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Seven-coordinated 2,2′ : 6′2″-terpyridinemolybdenum(II) complexes: synthesis, structure and reactivity of $[Mo(CO)(C_7H_8)(4,4',4''\text{-}R_3terpy)X]X'$ (R = H or ^tBu)

Thomas Daniel *, Hirotaka Nagao, Hiroshi Nakajima, Koji Tanaka, Akira Nakamura

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

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Abstract

The norbornadiene(terpyridine) complex $[Mo(CO)(C_7H_8)(terpy)I]I$ (**2a**) is prepared in two steps from $[Mo(CO)_4(C_7H_8)]$ (**1**), iodine and 2,2′ : 6′,2″-terpyridine. On treatment with either KPF_6 in methanol or $AgSbF_6$ in CH_2Cl_2 the more soluble salts $[Mo(CO)(C_7H_8)(terpy)I]PF_6$ (**2b**) and $[Mo(CO)(C_7H_8)(terpy)I]SbF_6$ (**2c**) are isolated with good yields. With 4,4′,4″-tri-tert-butyl-2,2′ : 6′,2″-terpyridine, in similar reactions the tert-butyl-substituted terpyridine compounds $[Mo(CO)(C_7H_8)(4,4',4''\text{-}^tBu_3terpy)I]X$ (X = I(**3a**), PF_6(**3b**) or SbF_6 (**3c**)) can be obtained, while the oxidation of **1** with two equivalents of $CuBr_2$ leads to the bromo(terpyridine) complexes $[Mo(CO)(C_7H_8)(terpy)Br]X$ (X = Br(**4a**), PF_6 (**4b**) or SbF_6 (**4c**)). The X-ray structural analysis for **4c** reveals an unusual arrangement for the ligands around the metal center. A triangle formed by the norbornadiene and the halogen is perpendicular to the plane formed by terpyridine and CO. The iodo compound **2a** as well as the bromo analogue **4a** reacts with a double quantity of $AgSbF_6$ by halogen abstraction to give a complex of the composition $\{[Mo(CO)(C_7H_8)(terpy)]_2(acetone)\}(SbF_6)_4$ (**5**). Treatment of **5** with two equivalents of PMe_3 affords the phosphine complex $[Mo(CO)(C_7H_8)(terpy)PMe_3](SbF_6)_2$–acetone (**6**). The similar compound $[Mo(CO)(C_7H_8)(terpy)NCCH_2CH_3](SbF_6)_2$ (**7**), which can be easily prepared from **5** and a fivefold excess of propionitrile, exists in acetone in a concentration-dependent equilibrium with **5**. In the presence of NaN_3 or NaCl, **5** yields the complexes $[Mo(CO)(C_7H_8)(terpy)X]SbF_6$ (X = N_3 (**8**) or Cl(**9**)). Whereas the azido compound **8** seems to be stable towards coordinating solvents, the chloro complex **9** slowly reacts in acetone.

Keywords: Molybdenum; Crystal structure; Terpyridene; Norbornadiene; Cationic complexes

1. Introduction

Whereas the 2,2′-bipyridines are well established ligands in the coordination chemistry of molybdenum [1], examples for 2,2′ : 6′,2″-terpyridine molybdenum complexes are very rare. Recently the synthesis of the compounds $[Mo(CO)_4(terpy)]$ [2] and $[Mo(CO)_4(4,4',4''\text{-}^tBu_3terpy)]$[3], which are analogoues to the bipyridine complexes $[Mo(CO)_4(R_2bipy)]$[4], have been reported. Even if these compounds show in solution a fluxional behavior with the two outer pyridine rings exchanging between the coordinated and the uncoordinated form, they contain the terpyridine or the tert-butyl-substituted terpyridine only as a bidentate ligand. Nevertheless, with the bis(terpyridine) complex $[Mo(terpy)_2]$, at least one example for a molybdenum complex, in which the terpyridine ligands coordinate via all three nitrogen atoms to the metal center, is also known [5].

We reported recently that the reaction of $[Mo(CO)_4(C_7H_8)]$ with iodine gives the norbornadienemolybdenum(II) compound $[Mo(CO)_2(C_7H_8)I_2]_n$ ($n \geqslant 1$), which on treatment with either 2,2′-bipyridine or 4,4′-di-tert-butyl-2,2′-bipyridine yields the seven-coordinated norbornadiene(bipyridine) complexes $[Mo(CO)(C_7H_8)(R_2bipy)I_2]$. In similar reactions the bromo analogues $[Mo(CO)(C_7H_8)(R_2bipy)Br_2]$ were obtained by oxidation of $[Mo(CO)_4(C_7H_8)]$ with two equivalents of $CuBr_2$ [6]. The present paper describes our results in the preparation of monocationic and dicationic norbornadiene(terpyridine) molybdenum(II) complexes of the gen-

* Corresponding author.

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eral composition $[Mo(CO)(C_7H_8)(R_3terpy)X]X'$ and $[Mo(CO)(C_7H_8)(R_3terpy)L](SbF_6)_2$.

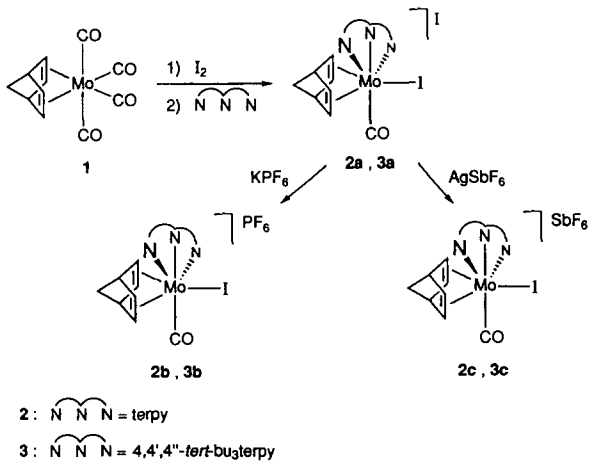
2. Results and discussion

2.1. Synthesis of $[Mo(CO)(C_7H_8)(4,4',4''\text{-}R_3terpy)X]X'$

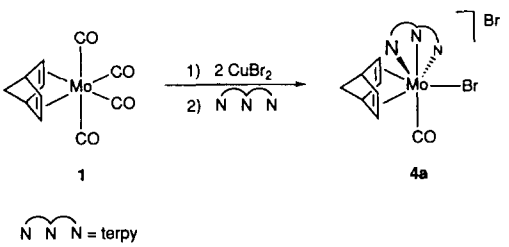
After stirring a 1 : 1 mixture of $[Mo(CO)_4(C_7H_8)]$ (**1**) and iodine in CH_2Cl_2 for 30 min at room temperature the compound $[Mo(CO)_4(C_7H_8)I_2]_n$ ($n \geq 1$) is formed with an almost quantitative yield. On treatment of a solution of $[Mo(CO)_4(C_7H_8)I_2]_n$ ($n \geq 1$) prepared in situ with an equivalent quantity of 2,2′ : 6′,2″-terpyridine the cationic norbornadiene(terpyridine) complex $[Mo(CO)(C_7H_8)(terpy)I]I$ (**2a**) separates as a red–brown solid and can be isolated with about 90% yield. While the characterization of **2a** by elemental analysis failed, correct analytical data are available for the tert-butyl-substituted analogue $[Mo(CO)(C_7H_8)(4,4',4''\text{-}{}^tBu_3terpy)I]I$ (**3a**), which is obtained in a similar reaction by using 4,4′,4″-tri-tert-butyl-2,2′ : 6′,2″-terpyridine instead of the non-substituted terpyridine as the starting material.

The difficulties in the purification of **2a** are connected with the poor solubility of this iodide salt in all tested organic solvents. Whereas **3a** is sufficiently soluble not only in acetone and CH_2Cl_2 but also in $CHCl_3$, a reasonable solubility for **2a** was only found in very polar solvents such as methanol or water.

