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Introduction

The ability of transition metals to form coordination compounds with alkenes was discovered almost two hundred years ago when W. C. Zeise¹ synthesized the first compound bearing π -bonded ethylene, K[PtCl₃(η^2 -C₂H₄)]·H₂O, 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

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 $[\{\eta^{5}:\kappa S-C_{5}H_{4}(CH_{2})_{2}SR\}M(CO)_{2}(\eta^{2}-C_{2}H_{3}Me)][BF_{4}]$ (M = Mo, W; R = Et, Ph). They are formed by protonation of allyl analogues $[\{\eta^{5}-C_{5}H_{4}(CH_{2})_{2}SR\}M(CO)_{2}(\eta^{3}-C_{3}H_{5})]$ 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 $[\{\eta^{5}:\kappa S-C_{5}H_{4}(CH_{2})_{2}SR\}W(CO)_{2}(\eta^{2}-C_{2}H_{3}Me)][BF_{4}]$ (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.

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 complexes¹¹ and by ruthenium compounds.^{10,12} The potential of iron catalysts is currently under comprehensive investigation.^{13–15} Gold(1)-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* = C₅Me₅; 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 $[(\eta^5-Ind')M(CO)_2(\eta^3-allyl)]$ (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 $[(\eta^3-C_3H_5)(MeCN)_2M(CO)_2Cl]$ (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 ¹H NMR and IR spectroscopy.

¹H spectra of the complexes **1–4** contained two sets of signals for the allyl ligand, expected for complexes of the $[(\eta^5-Cp')$ $M(CO)_2(\eta^3-C_3H_5)]$,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 HBF₄·Et₂O in dichloromethane at -40 °C afforded the complexes bearing η^2 -coordinated propene ligand [{ η^5 : κ S-C₅H₄(CH₂)₂SR}M(CO)₂(η^2 -CH₂CHCH₃)][BF₄] (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 ¹H NMR spectroscopy only owing to their thermal instability.

The ¹H NMR spectra of complexes **5** and **6**, measured at room temperature, contained two sets of signals attributed to two isomeric species of $[\{\eta^5:\kappa S-C_5H_4(CH_2)_2SR\}Mo(CO)_2(\eta^2-C_2H_3Me)][BF_4]$ 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 ($\delta = 1.8-2.3$ 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



Scheme 2 Synthesis of the precursors 1–4 and their protonation in a non-coordinating solvent: (I) $[(\eta^3-C_3H_5)(MeCN)_2M(CO)_2Cl]$ (M = Mo, W); (II) HBF₄·Et₂O, CH₂Cl₂, -40 °C.

able 1	Wavenumbers	(in ci	m ⁻¹) of	characteristic	infrared	bands
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Compound	$\nu_{\rm a}({\rm CO})$	$\nu_{s}(CO)$	$\nu(BF)$
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, ${}^{3}J({}^{1}\text{H}, {}^{1}\text{H}) = 6.5$ Hz, ${}^{4}J({}^{1}\text{H}, {}^{1}\text{H}) = 1.5$ 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, ¹H NMR, ¹³C NMR and IR spectroscopy. In both cases, only one set of signals was observed in ¹H NMR spectra attributed to single isomer (presumably isomer **a**). The coordinated



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.

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 \sim 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

Table 2	Selected bond	lenaths (Å)	and angles	(°) of mol	vbdenum and	tunasten o	complexes
				· / ······	,		

