cl_2]: δ = 25.9 (CH_2CHCH_3); 27.5 (CH_2CHCH_3); 45.5 (CH_2CHCH_3); 51.6 ($C_5H_4CH_2CH_2S$); 57.9 ($C_5H_4CH_2CH_2S$); 76.9 (C_5H_4); 84.4 (C_5H_4); 86.9 (C_5H_4); 95.1 (C_5H_4); 129.4 (C_6H_5); 130.7 (C_6H_5); 132.1 (C_6H_5); 139.0 (C_5H_4); 213.3 (CO); 214.3 (CO). IR (ATR, cm^{-1}): 2025 *vs.* [ν_a(CO)], 1915 *vs.* [ν_s(CO)], 1026 *vs.* [ν(BF)]. Single crystals of **8** suitable for X-ray diffraction analysis were prepared by overlayering of the acetonitrile solution of **8** with diethyl ether.

Synthesis of [{η^5:κ*S*-$C_5H_4(CH_2)_2SEt$}Mo(CO)$_2$(SMe_2)][BF_4] (9)

Compound **1** (119 mg, 0.34 mmol) was dissolved in 10 mL of dichloromethane, the solution was treated with Me_2S (50 μL, 0.68 mmol) cooled to 0 °C and treated with $HBF_4 \cdot Et_2O$ (46 μL, 0.34 mmol) dropwise. The color of the solution changed from orange to red immediately upon the addition of acid. The reaction mixture was stirred at room temperature for 16 h, the solvent was vacuum evaporated, and the crude product was purified by dissolution in a small amount of dichloromethane (~0.5 mL), the solution was cooled to −40 °C and subsequently the product was precipitated by the addition of diethyl ether (10 mL), the solvents were decanted and the solid was dried *in vacuo*. This process was repeated up to three times. Yield: 122 mg (0.27 mmol, 79%). Red solid. Anal. calc. for $C_{13}H_{19}S_2O_2MoBF_4$: C: 34.38; H: 4.22; S: 14.12. Found: C: 34.20; H: 4.07; S: 13.88. Positive-ion MS (acetone): *m*/*z* (%) = 369 (100) $[M]^+$. ^{1}H NMR [500 MHz, CD_2Cl_2, mixture 5 : 1 of isomers *cis* : *trans*]: δ = 1.38 (t, $^3J(^1H,^1H)$ = 7.3 Hz, 3H, SCH_2CH_3); 2.52 (s, 6H, $(CH_3)_2S$); 2.65–2.75 (m, 1H, $C_5H_4CH_2CH_2S$); 2.89–2.99 (m, 3H, 1H of $C_5H_4CH_2CH_2S$; 2H of SCH_2CH_3); 3.71–3.78 (m, 1H, $C_5H_4CH_2CH_2S$); 3.81–3.88 (m, 1H, $C_5H_4CH_2CH_2S$); 4.88–4.90 (m, 1H, C_5H_4 of *cis*); 5,03 (m, 1H, C_5H_4 of *trans*); 5.16–5.19 (m, 1H, C_5H_4 of *trans*); 5.35–5.36 (m, 1H, C_5H_4 of *trans*); 5.56 (s, 1H, C_5H_4 of *cis*); 5.64 (s,1H, C_5H_4 of *cis*); 6.19–6.10 (m, 1H, C_5H_4 of *trans*); 6.29 (s, 1H, C_5H_4 of *cis*). ^{13}C NMR [126 MHz, CD_2Cl_2]: δ = 13.7 (SCH_2CH_3 of *cis*); 13.9 (SCH_2CH_3 of *trans*); 25.9 (SCH_2CH_3); 28.2 ($(CH_3)_2S$ of *cis*); 28.5 ($(CH_3)_2S$ of *trans*); 34.1 ($C_5H_4CH_2CH_2S$ of *cis*); 36.3 ($C_5H_4CH_2CH_2S$ of *trans*); 54.0 ($C_5H_4CH_2CH_2S$ of *cis*); 66.2 ($C_5H_4CH_2CH_2S$ of *trans*); 82.8 (C_5H_4 of *cis*); 87.5 (C_5H_4 of *cis*); 89.2 (C_5H_4 of *cis*); 89.8 (C_5H_4 of *trans*); 92.7 (C_5H_4 of *trans*); 93.9 (C_5H_4 of *trans*); 95.4 (C_5H_4 of *trans*); 100.4 (C_5H_4 of *cis*); 130.9 (C_5H_4 of *trans*); 142.3 (C_5H_4 of *cis*); 230.6 (CO of *trans*); 235.8 (CO of *trans*); 241.8 (CO of *cis*); 244.2 (CO of *cis*). IR (ATR, cm^{-1}): 1975 *vs.* [ν_a(CO)], 1883 *vs.* [ν_s(CO)], 1019 *vs.* [ν(BF)]. Single crystals of **9**-*cis* suitable for X-ray diffraction analysis were prepared by the overlayering of dichloromethane solution of **9** with diethyl ether.