In order to make the cation $[Mo(CO)(C_7H_8)(terpy)I]^+$ more soluble we exchanged from the anion iodide to a larger anion. In the presence of equimolar quantities of either KPF_6 or NH_4PF_6 a suspension of **2a** in methanol reacts at room temperature within 1 h to give the complex $[Mo(CO)(C_7H_8)(terpy)I]PF_6$ (**2b**) with a good yield (Scheme 1). The analogous compound



Scheme 1.



Scheme 2.

$[Mo(CO)(C_7H_8)(terpy)I]SbF_6$ (**2c**) is obtained after stirring a 1 : 1 mixture of **2a** and $AgSbF_6$ in acetone for 30 min and separation of the formed silver iodide. While the PF_6 salt **2b** is reasonably soluble in acetone, the solubility for the SbF_6 salt **2c** is markedly increased. The analytical data found for **2b** and **2c** are in good agreement with the calculated data. Similarly, the tert-butyl-substituted complexes $[Mo(CO)(C_7H_8)(4,4',4''\text{-}tBu_3terpy)I]PF_6$ (**3b**) and $[Mo(CO)(C_7H_8)(4,4',4''\text{-}{}^tBu_3terpy)I]SbF_6$ (**3c**) can be synthesized.

The compounds **2** and **3** are characterized by IR and ^1H NMR spectroscopy. In the case when the solubility was sufficiently high, ^{13}C NMR spectra were additionally measured. Compared with the neutral bipyridine complexes $[Mo(CO)(C_7H_8)(R_2bipy)X_2]$ [6] for the cationic terpyridine compounds $[Mo(CO)(C_7H_8)(R_3terpy)X]X'$ the CO stretching frequencies are found to be 30–40 cm^{-1} higher in wavenumber. While the IR spectra in KBr show for all compounds two CO stretching frequencies at about 1920 and about 1940 cm^{-1}, in CH_2Cl_2 solution only one CO band at about 1940 cm^{-1} is observed.

From the NMR spectroscopy analysis of **2** and **3**, it can be concluded that the terpyridine is divided by a mirror plane and thus the tridentate coordination of this ligand is ensured. A second plane of symmetry through the two C=C double bonds and the CH_2 unit is observed for the norbornadiene ligand from both the ^1H and the ^{13}C NMR spectra. Therefore a pentagonal bipyramidal geometry, which was found as the molecular structure of the bipyridine complexes $[Mo(CO)(C_7H_8)(R_2bipy)X_2]$ [6], cannot be given in the case of the terpyridine complexes. Unfortunately single crystals which were good enough for an X-ray structural analysis were not available from **2** nor from **3**.

We solved this problem by the synthesis of the bromo(terpyridine) analogue $[Mo(CO)(C_7H_8)(terpy)Br]X$ (**4**). The reaction of $[Mo(CO)_4(C_7H_8)]$ (**1**) with two equivalents of $CuBr_2$ gives a green solution after separation of the precipitate of CuBr. Addition of 2,2′ : 6′,2″-terpyridine leads to the complex $[Mo(CO)(C_7H_8)(terpy)Br]Br$ (**4a**) with an 87% yield (Scheme 2). By methods similar to that described for the preparation of **2b** and **2c** (see Scheme 1) the more soluble salts

Table 1
Selected intramolecular bond distances (Å) and bond angles (°) in **4c**, with estimated standard deviations

Bond distances			
Mo–Br	2.6573(8)	Mo–C(17)	2.353(6)
Mo–N(1)	2.230(4)	Mo–C(18)	2.327(6)
Mo–N(2)	2.158(4)	Mo–C(19)	2.332(6)
Mo–N(3)	2.208(5)	Mo–C(20)	2.320(5)
Mo–C(1)	1.982(6)	O–C(1)	1.141(6)
Bond angles			
Br–Mo–N(1)	76.6(1)	N(2)–Mo–N(3)	73.3(2)
Br–Mo–N(2)	83.3(1)	N(1)–Mo–C(1)	102.9(2)
Br–Mo–N(3)	75.3(1)	N(2)–Mo–C(1)	163.4(2)
Br–Mo–C(1)	80.1(2)	N(3)–Mo–C(1)	101.9(2)
N(1)–Mo–N(2)	73.3(2)	Mo–C(1)–O	178.1(6)

$[Mo(CO)(C_7H_8)(terpy)Br]PF_6$ (**4b**) and $[Mo(CO)(C_7H_8)(terpy)Br]SbF_6$ (**4c**) are prepared. The spectroscopic data for **4** (for details see Section 3) are similar to those for the iodo derivatives **2** and **3** and thus need no further discussion.

2.2. Molecular structure of $[Mo(CO)(C_7H_8)(terpy)Br]SbF_6$ (4c)

The X-ray structural analysis of **4c** indeed infers a geometry for the cation $[Mo(CO)(C_7H_8)(terpy)Br]^+$, which is totally different from the pseudopentagonal bipyramidal structure found for the neutral bipyridine complex $[Mo(CO)(C_7H_8)(bipy)Br_2]$ [6]. As shown in Fig. 1, the arrangement of the ligands around the metal center is best described with a triangle formed by the norbornadiene and the halogen perpendicular to the plane formed by the terpyridine and the CO. Another probable description for this unusual geometry is an pseudo-octahedral fashion with the midpoint of the norbornadiene ligand occupying only one coordination site.

In either case it has to be mentioned that the rectangle formed by the terpyridine and CO is not ideal. The inflexibility of the terpyridine ligand fixes the angles N–Mo–N at 73.3(2)° and therefore widen the angles N–Mo–C(1) to about 102°. Furthermore it has to be noted that the molybdenum atom is not in plane with this square, but a little bit shifted to the side of the norbornadiene ligand. However, to our knowledge it is the first time that such an arrangement of the ligands is found for an molybdenum complex. For carbonyl(bipyridine) molybdenum(II) complexes besides the pseudopentagonal bipyramidal structure of $[Mo(CO)(C_7H_8)(bipy)Br_2]$ so far only capped octahedral, $[Mo(CO)_3(bipy)(SnCl_2Me)Cl]$ [7], and capped trigonal prism geometries, $[Mo(CO)_3(bipy)(HgCl_2)Cl]$ [8], have been reported.

Most of the bond distances observed for **4c** (Table 1)

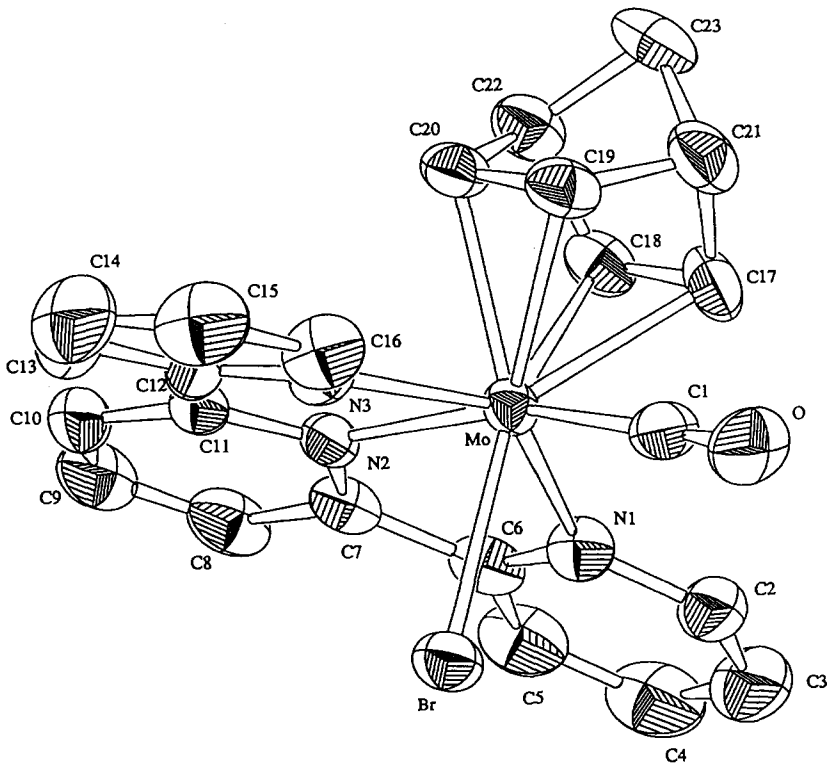


Fig. 1. Molecular structure of the cation $[Mo(CO)(C_7H_8)(terpy)Br]^+$ of **4c**.

