Norbornadiene(bipyridyl)molybdenum(II) Complexes: Synthesis, Structure and Reactivity of $[Mo(CO)(C_7H_8)(C_{10}H_6R_2N_2)X_2]$ (X = I, Br)☆

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The reaction of $[Mo(CO)_4(C_7H_8)]$ (**1**) with I_2 gave the norbornadienemolybdenum(II) complex $[Mo(CO)_2(C_7H_8)I_2]_{n\geq1}$ (**2**), which existed in an equilibrium of two isomeric forms. In acetonitrile, **2** reversibly formed the adduct $[Mo(CO)_2(C_7H_8)(NCCH_3)I_2]$ (**3**), whereas on treatment with 2,2′-bipyridine or 4,4′-di-2,2′-*t*Bu-bipyridine, it gave stable 7-coordinated molybdenum(II) complexes, $[Mo(CO)(C_7H_8)(C_{10}H_8N_2)I_2]$ (**4**) and $[Mo(CO)(C_7H_8)(C_{10}H_6tBu_2N_2)I_2]$ (**5**), in good yield. In similar reactions, the related dibromomolybdenum compounds $[Mo(CO)(C_7H_8)(C_{10}H_8N_2)Br_2]$ (**6**) and $[Mo(CO)(C_7H_8)(C_{10}H_6tBu_2N_2)Br_2]$ (**7**) were prepared by oxidation of **1** with two equivalents of $CuBr_2$. The X-ray structural analysis of **6** reveals that the geometry around the molybdenum atom is nearly perfectly pentagonal bipyramidal, with the CO and one of the bipyridyl rings perpendicular to the plane formed by the other ligands. The compounds **5** and **6** react with $AgSbF_6$ by halogen abstraction to give cationic complexes, $\{[Mo(CO)(C_7H_8)(C_{10}H_8N_2)Br]SbF_6\}_{n\geq1}$ (**8**) and $\{[Mo(CO)(C_7H_8)(C_{10}H_6tBu_2N_2)I]SbF_6\}_{n\geq1}$ (**9**): In acetone, **8** and **9** reversibly formed the adducts $[Mo(CO)(C_7H_8)(C_{10}H_8N_2)(acetone)Br]SbF_6$ (**8′**) and $[Mo(CO)(C_7H_8)(C_{10}H_6tBu_2N_2)(acetone)I]SbF_6$ (**9′**); while on treatment with PMe_3, the stable monomeric complexes, $[Mo(CO)(C_7H_8)(C_{10}H_8N_2)(PMe_3)Br]SbF_6$ (**10**) and $[Mo(CO)(C_7H_8)(C_{10}H_6tBu_2N_2)(PMe_3)I]SbF_6$ (**11**), were isolated in almost quantitative yield. In the presence of KBr, compound **8′** reverted to the dibromo complex **6**, whereas **9′** reacted to produce a 1:1:2 mixture of **5**, **7** and the bromo(iodo) complex $[Mo(CO)(C_7H_8)(C_{10}H_6tBu_2N_2)BrI]$ (**12**). The same mixture is available from the reaction of **5** with one equivalent of **7**.

Molybdenum(II) complexes are usually prepared through oxidation of the corresponding molybdenum(0) complex[1]. Typically halogens are added oxidatively[2]. Thus molybdenumhexacarbonyl forms two-centered dihalogen complexes $[Mo(CO)_4X_2]_2$, which readily exchange carbonyl groups for other ligands[3]. Reaction of $[Mo(CO)_3(NCCH_3)_3]$ with iodine or bromine gives the monomeric complexes $[Mo(CO)_3(NCCH_3)_2X_2]$. Their chemical properties were recently studied[4].

The norbornadienemolybdenum(0) complex $[Mo(CO)_4(C_7H_8)]$ is closely related to $[Mo(CO)_6]$ and $[Mo(CO)_3N(CCH_3)_3]$, and up to now, has mainly been used to synthesize other molybdenum(0) compounds[5]. For example, stirring with aniline at room temperature is sufficient to cause a total norbornadiene ligand exchange to form $[Mo(CO)_3(NH_2C_6H_5)_3]$, as shown by Werner and Prinz[6]. Here we report the oxidative addition of iodine to the complex $[Mo(CO)_4(C_7H_8)]$, the preparation of the 7-coordinated norbornadiene(bipyridyl)molybdenum(II) complexes $[Mo(CO)(C_7H_8)(C_{10}H_6R_2N_2)X_2]$, their transformation into cationic compounds $[Mo(CO)(C_7H_8)(C_{10}H_6R_2N_2)LX]SbF_6$, and a halogen ligand exchange in the dihalogen complex $[Mo(CO)(C_7H_8)(C_{10}H_6tBu_2N_2)IBr]$.

Reaction of $[Mo(CO)_4(C_7H_8)]$ (1) with I_2

The preparation and chemical behavior of dibromo(norbornadiene)tungsten(II) complexes have been reported by Davidson and coworkers[7]. Heating a suspension of $[W(CO)_4Br_2]_2$ in hexane, in the presence of an excess of norbornadiene, gave the 6-coordinated complex $[W(CO)_2(C_7H_8)Br_2]$. The octahedral structure with carbonyl ligands in the *trans* position was proven by X-ray crystal structure analysis[8].

After adding an equimolar amount of iodine to a CH_2Cl_2 solution of $[Mo(CO)_4(C_7H_8)]$ (**1**), the solution slowly darkens to reddish color and gas evolves. After evaporating all volatile compounds in vacuo, **2** remains as a reddish-brown powder in quantitative yield. The number of CO substituents can not be determined with mass spectrometry, however, elemental analysis confirms the formula $[Mo(CO)_2(C_7H_8)I_2]_{n\geq1}$ (**2**). ^1H- and ^{13}C-NMR spectra show two sets of lines for the norbornadiene ligands, which correspond to the two isomeric forms **2a** and **2b**, and the intensity of which vary from one sample to the next.

The structure of the two isomers can be further elucidated by studying their behaviour in coordinating solvents. In acetonitrile, **2** slowly converts to $[Mo(CO)_2(C_7H_8)(NCCH_3)I_2]$ (**3**). Prolonged drying of **3** in vacuo slowly removes the acetonitrile to form **2**, first through the formation of **2a** and then **2b**.