Synthesis of [{η^5:κ*S*-$C_5H_4(CH_2)_2SEt$}Mo(CO)$_2${$S(CH_2)_4$}][BF_4] (10)

The steps of synthesis followed the procedure for compound **9**, but with **1** (176 mg, 0.51 mmol), tetrahydrothiophene (67 μL,

0.76 mmol) and $HBF_4 \cdot Et_2O$ (70 μL, 0.52 mmol). Yield: 186 mg (0.39 mmol, 76%). Red solid. Anal. calc. for $C_{15}H_{21}S_2O_2MoBF_4$: C: 37.52; H: 4.41; S: 13.35. Found: C: 37.27; H: 4.19; S: 13.09. ^{1}H NMR [500 MHz, CD_2Cl_2, mixture 13 : 1 of isomers *cis* : *trans*]: δ = 1.37 (t, $^3J(^1H,^1H)$ = 7.3 Hz, 3H, SCH_2CH_3); 2.10–2.19 (m, 4H, $H^{3,3,4,4}$, C_4H_8S); 2.70–2.78 (m, 1H, $C_5H_4CH_2CH_2S$); 2.87–3.02 (m, 3H, 1H of $C_5H_4CH_2CH_2S$, 2H of SCH_2CH_3); 3.03–3.20 (m, 4H, $H^{2,2,5,5}$, C_4H_8S); 3.70–3.85 (m, 2H, $C_5H_4CH_2CH_2S$); 4.87–4.89 (m, 1H, C_5H_4 of *cis*); 5.06 (m, 1H, C_5H_4 of *trans*); 5.11 (m, 1H, C_5H_4 of *trans*); 5.54 (s, 1H, C_5H_4 of *cis*); 5.72 (s, 1H, C_5H_4 of *cis*); 6.09 (m, 1H, C_5H_4 of *trans*); 6.12 (m, 1H, C_5H_4 of *trans*); 6.23 (s, 1H, C_5H_4 of *cis*). ^{13}C NMR [126 MHz, CD_2Cl_2]: δ = 13.8 (SCH_2CH_3 of *cis*); 15.5 (SCH_2CH_3 of *trans*); 25.3 (SCH_2CH_3 of *trans*); 25.8 (SCH_2CH_3 of *cis*); 31.0 ($C^{3,4}$, C_4H_8S of *trans*); 31.2 ($C^{3,4}$, C_4H_8S of *cis*); 34.0 ($C_5H_4CH_2CH_2S$); 44.4 ($C^{2,5}$, C_4H_8S of *trans*); 45.0 ($C^{2,5}$, C_4H_8S of *cis*); 54.0 ($C_5H_4CH_2CH_2S$); 83.2 (C_5H_4 of *cis*); 87.4 (C_5H_4 of *cis*); 89.0 (C_5H_4 of *cis*); 89.9 (C_5H_4 of *trans*); 92.6 (C_5H_4 of *trans*); 93.9 (C_5H_4 of *trans*); 95.0 (C_5H_4 of *trans*); 100.6 (C_5H_4 of *cis*); 131.1 (C_5H_4 of *trans*); 142.1 (C_5H_4 of *cis*); 231.4 (CO of *trans*); 235.3 (CO of *trans*); 242.7 (CO of *cis*); 245.1 (CO of *cis*). IR (ATR, cm^{-1}): 1974 *vs.* [ν_a(CO)], 1882 *vs.* [ν_s(CO)], 1048 *vs.* [ν(BF)].