8a	9 -cis ^a	9 -cis ^a	9 -cis ^a	11 -cis	12 -cis	15-trans	16 -cis	18	19a
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)
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)
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)
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)
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)
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)
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)
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)
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)
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)
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)
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)
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)
	8a 1.9877(15) 2.027(3) 1.983(3) 2.5362(8) 2.210(2) 105.53(11) 123.04(10) 104.41(5) 133.96(8) 149.8(1) 102.9(1) 79.1(1) 77.53(7)	8a $9 \cdot cis^a$ $1.9877(15)$ $1.974(4)$ $2.027(3)$ $1.99(1)$ $1.983(3)$ $1.94(1)$ $2.5362(8)$ $2.509(2)$ $2.210(2)$ $2.546(3)$ $105.53(11)$ $117.9(3)$ $123.04(10)$ $122.4(4)$ $104.41(5)$ $107.75(16)$ $133.96(8)$ $118.14(17)$ $149.8(1)$ $134.4(3)$ $102.9(1)$ $119.4(3)$ $79.1(1)$ $74.3(5)$ $77.53(7)$ $76.38(9)$	8a9-cis ^a 9-cis ^a $1.9877(15)$ $1.974(4)$ $1.984(4)$ $2.027(3)$ $1.99(1)$ $2.00(1)$ $1.983(3)$ $1.94(1)$ $1.95(1)$ $2.5362(8)$ $2.509(2)$ $2.519(2)$ $2.210(2)$ $2.546(3)$ $2.530(2)$ $105.53(11)$ $117.9(3)$ $110.9(3)$ $123.04(10)$ $122.4(4)$ $123.7(3)$ $104.41(5)$ $107.75(16)$ $106.60(14)$ $133.96(8)$ $118.14(17)$ $124.13(14)$ $149.8(1)$ $134.4(3)$ $142.0(3)$ $102.9(1)$ $119.4(3)$ $112.2(3)$ $79.1(1)$ $74.3(5)$ $78.5(4)$ $77.53(7)$ $76.38(9)$ $75.53(8)$	8a9-cis ^a 9-cis ^a 9-cis ^a $1.9877(15)$ $1.974(4)$ $1.984(4)$ $1.984(5)$ $2.027(3)$ $1.99(1)$ $2.00(1)$ $2.01(1)$ $1.983(3)$ $1.94(1)$ $1.95(1)$ $2.01(1)$ $2.5362(8)$ $2.509(2)$ $2.519(2)$ $2.516(2)$ $2.210(2)$ $2.546(3)$ $2.530(2)$ $2.489(3)$ $105.53(11)$ $117.9(3)$ $110.9(3)$ $113.5(4)$ $123.04(10)$ $122.4(4)$ $123.7(3)$ $126.6(3)$ $104.41(5)$ $107.75(16)$ $106.60(14)$ $106.07(16)$ $133.96(8)$ $118.14(17)$ $124.13(14)$ $123.37(16)$ $149.8(1)$ $134.4(3)$ $142.0(3)$ $140.3(3)$ $102.9(1)$ $119.4(3)$ $112.2(3)$ $109.8(3)$ $79.1(1)$ $74.3(5)$ $78.5(4)$ $77.7(4)$ $77.53(7)$ $76.38(9)$ $75.53(8)$ $75.09(9)$	8a9- cis^a 9- cis^a 9- cis^a 11- cis $1.9877(15)$ $1.974(4)$ $1.984(4)$ $1.984(5)$ $1.9797(15)$ $2.027(3)$ $1.99(1)$ $2.00(1)$ $2.01(1)$ $2.006(4)$ $1.983(3)$ $1.94(1)$ $1.95(1)$ $1.96(1)$ $1.964(3)$ $2.5362(8)$ $2.509(2)$ $2.519(2)$ $2.516(2)$ $2.516(1)$ $2.210(2)$ $2.546(3)$ $2.530(2)$ $2.489(3)$ $2.5147(9)$ $105.53(11)$ $117.9(3)$ $110.9(3)$ $113.5(4)$ $117.67(11)$ $123.04(10)$ $122.4(4)$ $123.7(3)$ $126.6(3)$ $122.82(11)$ $104.41(5)$ $107.75(16)$ $106.60(14)$ $106.07(16)$ $107.42(5)$ $133.96(8)$ $118.14(17)$ $124.13(14)$ $123.37(16)$ $118.92(5)$ $149.8(1)$ $134.4(3)$ $142.0(3)$ $140.3(3)$ $134.7(1)$ $102.9(1)$ $119.4(3)$ $112.2(3)$ $109.8(3)$ $118.1(1)$ $79.1(1)$ $74.3(5)$ $78.5(4)$ $77.7(4)$ $75.4(1)$ $77.53(7)$ $76.38(9)$ $75.53(8)$ $75.09(9)$ $74.61(3)$	8a9-cis ^a 9-cis ^a 9-cis ^a 11-cis12-cis $1.9877(15)$ $1.974(4)$ $1.984(4)$ $1.984(5)$ $1.9797(15)$ $1.9820(9)$ $2.027(3)$ $1.99(1)$ $2.00(1)$ $2.01(1)$ $2.006(4)$ $2.000(2)$ $1.983(3)$ $1.94(1)$ $1.95(1)$ $1.96(1)$ $1.964(3)$ $1.963(2)$ $2.5362(8)$ $2.509(2)$ $2.519(2)$ $2.516(2)$ $2.5147(9)$ $2.532(5)$ $2.210(2)$ $2.546(3)$ $2.530(2)$ $2.489(3)$ $2.5147(9)$ $2.5314(5)$ $105.53(11)$ $117.9(3)$ $110.9(3)$ $113.5(4)$ $117.67(11)$ $113.30(6)$ $123.04(10)$ $122.4(4)$ $123.7(3)$ $126.6(3)$ $122.82(11)$ $125.97(6)$ $104.41(5)$ $107.75(16)$ $106.60(14)$ $106.07(16)$ $107.42(5)$ $107.93(3)$ $133.96(8)$ $118.14(17)$ $124.13(14)$ $123.37(16)$ $118.92(5)$ $120.98(3)$ $149.8(1)$ $134.4(3)$ $142.0(3)$ $140.3(3)$ $134.7(1)$ $138.43(6)$ $102.9(1)$ $119.4(3)$ $112.2(3)$ $109.8(3)$ $118.1(1)$ $113.03(6)$ $79.1(1)$ $74.3(5)$ $78.5(4)$ $77.7(4)$ $75.4(1)$ $76.74(8)$ $77.53(7)$ $76.38(9)$ $75.53(8)$ $75.09(9)$ $74.61(3)$ $75.17(2)$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	8a9-cis ^a 9-cis ^a 9-cis ^a 11-cis12-cis15-trans16-cis $1.9877(15)$ $1.974(4)$ $1.984(4)$ $1.984(5)$ $1.9797(15)$ $1.9820(9)$ $2.0023(18)$ $1.9880(11)$ $2.027(3)$ $1.99(1)$ $2.00(1)$ $2.01(1)$ $2.006(4)$ $2.000(2)$ $2.017(4)$ $1.975(2)$ $1.983(3)$ $1.94(1)$ $1.95(1)$ $1.96(1)$ $1.964(3)$ $1.963(2)$ $1.959(4)$ $1.965(2)$ $2.5362(8)$ $2.509(2)$ $2.519(2)$ $2.516(2)$ $2.516(1)$ $2.5232(5)$ $2.505(1)$ $2.5416(5)$ $2.210(2)$ $2.546(3)$ $2.530(2)$ $2.489(3)$ $2.5147(9)$ $2.5314(5)$ $2.490(1)$ $2.5395(6)$ $105.53(11)$ $117.9(3)$ $110.9(3)$ $113.5(4)$ $117.67(11)$ $113.30(6)$ $134.23(13)$ $114.69(8)$ $123.04(10)$ $122.4(4)$ $123.7(3)$ $126.6(3)$ $122.82(11)$ $125.97(6)$ $123.48(11)$ $115.15(7)$ $104.41(5)$ $107.75(16)$ $106.60(14)$ $106.07(16)$ $107.42(5)$ $107.93(3)$ $105.68(7)$ $120.36(4)$ $133.96(8)$ $118.14(17)$ $124.13(14)$ $123.37(16)$ $118.92(5)$ $120.98(3)$ $106.40(7)$ $121.60(4)$ $149.8(1)$ $134.4(3)$ $142.0(3)$ $140.3(3)$ $134.7(1)$ $138.43(6)$ $147.85(3)$ $124.84(7)$ $102.9(1)$ $119.4(3)$ $112.2(3)$ $109.8(3)$ $118.1(1)$ $113.03(6)$ $102.3(2)$ $123.23(6)$ $79.1(1)$ $74.3(5)$ $78.5(4)$ $77.7(4)$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$

^{*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 [{ $\eta^{5}:\kappa N-1-(C_{9}H_{6}N)C_{9}H_{6}$ }($\eta^{2}-C_{2}H_{3}Me$)W(CO)₂][BF₄]²¹ (0.068 Å) and calixarene tungsten(IV) complex [{p-Bu^t-calix[4]-(O)_{4}}W($\eta^{2}-C_{2}H_{3}Me$)], (0.058 Å).²⁵

Complexes of electron rich metals such as $Pt(\pi)^{29,30}$ and $Cu(\tau)^{24}$ 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 $Ta(\pi)$,²⁷ $Mo(\pi)$,²⁶ $W(\pi)^{21,31}$ and W(rv),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 $(21.9(3)^{\circ})$ fits into this range being close to value recently reported to structurally related indenyl tungsten(π) compound [{ $\eta^{5}:\kappa N-1-(C_{9}H_{6}N)$ C₉H₆}($\eta^{2}-C_{2}H_{3}Me$)W(CO)₂][BF₄]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.

¹H 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 ¹³C NMR spectra of **9**, **10** and **13**. They contain two sets of signals for the carbon atoms of the carbonyl ligands. The ¹H and ¹³C NMR spectra indicate low molecular symmetry of both isomers due to coordination of thioether side arm. The existence of two separate sets of signals for the ethylene spacers, observed in the ¹H 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 Xray 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(C₅)–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 $[(\eta^5-C_5H_5)Mo(CO)_2(\eta^3-C_3H_5)]$ 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). ¹H 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) ${\sf HBF}_4{\cdot}{\sf Et}_2{\sf O},\,{\sf CH}_2{\sf Cl}_2,\,1.1$ equiv. SR'_2, 0 °C.