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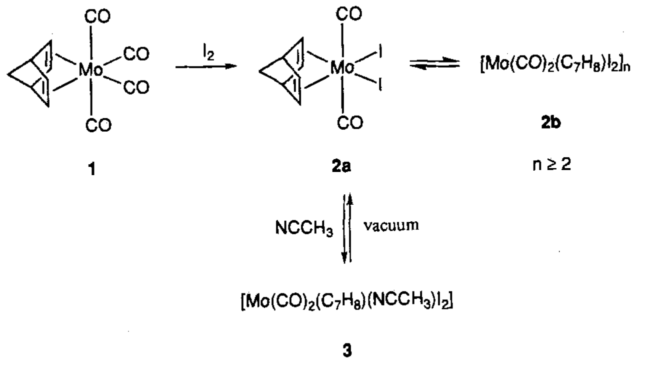
Scheme 1

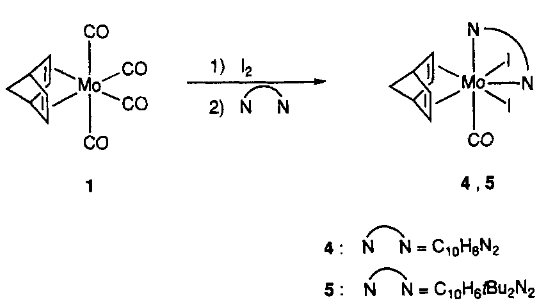


The spectroscopic data of **2a** is in accordance with spectroscopic data for $[W(CO)_2(C_7H_8)Br_2]$[7b]. Therefore we conclude a six-fold coordination for **2a** as shown in Scheme 1. We assume an iodine-bridged multi-centered structure $[Mo(CO)_2(C_7H_8)I_2]_{n\geq2}$ for **2b**, because we find 2 carbonyl signals in the ^{13}C spectra and at least 3 carbonyl stretching modes in the IR spectrum of **2b**. Furthermore, **2b** reacts much slower than **2a** with coordinating solvents.

Synthesis of Complexes $[Mo(CO)(C_7H_8)(C_{10}H_6R_2N_2)X_2]$ (4−7)

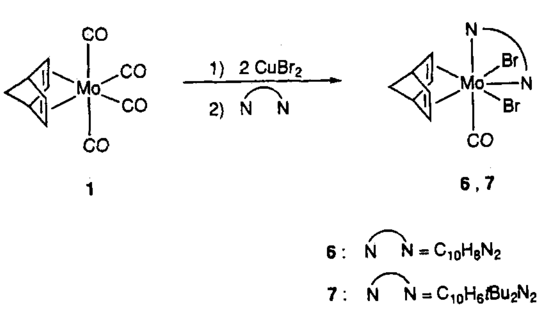
To make more stable complexes, we reacted **2** with bidentate ligands. It was known that $[W(CO)_2(C_7H_8)Br_2]$ and 2,2′-bipyridine react to form $[W(CO)(C_7H_8)(C_{10}H_8N_2)Br_2]$[7b]. Reaction of **2** with 2,2′-bipyridine in CH_2Cl_2 for one hour gives the 7-coordinated complex of $[Mo(CO)(C_7H_8)(C_{10}H_8N_2)I_2]$ (**4**) in a yield of 89%. $[Mo(CO)(C_7H_8)(C_{10}H_6tBu_2N_2)I_2]$ (**5**) is made in the same fashion. In these syntheses of **4** and **5**, $[Mo(CO)_3(C_{10}H_8N_2)I_2]$[9] and $[Mo(CO)_3(C_{10}H_6tBu_2N_2)I_2]$[10], respectively, were formed as by-products and were identified through comparison of spectroscopic data with authentic samples.

Scheme 2



The bromo analogues of **4** and **5** can not be prepared by oxidative addition of bromine. Compound **1**, bromine and 2,2′-bipyridine not only form $[Mo(CO)(C_7H_8)(C_{10}H_8N_2)Br_2]$ (**6**), but also a paramagnetic impurity, which could not be removed despite repeated recrystallizations. Compounds **6** and **7** can be formed with a two-fold excess of $CuBr_2$ as oxidizing agent in CH_2Cl_2 and subsequent treatment with 2,2′-bipyridine (for **6**) or 4,4′-di-*t*Bu-2,2′-bipyridine (for **7**) in yields of approximately 90%.

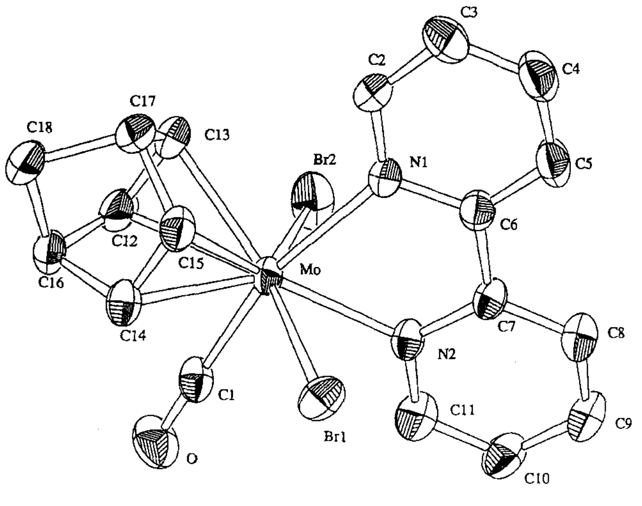
Scheme 3



The norbornadiene complexes **4**−**7** are violet and reddish-violet solids which can be stored for weeks at room temp. without decomposition. Data from the ^1H and ^{13}C spectra led us to conclude, that a mirror plane intersects the C=C double bonds of the norbornadiene ligand. Each proton and carbon of the bipyridyl have their own signal, therefore the two pyridine rings coordinate unsymmetrically.

Figure 1 shows a projection of the crystal structure of **6**. The ligands are coordinated in a slightly twisted pentagonal bipyramidal arrangement which is centered around the metal. The carbonyl ligand and one of the pyridine rings protrude out of the plane formed by the other ligands. The structure deviates from ideal pentagonal bipyramidal geometry is deviated due to the *trans* orientation of carbonyl ligand and pyridine ring. The rigid nature of the bipyridyl ligand, which has a N1−Mo−N2 angle of 72.7(1)°, explains the compression of the N1−Mo−C1 angle to 165.3(2)°.