Synthesis of [{η^5:κ*S*-$C_5H_4(CH_2)_2SEt$}Mo(CO)$_2${κ*S*-S$(CH_2)_4$O}][BF_4] (11)

The steps of synthesis followed the procedure for compound **9**, but with **1** (139 mg, 0.40 mmol), 1,4-oxathiane (56 μL, 0.60 mmol) and $HBF_4 \cdot Et_2O$ (55 μL, 0.40 mmol). Yield: 147 mg (0.30 mmol, 74%). Red solid. Anal. calc. for $C_{15}H_{21}S_2O_3MoBF_4$: C: 36.31; H: 4.27; S: 12.92. Found: C: 36.10; H: 4.09; S: 12.69. Positive-ion MS (acetone): *m*/*z* (%) = 411 (100) $[M]^+$. ^{1}H NMR [500 MHz, CD_2Cl_2]: δ = 1.38 (t, $^3J(^1H,^1H)$ = 7.4 Hz, 3H, SCH_2CH_3); 2.66–2.73 (m, 1H, $C_5H_4CH_2CH_2S$); 2.75–2.81 (m, 2H, CH_2, SCH_2CH_3); 2.90–3.00 (m, 4H of OC_4H_8S, 1H of $C_5H_4CH_2CH_2S$); 3.70–3.76 (m, 1H, $C_5H_4CH_2CH_2S$); 3.84–3.92 (m, 1H, $C_5H_4CH_2CH_2S$); 3.96–4.04 (m, 4H, OC_4H_8S); 4.86–4.87 (m, 1H, C_5H_4); 5.58 (s, 1H, C_5H_4); 5.69 (s, 1H, C_5H_4); 6.38 (s, 1H, C_5H_4). ^{13}C NMR [126 MHz, CD_2Cl_2]: δ = 13.7 (SCH_2CH_3); 26.0 ($C_5H_4CH_2CH_2S$); 34.1 (OC_4H_8S); 38.4 (SCH_2CH_3); 54.0 ($C_5H_4CH_2CH_2S$); 68.9 (OC_4H_8S); 82.6 (C_5H_4); 87.2 (C_5H_4); 89.2 (C_5H_4); 100.0 (C_5H_4); 142.5 (C_5H_4); 241.5 (CO); 243.5 (CO). IR (ATR, cm^{-1}): 1986 *vs.* [ν_a(CO)], 1885 *vs.* [ν_s(CO)], 1026 *vs.* [ν(BF)]. Single crystals of **11**-*cis* suitable for X-ray diffraction analysis were prepared by overlayering of the dichloromethane solution of **11** with diethyl ether.

Synthesis of [{η^5:κ*S*-$C_5H_5(CH_2)_2SPh$}Mo(CO)$_2$(SMe_2)][BF_4] (12)