Scheme 4 Synthesis of the thioether complexes 15–17: (I) HBF₄·Et₂O, CH₂Cl₂, 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.

cyclopentadienyl hydrogens, and one set of signals of given coordinated thioether. The integral intensities of the signals prove that two thioether ligands are coordinated. ¹³C 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(π) stronger than thioethers²¹ 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) compounds³³ 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.



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

Compounds **1** reacts with HBF₄·Et₂O 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 $[(\eta^5-C_5H_5)Mo(CO)_2(\eta^3-C_3H_5)]$ by HBF₄·Et₂O in presence of acetonitrile is well described in literature,^{35,36} we decided to study the protonation with another strong acid CF₃SO₃H. The reaction was done in acetonitrile at 0 °C. ¹H NMR spectrum in CD₂Cl₂ 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 $[(\eta^5-C_5H_5)Mo(CO)_2(MeCN)_2](CF_3-SO_3)$ (**19a**) in a pure form and dissolution in CD₂Cl₂ leads to



Scheme 6 Synthesis of 19a and its transformation to 19b: (I) CF₃SO₃H, MeCN, 0 $^{\circ}$ C (II) CD₂Cl₂.

partial exchange of acetonitrile ligand with triflate. Such interpretation well correlates with formation equimolar amounts of **19b** and free acetonitrile, evidenced by the ¹H 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 $[(\eta^5-C_5H_5)Mo(CO)_2(-NCMe)_2][BF_4]^{.35}$

Conclusions

This study describes protonation of allyl ligand in molybdenum and tungsten complexes $[(\eta^5-Cp')(\eta^3-allyl)M(CO)_2]$ (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 $[{\eta^5:\kappa S-C_5H_4(CH_2)_2SR}Mo(CO)_2(\eta^2 C_2H_3Me$][BF₄] (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 $[\{\eta^5:\kappa S-C_5H_4(CH_2)_2SR\}Mo(CO)_2(SR'_2)][BF_4]$ 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 analogue without intramolecular coordination $[(\eta^5-C_5H_5)]$ Mo(CO)₂(SMe₂)₂[BF₄] formed by protonation of cyclopentadienyl complex $[(\eta^5-C_5H_5)Mo(CO)_2(\eta^3-C_3H_5)]$ 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: $[(\eta^5-C_5H_5)Mo(CO)_2(\eta^3-C_3H_5)];^{38}$ $[(\eta^3-C_3H_5)(MeCN)_2-Mo(CO)_2CI];^{39} [(\eta^3-C_3H_5)(EtCN)_2W(CO)_2CI].^{40}$

Methods

¹H, ¹³C{¹H}, ¹³C-APT, ¹H–¹H COSY and ¹H–¹³C 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 Me₄Si. 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 μ L 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 microfocus CuKa/MoKa 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 software⁴¹ 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 SHELXT⁴³ and SHELXS⁴⁴ structure solution program using intrinsic phasing (9-cis, 12-cis, 16-cis and 19a) and direct methods (11-cis) and refined with the SHELXL⁴⁵ 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 CuK α (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 F² (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 $U_{iso}(H) = 1.5$ $U_{\rm eq}$ (pivot atom) for methyl moiety.

Synthesis of C₅H₅(CH₂)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(CH₂)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 \times 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. ¹H NMR [400 MHz, CDCl₃, 1:1 mixture of 1- and 2-isomers (a: **b**]: $\delta = 1.27$ (t, ${}^{3}J({}^{1}H, {}^{1}H) = 7.4$ Hz, 3H, SCH₂CH₃); 2.57 (q, ${}^{3}J({}^{1}H, {}^{1}H) = 7.4 \text{ Hz}, 2H, SCH_{2}CH_{3}$; 2.63–2.76 (m, 4H of a and 4H **b**, $C_5H_5CH_2CH_2S$; 2.93 (q, ${}^{3}J({}^{1}H, {}^{1}H) = 1.4$ 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, H⁴ of **a**,

C₅H₅); 6.22 (s, H⁴ of **b**, C₅H₅); 6.28 (dq, ${}^{3}J({}^{1}H,{}^{1}H) = 5.4$ Hz, ${}^{4}J({}^{1}H,{}^{1}H) = 1.5$ Hz, H³ of **b**, C₅H₅); 6.41–6.47 (m, 3H, H^{3,2} of **a**, H¹ of **b**, C₅H₅).

Synthesis of C₅H₅(CH₂)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 $Cl(CH_2)_2$ SPh. 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, CDCl₃, 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**, $C_5H_5CH_2CH_2S$); 6.22 (s, 1H, H⁴ of **a**, C_5H_5); 6.37 (s, 1H, H⁴ of **b**, C_5H_5); 7.29 (t, ${}^{3}J({}^{1}H,{}^{1}H) = 7.2$ Hz, 2H of **a** and 2H of **b**, $H^{2,6}C_{6}H_5$); 7.47 (d, ${}^{3}J({}^{1}H,{}^{1}H) = 7.5$ Hz, 1H of **a** and 1H of **b**, H⁴ C_6H_5).

Synthesis of $[{\eta^5-C_5H_4(CH_2)_2SEt}Mo(CO)_2(\eta^3-C_3H_5)]$ (1)

C₅H₅(CH₂)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 $[(\eta^3-C_3H_5)(MeCN)_2Mo(CO)_2Cl]$ (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 \times 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 C14H18SO2MO: 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*]: $\delta = 0.91$ (d, ${}^{3}J({}^{1}H, {}^{1}H)$ = 10.8 Hz, 2H, H^{anti} of *exo*, C₃H₅); 1.22 (t, ${}^{3}/({}^{1}H, {}^{1}H) = 7.3$ Hz, 3H, SCH₂CH₃); 1.65 (d, ${}^{3}J({}^{1}H, {}^{1}H) = 10.5$ Hz, 2H, H^{anti} of endo, C₃H₅); 2.47 (t, ${}^{3}I({}^{1}H, {}^{1}H) = 7.4$ Hz, 2H, C₅H₄CH₂CH₂S); 2.52 (q, ${}^{3}I({}^{1}H, {}^{1}H)$ = 7.3 Hz, 2H, SCH₂CH₃); 2.64 (t, ${}^{3}J({}^{1}H, {}^{1}H) = 7.4$ Hz, 2H, C₅- $H_4CH_2CH_2S$; 2.74 (d, ${}^{3}J({}^{1}H, {}^{1}H) = 7.0$ Hz, 2H, H^{syn} of *exo*, C_3H_5); 2.78-2.83 (m, 2H, H^{syn} of endo, C₃H₅); 3.59-3.69 (m, 1H, H^{meso} of endo, C_3H_5 ; 3.92 (tt, ${}^{3}J({}^{1}H, {}^{1}H) = 10.8$ Hz, ${}^{4}J({}^{1}H, {}^{1}H) = 7.0$ Hz, 1H, H^{meso} of exo, C₃H₅); 5.17 (s, 2H, C₅H₄); 5.22 (s, 2H, C₅H₄). IR (ATR, cm⁻¹): 1935 vs. $[\nu_{a}(CO)]$, 1850 vs. $[\nu_{s}(CO)]$.