are in good agreement with those found for the neutral bipyridine complex $[Mo(CO)(C_7H_8)(bipy)Br_2]$ [6]. Nevertheless, the distance between the metal center and the N atom of the middle pyridine ring is at 2.158(4) Å very short. With 2.277(4) Å in the bipyridine complex the bond length between the molybdenum atom and the nitrogen in the *trans* position to the CO ligand was found to be more than 0.1 Å longer. This of course has some influence on the carbonyl ligand. In the molecular structure of $[Mo(CO)(C_7H_8)(bipy)Br_2]$, distances of 1.931(5) Å for Mo–C(1) and 1.150(5) Å for O–C(1) have been found. For the cation $[Mo(CO)(C_7H_8)(terpy)Br]^+$, the bond length Mo–C(1) is at 1.982(6) Å longer by 0.05 Å, while the distance O–C(1) is with 1.141 Å slightly shorter. The fact that, compared with the neutral compounds $[Mo(CO)(C_7H_8)(R_2bipy)X_2]$, the CO bond is strengthened in the cationic terpyridine complexes $[Mo(CO)(C_7H_8)(R_3terpy)X]X'$ is consistent with the IR spectroscopy data.

2.3. Reactivity of $[Mo(CO)(C_7H_8)(terpy)X]X$ (X = I(2a) or Br(4a))

When we studied the reactivity of the neutral norbornadiene(bipyridine) complexes $[Mo(CO)(C_7H_8)(R_2bipy)X_2]$ we observed that one of the halogeno ligands can be easily abstracted with $AgSbF_6$. The resulting coordination polymers $\{[Mo(CO)(C_7H_8)(R_2bipy)X]SbF_6\}_n$ ($n \geqslant 1$) were found to be reactive both towards neutral and anionic ligands, yielding compounds of the general type $[Mo(CO)(C_7H_8)(R_2bipy)(L)X]SbF_6$ and $[Mo(CO)(C_7H_8)(R_2bipy)XX']$ [6]. A similar reactivity for the cationic norbornadiene(terpyridine) complexes would offer, besides other monocationic compounds $[Mo(CO)(C_7H_8)(terpy)X]SbF_6$, also dicationic complexes $[Mo(CO)(C_7H_8)(terpy)L](SbF_6)_2$.

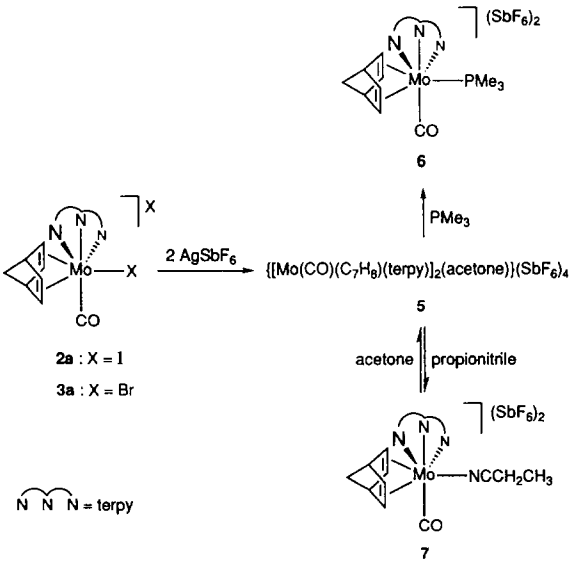
On treatment with two equivalents of $AgSbF_6$ suspensions of the iodo complex $[Mo(CO)(C_7H_8)(terpy)I]I$ (**2a**) as well as the bromo analogue $[Mo(CO)(C_7H_8)(terpy)Br]Br$ (**4a**) in acetone leads to red–orange solutions. In either case after separation of the precipitated silver halide the compound $\{[Mo(CO)(C_7H_8)(terpy)]_2(acetone)\}(SbF_6)_4$ (**5**) is isolated as an orange–red solid with about 85% yield.

The composition of **5** is ensured by its spectroscopic data. Similar to those of the compounds **2** and **3** the IR spectra of **5** in solution show only one CO stretching frequency, while two CO bands are visible for the spectrum measured in KBr. Besides these two, another band at 1645 cm^{-1}, which is assigned to a coordinated acetone, can be observed. The ^1H and the ^{13}C NMR spectrum of **5** in acetone-d_6 indicates the existence of two different $[Mo(CO)(C_7H_8)(terpy)]^{2+}$ units and one molecule of acetone in the ratio 1 : 1 : 1. Since the resonances observed for acetone correspond to the chemical shifts for uncoordinated acetone, this molecule should be only weakly coordinated to the metal center.

Although the spectroscopic data leave no doubt about the composition of **5**, we are so far not able to ensure its structure. For a dimeric complex $\{[Mo(CO)(C_7H_8)(terpy)]_2(\mu\text{-acetone})\}(SbF_6)_4$ with the acetone molecule bridging the two $[Mo(CO)(C_7H_8)(terpy)]^{2+}$ units, **5** seems to be too soluble in acetone. On the contrary the fact that the absence of concentration dependence in the NMR spectra measured in acetone-d_6 was observed gives an argument against the existence of **5** as a mixture of a seven-coordinated compound $[Mo(CO)(C_7H_8)(terpy)(acetone)](SbF_6)_2$ and a six-coordinated complex $[Mo(CO)(C_7H_8)(terpy)](SbF_6)_2$. However, as explained hereafter, **5** is a good precursor for the synthesis of dicationic complexes $[Mo(CO)(C_7H_8)(terpy)L](SbF_6)_2$ as well as monocationic compounds $[Mo(CO)(C_7H_8)(terpy)X]SbF_6$.

After stirring of an solution of **5** prepared in situ in acetone with a slight excess of PMe_3, the phosphine complex $[Mo(CO)(C_7H_8)(terpy)PMe_3](SbF_6)_2 \cdot$ acetone (**6**) can be isolated with a good yield. Compound **6** crystallizes with one molecule of acetone, which could not be removed by washing with other solvents or drying in vacuum. The fact that this acetone molecule is not in contact with the metal center is indicated by the IR spectrum of **6** measured in KBr. The NMR spectroscopy data of **6** are in good agreement with those observed for the monocationic compounds $[Mo(CO)(C_7H_8)(R_3terpy)X]X'$ and therefore the dication $[Mo(CO)(C_7H_8)(terpy)PMe_3]^{2+}$ should show a structure similar to that suggested in Scheme 3.

Under conditions similar to those used for the preparation of the phosphine complex **6**, $\{[Mo(CO)(C_7H_8)$-



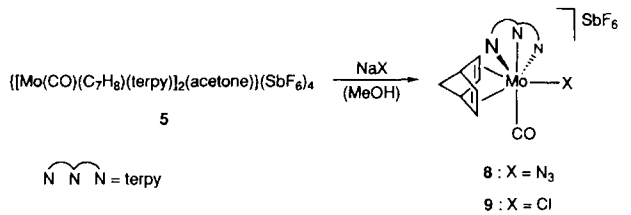
Scheme 3.