The steps of synthesis followed the procedure for compound **9**, but with **2** (98 mg, 0.25 mmol), Me_2S (37 μL, 0.50 mmol) and $HBF_4 \cdot Et_2O$ (33 μL, 0.25 mmol). Yield: 98 mg (0.20 mmol, 78%). Red solid. Anal. calc. for $C_{17}H_{19}S_2O_2MoBF_4$: C: 40.66; H: 3.81; S: 12.77. Found: C: 40.38; H: 3.57; S: 12.52. Positive-ion MS (acetone): *m*/*z* (%) = 355 (100) $[M - SC_2H_6]^+$. ^{1}H NMR [400 MHz, CD_2Cl_2]: δ = 2.53 (s, 6H, $(CH_3)_2S$); 2.72–2.81 (m, 1H, $C_5H_4CH_2CH_2S$); 2.93–3.01 (m, 1H, $C_5H_4CH_2CH_2S$); 3.87–3.95 (m, 1H, $C_5H_4CH_2CH_2S$); 4.19–4.28 (m, 1H, $C_5H_4CH_2CH_2S$); 4.96 (s, 1H, C_5H_4); 5.56 (s, 1H, C_5H_4); 5.85 (s,1H, C_5H_4); 6.39 (s, 1H, C_5H_4); 7.50–7.58 (m, 5H, C_6H_5). ^{13}C NMR [126 MHz, CD_2Cl_2]: δ = 27.0 ($C_5H_4CH_2CH_2S$); 28.3 ($(CH_3)_2S$); 61.3 ($C_5H_4CH_2CH_2S$); 82.8 (C_5H_4); 87.2 (C_5H_4); 89.5 (C_5H_4); 100.8 (C_5H_4); 130.6 (C_6H_5); 131.6 (C_6H_5); 131.8 (C_6H_5); 142.1 (C_5H_4); 240.2 (CO); 243.9 (CO). IR (ATR, cm^{-1}): 1978 *vs.* [ν_a(CO)], 1890 *vs.* [ν_s(CO)], 1022 *vs.* [ν(BF)]. Single crystals of **12**-*cis* suitable for X-ray diffraction analysis were prepared by the overlayering of dichloromethane solution of **12** with hexane.

Synthesis of [{η^5:κS-$C_5H_4(CH_2)_2SPh$}Mo(CO)$_2${S$(CH_2)_4$}][BF_4] (13)

The steps of synthesis followed the procedure for compound **9**, but with **2** (68 mg, 0.17 mmol), tetrahydrothiophene (22 μL, 0.25 mmol) and $HBF_4 \cdot Et_2O$ (23 μL, 0.17 mmol). Yield: 80 mg (0.15 mmol, 89%). Red solid. Anal. calc. for $C_{19}H_{21}S_2O_2MoBF_4$: C: 43.20; H: 4.01; S: 12.14. Found: C: 42.98; H: 3.83; S: 11.96. Positive-ion MS (acetone): *m*/*z* (%) = 443 (100) $[M]^+$. ^{1}H NMR [500 MHz, CD_2Cl_2, mixture 5 : 2 of isomers *cis* : *trans*]: δ = 2.07–2.21 (m, 4H, $H^{3,3,4,4}$, C_4H_8S); 2.37–2.48 (m, 1H, $C_5H_4CH_2CH_2S$ of *trans*); 2.62–2.71 (m, 1H, $C_5H_4CH_2CH_2S$ of *trans*); 2.74–2.85 (m,1H, $C_5H_4CH_2CH_2S$ of *cis*); 2.90–3.00 (m, 1H, $C_5H_4CH_2CH_2S$ of *cis*); 3.17 (t, $^3J(^1H,^1H)$ = 5.8 Hz, 4H, $H^{2,2,5,5}$, C_4H_8S); 3.52–3.61 (m, 1H, $C_5H_4CH_2CH_2S$ of *trans*); 3.73–3.80 (m, 1H, $C_5H_4CH_2CH_2S$ of *trans*); 3.94 (dt, $^2J(^1H,^1H)$ = 12.7 Hz, $^3J(^1H,^1H)$ = 5.3 Hz, 1H, $C_5H_4CH_2CH_2S$ of *cis*); 4.15–4.22 (m, 1H, $C_5H_4CH_2CH_2S$ of *cis*); 4.97 (d, $^3J(^1H,^1H)$ = 1.4 Hz, 1H, C_5H_4 of *cis*); 5.15 (s, 1H, C_5H_4 of *trans*); 5.24 (s, 1H, C_5H_4 of *trans*); 5.54 (s, 1H, C_5H_4 of *cis*); 5.87 (s, 1H, C_5H_4 of *cis*); 6.17 (s, 1H, C_5H_4 of *trans*); 6.35 (s, 1H, C_5H_4 of *cis*); 6.42 (s, 1H, C_5H_4 of *trans*); 7.49–7.54 (m, 5H, C_6H_5 of *cis*); 7.55–7.57 (m, 3H, C_6H_5 of *trans*); 7.63–7.66 (m, 2H, C_6H_5 of *trans*). ^{13}C NMR [126 MHz, CD_2Cl_2]: δ = 26.7 ($C_5H_4CH_2CH_2S$); 31.0 (SC_4H_8); 31.2 (SC_4H_8); 44.4 (SC_4H_8); 45.0 (SC_4H_8); 61.5 ($C_5H_4CH_2CH_2S$); 83.3 (C_5H_4 of *cis*); 87.2 (C_5H_4 of *cis*); 89.1 (C_5H_4 of *cis*); 90.4 (C_5H_4 of *trans*); 92.7 (C_5H_4 of *trans*); 94.6 (C_5H_4 of *trans*); 95.2 (C_5H_4 of *trans*); 101.1 (C_5H_4 of *cis*); 130.5 (C_6H_5); 130.6 (C_6H_5); 131.9 (C_6H_5); 141.5 (C_5H_4); 231.3 (CO of *trans*); 232.3 (CO of *trans*); 241.3 (CO of *cis*); 244.8 (CO of *cis*). IR (ATR, cm^{-1}): 1978 *vs.* [ν_a(CO)], 1890 *vs.* [ν_s(CO)], 1022 *vs.* [ν(BF)].