Synthesis of $[(\eta^{5}-C_{5}H_{4}(CH_{2})_{2}SPh)Mo(CO)_{2}(\eta^{3}-C_{3}H_{5})]$ (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 $[(\eta^3-C_3H_5)(MeCN)_2-Mo(CO)_2Cl]$ (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*]: $\delta = 0.91$ (d, ${}^{3}J({}^{1}H, {}^{1}H) = 10.8$ Hz, 2H, H^{anti} of *exo*, C_3H_5); 1.63 (d, ${}^{3}J({}^{1}H, {}^{1}H)$

= 10.4 Hz, 2H, H^{anti} of endo, C_3H_5); 2.54 (t, ${}^{3}J({}^{1}H, {}^{1}H) = 7.5$ Hz, 2H, $C_5H_5CH_2CH_2SPh$); 2.73 (d, ${}^{3}J({}^{1}H, {}^{1}H) = 6.9$ Hz, 2H, H^{syn} of exo, C_3H_5); 2.80 (d, ${}^{3}J({}^{1}H, {}^{1}H) = 5.3$ Hz, 2H, H^{syn} of endo, C_3H_5); 3.01 (t, ${}^{3}J({}^{1}H, {}^{1}H) = 7.5$ Hz, 2H, $C_5H_5CH_2CH_2SPh$); 3.59–3.67 (m, 1H, H^{meso} of endo, C_3H_5); 3.90 (tt, ${}^{3}J({}^{1}H, {}^{1}H) = 10.7$ Hz, ${}^{3}J({}^{1}H, {}^{1}H) = 7.1$ 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, ${}^{3}J({}^{1}H, {}^{1}H) = 7.1$ 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 $[\{\eta^5 - C_5 H_4 (CH_2)_2 SEt\} W (CO)_2 (\eta^3 - C_3 H_5)]$ (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 $[(\eta^3-C_3H_5)(EtCN)_2-W(CO)_2Cl]$ (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, C₆D₆, 5 : 2 mixture of isomers *exo* : *endo*]: $\delta = 1.03$ (t, ${}^{3}J({}^{1}H,{}^{1}H) =$ 7.4 Hz, 3H, SCH₂CH₃); 1.08–1.15 (m, 2H, H^{anti} of *exo* and *endo*, C₃H₅); 2.12 (t, ${}^{3}J({}^{1}H,{}^{1}H) =$ 7.1 Hz, 2H, C₅H₄CH₂CH₂S); 2.19 (q, ${}^{3}J({}^{1}H,{}^{1}H) =$ 7.3 Hz, 2H, SCH₂CH₃); 2.26 (t, ${}^{3}J({}^{1}H,{}^{1}H) =$ 6.8 Hz, 2H, C₅H₄CH₂CH₂S); 2.38 (d, ${}^{3}J({}^{1}H,{}^{1}H) =$ 6.1 Hz, 2H, H^{syn} of *exo*, C₃H₅); 2.61–2.67 (m, 2H, H^{syn} of *endo*, C₃H₅); 2.84–2.95 (m, 1H^{meso} of *exo*, C₃H₅); 3.51–3.62 (m, 1H^{meso} of *endo*, C₃H₅); 4.50 (s, 2H, C₅H₄); 4.57 (s, 2H, C₅H₄). IR (ATR, cm⁻¹): 1929 *vs*. [ν_a (CO)], 1840 *vs*. [ν_s (CO)].

Synthesis of $[\{\eta^5 - C_5 H_4 (CH_2)_2 SPh\} W (CO)_2 (\eta^3 - C_3 H_5)]$ (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 $[(\eta^3-C_3H_5)(EtCN)_2-W(CO)_2Cl]$ (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, CDCl₃, 2 : 1 mixture of isomers *exo* : *endo*]: $\delta = 1.19$ (d, ${}^3J({}^{1}H,{}^{1}H) = 9.9$ 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, ${}^{3}J({}^{1}H,{}^{1}H) = 7.5$ Hz, 2H, $C_5H_4CH_2-CH_2S$); 2.72 (d, ${}^{3}J({}^{1}H,{}^{1}H) = 5.9$ 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, ${}^{3}J({}^{1}H,{}^{1}H) = 7.4$ 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*. [v_a (CO)], 1839 *vs*. [v_s (CO)].

Synthesis of $[{\eta^5:\kappa S-C_5H_4(CH_2)_2SEt}Mo(CO)_2(\eta^2-C_2H_3Me)]$ [BF₄] (5)

Compound 1 (252 mg, 0.73 mmol) was dissolved in 10 mL of dichloromethane, the solution was cooled to $-40 \,^{\circ}\text{C}$ and treated with HBF₄·Et₂O (98 µL, 0.73 mmol) dropwise. The solution was stirred at $-40 \,^{\circ}\text{C}$ 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 $-40 \,^{\circ}\text{C}$ and to measure the ¹H NMR spectra directly after isolation. Yield: 316 mg (0.60 mmol,

82%). Orange solid. ¹H NMR [500 MHz, CD_2Cl_2 , 4 : 5 mixture of isomers **a** : **b**]: δ = 1.27 (t, ³*J*(¹H, ¹H) = 7.4 Hz, 3H of **b**, SCH₂*CH*₃); 1.31 (t, ³*J*(¹H, ¹H) = 7.4 Hz, 3H of **a**, SCH₂*CH*₃); 1.88 (d, ³*J*(¹H, ¹H) = 5.5 Hz, 3H of **a**, CH₂CHCH₃); 2.21 (d, ³*J*(¹H, ¹H) = 6.0 Hz, 3H of **b**, CH₂CHCH₃); 4.90 (s, 1H of **b**, C₅H₄); 4.95 (s, 1H of **a**, C₅H₄); 5.35 (s, 1H of **b**, C₅H₄); 6.08 (s, 1H of **a**, C₅H₄); 6.10 (s, 1H of **b**, C₅H₄); 6.25 (s, 1H of **a**, C₅H₄); 6.35 (s, 1H of **b**, C₅H₄).