Figure 1. Projection of the crystal structure of **6**; selected bond lengths [Å] and angles [°]: Mo−Br1 2.6809(6), Mo−Br2 2.6496(7), Mo−N1 2.277(4), Mo−N2 2.226(4), Mo−C1 1.931(5), O−C1 1.150(5); N1−Mo−C1 165.3(2), N1−Mo−N2 72.7(1), Br1−Mo−N1 85.2(1), Br1−Mo−N2 72.61(9), Br1−Mo−C1 89.6(1), N2−Mo−C1 92.6(2)

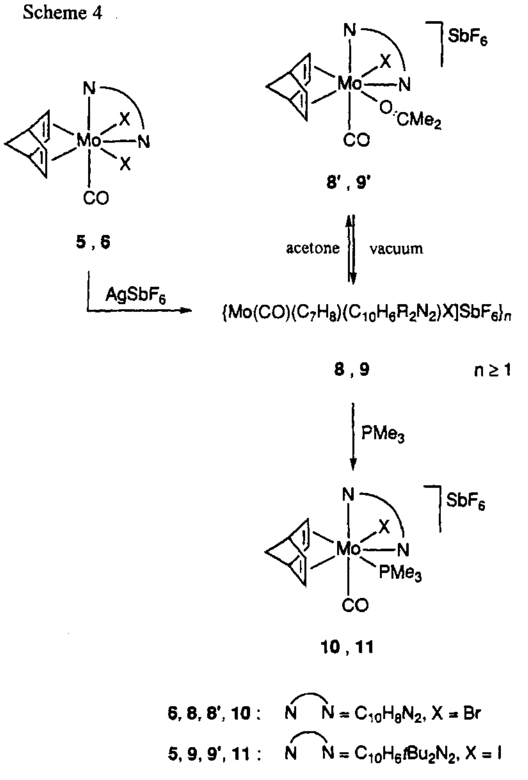


As far as we know, **6** is the first carbonylmolybdenum(II) complex with a pentagonal bipyramidal arrangement of the ligands[11]. Other 7-coordinated molybdenum(II) compounds often show capped octahedral (e.g., $[Mo(CO)_3(C_{10}H_8N_2)(SnMeCl_2)Cl]$[12]) and capped trigonal prismatic geometries (e.g., $[Mo(CO)_3(C_{10}H_8N_2)(HgCl)Cl]$[13]).

Reactions of Complexes 5 and 6

Cationic compounds are formed from the neutral complexes $[Mo(CO)(C_7H_8)(C_{10}H_6R_2N_2)X_2]$ via abstraction of one of the halogen ligands. Treatment of **6** with an equimolar amount of $AgSbF_6$ in CH_2Cl_2 produces $\{[Mo(CO)(C_7H_8)(C_{10}H_8N_2)Br]SbF_6\}_{n\geq1}$ (**8**) in good yield as a reddish brown solid. Acetone can also be used as a reaction medium but must be removed from the product with extensive drying or repeated washings with pentane. The elemental analysis confirms the molecular formula of **8**. The carbonyl stretching vibration of **8** is shifted 65 cm^{-1} to higher wavenumbers in comparison with the starting material **6**, indicating the carbonyl bond has become stronger. NMR-spectroscopic data in [D$_6$]acetone let us conclude, that the bipyridyl ligand coordinates unsymmetrically to the metal center as in **6**. Separate signals exist for each H and C atom of the norbornadiene ligand in **8**.

Scheme 4



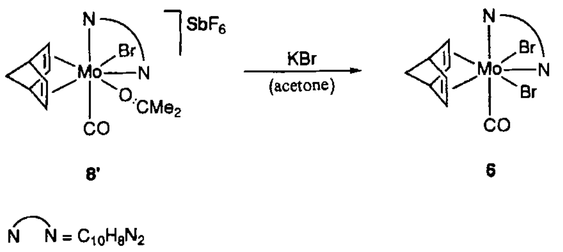
Compound $\{[Mo(CO)(C_7H_8)(C_{10}H_6tBu_2N_2)I]SbF_6\}_{n\geq1}$ (**9**) can be obtained from **5** in over 90% yield, in the same way that **8** was obtained from **6**. The mass spectrum of **9** shows the M^+ and the M^+ − CO corresponding to $\{[Mo(CO)(C_7H_8)(C_{10}H_8N_2)I]^+\}_1$. Furthermore, ions of higher molar mass, but with a mass still lower than that of the dication $\{[Mo(CO)(C_7H_8)(C_{10}H_8N_2)I]^+\}_2$ can be found; but they cannot be attributed unambiguously to fragments of multi-centered complexes.

The di-*tert*-butylbipyridyl ligand improve the solubility of **9**. NMR spectra of **9** can be measured in chloroform and methylene dichloride, as well as in solvents with far worse coordinating power, and reveal a large number of line sets. Spectra made in acetone show signals analogous to those of **8**. At −50 °C only some signals of the norbornadiene protons are slightly broadened; at room temp. a large number of signals are broadened.

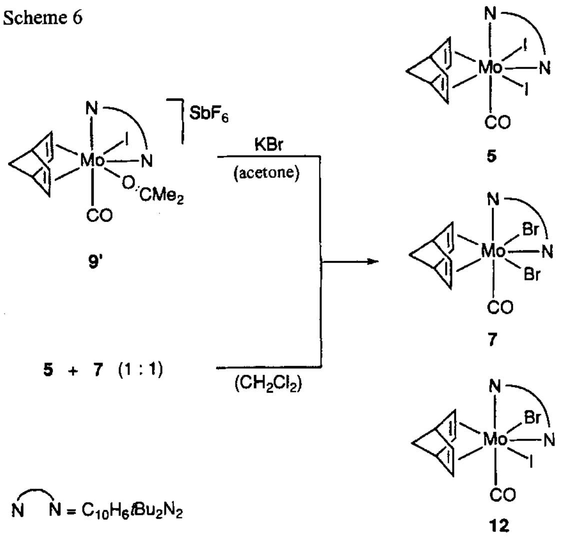
These observations led us to conclude, that the 6-coordinated cations $[Mo(CO)(C_7H_8)(C_{10}H_8R_2N_2)X]^+$, resulting from the abstraction of a halogen from $[Mo(CO)(C_7H_8)(C_{10}H_8R_2N_2)X_2]$, are stabilized by the formation of halogen-bridged coordination polymers $\{[Mo(CO)(C_7H_8)(C_{10}H_6R_2N_2)X]^+\}_{n\geq2}$. Those halogen bridges further react, reversibly cleaving in acetone, to form the 7-coordinated adducts $[Mo(CO)(C_7H_8)(C_{10}H_8N_2)(acetone)Br]SbF_6$ (**8'**) and $[Mo(CO)(C_7H_8)(C_{10}H_6tBu_2N_2)(acetone)I]SbF_6$ (**9'**). Also the addition of trimethylphosphane to **8** or **9** in acetone gives the stable products $[Mo(CO)(C_7H_8)(C_{10}H_8N_2)(PMe_3)Br]SbF_6$ (**10**) and $[Mo(CO)(C_7H_8)(C_{10}H_6tBu_2N_2)(PMe_3)I]SbF_6$ (**11**), respectively, in yields of higher than 90% (see Scheme 4).

Compound **8** reacts slowly with solid KBr in acetone to form a violet solid, which, according to its spectroscopic data, is **6**. Analogously, **9** and KBr gives a solid with molecular formula of $[Mo(CO)(C_7H_8)(C_{10}H_6tBu_2N_2)BrI]$ (**12**).