Synthesis of [{η^5:κ*S*-$C_5H_4(CH_2)_2SPh$}Mo(CO)$_2${κ*S*-S$(CH_2)_4$O}][BF_4] (14)

The steps of synthesis followed the procedure for compound **9**, but with **2** (198 mg, 0.50 mmol), 1,4-oxathiane (70 μL, 0.75 mmol) and $HBF_4 \cdot Et_2O$ (67 μL, 0.50 mmol). Yield: 221 mg (0.41 mmol, 81%). Red solid. Anal. calc. for $C_{19}H_{21}S_2O_3MoBF_4$: C: 41.93; H: 3.89; S: 11.78. Found: C: 41.67; H: 3.66; S: 11.57. Positive-ion MS (acetone): *m*/*z* (%) = 355 (100) $[M - OC_4H_8S]^+$. ^{1}H NMR [500 MHz, CD_2Cl_2]: δ = 2.63–2.83 (m, 2H, $C_5H_4CH_2CH_2S$); 2.93–3.06 (m, 4H, OC_4H_8S); 3.86–3.96 (1H, $C_5H_4CH_2CH_2S$); 3.99 (s, 4H, OC_4H_8S); 4.22–4.30 (m, 1H, $C_5H_4CH_2CH_2S$); 4.94 (s, 1H, C_5H_4); 5.58 (s, 1H, C_5H_4); 5.86 (s, 1H, C_5H_4); 6.47 (s, 1H, C_5H_4); 7.49–7.58 (m, 5H, C_6H_5). ^{13}C NMR [126 MHz, CD_2Cl_2]: δ = 27.0 ($C_5H_4CH_2CH_2S$); 38.6 (OC_4H_8S); 54.4 ($C_5H_4CH_2CH_2S$); 69.0 (OC_4H_8S); 82.8 (C_5H_4); 87.0 (C_5H_4); 89.4 (C_5H_4); 100.6 (C_5H_4); 130.6 (C_6H_5); 131.5 (C_6H_5); 131.6 (C_6H_5); 142.0 (C_5H_4); 240.1 (CO); 243.4 (CO). IR (ATR, cm^{-1}): 1984 *vs.* [ν_a(CO)], 1901 *vs.* [ν_s(CO)], 1030 *vs.* [ν(BF)].