Synthesis of $[{\eta^5:\kappa S-C_5H_4(CH_2)_2SPh}Mo(CO)_2(\eta^2-C_2H_3Me)]$ [BF₄] (6)

The steps of synthesis followed the procedure for compound 5, but with 2 (105 mg, 0.27 mmol), HBF₄·Et₂O (38 µL, 0.28 mmol). Yield: 101 mg (0.21 mmol, 79%). Orange solid. ¹H NMR [500 MHz, CD₂Cl₂, 3:5 mixture of isomers **a**: **b**]: $\delta = 1.98$ (d, ${}^{3}J({}^{1}\text{H},{}^{1}\text{H}) = 5.7$ Hz, 3H of **a**, CH₂CHCH₃); 2.24 (d, ${}^{3}J({}^{1}\text{H},{}^{1}\text{H}) =$ 6.0 Hz, 3H of **b**, CH₂CHCH₃); 4.96 (s, 1H of **b**, C₅H₄); 5.10 (s, 2H of **a**, C₅H₄); 5.36 (s, 1H of **b**, C₅H₄); 5.37 (s, 1H of **b**, C₅H₄); 6.33 (s, 1H of **a**, C₅H₄); 6.35 (s, 1H of **a**, C₅H₄); 6.43 (s, 1H of **b**, C₅H₄).

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

Compound 3 (731 mg, 1.68 mmol) was dissolved in 10 mL of acetonitrile, the solution was cooled to 0 °C and treated with HBF₄·Et₂O (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 C₁₄H₁₉SO₂WBF₄: 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) $[M - C_3H_6]^+$. ¹H NMR [500 MHz, CD_2Cl_2]: $\delta = 1.22$ (t, ${}^{3}J({}^{1}H, {}^{1}H) = 7.4$ Hz, 3H, SCH_2CH_3 ; 2.09 (d, ${}^{3}J({}^{1}H, {}^{1}H) = 5.2$ Hz, 3H, CH_2CHCH_3); 2.64 (d, ${}^{3}J({}^{1}H,{}^{1}H) = 10.0$ Hz, 2H, $CH_{2}CHCH_{3}$; 2.75–2.80 (m, 1H, SCH₂CH₃); 2.82-2.89 (m, 1H, C₅H₄CH₂CH₂S); 2.92-3.00 (m, 1H, SCH_2CH_3 ; 3,12 (ddd, ${}^{3}J({}^{1}H,{}^{1}H) = 14.6$ Hz, ${}^{4}J({}^{1}H,{}^{1}H) = 5.4$ Hz, ${}^{5}J({}^{1}H, {}^{1}H) = 2.2$ Hz, 1H, $C_{5}H_{4}CH_{2}CH_{2}S$; 3.18–3.26 (m, 1H, CH_2CHCH_3 ; 3.77 (td, ${}^{3}J({}^{1}H, {}^{1}H) = 13.7$ Hz, ${}^{4}J({}^{1}H, {}^{1}H) = 5.5$ Hz, 1H, $C_5H_4CH_2CH_2S$; 3.89 (ddd, ${}^{3}J({}^{1}H, {}^{1}H) = 10.9$ Hz, ${}^{4}J({}^{1}H, {}^{1}H) =$ 4.7 Hz, ${}^{5}J({}^{1}H, {}^{1}H) = 2.8$ Hz, 1H, $C_{5}H_{4}CH_{2}CH_{2}S$; 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). ¹³C NMR [126 MHz, CD₂Cl₂]: δ = 13.6 (SCH₂CH₃); 25.9 (CH₂-CHCH₃); 26.5 ($C_5H_4CH_2CH_2S$); 34.8 (SCH₂CH₃); 45.0 (CH₂-CHCH₃); 51.4 (C₅H₄CH₂CH₂S); 51.8 (CH₂CHCH₃); 76.1 (C₅H₄); 85.1 (C₅H₄); 88.0 (C₅H₄); 94.0 (C₅H₄); 139.8 (C₅H₄); 214.0 (CO); 214.7 (CO). IR (ATR, cm⁻¹): 2025 vs. $[\nu_{a}(CO)]$, 1946 vs. $[\nu_{s}(CO)]$, 1034 vs. [v(BF)].

Synthesis of $[{\eta^5:\kappa S-C_5H_4(CH_2)_2SPh}W(CO)_2(\eta^2-C_2H_3Me)]$ [BF₄] (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) $[M - C_3H_6]^+$. ¹H NMR [500 MHz, CD_2Cl_2]: $\delta = 2.14$ (d, ${}^{3}J({}^{1}H,{}^{1}H) = 4.7$ Hz, 3H, CH₂CHCH₃); 2.45–2.57 (m, 1H, C₅H₄- CH_2CH_2S ; 2.66 (dd, ${}^{2}J({}^{1}H, {}^{1}H) = 11.8 \text{ Hz}, {}^{3}J({}^{1}H, {}^{1}H) = 5.3 \text{ Hz}, 1H$, C₅H₄CH₂CH₂S); 2.99–3.11 (m, 2H, CH₂CHCH₃); 3.52 (s, 1H, CH₂CHCH₃); 3.97-4.04 (m, 1H, C₅H₄CH₂CH₂S); 4.12-4.19 (m, 1H, C₅H₄CH₂CH₂S); 5.07 (s, 1H, C₅H₄); 5.16 (s, 1H, C₅H₄); 6.45 $(s, 1H, C_5H_4); 6.53 (s, 1H, C_5H_4); 7.51 (5H, C_6H_5).$ ¹³C NMR [126 MHz, CD_2Cl_2]: $\delta = 25.9$ (CH₂CHCH₃); 27.5 (CH₂CHCH₃); 45.5 (CH₂CHCH₃); 51.6 (C₅H₄CH₂CH₂S); 57.9 (C₅H₄CH₂CH₂S); 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 (C₆H₅); 132.1 (C₆H₅); 139.0 (C₅H₄); 213.3 (CO); 214.3 (CO). IR (ATR, cm⁻¹): 2025 vs. $[\nu_a(CO)]$, 1915 vs. $[\nu_s(CO)]$, 1026 vs. $[\nu(BF)]$. 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 $[{\eta^5: \kappa S-C_5H_4(CH_2)_2SEt}Mo(CO)_2(SMe_2)][BF_4]$ (9)