$(terpy)]_2(acetone)\}(SbF_6)_4$ (**5**) reacts with a five-fold excess of propionitrile to give the compound $[Mo(CO)(C_7H_8)(terpy)NCCH_2CH_3](SbF_6)_2$ (**7**) with 91% yield. Most of the spectroscopic data of **7** are in good agreement with that observed for **6**. Nevertheless, the resonance assigning the H(6) proton of the terpyridine ligand and one of the signals for the =CH protons of the norbornadiene ligand are considerably shifted. In the ^1H NMR spectrum of **7** measured in acetone-d_6 the H(6) atom is observed together with the H(5) proton as one signal at $\delta = 7.97$ ppm, which could be ensured by the selective decoupling of all proton resonances of the terpyridine ligand.

Moreover, the NMR spectroscopy analysis of **7** gives information that **7** exists in acetone in a concentration-dependent equilibrium with **5**. While in concentrated solutions **7** was found to be the major component, the equilibrium is more and more on the side of **5** on lowering the concentration. Exclusively the propionitrile complex **7** can be observed on treatment of a solution of **7** in acetone-d_6 with more than a double excess of propionitrile.

In the presence of anionic ligands, **5** reverts to monocationic complexes of the general type $[Mo(CO)(C_7H_8)(terpy)X]SbF_6$. After stirring a solution of **5** synthesized in situ in methanol with equimolar quantities of NaN_3 or NaCl for some hours at room temperature the complexes $[Mo(CO)(C_7H_8)(terpy)N_3]SbF_6$ (**8**) and $[Mo(CO)(C_7H_8)(terpy)Cl]SbF_6$ (**9**) separate as red–violet solids and can be isolated with good yields (Scheme 4).

The NMR spectroscopy data observed for the azido complex **8** are in good agreement with those found for the bromo and iodo analogue, whereas the ^1H NMR spectrum of the chloro compound **9** is better comparable with that measured for the propionitrile compound **7**. Again the signals for the H(6) and the H(5) protons in the terpyridine ligand show exactly the same chemical shift. The ^{13}C NMR spectroscopy analysis of **9** failed, because this complex slowly reacts in acetone to give an unidentified compound. So far we were not able to isolate this compound, but it could be ensured by its NMR spectroscopy data that it is not **5**.



Scheme 4.

3. Experimental section

All reactions were carried out under an atmosphere of argon and in carefully dried solvents. The starting materials $[Mo(CO)_4(C_7H_8)]$ (**1**) [9] and 4,4′,4″-tri-tert-butyl-2,2′ : 6′,2″-terpyridine [10] were prepared by published methods. IR, Shimadzu FT IR–8200D; NMR, JEOL EX 270 FT NMR. Decomposition points were determined using an Yanaco Micro melting-point apparatus.

3.1. Preparation of $[Mo(CO)(C_7H_8)(terpy)I]I$ (2a)

A solution of **1** (478 mg, 1.59 mmol) in 20 ml of CH_2Cl_2 was treated with I_2 (403 mg, 1.59 mmol) and the mixture was stirred for 30 min at room temperature. After addition of 2,2′ : 6′,2″-terpyridine (371 mg, 1.59 mmol) stirring was continued for 1 h and 20 ml of ether was added. The red–brown solid that separated was filtered off, washed with CH_2Cl_2 : ether (1 : 1) and dried in vacuum, (yield, 998 mg (89%); decomposition temperature, 184°C). Anal. Found: C, 36.51; H, 2.76; N, 5.51. $C_{23}H_{19}I_2MoN_3O$ calc.: C, 39.29; H, 2.72; N, 5.98%. IR (KBr): ν(CO) 1937 (vs), 1925 (vs) cm^{-1}. ^1H NMR (acetone-d_6, 270 MHz): δ 8.95 (d; J(HH) = 7.9 Hz; 2H; H(9)), 8.87 (d; J(HH) = 8.1 Hz; 2H; H(3)), 8.68 (d; J(HH) = 5.7 Hz; 2H; H(6)), 8.67 (t; J(HH) = 7.9 Hz; 1H; H(10)), 8.35 (ddd; J(HH) = 8.1, 7.8 and 1.3 Hz; 2H; H(4)), 7.70 (ddd; J(HH) = 7.8, 5.7 and 1.3 Hz; 2H; H(5)), 4.31 and 2.23 (both ddd; J(HH) = 4.0, 4.0 and 1.0 Hz; both 2H; =CH and =CH′), 4.02 and 2.98 (both m; both 1H; CH and CH′), 1.37 (s, br; 2H; CH_2) ppm.

3.2. Preparation of $[Mo(CO)(C_7H_8)(4,4',4''\text{-}{}^tBu_3\text{-}terpy)I]I$ (3a)

A solution of **1** (426 mg, 142 mmol) in 10 ml of CH_2Cl_2 was treated with I_2 (360 mg, 1.42 mmol) and the mixture was stirred for 30 min at room temperature. After addition of 4,4′,4″-tri-tert-butyl-2,2′ : 6′,2″-terpyridine (570 mg, 1.42 mmol), stirring was continued for 1 h and 30 ml of ether was added. The red solid that separated was filtered off, washed with CH_2Cl_2: ether (1 : 3) and dried in vacuum, (yield, 918 mg (74%); decomposition temperature, 181°C). Anal. Found: C, 48.49; H, 5.04; N, 4.81. $C_{35}H_{43}I_2MoN_3O$ calc.: C, 48.24; H, 4.97; N, 4.82%. IR (KBr): ν(CO) 1928 (sh), 1909 (vs) cm^{-1}. IR (CH_2Cl_2): ν(CO) 1937 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz): δ 8.62 (s; 2H; H(9)), 8.55 (d; J(HH) = 2.0 Hz; 2H; H(3)), 8.27 (d; J(HH) = 5.9 Hz; 2H; H(6)), 7.41 (dd; J(HH) = 5.9 and 2.0 Hz; 2H; H(5)), 3.95 and 3.19 (both s, br; both 1H; CH and CH′), 3.90 and 2.10 (both dd, br; J(HH) = 4.4 and 4.4 Hz; both 2H; =CH and =CH′), 1.71 (s; 9H;

C(10)CCH$_3$), 1.48 (s; 18H; C(4)CCH$_3$), 1.38 (s, br; 2H; CH$_2$) ppm. ^{13}C NMR ($CDCl_3$, 67.8 MHz): δ 222.64 (CO), 164.98, 164.94, 154.85, 154.40, 152.54, 125.16, 122.16 and 122.12 (C(2)–C(10)), 66.84, 63.23, 57.76, 44.10 and 42.39 (=CH,=CH′, CH, CH′ and CH$_2$), 36.74 (C(10)*C*CH$_3$), 36.07 (C(4)*C*CH$_3$), 31.14 (C(10)C*C*H$_3$), 30.61 (C(4)C*C*H$_3$) ppm.

3.3. Preparation of [Mo(CO)(C_7H_8)(terpy)I]PF_6 (2b)

A suspension of **2a** (217 mg, 0.31 mmol) in 10 ml of methanol was treated with KPF_6 (60 mg, 0.33 mmol) and the mixture was stirred for 1 h at room temperature. The red solid that separated was filtered off, washed with methanol and ether and dried in vacuum, (yield, 196 mg (88%); decomposition temperature, 182°C). Anal. Found: C, 38.06; H, 2.82; N, 5.61. $C_{23}H_{19}F_6IMoN_3OP$ calc.: C, 38.30; H, 2.66; N, 5.83%. IR (KBr): ν(CO) 1947 (vs), 1929(vs), ν(PF) 850(vs) cm^{-1}. ^{1}H NMR (acetone-d_6, 270 MHz): δ 8.95 (d; J(HH) = 7.9 Hz; 2H; H(9)), 8.87 (dd; J(HH) = 7.9 and 1.3 Hz; 2H; H(3)), 8.69 (dd; J(HH) = 5.6 and 1.3 Hz; 2H; H(6)), 8.67 (t; J(HH) = 7.9 Hz; 1H; H(10)), 8.35 (ddd; J(HH) = 7.9, 7.9 and 1.3 Hz; 2H; H(4)), 7.70 (ddd; J(HH) = 7.9, 5.6 and 1.3 Hz; 2H; H(5)), 4.31 and 2.22 (both dd; J(HH) = 4.3 and 4.3 Hz; both 2H; =CH and =CH′), 4.00 and 2.97 (both m; both 1H; CH and CH′), 1.37 (s, br; 2H; CH$_2$) ppm.