Synthesis of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(SMe_2)_2][BF_4]$ (15)

The steps of synthesis followed the procedure for compound **9**, but with $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ (120 mg, 0.47 mmol), Me_2S (104 μL, 1.41 mmol) and $HBF_4\cdot Et_2O$ (63 μL, 0.47 mmol). Yield: 157 mg (0.37 mmol, 78%). Red solid. Anal. calc. for $C_{11}H_{17}S_2O_2MoBF_4$: C: 30.86; H: 4.00; S: 14.98. Found: C: 30.62; H: 3.77; S: 14.74. Positive-ion MS (acetone): *m*/*z* (%) = 335 (100) $[M - 2\ SC_2H_6 + 2\ C_3H_6O]^+$. ^{1}H NMR [500 MHz, CD_2Cl_2]: δ = 2.52 (s, 12H, $(CH_3)_2S$); 5.76 (s, 5H, C_5H_5). ^{13}C NMR [126 MHz, CD_2Cl_2]: δ = 26.9 ($(CH_3)_2S$); 95.7 (C_5H_5); 244.9 (CO). IR (ATR, cm^{-1}): 1982 *vs.* [ν_a(CO)], 1888 *vs.* [ν_s(CO)], 1029 *vs.* [ν(BF)]. Single crystals of **15**-*trans* suitable for X-ray diffraction analysis were prepared by overlayering of the dichloromethane solution of **15** with diethyl ether.

Synthesis of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{(CH_2)_4S\}_2][BF_4]$ (16)

The steps of synthesis followed the procedure for compound **9**, but with $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ (109 mg, 0.42 mmol), tetrahydrothiophene (93 μL, 1.05 mmol) and $HBF_4\cdot Et_2O$ (57 μL, 0.42 mmol)). Yield: 169 mg (0.35 mmol, 84%). Red solid. Anal. calc. for $C_{15}H_{21}S_2O_2MoBF_4$: C: 37.52; H: 4.41; S: 13.35. Found: C: 37.25; H: 4.14; S: 13.11. Positive-ion MS (acetone): *m*/*z* (%) = 307 (100) $[M - SC_4H_8]^+$. ^{1}H NMR [500 MHz, CD_2Cl_2]: δ = 2.15–2.18 (m, 4H, $H^{3,3,4,4}$, C_4H_8S); 3.08–3.20 (m, 4H, $H^{2,2,5,5}$, C_4H_8S); 5.72 (s, 5H, C_5H_5). ^{13}C NMR [126 MHz, CD_2Cl_2]: δ = 31.2 ($C^{3,4}$, C4H8S); 44.2 ($C^{2,5}$, C_4H_8S); 95.8 (C_5H_5); 246.1 (CO). IR (ATR, cm^{-1}): 1960 *vs.* [ν_a(CO)], 1898 *vs.* [ν_s(CO)], 1027 *vs.* [ν(BF)]. Single crystals of **16**-*cis* suitable for X-ray diffraction analysis were prepared by overlayering of the dichloromethane solution of **16** with diethyl ether.

Synthesis of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2\{\kappa S\text{-}S(CH_2)_4O\}_2][BF_4]$ (17)

The steps of synthesis followed the procedure for compound **9**, but with $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ (180 mg, 0.70 mmol), 1,4-oxathiane (164 μL, 1.75 mmol) and $HBF_4\cdot Et_2O$ (95 μL, 0.70 mmol). Yield: 295 mg (0.58 mmol, 82%). Red solid. Anal. calc. for $C_{15}H_{21}S_2O_4MoBF_4$: C: 35.17; H: 4.13; S: 12.52. Found: C: 34.93; H: 3.89; S: 12.30. Positive-ion MS (acetone): *m*/*z* (%) = 295 (100) $[M - OC_4H_8S - CO]^+$. ^{1}H NMR [500 MHz, CD_2Cl_2]: δ = 2.79–2.83 (m, 4H, OC_4H_8S); 3.00–3.04 (m, 4H, OC_4H_8S); 4.01–4.04 (m, 8H, OC_4H_8S); 5.79 (s, 5H, C_5H_5). ^{13}C NMR [126 MHz, CD_2Cl_2]: δ = 37.6 (OC_4H_8S); 69.0 (OC_4H_8S); 95.7 (C_5H_5); 243.9 (CO). IR (ATR, cm^{-1}): 1981 *vs.* [ν_a(CO)], 1903 *vs.* [ν_s(CO)], 1049 *vs.* [ν(BF)].