Compound 1 (119 mg, 0.34 mmol) was dissolved in 10 mL of dichloromethane, the solution was treated with Me2S (50 µL, 0.68 mmol) cooled to 0 °C and treated with HBF₄·Et₂O (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 C₁₃H₁₉S₂O₂MoBF₄: 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 $(\%) = 369 (100) [M]^+$. ¹H NMR [500 MHz, CD₂Cl₂, mixture 5 : 1 of isomers *cis*: *trans*]: $\delta = 1.38$ (t, ${}^{3}J({}^{1}H, {}^{1}H) = 7.3$ Hz, 3H, SCH₂CH₃); 2.52 (s, 6H, (CH₃)₂S); 2.65–2.75 (m, 1H, C₅H₄CH₂CH₂S); 2.89–2.99 (m, 3H, 1H of C₅H₄CH₂CH₂S; 2H of SCH₂CH₃); 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, C₅H₄ of *cis*); 5,03 (m, 1H, C₅H₄ 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, C₅H₄ of cis); 6.19-6.10 (m, 1H, C₅H₄ of trans); 6.29 (s, 1H, C₅H₄ of *cis*). ¹³C NMR [126 MHz, CD₂Cl₂]: $\delta = 13.7$ (SCH₂CH₃ of *cis*); 13.9 (SCH₂CH₃ of *trans*); 25.9 (SCH₂CH₃); 28.2 ((CH₃)₂S of *cis*); 28.5 ((CH₃)₂S of *trans*); 34.1 (C₅H₄CH₂CH₂S of *cis*); 36.3 (C₅H₄CH₂CH₂S of *trans*); 54.0 (C₅H₄CH₂CH₂S of *cis*); 66.2 (C5H4CH2CH2S of trans); 82.8 (C5H4 of cis); 87.5 (C5H4 of cis); 89.2 (C₅H₄ of *cis*); 89.8 (C₅H₄ of *trans*); 92.7 (C₅H₄ of *trans*); 93.9 (C₅H₄ of trans); 95.4 (C₅H₄ of trans); 100.4 (C₅H₄ of cis); 130.9 (C₅H₄ of *trans*); 142.3 (C₅H₄ 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. $[\nu_{a}(CO)]$, 1883 vs. $[\nu_{s}(CO)]$, 1019 vs. $[\nu(BF)]$. 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 $[{\eta^5: \kappa S-C_5H_4(CH_2)_2SEt}Mo(CO)_2{S(CH_2)_4}][BF_4](10)$

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

0.76 mmol) and HBF₄·Et₂O (70 µL, 0.52 mmol). Yield: 186 mg (0.39 mmol, 76%). Red solid. Anal. calc. for C₁₅H₂₁S₂O₂MoBF₄: C: 37.52; H: 4.41; S: 13.35. Found: C: 37.27; H: 4.19; S: 13.09. ¹H NMR [500 MHz, CD₂Cl₂, mixture 13 : 1 of isomers *cis* : *trans*]: $\delta =$ 1.37 (t, ${}^{3}J({}^{1}H, {}^{1}H) = 7.3$ Hz, 3H, SCH₂CH₃); 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 C₅H₄CH₂CH₂S, 2H of SCH₂CH₃); 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, C₅H₄ of *cis*); 5.06 (m, 1H, C₅H₄ of *trans*); 5.11 (m, 1H, C₅H₄ of trans); 5.54 (s, 1H, C₅H₄ of cis); 5.72 (s, 1H, C₅H₄ of cis); 6.09 (m, 1H, C₅H₄ of *trans*); 6.12 (m, 1H, C₅H₄ of *trans*); 6.23 (s, 1H, C_5H_4 of *cis*). ¹³C NMR [126 MHz, CD_2Cl_2]: $\delta = 13.8$ (SCH₂CH₃ of cis); 15.5 (SCH₂CH₃ of trans); 25.3 (SCH₂CH₃ of trans); 25.8 (SCH₂CH₃ of *cis*); 31.0 (C^{3,4}, C₄H₈S of *trans*); 31.2 (C^{3,4}, C₄H₈S of cis); 34.0 (C₅H₄CH₂CH₂S); 44.4 (C^{2,5}, C₄H₈S of trans); 45.0 (C^{2,5}, C₄H₈S of *cis*); 54.0 (C₅H₄CH₂CH₂S); 83.2 (C₅H₄ of *cis*); 87.4 (C₅H₄ of cis); 89.0 (C₅H₄ of cis); 89.9 (C₅H₄ of trans); 92.6 (C₅H₄ of trans); 93.9 (C₅H₄ of trans); 95.0 (C₅H₄ of trans); 100.6 (C₅H₄ of *cis*); 131.1 (C₅H₄ of *trans*); 142.1 (C₅H₄ 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. $[\nu_{a}(CO)]$, 1882 vs. $[\nu_{s}(CO)]$, 1048 vs. $[\nu(BF)]$.

Synthesis of [$\{\eta^5:\kappa S-C_5H_4(CH_2)_2SEt\}Mo(CO)_2\{\kappa S-S(CH_2)_4O\}$] [BF₄] (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 HBF₄·Et₂O (55 µL, 0.40 mmol). Yield: 147 mg (0.30 mmol, 74%). Red solid. Anal. calc. for C₁₅H₂₁S₂O₃MoBF₄: 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]⁺. ¹H NMR [500 MHz, CD_2Cl_2]: $\delta = 1.38$ (t, ${}^{3}J({}^{1}H, {}^{1}H) = 7.4$ Hz, 3H, SCH₂CH₃); 2.66–2.73 (m, 1H, C₅H₄CH₂CH₂S); 2.75–2.81 (m, 2H, CH₂, SCH₂CH₃); 2.90-3.00 (m, 4H of OC₄H₈S, 1H of C₅H₄CH₂-CH₂S); 3.70-3.76 (m, 1H, C₅H₄CH₂CH₂S); 3.84-3.92 (m, 1H, C₅H₄CH₂CH₂S); 3.96-4.04 (m, 4H, OC₄H₈S); 4.86-4.87 (m, 1H, C₅H₄); 5.58 (s, 1H, C₅H₄); 5.69 (s, 1H, C₅H₄); 6.38 (s, 1H, C₅H₄). ¹³C NMR [126 MHz, CD_2Cl_2]: $\delta = 13.7$ (SCH₂CH₃); 26.0 (C₅H₄-CH₂CH₂S); 34.1 (OC₄H₈S); 38.4 (SCH₂CH₃); 54.0 (C₅H₄CH₂- CH_2S ; 68.9 (OC_4H_8S); 82.6 (C_5H_4); 87.2 (C_5H_4); 89.2 (C_5H_4); 100.0 (C₅H₄); 142.5 (C₅H₄); 241.5 (CO); 243.5 (CO). IR (ATR, cm⁻¹): 1986 vs. $[\nu_{a}(CO)]$, 1885 vs. $[\nu_{s}(CO)]$, 1026 vs. $[\nu(BF)]$. 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 $[{\eta^5: \kappa S-C_5H_5(CH_2)_2SPh}Mo(CO)_2(SMe_2)][BF_4]$ (12)