3.4. Preparation of [Mo(CO)(C_7H_8)(terpy)I]SbF_6 (2c)

A suspension of **2a** (186 mg, 0.27 mmol) in 10 ml of acetone was slowly treated with a solution of $AgSbF_6$ (91 mg, 0.27 mmol) in 10 ml of acetone and the mixture was stirred for 30 min at room temperature and then filtered through cellulose. The filtrate was concentrated to about 5 ml in vacuum, and 30 ml of ether was added. The red solid that separated was filtered off, washed with pentane and dried in vacuum (yield, 191 mg (89%); decomposition temperature, 162°C). Anal. Found: C, 33.41; H, 2.46; N, 4.84. $C_{23}H_{19}F_6IMoN_3OSb$ calc.: C, 34.02; H, 2.36; N, 5.18%. IR (KBr): ν(CO) 1943(vs), 1930(vs), ν(SbF) 660(vs) cm^{-1}. IR (CH_2Cl_2): ν(CO) 1941(vs), ν(SbF) 660(vs)cm^{-1} ^{1}H NMR (acetone-d_6, 270 MHz): δ 8.93 (d; J(HH) = 7.9 Hz; 2H; H(9)), 8.85 (dd; J(HH) = 8.0 and 1.3 Hz; 2H; H(3)), 8.68 (dd; J(HH) = 5.7 and 1.3 Hz; 2H; H(6)), 8.65 (dd; J(HH) = 7.9 and 7.9 Hz; 1H; H(10)), 8.34 (ddd; J(HH) = 8.0, 7.8 and 1.3 Hz; 2H; H(4)), 7.69 (ddd; J(HH) = 7.8, 5.7 and 1.3 Hz; 2H; H(5)), 4.31 and 2.22 (both ddd; J(HH) = 4.1, 4.1 and 1.0 Hz; both 2H; =CH and =CH′), 3.99 and 2.97 (both m; both 1H; CH and CH′), 1.37 (dd; J(HH) = 1.3 and 1.3 Hz; 2H; CH$_2$) ppm. ^{13}C NMR (acetone-d_6, 67.8 MHz): δ 224.63 (CO), 156.84, 156.57, 155.34, 141.89, 141.86, 130.10, 126.64 and 126.04 (C(2)–C(10)), 68.15, 64.93, 58.93, 45.56 and 43.55 (=CH, =CH′, CH, CH′ and CH$_2$) ppm.

3.5. Preparation of [Mo(CO)(C_7H_8)(4,4′,4″-^{t}Bu$_3$-terpy)I]PF_6 (3b)

A suspension of **3a** (119 mg, 0.15 mmol) in 10 ml of methanol was treated with KPF_6 (30 mg, 0.16 mmol) and the mixture was stirred for 1 h at room temperature. The solvent was removed in vacuum and the residue extracted three times with 5 ml of CH_2Cl_2. The combined extracts were taken to dryness under vacuum and the residue recrystallized from CH_2Cl_2: ether to give an red solid (yield, 123 mg (95%); decomposition, temperature, 158°C). Anal. Found: C, 47.43; H, 4.90; N, 4.70. $C_{35}H_{43}F_6IMoN_3OP$ calc.: C, 47.26; H, 4.87; N, 4.72%. IR (KBr): ν(CO) 1934(vs), 1910(vs), ν(PF) 850(vs) cm^{-1}. IR (CH_2Cl_2): ν(CO) 1938(vs), ν(PF) 850(vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 8.40 (s; 2H; H(9)), 8.33 (d; J(HH) = 1.8 Hz; 2H; H(3)), 8.25 (d; J(HH) = 6.0 Hz; 2H; H(6)), 7.42 (dd; J(HH) = 6.0 and 1.8 Hz; 2H; H(5)), 3.91 and 3.03 (both s, br; both 1H; CH and CH′), 3.90 and 2.03 (both dd, br; J(HH) = 4.3 and 4.3 Hz; both 2H; =CH and =CH′), 1.62 (s; 9H; C(10)CCH3), 1.43 (s; 18H; C(4)CCH3), 1.34 (s, br; 2H; CH$_2$) ppm. ^{13}C NMR ($CDCl_3$, 67.8 MHz): δ 222.72 (CO), 164.93, 164.88, 154.74, 154.46, 152.33, 125.16, 121.22 and 121.20 (C(2)–C(10)), 66.75, 63.31, 57.66, 43.94 and 41.80 (=CH,=CH′, CH, CH′ and CH$_2$), 36.34 (C(10)*C*CH$_3$), 35.84 (C(4)*C*CH$_3$), 30.50 (C(10)C*C*H$_3$), 30.22 (C(4)C*C*H$_3$) ppm.

3.6. Preparation of [Mo(CO)(C_7H_8)(4,4′,4″-^{t}Bu$_3$-terpy)I]SbF_6 (3c)

A solution of **3a** (248 mg, 0.30 mmol) in 10 ml of CH_2Cl_2 was slowly treated with a solution of $AgSbF_6$ (104 mg, 0.30 mmol) in 10 ml of CH_2Cl_2 and the mixture was stirred for 30 min at room temperature and then filtered through cellulose. The filtrate was concentrated to about 5 ml in vacuum, and 50 ml of ether was added. The red solid that separated was filtered off, washed with pentane and dried in vacuum (yield, 247 mg (83%); decomposition temperature, 179°C). Anal. Found: C, 42.41; H, 4.40; N, 4.19. $C_{35}H_{43}F_6IMoN_3OSb$ calc.: C, 42.88; H, 4.42; N, 4.29%. IR (KBr): ν(CO) 1932(vs), 1913(vs), ν(SbF) 660(vs) cm^{-1}. IR (CH_2Cl_2): ν(CO) 1938 (vs), ν(SbF) 660(vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 8.41 (s; 2H; H(9)), 8.34 (d; J(HH) = 2.0 Hz; 2H; H(3)), 8.23 (d; J(HH) = 5.9 Hz; 2H; H(6)), 7.41 (dd; J(HH) = 5.9 and 2.0 Hz; 2H; H(5)), 3.88 and 2.98 (both s, br; both 1H; CH and CH′), 3.91 and 2.03 (both dd, br; J(HH) = 4.4 and 4.4 Hz; both 2H; =CH and =CH′), 1.61 (s; 9H; C(10)CCH3), 1.42 (s; 18H; C(4)CCH3), 1.33 (s, br; 2H; CH$_2$) ppm. ^{13}C NMR ($CDCl_3$, 67.8 MHz): δ 222.72 (CO), 164.99,

164.93, 154.73, 154.52, 152.32, 125.19, 121.24 and 121.13 (C(2)–C(10)), 66.67, 63.34, 57.67, 43.92 and 41.84 (=CH, =CH′, CH, CH′ and CH_2), 36.34 (C(10)CCH_3), 35.83 (C(4)CCH_3), 30.50 (C(10)CCH_3), 30.20 (C(4)CCH_3) ppm.