Scheme 5



Scheme 6



^{1}H- and ^{13}C-NMR spectra at −45°C show three sets of lines with an integral of 1:1:2. The two sets of signals with lower intensity correspond to **5** and **7**, the signals with high intensity correspond to **12**. At room temp., the signals for the norbornadiene and the di-*tert*-butyl-bipyridyl ligands were broader.

A mixture of **5** and **7** in CH_2Cl_2 at room temperature equilibrates to a mixture of **5**, **7** and **12**. We suggest that the mechanism of the halogen exchange involves an intermediate cationic species of the general formula [$Mo(CO)(C_7H_8)(C_{10}H_6tBu_2N_2)X$]X'.

Experimental

All reactions were carried out under argon atmosphere and with carefully dried solvents. The synthesis of [$Mo(CO)_4(C_7H_8)$] (**1**)[6] and 4,4'-di-*t*Bu-2,2'-bipyridine[14] were performed according to literature methods. – Melting and decomposition points: Yanaco Micro Melting Pont Apparatus. – IR: Shimadzu FT IR-8200D. – NMR: Jeol EX 270 FTNMR; ^{13}C NMR: C,H-decoupled. Sharp singlets were obtained when not indicated otherwise. – MS: Shimadzu-Kratos Concept 1S.

[Mo(CO)$_2$(C$_7$H$_8$)I$_2$]$_{n\geq 1}$ (**2**): A solution of 412 mg (1.37 mmol) **1** in 10 ml CH_2Cl_2 was treated with 348 mg (1.37 mmol) iodine. The dark red solution was stirred for 1 h at room temp. and then the solvent was removed under vacuum to yield a red-brown microcrystalline solid. Yield: 679 mg (99%); dec. 109°C. – MS (70 eV), *m/z* (%)[15]: 528 (0.4) [M$^+$ + CO], 500 (0.7) [M$^+$], 472 (2.4) [M$^+$ – CO], 345 (0.5) [M$^+$ – I], 316 (0.7) [M$^+$ – CO – I], 218 (0.4) [M$^+$ – 2 I]. – IR (KBr): $\tilde{\nu}$ = 2082 (s), 2071 (m), 2020 (s), 1991 (s) and 1933 (m) cm^{-1} [ν(CO)]. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2077 (m), 2053 (w), 2025 (m) and 1993 (s) cm^{-1} [ν(CO)]. – The IR and NMR spectra indicate that **2** exists as an equilibrium between the two isomers, **2a** and **2b**. **2a**: IR (CH_2Cl_2): $\tilde{\nu}$ = 2062 (w) and 1998 (s) cm^{-1} [ν(CO)]. – ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 4.27 [t, *J*(HH) = 2.6 Hz, 4H, =CH], 3.97 (m, 2H, CH), 1.10 [t, *J*(HH) = 1.3 Hz, 2H, CH_2]. – ^{13}C-NMR ($CDCl_3$, 67.8 MHz): δ = 213.78 (CO), 60.20 (CH), 59.37 (=CH), 44.68 (CH_2). **2b**: ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 5.08 [t, *J*(HH) = 2.6 Hz, 4H, =CH], 3.77 (m, 2H, CH), 1.61 [t, *J*(HH) = 1.3 Hz, 2H, CH_2]. – ^{13}C NMR ($CDCl_3$, 67.8 MHz): δ = 202.13 and 194.58 (CO), 70.23 (=CH), 67.40 (CH), 45.11 (CH_2). **2a/2b**: $C_9H_8I_2MoO_2$ (497.9): calcd. C 21.71, H 1.62; found C 21.84, H 1.61.

Reaction of **2** *in Acetonitrile:* A suspension of 150 mg (0.32 mmol) **2** in 10 ml acetonitrile was stirred for 2 h at room temperature; and then the solvent from the resulting yellow solution was removed under vacuum. After 2 hours, a red oil was obtained which was composed of [$Mo(CO)_2(C_7H_8)(NCCH_3)I_2$] (**3**) and a small amount of **2a** (5–10%). – IR (CH_3CN): $\tilde{\nu}$ = 2312 (w) [ν(CN)], 2011 (w) and 1955 (s) cm^{-1} [ν(CO)]. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2312 (w) [ν(CN)], 1951 (s) cm^{-1} [ν(CO)]. – ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 4.73 and 4.08 [dd, *J*(HH) = 4.3 and 4.3 Hz, each 2H, =CH and =CH'], 4.07 and 3.81 (m, each 1H, CH and CH'), 2.76 (s, 3H, CH_3), 1.18 (s, 2H, CH_2). – ^{13}C NMR ($CDCl_3$, 67.8 MHz): δ = 224.95 (CO), 126.93 (CH_3), 64.12, 63.28, 59.75, 45.42 and 45.32 (=CH, =CH', CH, CH' and CH_2), 2.87 (br. s, NC).

[Mo(CO)(C$_7$H$_8$)(C$_{10}$H$_8$N$_2$)I$_2$] (**4**): A solution of 448 mg (1.49 mmol) **1** in 10 ml CH_2Cl_2 was treated with 378 mg (1.49 mmol) of iodine. After 1 h of stirring at room temp., 233 mg (1.49 mmol) 2,2'-bipyridine was added to the dark red solution and the solution was stirred 1 more hour. A violet suspension was formed to which was added 30 ml of ether. After the supernatant was decanted, the residue was washed twice with 10 ml portions of ether and dried under high vacuum to produce a violet microcrystalline solid. Yield: 829 mg (89%); dec. 184°C. – IR (KBr): $\tilde{\nu}$ = 1889 (s) cm^{-1} [ν(CO)]. – ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 9.82 and 9.76 [d, *J*(HH) = 5.3 Hz, each 1H, 6-H and 6-H'], 8.30 and 8.15 [d, *J*(HH) = 7.9 Hz, each 1H, 3-H and 3-H'], 8.06 and 8.03 [dd, *J*(HH) = 7.9 and 6.9 Hz, each 1H, 4-H and 4-H'], 7.61 and 7.48 [dd, *J*(HH) = 6.9 and 5.3 Hz, each 1H, 5-H and 5-H'], 4.87 and 4.30 [br. dd, *J*(HH) = 4.2 and 4.2 Hz, each 2H, =CH and =CH'], 3.95 and 3.62 (br. s, each 1H, CH and CH'), 1.65 (br. s, 2H, CH_2). – $C_{18}H_{16}I_2MoN_2O$ (626.1): calcd. C 34.53, H 2.56, N 4.47; found C 34.50, H 2.72, N 4.62.