The steps of synthesis followed the procedure for compound **9**, but with **2** (98 mg, 0.25 mmol), Me₂S (37 µL, 0.50 mmol) and HBF₄·Et₂O (33 µL, 0.25 mmol). Yield: 98 mg (0.20 mmol, 78%). Red solid. Anal. calc. for C₁₇H₁₉S₂O₂MoBF₄: 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 - SC₂H₆]⁺. ¹H NMR [400 MHz, CD₂Cl₂]: δ = 2.53 (s, 6H, (CH₃)₂S); 2.72–2.81 (m, 1H, C₅H₄CH₂-CH₂S); 2.93–3.01 (m, 1H, C₅H₄CH₂CH₂S); 3.87–3.95 (m, 1H, C₅H₄CH₂CH₂S); 4.19–4.28 (m, 1H, C₅H₄CH₂CH₂S); 4.96 (s, 1H, C₅H₄); 5.85 (s, 1H, C₅H₄); 6.39 (s, 1H, C₅H₄);

7.50–7.58 (m, 5H, C₆H₅). ¹³C NMR [126 MHz, CD₂Cl₂]: δ = 27.0 (C₅H₄CH₂CH₂S); 28.3 ((CH₃)₂S); 61.3 (C₅H₄CH₂CH₂S); 82.8 (C₅H₄); 87.2 (C₅H₄); 89.5 (C₅H₄); 100.8 (C₅H₄); 130.6 (C₆H₅); 131.6 (C₆H₅); 131.8 (C₆H₅); 142.1 (C₅H₄); 240.2 (CO); 243.9 (CO). IR (ATR, cm⁻¹): 1978 *vs.* [*v*_a(CO)], 1890 *vs.* [*v*_s(CO)], 1022 *vs.* [*v*(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 $[\{\eta^5:\kappa S-C_5H_4(CH_2)_2SPh\}Mo(CO)_2\{S(CH_2)_4\}][BF_4]$ (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 HBF4·Et2O (23 µL, 0.17 mmol). Yield: 80 mg (0.15 mmol, 89%). Red solid. Anal. calc. for C19H21S2O2MoBF4: C: 43.20; H: 4.01; S: 12.14. Found: C: 42.98; H: 3.83; S: 11.96. Positiveion MS (acetone): m/z (%) = 443 (100) [M]⁺. ¹H NMR [500 MHz, CD_2Cl_2 , mixture 5 : 2 of isomers *cis* : *trans*]: $\delta = 2.07-2.21$ (m, 4H, H^{3,3,4,4}, C₄H₈S); 2.37–2.48 (m, 1H, C₅H₄CH₂CH₂S of *trans*); 2.62– 2.71 (m, 1H, C₅H₄CH₂CH₂S of trans); 2.74–2.85 (m,1H, C₅H₄-CH₂CH₂S of cis); 2.90-3.00 (m, 1H, C₅H₄CH₂CH₂S of cis); 3.17 (t, ${}^{3}I({}^{1}H, {}^{1}H) = 5.8$ Hz, 4H, H^{2,2,5,5}, C₄H₈S); 3.52–3.61 (m, 1H, C₅H₄-CH₂CH₂S of trans); 3.73-3.80 (m, 1H, C₅H₄CH₂CH₂S of trans); 3.94 (dt, ${}^{2}J({}^{1}H, {}^{1}H) = 12.7$ Hz, ${}^{3}J({}^{1}H, {}^{1}H) = 5.3$ Hz, 1H, C₅H₄CH₂-CH₂S of cis); 4.15-4.22 (m, 1H, C₅H₄CH₂CH₂S of cis); 4.97 (d, ${}^{3}J({}^{1}H, {}^{1}H) = 1.4$ Hz, 1H, C₅H₄ of *cis*); 5.15 (s, 1H, C₅H₄ of *trans*); 5.24 (s, 1H, C₅H₄ of *trans*); 5.54 (s, 1H, C₅H₄ of *cis*); 5.87 (s, 1H, C₅H₄ of *cis*); 6.17 (s, 1H, C₅H₄ of *trans*); 6.35 (s, 1H, C₅H₄ of *cis*); 6.42 (s, 1H, C₅H₄ of trans); 7.49-7.54 (m, 5H, C₆H₅ of cis); 7.55-7.57 (m, 3H, C₆H₅ of *trans*); 7.63–7.66 (m, 2H, C₆H₅ of *trans*). ¹³C NMR [126 MHz, CD_2Cl_2]: $\delta = 26.7 (C_5H_4CH_2CH_2S)$; 31.0 (SC₄H₈); 31.2 (SC_4H_8) ; 44.4 (SC_4H_8) ; 45.0 (SC_4H_8) ; 61.5 $(C_5H_4CH_2CH_2S)$; 83.3 (C₅H₄ of *cis*); 87.2 (C₅H₄ of *cis*); 89.1 (C₅H₄ of *cis*); 90.4 (C₅H₄ of trans); 92.7 (C₅H₄ of trans); 94.6 (C₅H₄ of trans); 95.2 (C₅H₄ of trans); 101.1 (C_5H_4 of cis); 130.5 (C_6H_5); 130.6 (C_6H_5); 131.9 (C₆H₅); 141.5 (C₅H₄); 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. $[\nu_a(CO)]$, 1890 vs. [v_s(CO)], 1022 vs. [v(BF)].

Synthesis of [$\{\eta^5:\kappa S-C_5H_4(CH_2)_2SPh\}Mo(CO)_2\{\kappa S-S(CH_2)_4O\}$] [BF₄] (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 HBF₄·Et₂O (67 µL, 0.50 mmol). Yield: 221 mg (0.41 mmol, 81%). Red solid. Anal. calc. for C₁₉H₂₁S₂O₃MoBF₄: 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) $[M - OC_4H_8S]^+$. ¹H NMR [500 MHz, CD_2Cl_2]: $\delta = 2.63-2.83$ (m, 2H, $C_5H_4CH_2$ -CH₂S); 2.93-3.06 (m, 4H, OC₄H₈S); 3.86-3.96 (1H, C₅H₄CH₂- CH_2S); 3.99 (s, 4H, OC_4H_8S); 4.22–4.30 (m, 1H, $C_5H_4CH_2CH_2S$); 4.94 (s, 1H, C₅H₄); 5.58 (s, 1H, C₅H₄); 5.86 (s, 1H, C₅H₄); 6.47 (s, 1H, C₅H₄); 7.49–7.58 (m, 5H, C₆H₅). ¹³C NMR [126 MHz, CD_2Cl_2]: $\delta = 27.0 (C_5H_4CH_2CH_2S)$; 38.6 (OC_4H_8S); 54.4 (C_5H_4 -CH₂CH₂S); 69.0 (OC₄H₈S); 82.8 (C₅H₄); 87.0 (C₅H₄); 89.4 (C₅H₄); 100.6 (C₅H₄); 130.6 (C₆H₅); 131.5 (C₆H₅); 131.6 (C₆H₅); 142.0 (C_5H_4) ; 240.1 (CO); 243.4 (CO). IR (ATR, cm⁻¹): 1984 vs. $[\nu_a(CO)]$, 1901 vs. $[\nu_s(CO)]$, 1030 vs. $[\nu(BF)]$.