Synthesis of $[\{\eta^5\text{:}\kappa S\text{-}C_5H_4(CH_2)_2SEt\}Mo(CO)_2(NCMe)][BF_4]$ (18)

The steps of synthesis followed the procedure for compound **7**, but with **1** (391 mg, 1.13 mmol) and $HBF_4\cdot Et_2O$ (152 μL, 1.13 mmol). Yield: 454 mg (1.05 mmol, 93%). Red solid. Anal. calc. for $C_{13}H_{16}SO_2NMoBF_4$: C: 36.05; H: 3.72; N: 3.23; S: 7.40. Found: C: 35.88; H: 3.47; N: 2.98; S: 7.17. Positive-ion MS (acetone): *m*/*z* (%) = 365 (100) $[M - MeCN + C_3H_6O]^+$. ^{1}H NMR [500 MHz, CD_2Cl_2]: δ = 1.39 (t, $^3J(^1H,^1H)$ = 7.2 Hz, 3H, SCH_2CH_3); 2.54 (s, 3H, CH_3CN); 2.59–2.66 (m, 1H, $C_5H_4CH_2CH_2S$); 2.81–2.95 (m, 2H, SCH_2CH_3); 2.93–2.99 (m, 1H, $C_5H_4CH_2CH_2S$); 3.65–3.71 (m, 1H, $C_5H_4CH_2CH_2S$); 4.04–4.12 (m, 1H, $C_5H_4CH_2CH_2S$); 4.82 (s, 1H, C_5H_4); 5.44 (s, 1H, C_5H_4); 5.76 (s, 1H, C_5H_4); 6.52 (s, 1H, C_5H_4). ^{13}C NMR [126 MHz, CD_2Cl_2]: δ = 5.5 (CH_3, CH_3CN); 13.7 (SCH_2CH_3); 25.9 ($C_5H_4CH_2CH_2S$); 33.4 (SCH_2CH3); 53.9 (C_5H_4-CH_2CH_2S); 83.6 (C_5H_4); 87.8 (C_5H_4); 88.0 (C_5H_4); 104.9 (C_5H_4); 142.2 (C_5H_4); 144.7 (CN, CH_3CN); 244.2 (CO); 247.8 (CO). IR (ATR, cm^{-1}): 1994 *vs.* [ν_a(CO)], 1886 *vs.* [ν_s(CO)], 1054 *vs.* [ν(BF)]. Single crystals of **18** suitable for X-ray diffraction analysis were prepared by overlayering of the dichloromethane solution of **18** with hexane.

Synthesis of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(MeCN)_2](CF_3SO_3)$ (19)

The steps of synthesis followed the procedure for compound **7**, but with $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ (109 mg, 0.42 mmol) and CF_3SO_3H (37 μL, 0.42 mmol). Yield: 150 mg (0.33 mmol, 80%). Red solid. Anal. calc. for $C_{12}H_{11}N_2SO_5MoF_3$: C: 32.16; H: 2.47; N: 6.25; S: 7.15. Found: C: 31.93; H: 2.22; N: 6.02; S: 6.87. ^{1}H NMR [400 MHz, CD_2Cl_2, 6 : 5 mixture of complexes $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(MeCN)_2](CF_3SO_3)$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(MeCN)(CF_3SO_3)]$ (**a** : **b**)]: δ = 1.97 (s, 3H, free CH_3CN); 2.50 (s, 3H, CH_3CN of **b**); 2.55 (s, 6H, CH_3CN of **a**); 5.74 (s, 5H, C_5H_5 of **b**); 5.75 (s, 5H, C_5H_5 of **a**). IR (ATR, cm^{-1}): 1990 *vs.* [ν_a(CO)], 1882 *vs.* [ν_s(CO)], 1261 *vs.* [$\nu_a(SO_3)$], 1224 m [$\nu_s(CF_3)$], 1151 s [ν_a(CO)], 1032 s [$\nu_s(SO_3)$]. Single crystals of **19** suitable for X-ray diffraction analysis were prepared by overlayering of the acetonitrile solution of **19** with diethyl ether.

Author contributions

The authors contributed equally.

Conflicts of interest

There are no conflicts to declare.

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