[Mo(CO)(C$_7$H$_8$)(C$_{10}$H$_6$tBu$_2$N$_2$)I$_2$] (**5**): The reaction was performed as described for **4**, using 436 mg (1.45 mmol) **1**, 368 mg (1.45 mmol) iodine and 390 mg (1.45 mmol) 4,4'-di-*t*Bu-2,2'-bipyridine. A violet solution is formed to which was slowly added 20 ml of ether and then 20 ml of pentane. A precipitate formed and the supernatant was decanted. The precipitate was then washed twice with 10 ml portions of ether and dried under high vacuum to produce a red-violet crystalline solid. Yield: 832 mg (78%); dec. 176°C. – IR (KBr): $\tilde{\nu}$ = 1893 (s) cm^{-1} [ν(CO)]. – ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 9.66 and 9.60 [d, *J*(HH) = 5.9 Hz, each 1H, 6-H and 6-H'], 8.20 and 8.06 [d, *J*(HH) = 2.0 Hz, each 1H, 3-H and 3-H'], 7.56 and 7.45 [dd, *J*(HH) = 5.9 and 2.0 Hz, each 1H, 5-H and 5-H'], 4.83 and 4.27 (br. s, each 2H, =CH and =CH'), 3.92 and 3.60 (br. s, each 1H, CH and CH'), 1.61 (br. s, 2H, CH_2), 1.48 and 1.43 (s, each 9H, C-4CCH_3 and C-4'CCH_3). – ^{13}C NMR ($CDCl_3$, 67.8 MHz): δ = 229.05 (CO), 163.54, 162.76, 157.56, 155.47, 154.21, 153.08, 123.85, 122.54, 120.06 and 119.14 (C-2–C-6 and C-2'–C-6'), 63.61, 62.26, 53.75, 44.19 and 43.84 (=CH, =CH', CH, CH' and CH_2), 35.57 and 35.37 (C-4*C*CH_3 and C-4'*C*CH_3), 30.42 and 30.27 (C-4C*C*H_3 and C-4'C*C*H_3). – $C_{26}H_{32}I_2MoN_2O$ (738.3): calcd. C 42.30, H 4.37, N 3.79; found C 41.75, H 4.06, N 3.56.

[Mo(CO)(C$_7$H$_8$)(C$_{10}$H$_8$N$_2$)Br$_2$] (**6**): A solution of 416 mg (1.39 mmol) **1** in 10 ml CH_2Cl_2 was treated with 620 mg (2.78 mmol) $CuBr_2$ and stirred at room temp. for 1 h. Then the CuBr was filtered off to leave a dark green filtrate to which was added 217 mg (1.39 mmol) 2,2'-bipyridine and stirred for another hour. A violet suspension was formed which was treated with 20 ml of pentane. The supernatant was decanted and the residue was washed twice, each time with 10 ml of pentane and dried under high vacuum to produce a red-violet microcrystalline powder. Yield: 698 mg (94%); dec. 188°C. – IR (KBr): $\tilde{\nu}$ = 1884 (s) cm^{-1} [ν(CO)]. – ^{1}H NMR ($CDCl_3$, 270 MHz)[16]: δ = 9.59 [dd, *J*(HH) = 5.5 and 1.2 Hz, 1H, 6-H], 9.54 [dd, *J*(HH) = 5.3 and 1.4 Hz, 1H, 6-H'], 8.26 [dd, *J*(HH) = 8.3 and 1.3 Hz, 1H, 3-H], 8.14 [dd, *J*(HH) = 8.1 and 1.4 Hz, 1H, 3-H'], 8.02 [ddd, *J*(HH) = 8.1, 7.6 and 1.4 Hz, 1H, 4-H'], 8.01 [dd, *J*(HH) = 8.3, 7.4 and 1.2 Hz, 1H, 4-H], 7.57 [ddd, *J*(HH) = 7.4, 5.5 and 1.3 Hz, 1H, 5-H], 7.54 [ddd, *J*(HH) = 7.6, 5.3 and 1.4 Hz, 1H, 5-H'], 4.48 [ddd, *J*(HH) = 4.2, 3.8 and 0.7 Hz, 2H, =CH], 3.96 (m, 1H, CH'), 3.92 [ddd, *J*(HH) = 4.2, 3.6 and 0.7 Hz, 2H, =CH'], 3.65 (m, 1H, CH), 1.76 [dd, *J*(HH) = 1.3 and 1.2 Hz, 2H, CH_2]. – $C_{18}H_{16}Br_2MoN_2O$ (532.1): calcd. C 40.63, H 3.41, N 5.26; found C 40.20, H 3.18, N 5.48.

[Mo(CO)(C$_7$H$_8$)(C$_{10}$H$_6$tBu$_2$N$_2$)Br$_2$] (**7**): The reaction was conducted as described for **6** using 218 mg (0.73 mmol) **1**, 324 mg (1.45 mmol) $CuBr_2$ and 292 mg (0.73 mmol) 4,4'-di-*t*Bu-2,2'-bipyridine. A violet solution is formed that was reduced in volume by approximately 5 ml, and then treated with 30 ml of pentane. The supernatant was then decanted and the precipitate washed

twice with 10 ml portions of pentane. The substance was then dried under high vacuum to yield a violet crystalline solid. Yield: 406 mg (87%); dec. 176°C. – IR (KBr): $\tilde{\nu}$ = 1891 (s) cm^{-1} [ν(CO)]. – ^1H NMR ($CDCl_3$, 270 MHz): δ = 9.46 and 9.39 [d, J(HH) = 5.9 Hz, each 1 H, 6-H and 6-H′], 8.18 and 8.06 [d, J(HH) = 2.0 Hz, each 1 H, 3-H and 3-H′], 7.53 and 7.51 [dd, J(HH) = 5.9 and 2.0 Hz, each 1 H, 5-H and 5-H′], 4.45 and 3.89 [br. dd, J(HH) = 4.3 and 4.3 Hz, each 2 H, =CH and =CH′], 3.92 and 3.49 (br. s, each 1 H, CH and CH′), 1.74 (br. s, 2 H, CH_2), 1.45 and 1.43 (s, each 9 H, C-4CCH_3 and C-4′CCH_3). – ^{13}C NMR ($CDCl_3$, 67.8 MHz): δ = 228.06 (CO), 163.13, 162.76, 157.03, 153.10, 152.89, 152.60, 124.26, 122.51, 120.02 and 119.03 (C-2–C6 and C-2′–C-6′), 66.56, 60.32, 57.28, 43.20 and 42.34 (=CH, =CH′, CH, CH′ and CH_2), 35.51 and 35.34 (C-4*C*CH_3 and C-4′*C*CH_3), 30.39 and 30.36 (C-4C*C*H_3 and C-4′C*C*H_3). – $C_{26}H_{32}Br_2MoN_2O$ (644.3): calcd. C 48.47, H 5.01, N 4.35; found C 48.58, H 4.96, N 4.49.