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

The steps of synthesis followed the procedure for compound **9**, but with $[(\eta^5 - C_5H_5)Mo(CO)_2(\eta^3 - C_3H_5)]$ (120 mg, 0.47 mmol), Me₂S (104 µL, 1.41 mmol) and HBF₄·Et₂O (63 µL, 0.47 mmol). Yield: 157 mg (0.37 mmol, 78%). Red solid. Anal. calc. for C₁₁-H₁₇S₂O₂MoBF₄: 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 SC₂H₆ + 2 C₃H₆O]⁺. ¹H NMR [500 MHz, CD₂Cl₂]: δ = 2.52 (s, 12H, (CH₃)₂S); 5.76 (s, 5H, C₅H₅). ¹³C NMR [126 MHz, CD₂Cl₂]: δ = 26.9 ((CH₃)₂S); 95.7 (C₅H₅); 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 $[(\eta^5-C_5H_5)Mo(CO)_2\{(CH_2)_4S\}_2][BF_4]$ (16)

The steps of synthesis followed the procedure for compound **9**, but with $[(\eta^5-C_5H_5)Mo(CO)_2(\eta^3-C_3H_5)]$ (109 mg, 0.42 mmol), tetrahydrothiophene (93 µL, 1.05 mmol) and HBF₄·Et₂O (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) $[M - SC_4H_8]^+$. ¹H NMR [500 MHz, CD₂Cl₂]: δ = 2.15–2.18 (m, 4H, H^{3,3,4,4}, C₄H₈S); 3.08–3.20 (m, 4H, H^{2,2,5,5}, C₄H₈S); 5.72 (s, 5H, C₅H₅). ¹³C NMR [126 MHz, CD₂Cl₂]: δ = 31.2 (C^{3,4}, C4H8S); 44.2 (C^{2,5}, C₄H₈S); 95.8 (C₅H₅); 246.1 (CO). IR (ATR, cm⁻¹): 1960 *vs.* [v_a (CO)], 1898 *vs.* [v_s (CO)], 1027 *vs.* [v(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 $[(\eta^5 - C_5 H_5)Mo(CO)_2 \{\kappa S - S(CH_2)_4 O\}_2][BF_4]$ (17)

The steps of synthesis followed the procedure for compound **9**, but with $[(\eta^5-C_5H_5)Mo(CO)_2(\eta^3-C_3H_5)]$ (180 mg, 0.70 mmol), 1,4-oxathiane (164 µL, 1.75 mmol) and HBF₄·Et₂O (95 µL, 0.70 mmol). Yield: 295 mg (0.58 mmol, 82%). Red solid. Anal. calc. for C₁₅H₂₁S₂O₄MoBF₄: 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) $[M - OC_4H_8S - CO]^+$. ¹H NMR [500 MHz, CD₂Cl₂]: δ = 2.79–2.83 (m, 4H, OC₄H₈S); 3.00–3.04 (m, 4H, OC₄H₈S); 4.01–4.04 (m, 8H, OC₄H₈S); 5.79 (s, 5H, C₅H₅). ¹³C NMR [126 MHz, CD₂Cl₂]: δ = 37.6 (OC₄H₈S); 69.0 (OC₄H₈S); 95.7 (C₅H₅); 243.9 (CO). IR (ATR, cm⁻¹): 1981 *vs*. [ν_a (CO)], 1903 *vs*. [ν_s (CO)], 1049 *vs*. [ν (BF)].

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

The steps of synthesis followed the procedure for compound 7, but with 1 (391 mg, 1.13 mmol) and HBF₄·Et₂O (152 µL, 1.13 mmol). Yield: 454 mg (1.05 mmol, 93%). Red solid. Anal. calc. for C₁₃H₁₆SO₂NMoBF₄: 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 + C₃H₆O]⁺. ¹H NMR [500 MHz, CD₂Cl₂]: δ = 1.39 (t, ³*J*(¹H, ¹H) = 7.2 Hz, 3H, SCH₂CH₃); 2.54 (s, 3H, CH₃CN); 2.59–2.66 (m, 1H, C₅H₄CH₂CH₂S); 2.81–2.95 (m,

2H, SCH₂CH₃); 2.93–2.99 (m, 1H, C₅H₄CH₂CH₂S); 3.65–3.71 (m, 1H, C₅H₄CH₂CH₂S); 4.04–4.12 (m, 1H, C₅H₄CH₂CH₂S); 4.82 (s, 1H, C₅H₄); 5.44 (s, 1H, C₅H₄); 5.76 (s, 1H, C₅H₄); 6.52 (s, 1H, C₅H₄). ¹³C NMR [126 MHz, CD₂Cl₂]: $\delta = 5.5$ (CH₃, CH₃CN); 13.7 (SCH₂CH₃); 25.9 (C₅H₄CH₂CH₂S); 33.4 (SCH₂CH3); 53.9 (C₅H₄-CH₂CH₂S); 83.6 (C₅H₄); 87.8 (C₅H₄); 88.0 (C₅H₄); 104.9 (C₅H₄); 142.2 (C₅H₄); 144.7 (CN, CH₃CN); 244.2 (CO); 247.8 (CO). IR (ATR, cm⁻¹): 1994 *vs.* [*v*_a(CO)], 1886 *vs.* [*v*_s(CO)], 1054 *vs.* [*v*(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 $[(\eta^{5}-C_{5}H_{5})Mo(CO)_{2}(MeCN)_{2}](CF_{3}SO_{3})$ (19)

The steps of synthesis followed the procedure for compound 7, but with $[(\eta^5 - C_5 H_5)Mo(CO)_2(\eta^3 - C_3 H_5)]$ (109 mg, 0.42 mmol) and CF₃SO₃H (37 µL, 0.42 mmol). Yield: 150 mg (0.33 mmol, 80%). Red solid. Anal. calc. for C12H11N2SO5MoF3: 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. ¹H NMR [400 MHz, CD_2Cl_2 , 6:5 mixture of complexes [(η^5 -C₅H₅)] $Mo(CO)_2(MeCN)_2](CF_3SO_3)$ and $[(\eta^{5}-C_{5}H_{5})Mo(CO)_{2}(-$ MeCN)(CF₃SO₃)] (**a** : **b**)]: $\delta = 1.97$ (s, 3H, free CH₃CN); 2.50 (s, 3H, CH₃CN of **b**); 2.55 (s, 6H, CH₃CN of **a**); 5.74 (s, 5H, C₅H₅ of **b**); 5.75 (s, 5H, C₅H₅ of **a**). IR (ATR, cm⁻¹): 1990 *vs*. [ν_{a} (CO)], 1882 vs. $[\nu_{s}(CO)]$, 1261 vs. $[\nu_{a}(SO_{3})]$, 1224 m $[\nu_{s}(CF_{3})]$, 1151 s $[\nu_{a}(CO)]$, 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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