3.7. Preparation of [Mo(CO)(C_7H_8)(terpy)Br]Br (4a)

A solution of **1** (314 mg, 1.05 mmol) in 30 ml of CH_2Cl_2 was treated with $CuBr_2$ (467 mg, 2.09 mmol) and the mixture was stirred for 1 h at room temperature and then filtered though cellulose. The filtrate was treated with 2,2′ : 6′,2″-terpyridine (245 mg, 1.05 mmol), stirring was continued for 1 h and 30 ml of ether was added. The red–brown solid that separated was filtered off, washed with CH_2Cl_2 : ether (1 : 1) and dried in vacuum (yield, 559 mg (87%); decomposition temperature, 163°C). Anal. Found: C, 44.79; H, 3.40; N, 6.81. $C_{23}H_{19}Br_2MoN_3O$ calc.: C, 45.35; H, 3.14; N, 6.90%. IR (KBr): ν(CO) 1927(vs) cm^{-1}. ^1H NMR (acetone-d_6, 270 MHz): δ 9.00 (d; J(HH) = 7.9 Hz; 2H; H(9)), 8.91 (dd; J(HH) = 8.2 and 1.3 Hz; 2H; H(3)), 8.65 (t; J(HH) = 7.9 Hz; 1H; H(10)), 8.60 (dd; J(HH) = 5.6 and 1.3 Hz; 2H; H(6)), 8.35 (ddd; J(HH) = 8.2, 7.8 and 1.3 Hz; 2H; H(4)), 7.74 (ddd; J(HH) = 7.8, 5.6 and 1.3 Hz; 2H; H(5)), 4.36 and 2.39 (both ddd; J(HH) = 4.3, 4.3 and 1.0 Hz; both 2H; =CH and =CH′), 3.97 and 3.01 (both s, br; both 1H; CH and CH′), 1.35 (dd; J(HH) = 1.3 and 1.3 Hz; 2H; CH_2).

3.8. Preparation of [Mo(CO)(C_7H_8)(terpy)Br]PF_6 (4b)

A solution of **4a** (55 mg, 0.09 mmol) in 15 ml of methanol was treated with KPF_6 (20 mg, 0.11 mmol) and the mixture was stirred for 1 h at room temperature. The red solid that separated was filtered off, washed with methanol and ether and dried in vacuum (yield, 49 mg (78%); decomposition temperature 168°C). Anal. Found: C, 40.52; H, 3.16; N, 5.92. $C_{23}H_{19}BrF_6MoN_3OP$ calc.: C, 40.97; H, 2.84; N, 6.23%. IR (KBr): ν(CO) 1952(vs), 1938(vs), ν(PF) 850(vs) cm^{-1}. ^1H NMR (acetone-d_6, 270 MHz): δ 8.91 (d; J(HH) = 7.9 Hz; 2H; H(9)), 8.82 (ddd; J(HH) = 7.9, 1.3 and 0.7 Hz; 2H; H(3)), 8.65 (dd; J(HH) = 7.9 and 7.9 Hz; 1H; H(10)), 8.60 (ddd; J(HH) = 5.6, 1.7 and 0.7 Hz; 2H; H(6)), 8.35 (ddd; J(HH) = 7.9, 7.9 and 1.7 Hz; 2H; H(4)), 7.75 (ddd; J(HH) = 7.9, 5.6 and 1.3 Hz; 2H; H(5)), 4.35 and 2.39 (both ddd; J(HH) = 4.3, 4.3 and 1.3 Hz; both 2H; =CH and =CH′), 3.97 and 3.00 (both m; both 1H; CH and CH′), 1.36 (s, br; 2H; CH_2) ppm.

3.9. Preparation of [Mo(CO)(C_7H_8(terpy)Br]SbF_6 (4c)

A suspension of **4a** (347 mg, 0.57 mmol) in 20 ml of acetone was slowly treated with a solution of $AgSbF_6$ (196 mg, 0.57 mmol) in 10 ml of acetone and the mixture was stirred for 1 h at room temperature and then filtered through cellulose. The filtrate was concentrated to about 10 ml in vacuum, and 50 ml of ether was added. The red solid that separated was filtered off, washed with ether and dried in vacuum (yield, 392 mg (90%); decomposition temperature, 157°C). Anal. Found: C, 35.72; H, 2.71; N, 5.36. $C_{23}H_{19}BrF_6MoN_3OSb$ calc.: C, 36.11; H, 2.50; N, 5.49%. IR (KBr): ν(CO) 1939(vs), ν(SbF) 660(vs) cm^{-1}. ^1H NMR (acetone-d_6, 270 MHz): δ 8.91 (d; J(HH) = 7.9 Hz; 2H; H(9)), 8.82 (ddd; J(HH) = 8.2, 1.3 and 1.0 Hz; 2H; H(3)), 8.65 (dd; J(HH) = 7.9 and 7.9 Hz; 1H; H(10)), 8.60 (ddd; J(HH) = 5.6, 1.7 and 1.0 Hz; 2H; H(6)), 8.35 (ddd; J(HH) = 8.2, 7.6 and 1.7 Hz; 2H; H(4)), 7.75 (ddd; J(HH) = 7.6, 5.6 and 1.3 Hz; 2H; H(5)), 4.35 and 2.39 (both ddd; J(HH) = 4.2, 4.2 and 1.3 Hz; both 2H; =CH and =CH′), 3.97 and 2.99 (both m; both 1H; CH and CH′), 1.36 (dd; J(HH) = 1.3 and 1.3 Hz; 2H; CH_2) ppm. ^{13}C NMR (acetone-d_6, 67.8 MHz): δ 224.91 (CO), 157.01, 156.24, 154.41, 142.01, 141.94, 130.44, 126.46 and 125.96 (C(2)–C(10)), 66.15, 63.99, 58.70, 45.30 and 43.77 (=CH, =CH′, CH, CH′ and CH_2) ppm.

3.10. Preparation of {[Mo(CO)(C_7H_8)(terpy)]$_2$-(acetone)}$(SbF_6)_4$ (5)

(i) A suspension of **2a** (112 mg, 0.16 mmol) in 20 ml of acetone was slowly treated with a solution of $AgSbF_6$ (109 mg, 0.32 mmol) in 10 ml of acetone and the mixture was stirred for 30 min at room temperature and then filtered through cellulose. The filtrate was taken to dryness under vacuum and the residue washed with CH_2Cl_2 : pentane (1 : 1) three times to give an orange–red solid (yield, 127 mg (84%); decomposition temperature, 154°C).

(ii) As described for (i) but starting from **4a** (224 mg, 0.37 mmol) and $AgSbF_6$ (253 mg, 0.74 mmol) gave a yield of 303 mg (86%). Anal. Found: C, 30.27; H, 2.34; N, 4.55. $C_{49}H_{44}F_{24}Mo_2N_6O_3Sb_4$ calc.: C, 30.98; H, 2.33; N, 4.22%. IR (KBr): ν(CO) 1970(vs), 1935(sh), ν(C=O) 1645(m), ν(SbF) 660(vs) cm^{-1}. IR (acetone): ν(CO) 1946(vs), ν(SbF), 660(vs) cm^{-1}. ^1H NMR (acetone-d_6, 270 MHz): δ 8.99 and 8.92 (both d; J(HH) = 7.9 Hz; both 2H; H(9)), 8.89 and 8.86 (both dd; J(HH) = 7.9 and 1.3 Hz; both 2H; H(3)), 8.81 (dd; J(HH) = 5.3 and 1.7 Hz; 2H; H(6)), 8.74 and 8.73 (both dd; J(HH) = 7.9 and 7.9 Hz; both 1H; H(10)), 8.53 and 8.45 (both ddd; J(HH) = 7.9, 7.6 and 1.7 Hz; both 2H; H(4)), 8.11 (dd; J(HH) = 5.9 and 1.7 Hz; 2H; H(6)), 8.00 (ddd; J(HH) = 7.6, 5.9 and 1.3 Hz; 2H; H(5)), 7.94 (ddd; J(HH) = 7.6, 5.3 and 1.3 Hz; 2H; H(5)), 4.97 (dd; J(HH) = 4.3 and 4.3 Hz; 2H; =CH), 4.76 (ddd; J(HH) = 4.3, 4.3 and 1.3 Hz; 2H; =CH), 4.14 (m, 3H, =CH and CH), 4.02, 3.96 and 3.15 (all m; all 1H; CH), 2.82 (ddd; J(HH) = 4.3, 4.3 and 1.0 Hz; 2H;

=CH), 2.16 (s; 2H; CH_2), 2.09 (s; 6H; acetone), 1.43 (t; J(HH) = 1.3 Hz; 2H; CH_2) ppm. ^{13}C NMR (acetone-d_6, 67.8 MHz): δ 224.71 and 217.75 (CO), 158.50, 157.70, 157.23, 156.92, 154.24, 150.83, 145.31, 144.21, 143.89, 143.44, 131.74, 130.94, 127.04, 127.02, 126.65 and 126.19 (C(2)–C(10)), 72.62, 68.83, 67.40, 67.37, 66.41, 60.33, 59.49, 44.96, 44.10, 43.93 and 42.54 (=CH, CH, and CH_2), 31.46 (s; acetone) ppm.