$\{[Mo(CO)(C_7H_8)(C_{10}H_8N_2)Br]SbF_6\}_{n\geq 1}$ (**8**): A solution of 241 mg (0.70 mmol) $AgSbF_6$ in 10 ml CH_2Cl_2 was added to a suspension of 373 mg (0.70 mmol) **6** in 10 ml CH_2Cl_2; then the reaction mixture was stirred for 1 h at room temp. The AgBr was separated from the red-brown solution by filtration and then 50 ml of pentane was added to the solution. The supernatant was decanted from the resulting precipitate and the precipitate washed twice with 10 ml portions of pentane and then dried under high vacuum to give a red-brown microcrystalline powder. Yield: 453 mg (94%); dec. 174°C. – IR (KBr): $\tilde{\nu}$ = 1949 (s) [ν(CO)], 660 (s) cm^{-1} [ν(SbF)]. – ^1H NMR ([D_6]acetone, 270 MHz): δ = 9.42 [dd, J(HH) = 5.3 and 1.3 Hz, 1 H, 6-H], 8.85 [dd, J(HH) = 8.2 and 1.0 Hz, 1 H, 3-H], 8.76 [dd, J(HH) = 7.9 and 1.0 Hz, 1 H, 3-H′], 8.58 [dd, J(HH) = 5.6 and 1.3 Hz, 1 H, 6-H′], 8.42 [ddd, J(HH) = 7.9, 7.6 and 1.3 Hz, 1 H, 4-H′], 8.32 [ddd, J(HH) = 8.2, 7.3 and 1.3 Hz, 1 H, 4-H], 7.93 [ddd, J(HH) = 7.3, 5.3 and 1.0 Hz, 1 H, 5-H], 7.70 [ddd, J(HH) = 7.6, 5.6 and 1.0 Hz, 1 H, 5-H′], 4.41, 4.20, 3.65 and 2.50 [dd, J(HH) = 4.3 and 4.3 Hz, each 1 H, =CH, =CH′, =CH″ and =CH‴], 3.92 and 3.37 (br. s, each 1 H, CH and CH′), 1.61 and 1.49 [d, J(HH) = 9.4 Hz, each 1 H, CH_2]. – ^{13}C NMR ([D_6]acetone, 67.8 MHz): δ = 225.21 (CO), 156.66, 154.81, 154.08, 153.89, 142.51, 141.51, 129.63, 128.31, 126.28 and 126.22 (C-2–C-6 and C-2′–C-6′), 67.61, 67.29, 66.81, 66.21, 59.40, 45.30 and 43.35 (=CH, =CH′, =CH″, =CH‴, CH, CH′ and CH_2). – $C_{18}H_{16}BrF_6MoN_2OSb$ (687.9): calcd. C 31.43, H 2.34, N 4.07; found C 31.00, H 2.55, N 4.13.

$\{[Mo(CO)(C_7H_8)(C_{10}H_6tBu_2N_2)I]SbF_6\}_{n\geq 1}$ (**9**): To a solution of 587 mg (0.80 mmol) **5** in 20 ml CH_2Cl_2, a solution of 273 mg (0.80 mmol) $AgSbF_6$ in 10 ml CH_2Cl_2 was slowly added and stirred at room temp. for 1 h. The AgI was separated by filtration and to the red-brown filtrate was added 50 ml of pentane. The supernatant was decanted and the precipitate washed twice with 10 ml portions of pentane and dried under high vacuum to yield a red-brown microcrystalline powder. Yield: 623 mg (93%); dec. 187°C. – MS (70 eV), m/z (%)[15]: 613 (39) [M^+], 585 (33) [M^+ – CO]. – IR (KBr): $\tilde{\nu}$ = 1942 (s) [ν(CO)], 660 (s) cm^{-1} [ν(SbF)]. – ^1H NMR ([D_6]acetone, 270 MHz, 25°C): δ = 9.35 and 8.47 (br. s, each 1 H, 6-H and 6-H′), 8.88 and 8.76 (br. s, each 1 H, 3-H and 3-H′), 7.94 [dd, J(HH) = 5.6 and 1.7 Hz, 1 H, 5-H], 7.64 [dd, J(HH) = 5.0 Hz, 1 H, 5-H′], 4.28, 4.13, 3.48 and 2.23 (br. s, each 1 H, =CH, =CH′, =CH″ and =CH‴), 3.93 and 3.32 (br. s, each 1 H, CH and CH′), 1.52 and 1.43 (s, each 9 H, C-4CCH_3 and C-4′CCH_3), signals for CH_2 could not be assigned unequivocally. – ^1H NMR ([D_6]acetone, 270 MHz, –50°C): δ = 9.41 and 8.46 [d, J(HH) = 5.6 Hz, each 1 H, 6-H and 6-H′], 9.01 and 8.89 (s, each 1 H, 3-H and 3-H′), 7.91 and 7.60 [d, J(HH) = 5.6 Hz, each 1 H, 5-H and 5-H′], 4.32, 4.06, 3.35 and 2.27 [br. dd, J(HH) = 4.3 and 4.3 Hz, each 1 H, =CH, =CH′, =CH″ and =CH‴], 3.93 and 3.30 (br. s, each 1 H, CH and CH′), 1.47 and 1.37 (s, each 9 H, C-4CCH_3 and C-4′CCH_3), signals for CH_2 could not be assigned unequivocally. – ^{13}C NMR ([D_6]acetone, 67.8 MHz, 25°C): δ = 167.09, 165.82, 156.9 (br. s), 155.08, 154.56, 153.5 (br. s), 126.42, 125.24, 123.47 and 123.28 (C-2–C-6 and C-2′–C-6′), 68.9 (br. s), 67.7 (br. s), 67.3 (br. s), 66.7 (br. s), 59.2 (br. s), 45.48 and 43.2 (br. s, =CH, =CH′, =CH″, =CH‴, CH, CH′ and CH_2), 37.40 and 37.24 (C-4*C*CH_3 and C-4′*C*CH_3), 31.36 and 31.12 (C-4C*C*H_3 and C-4′C*C*H_3), signal for CO no localized. – ^{13}C NMR ([D_6]acetone, 67.8 MHz, –50°C): δ = 225.57 (CO), 166.32, 165.09, 156.38, 154.48, 154.45, 153.08, 126.00, 124.77, 123.55 and 123.41 (C-2–C-6 and C-2′–C-6′), 68.57, 68.09, 66.73, 66.42, 58.68, 44.99 and 42.62 (=CH, =CH′, =CH″, =CH‴, CH, CH′ and CH_2), 37.14 and 36.99 (C-4*C*CH_3 and C-4′*C*CH_3), signals for C-4C*C*H_3 and C-4′C*C*H_3 could not be assigned unequivocally. – $C_{26}H_{32}F_6IMoN_2OSb$ (847.1): calcd. C 36.86, H 3.81, N 3.31; found C 36.73, H 3.78, N 3.24.

$[Mo(CO)(C_7H_8)(C_{10}H_8N_2)(PMe_3)Br]SbF_6$ (**10**): A 1 M solution of PMe_3 in THF (0.2 ml) was slowly added to a suspension of 100 mg (0.15 mmol) **8** in 5 ml CH_2Cl_2 and then stirred for 30 min at room temp. Ether (50 ml) was then added to the resulting red solution. The supernatant was decanted and the precipitate washed twice with 10 ml portions of pentane and dried under high vacuum to produce an orange-red microcrystalline powder. Yield: 108 mg (97%); dec. 174°C. – IR (KBr): $\tilde{\nu}$ = 1916 (s) and 1907 (s) [ν(CO)], 660 (s) cm^{-1} [ν(SbF)]. – IR (CH_2Cl_2): $\tilde{\nu}$ = 1913 (s) [ν(CO)], 660 (s) cm^{-1} [ν(SbF)]. – ^1H NMR ([D_6]acetone, 270 MHz): δ = 9.58 [dd, J(HH) = 5.3 and 1.3 Hz, 1 H, 6-H], 8.88 [dd, J(HH) = 8.3 and 1.3 Hz, 2 H, 3-H and 3-H′], 8.54 [dd, J(HH) = 5.6 and 1.3 Hz, 1 H, 6-H′], 8.45 and 8.41 [ddd, J(HH) = 8.3, 7.6 and 1.3 Hz, each 1 H, 4-H and 4-H′], 7.96 [ddd, J(HH) = 7.6, 5.3 and 1.3 Hz, 1 H, 5-H], 7.84 [ddd, J(HH) = 7.6, 5.6 and 1.3 Hz, 1 H, 5-H′], 4.68, 4.45, 4.24 and 2.16 [dd, J(HH) = 4.3 and 4.3 Hz, each 1 H, =CH, =CH′, =CH″ and =CH‴], 3.90 and 3.32 (br. s, each 1 H, CH and CH′), 1.68 [d, J(HH) = 8.9 Hz, 1 H, one H from CH_2], 1.50 [d, J(HH) = 9.3 Hz, 1 H, one H from CH_2], 1.10 [d, J(PH) = 10.2 Hz, 9 H, PCH_3]. – ^{13}C NMR ([D_6]acetone, 67.8 MHz): δ = 226.26 [d, J(PC) = 18.7 Hz, CO], 155.98, 155.85, 155.83, 154.55 [d, J(PC) = 3.7 Hz], 142.72 [d, J(PC) = 2.8 Hz], 141.36, 130.68 [d, J(PC) = 3.7 Hz], 128.95, 127.16 [d, J(PC) = 2.8 Hz] and 126.45 (C-2–C-6 and C-2′–C-6′), 76.67, 75.58 [d, J(PC) = 3.7 Hz], 72.75, 69.03, 62.39, 46.29 and 44.93 [d, J(PC) = 1.8 Hz, =CH, =CH′, =CH″, =CH‴, CH, CH′ and CH_2], 16.14 [d, J(PC) = 29.4 Hz, PCH_3]. – $C_{21}H_{25}BrF_6MoN_2OPSb$ (764.0): calcd. C 33.01, H 3.30, N 3.67; found C 32.68, H 3.31, N 3.71.

$[Mo(CO)(C_7H_8)(C_{10}H_6tBu_2N_2)(PMe_3)I]SbF_6$ (**11**): The reaction was performed as described for **10** using 197 mg (0.23 mmol) **9** and 0.3 ml of a 1 M solution of PMe_3 in THF. A brown solution is formed which was reduced in volume by approximately 3 ml. Ether (50 ml) was added to the concentrated reaction mixture and cooled to –20°C. After several hous an orange-red microcrystalline solid precipitated which was recovered by filtration and washed twice with 10 ml portions of pentane and dried under high vacuum. Yield: 205 mg (95%); dec. 171°C. – IR (KBr): $\tilde{\nu}$ = 1909 (s) [ν(CO)], 660 (s) cm^{-1} [ν(SbF)]. – ^1H NMR ([D_6]acetone, 270 MHz): δ = 9.72 [d, J(HH) = 6.0 Hz, 1 H, 6-H], 8.90 and 8.86 [d, J(HH) = 2.0 Hz, each 1 H, 3-H and 3-H′], 8.41 [dd, J(PH) = 2.3, J(HH) = 6.0 Hz, 1 H, 6-H′], 7.94 and 7.82 [dd, J(HH) = 6.0 and 2.0 Hz, each 1 H, 5-H and 5-H′], 4.79, 4.69, 4.62 and 2.12 [dd, J(HH) = 4.3 and 4.3 Hz, each 1 H, =CH, =CH′, =CH″ and =CH‴], 3.88 and 3.30 (m, each 1 H, CH and CH′), 1.72 and 1.67 [d, J(HH) = 9.2 Hz, each 1 H, CH_2], 1.51 and 1.44 (s, each 9 H, C-

4CCH$_3$ and C-4'CCH$_3$), 1.20 [d, *J*(PH) = 9.9 Hz, 9H, PCH$_3$]. – ^{13}C NMR ([D$_6$]acetone, 67.8 MHz): δ = 226.21 [d, *J*(PC) = 18.4 Hz, CO], 167.55 [d, *J*(PC) = 2.8 Hz], 166.09, 157.17, 155.94, 155.40 [d, *J*(PC) = 3.7 Hz], 154.79 [d, *J*(PC) = 3.7 Hz], 127.62 [d, *J*(PC) = 3.7 Hz], 126.08, 124.37 [d, *J*(PC) = 1.8 Hz] and 123.56 (C-2–C-6 and C-2'–C-6'), 73.20, 72.85, 69.21, 69.08, 63.73, 46.49 and 45.31 [d, *J*(PC) = 1.8 Hz, =CH, =CH', =CH'', =CH''', CH, CH' and CH$_2$], 37.47 and 37.30 (C-4*C*CH$_3$ and C-4'*C*CH$_3$), 31.32 and 31.19 (C-4C*C*H$_3$ and C-4'C*C*H$_3$), 18.60 [d, *J*(PC) = 29.4 Hz, PCH$_3$]. – $C_{29}H_{41}F_6IMoN_2OPSb$ (923.2): calcd. C 37.73, H 4.48, N 3.03; found C 37.39, H 4.35, N 2.98.

Reactions of **8** *with KBr:* A solution of 126 mg (0.18 mmol) **8** in 10 ml acetone was treated with 22 mg (0.19 mmol) KBr and stirred for 3 h at room temp. The supernatant was decanted from the precipitate which had formed; and the precipitate was washed twice with 10 ml portions of ether and dried under high vacuum to produce **6** a crystalline violet solid. Yield: 82 mg (84%). The identification of **6** was confirmed by the comparison of its IR- and ^{1}H-NMR-spectroscopic data with that of an authentic sample.