3.11. Preparation of $[Mo(CO)(C_7H_8)(terpy)PMe_3](SbF_6)_2 \cdot$ acetone (6)

A suspension of **2a** (320 mg, 0.46 mmol) in 20 ml of acetone was slowly treated with a solution of $AgSbF_6$ (312 mg, 0.91 mmol) in 10 ml of acetone and the mixture was stirred for 1 h at room temperature and then filtered through cellulose. The filtrate was treated with 0.5 ml of a 1 molar solution of PMe_3 in tetrahydrofuran, stirring was continued for 30 min and 50 ml of ether was added. The orange–red solid that separated was filtered off, washed with ether and dried in vacuum (yield, 381 mg (79%), decomposition temperature, 197°C). Anal. Found: C, 32.79; H, 3.13; N, 3.98. $C_{29}H_{34}F_{12}MoN_3O_2PSb_2$ calc.: C, 33.02; H, 3.25; N, 3.98%. IR (KBr): ν(CO) 1934(vs), ν(C=O) 1700(s), ν(SbF) 660(vs) cm^{-1}. ^{1}H NMR (acetone-d_6, 270 MHz): δ 9.07 (d; J(HH) = 8.3 Hz; 2H; H(9)), 9.04 (dd; J(HH) = 8.3 and 1.3 Hz; 2H; H(3)), 8.78 (dt; J(PH) = 1.7 Hz, J(HH) = 8.3 Hz; 1H; H(10)), 8.62 (dd; J(HH) = 5.6 and 1.7 Hz; 2H; H(6)), 8.55 (ddd; J(HH) = 8.3, 7.9 and 1.7 Hz; 2H; H(4)), 7.93 (ddd; J(HH) = 7.9, 5.6 and 1.3 Hz; 2H; H(5)), 4.97 and 2.59 (both dd; J(HH) = 4.3 and 4.3 Hz; both 2H; =CH and =CH′), 4.16 and 3.12 (both s, br; both 1H; CH and CH′), 2.09 (s; 6H; acetone), 1.50 (s; 2H; CH_2), 1.05 (d; J(PH) = 10.6 Hz; 9H; PCH_3) ppm. ^{13}C NMR (acetone-d_6, 67.8 MHz): δ 224.67 (d; J(PC) = 21.1 Hz; CO), 156.67 (d; J(PC) = 1.8 Hz), 155.90 (s), 155.38 (d; J(PC) = 2.8 Hz), 143.64 (d; J(PC) = 2.8 Hz), 142.52 (d; J(PC) = 1.8 Hz), 131.30 (d; J(PC) = 1.8 Hz), 127.96 (s) and 127.37 (s; C(2)–C(10)), 79.30 (s), 75.11 (s), 60.98 (s), 46.14 (s) and 45.84 (d; J(PC) = 1.8 Hz; =CH, =CH′, CH, CH′ and CH_2), 31.44 (s; acetone), 12.24 (d; J(PC) = 28.5 Hz; PCH_3) ppm.

3.12. Preparation of $[Mo(CO)(C_7H_8)(terpy)NCCH_2CH_3](SbF_6)_2$ (7)

A suspension of **2a** (235 mg, 0.33 mmol) in 20 ml of acetone was slowly treated with a solution of $AgSbF_6$ (230 mg, 0.67 mmol) in 10 ml of acetone and the mixture was stirred for 1 h at room temperature and then filtered through cellulose. The filtrate was treated with propionitrile (120 μl, 1.68 mmol), stirring was continued for 30 min and 50 ml of ether was added. The orange–red solid that separated was filtered off, washed with ether and dried in vacuum (yield, 296 mg (91%); decomposition temperature, 153°C). Anal. Found: C, 31.83; H, 2.57; N, 5.55. $C_{26}H_{24}F_{12}MoN_4OSb_2$ calc.: C, 32.00; H, 2.48; N, 5.74%. IR (KBr): ν(CN) 2283(w), ν(CO) 1991(vs), 1953(vs), ν(SbF) 660(vs) cm^{-1}. IR (CH_2Cl_2): ν(CN) 2291(w), ν(CO) 1975(vs), ν(SbF) 660(vs) cm^{-1}. ^{1}H NMR (acetone-d_6, 270 MHz): δ 8.99 (d; J(HH) = 7.9 Hz; 2H; H(9)), 8.85 (ddd; J(HH) = 7.9, 1.3 and 1.3 Hz; 2H; H(3)), 8.73 (dd; J(HH) = 7.9 and 7.9 Hz; 1H; H(10)), 8.43 (ddd; J(HH) = 7.9, 5.3 and 5.3 Hz; 2H; H(4)), 7.97 (dd; J(HH) = 5.3 and 1.3 Hz; 4H; H(5) and H(6)), 4.93 and 4.29 (both dd; J(HH) = 4.3 and 4.3 Hz; both 2H; =CH and =CH′), 4.11 and 3.95 (both m; both 1H; CH and CH′), 2.48 (q; J(HH) = 7.6 Hz; 2H; CH_2CH_3), 2.13 (t; J(HH) = 1.0 Hz; 2H; CH_2), 0.97 (t; J(HH) = 7.6 Hz; 3H; CH_2CH_3) ppm. ^{13}C NMR (acetone-d_6, 67.8 MHz): δ 214.49 (CO), 157.49, 157.04, 156.95, 145.04, 143.21, 130.90, 127.19 and 126.36 (C(2)–C(10)), 133.76 (CN), 71.09, 68.64, 60.44, 43.23 and 42.65 (=CH, =CH′, CH, CH′ and CH_2), 13.50 and 10.59 (CH_2CH_3 and CH_2CH_3) ppm.

3.13. Preparation of $[Mo(CO)(C_7H_8)(terpy)N_3]SbF_6$ (8)

A suspension of **4a** (320 mg, 0.53 mmol) in 20 ml of acetone was slowly treated with a solution of $AgSbF_6$ (361 mg, 1.05 mmol) in 10 ml of acetone and the mixture was stirred for 30 min at room temperature and then filtered through cellulose. The filtrate was taken to dryness under vacuum, the residue solved in 20 ml of methanol and NaN_3 (35 mg, 0.54 mmol) was added. The violet–red solid that separated by stirring for 2 h was filtered off, washed with methanol and ether and dried in vacuum (yield, 293 mg (77%); decomposition temperature, 128°C). Anal. Found: C, 37.63; H, 2.73; N, 11.24. $C_{23}H_{19}F_6MoN_6OSb$ calc.: C, 37.99; H, 2.63; N, 11.56%. IR (KBr): ν(N3) 2045(vs), ν(CO) 1938(vs), ν(SbF) 660(vs) cm^{-1}. ^{1}H NMR (acetone-d_6, 270 MHz): δ 8.83 (d; J(HH) = 7.9 Hz; 2H; H(9)), 8.78 (dd; J(HH) = 7.9 and 1.3 Hz; 2H; H(3)), 8.60 (dd; J(HH) = 7.9 and 7.9 Hz; 1H; H(10)), 8.54 (dd; J(HH) = 5.6 and 1.3 Hz; 2H; H(6)), 8.37 (ddd; J(HH) = 7.9, 7.6 and 1.3 Hz; 2H; H(4)), 7.80 (ddd; J(HH) = 7.6, 5.6 and 1.3 Hz; 2H; H(5)), 4.39 (dd; J(HH) = 4.3 and 4.3 Hz; 2H; =CH), 3.89 and 3.02 (both s, br; both 1H; CH and CH′), 2.47 (dd; J(HH) = 4.6 and 4.6 Hz; 2H; =CH′), 1.30 (s; 2H; CH_2) ppm. ^{13}C NMR (acetone-d_6, 67.8 MHz): δ 225.24 (CO), 157.04, 155.74, 153.26, 142.28, 142.21, 130.75, 126.43 and 125.95 (C(2)–C(10)), 66.86, 64.68, 58.37, 45.29 and 44.53 (=CH, =CH′, CH, CH′ and CH_2) ppm.

3.14. Preparation of $[Mo(CO)(C_7H_8)(terpy)Cl]SbF_6$ (9)

A suspension of **2a** (309 mg, 0.44 mmol) in 20 ml of acetone was slowly treated with a solution of $AgSbF_6$

(302 mg, 0.88 mmol) in 10 ml of acetone and the mixture was stirred for 30 min at room temperature and then filtered through cellulose. The filtrate was taken to dryness under vacuum, the residue solved in 20 ml of methanol and NaCl (30 mg, 0.51 mmol) was added. The violet–red solid that separated by stirring for 3 h was filtered of, washed with methanol and ether and dried in vacuum (yield, 283 mg (90%); decomposition temperature, 164°C). Anal. Found: C, 38.23; H, 2.76; N, 5.76. $C_{23}H_{19}ClF_6MoN_3OSb$ calc.: C, 38.34; H, 3.22; N, 5.83%. IR (KBr): ν(CO) 1923(vs), ν(SbF) 660(vs) cm^{-1}. ^1H NMR (acetone-d_6, 270 MHz): δ 8.92 (d; J(HH) = 8.3 Hz; 2H; H(9)), 8.80 (ddd; J(HH) = 7.9, 1.3 and 1.3 Hz; 2H; H(3)), 8.64 (dd; J(HH) = 8.3 and 8.3 Hz; 1H; H(10)), 8.36 (ddd; J(HH) = 7.9, 5.3 and 5.3 Hz; 2H; H(4)), 7.91 (dd; J(HH) = 5.3 and 1.3 Hz; 4H; H(5) and H(6)), 4.58 and 3.64 (both dd; J(HH) = 4.3 and 4.3 Hz; both 2H; =CH and =CH′), 3.91 and 3.86 (both m; both 1H; CH and CH′), 2.82 (s; 2H; CH_2) ppm.

3.15. Crystal structure analysis of 4c

Single crystals were grown from CH_2Cl_2: pentane. Crystal data: monoclinic; space group, $P2_1/a$ (No. 14); a = 14.2114(1) Å, b = 13.860(1) Å and c = 12.673(1) Å; V = 2495.9(3) Å^3; Z = 4, d_{calc} = 2.036 g cm^{-3}; μ(Mo Kα) = 32.55 cm^{-1}; crystal size, 0.2 × 0.15 × 0.15 mm: Enraf–Nonius CAD4 FR590 diffractometer: Mo Kα radiation (λ = 0.710 69 Å); graphite monochromator; T = 293 K; ω–2Θ scan; maximum 2Θ = 54.9°; 6225 reflections were measured, 4516 were regarded as being observed ($F_0 > 3\sigma(F_0)$); intensity data were corrected by Lorentz and polarization effects; empirical absorption correction was applied by using the program DIFABS [11]; minimum transmission was

Table 2
Positional parameters for **4c**, with estimated standard deviations

Atom	x	y	z	B_{eq} (Å)
Sb	0.229854(38)	0.193932(43)	0.197045(44)	5.71(1)
Mo	0.097579(30)	0.753179(32)	0.271411(37)	2.368(9)
Br	0.230097(40)	0.659940(44)	0.382168(51)	3.53(1)
F(1)	0.20531(48)	0.30229(43)	0.27086(53)	11.2(2)
F(2)	0.09941(38)	0.18700(56)	0.17479(52)	11.8(2)
F(3)	0.21383(52)	0.11964(58)	0.31953(50)	13.4(3)
F(4)	0.24370(47)	0.07722(43)	0.12855(55)	11.7(2)
F(5)	0.35288(38)	0.19538(43)	0.22609(77)	14.1(3)
F(6)	0.23573(47)	0.25331(44)	0.07046(52)	11.4(2)
O	0.27742(27)	0.85629(32)	0.19061(40)	4.9(1)
N(1)	0.10256(30)	0.60906(32)	0.19353(37)	3.0(1)
N(2)	0.00406(29)	0.66019(31)	0.35646(35)	2.6(1)
N(3)	0.08922(30)	0.81253(33)	0.43263(38)	3.0(1)
C(1)	0.21117(38)	0.81840(40)	0.21838(50)	3.3(1)
C(2)	0.15900(43)	0.58535(45)	0.11355(49)	3.8(1)
C(3)	0.15123(54)	0.49689(55)	0.06384(57)	5.2(2)
C(4)	0.08494(58)	0.43177(51)	0.09530(62)	5.5(2)
C(5)	0.02708(48)	0.45560(44)	0.17608(57)	4.4(2)
C(6)	0.03669(39)	0.54476(40)	0.22496(48)	3.2(1)
C(7)	−0.01743(36)	0.57291(39)	0.31767(47)	3.0(1)
C(8)	−0.08064(40)	0.51364(43)	0.36952(56)	3.9(1)
C(9)	−0.11757(41)	0.54495(48)	0.46216(60)	4.4(2)
C(10)	−0.08927(41)	0.63096(49)	0.50554(52)	4.1(1)
C(11)	−0.02467(36)	0.68687(40)	0.45200(45)	3.0(1)
C(12)	0.02313(37)	0.77379(41)	0.49523(45)	3.0(1)
C(13)	0.00707(48)	0.80891(50)	0.59458(54)	4.4(2)
C(14)	0.06086(58)	0.88419(61)	0.63215(58)	5.8(2)
C(15)	0.12859(53)	0.92499(52)	0.57059(62)	5.2(2)
C(16)	0.14032(43)	0.88678(46)	0.47108(53)	4.1(2)
C(17)	0.06558(46)	0.79882(45)	0.09537(47)	3.8(1)
C(18)	−0.01562(41)	0.75541(42)	0.13570(47)	3.4(1)
C(19)	0.05959(40)	0.91307(40)	0.23182(51)	3.4(1)
C(20)	−0.02155(38)	0.86766(39)	0.26963(49)	3.2(1)
C(21)	0.05115(45)	0.90732(46)	0.11191(52)	4.1(2)
C(22)	−0.07819(41)	0.83506(45)	0.17281(51)	3.7(1)
C(23)	−0.05666(48)	0.91574(46)	0.09401(54)	4.5(2)

[a] Anisotropically refined atoms are given in form of the isotropic equivalent displacement parameter defined as $(\frac{4}{3})[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

84%. The structure was solved by heavy-atom Patterson methods; atomic coordinates (Table 2) and anisotropic thermal parameters of the non-hydrogen atoms were refined by the full-matrix least-squares method (325 parameters; $w = 1/\sigma^2(F_0)$. The hydrogen atoms were placed in calculated positions (distance C–H, 0.95 Å). $R = 0.049$ and $R_w = 0.051$; rate of number of reflections to number of parameters, 13.9; residual electron density, +2.59, −2.61 electrons $Å^{-3}$. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbh, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-59027, the names of the authors and the journal citation.

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