Reaction of **9** *with KBr:* A solution of 196 mg (0.23 mmol) **9** in 15 ml acetone was treated with 27 mg (0.23 mmol) KBr and stirred for 1 h at room temp. A violet solution was formed that was brought to dryness under vacuum. The residue was extracted three times with 10 portions of toluene/CH$_2$Cl$_2$ (1:1). The combined extracts were reduced in volume by 5 ml and treated with 50 ml of pentane. The supernatant was decanted from the resulting precipitate; and the precipitate was washed twice with 10 ml portions of pentane and dried under high vacuum to produce a violet microcrystalline powder. Yield: 143 mg (90%); dec. 179°C. – IR (KBr): $\tilde{\nu}$ = 1892 (s) cm^{-1} [ν(CO)]. – ^{1}H-NMR (CDCl$_3$, 270 MHz, 25°C): δ = 9.5 (vbr. s, 2H, 6-H and 6-H'), 8.20 and 8.08 (s, each 1H, 3-H and 3-H'), 7.55 and 7.49 (br. s, each 1H, 5-H and 5-H'), 4.8, 4.5 and 4.2 (vbr. s, each 1H, =CH, =CH' and =CH''), 3.93 (br. s, 2H, =CH''' and CH), 3.62 (br. s, 1H, CH'), 1.72 (br. s, 2H, CH$_2$), 1.50 and 1.47 (s, each 9H, C-4CCH$_3$ and C-4'CCH$_3$). – ^{13}C NMR (CDCl$_3$, 67.8 MHz, 25°C): δ = 228.6 (vbr. s, CO), 163.4 (vbr. s), 162.76, 157.2 (vbr. s), 154.1 (vbr. s), 152.8 (vbr. s), 124.05 (br. s), 122.59, 120.03 and 119.13 (C-2–C-6 and C-2'–C-6'), 66.8, 63.3, 61.2, 60.6, 58.4, 57.3, 53.8, 52.7, 43.8 and 43.0 (vbr. s, =CH, =CH', =CH'', =CH''', CH, CH' and CH$_2$), 35.53 and 35.34 (C-4*C*CH$_3$ and C-4'*C*CH$_3$), 30.42 and 30.31 (C-4C*C*H$_3$ and C-4'C*C*H$_3$). – The NMR spectra measured at –45°C show a 1:1:2 equilibrium mixture of **5**, **7** and [Mo(CO)(C$_7$H$_8$)(C$_{10}$H$_6$*t*Bu$_2$N$_2$)BrI] (**12**): – **12**: ^{1}H NMR (CDCl$_3$, 270 MHz, –45°C): δ = 9.58 [d, *J*(HH) = 5.9 Hz, 1H, 6-H], 9.49 [d, *J*(HH) = 6.3 Hz, 1H, 6-H'], 8.22 and 8.10 [d, *J*(HH) = 2.0 Hz, each 1H, 3-H and 3-H'], 7.61 [dd, *J*(HH) = 5.9 and 2.0 Hz, 1H, 5-H], 7.55 [dd, *J*(HH) = 6.3 and 2.0 Hz, 1H, 5-H'], 4.77, 4.54, 4.28 and 3.90 [dd, *J*(HH) = 4.3 and 4.3 Hz, each 1H, =CH, =CH', =CH'', =CH''', CH and CH'], 4.27 and 3.66 (m, each 1H, CH and =CH'), 1.75 [br. d, *J*(HH) = 11.2 Hz, 1H, one H from CH$_2$], 1.67 [br. d, *J*(HH) = 11.7 Hz, 1H, one H from CH$_2$], 1.47 and 1.44 (s, each 9H, C-4CCH$_3$ and C-4'CCH$_3$). – ^{13}C NMR (CDCl$_3$, 67.8 MHz, –45°C): δ = 228.25 (CO), 163.05, 162.49, 156.49, 153.86, 152.90, 152.78, 124.31, 122.79, 120.10 and 119.24 (C-2–C-6 and C-2'–C-6'), 63.12, 61.13, 58.05, 52.62, 43.48 and 42.85 (=CH, =CH', =CH'', =CH''', CH, CH' and CH$_2$), 35.49 and 35.28 (C-4*C*CH$_3$ and C-4'*C*CH$_3$), 30.27 and 30.16 (C-4C*C*H$_3$ and C-4'C*C*H$_3$). – **5**/**7**/**12**: $C_{26}H_{32}BrIMoN_2O$ (691.3): calcd. C 45.17, H 4.67, N 4.05; found C 44.78, H 4.54, N 3.87.

Reaction of **5** *with* **7**: A solution of 50 mg (0.07 mmol) **5** in 3 ml CH$_2$Cl$_2$ was treated with 44 mg (0.07 mmol) **7** and stirred at room temp. for 2 h. Pentane (30 ml) was then added to the violet solution and the supernatant decanted from the resulting violet crystalline solid. This solid was washed twice with 10 ml portions of pentane and dried under high vacuum. Yield: 89 mg (95%). The identification of the 1:1:2 mixture of **5**, **7** and **12** was achieved through the comparison of the ^{1}H- and ^{13}C-NMR-spectroscopic data, collected at –45°C, with that of an authentic sample.

Crystal Structure Analysis of **6**[17]: Crystallization solvent CH$_2$Cl$_2$/pentane; $C_{18}H_{16}Br_2MoN_2O$ (532.1); Crystal size 0.2 × 0.2 × 0.15 mm; monoclinic; space group $P2_1/a$ (Nr. 14); Z = 4; a = 14.653(2), b = 14.249(3), c = 8.3808(7) Å; β = 94.436(8)°; V = 1744.6(3) Å^3; $d_{calc.}$ = 2.03 gcm^{-3}; Mo-K_α (λ = 0.71069 Å); graphite-monochromated; Enraf-Nonius-CAD4-FR590 diffractometer; ω/2Θ-scan; range 2Θ$_{max}$ = 60°; measured reflections 5591; independent reflections: 3040 [$F_o > 3\sigma(F_o)$]; empirical absorption correction DIFABS-program (min. transmission 89.0%); structure solution through direct methods (SAPI 91) anisotropic determination of the non-hydrogen atoms; hydrogen atoms not determined. R = 0.039; Rw = 0.033 [$w = 1/\sigma^2(F_o)$]; reflection/parameter ratio: 14.0; residual electron density: +0.69/–0.78 e/Å^3.

☆ Dedicated to Professor Dr. *Helmut Werner* on the occasion of his birthday.

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[15] The reported m/z refers to the isotope ^{98}Mo; the other isotopes were found in the position and intensity of the natural distribution of Molybdenum.

[16] The signal assignment is based on selective decoupling of all resonances.

[17] Further information regarding the crystal structure investigations may be obtained by writing Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, and quoting the depository number CSD-58988, the names of the authors and the journal citation.

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