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Fluxional behavior of tert-butyl-substituted 2,2′ : 6′2″-terpyridylmolybdenum(0) and 2,2′-bipyridylmolybdenum(II) complexes: enhanced solubility and ease in NMR study caused by the tert-butyl group

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Abstract

Reaction of $[Mo(CO)_4(norbornadiene)]$ with 4,4′,4″-tri-tert-butyl-2,2′ : 6′,2″-terpyridine afforded the complex $[Mo(CO)_4(4,4',4''\text{-}{}^tBu_3terpy)]$ (**2**), which in solution shows fluxional behavior, observed by ^1H and ^{13}C NMR studies at between 25 and −70°C. $[Mo(CO)_4(4,4'\text{-}{}^tBu_2bipy)]$ (**1**) reacts with I_2 and $SnBr_4$ by oxidative addition to give molybdenum(II) complexes, $[Mo(CO)_3(4,4'\text{-}{}^tBu_2bipy)I_2]$ (**3**) and $[Mo(CO)_3(4,4'\text{-}{}^tBu_2bipy)(SnBr_3)Br]$ (**4**). The related compounds $[Mo(CO)_3(4,4'\text{-}{}^tBu_2bipy)X_2]$ (X = Br(**5**) or Cl(**6**)) have been prepared by oxidation of **1** with two equivalents of CuX_2. The IR spectra of **3** in different polar solvents suggest that this compound exists in solution in two isomeric forms, which are in equilibrium. The NMR spectra of **3**, **5** and **6** are temperature dependent, indicating their dynamic behavior in solution. $\Delta G^{\ddagger}$ values for the fluxional process of about 47 kJ mol^{-1} and about 53 kJ mol^{-1} have been obtained for **5** and **6** respectively. Low temperature ^{13}C NMR studies of **4** have shown that this compound in solution has a different kind of fluxional behavior.

Keywords: Molybdenum; Di-*t*butyl-2,2′-bipyridine; Tri-*t*butyl-2,2′:6,2″-terpyridine; Dynamic behavior; Temperature-dependent NMR

1. Introduction

When we prepared the norbornadienemolybdenum(II) compounds $[Mo(CO)(norbornadiene)(4,4'\text{-}R_2bipy)X_2]$ from $[Mo(CO)_4(norbornadiene)]$ [1], we obtained unexpected byproducts, the tricarbonyl complexes $[Mo(CO)_3(4,4'\text{-}R_2bipy)X_2]$ (R = H, or ^{t}Bu; X = Br or I). As early as 1962, Stiddard described that the compounds $[Mo(CO)_3(bipy)X_2]$ (X = Br or I) can be prepared more easily by using $[Mo(CO)_4(bipy)]$ as the starting material [2]. Oxidative addition of I_2 or Br_2 is thus reported to give the bipyridylmolybdenum(II) complexes with a good yield. In the same paper he reported that the IR spectra of the diiodo compound in $CHCl_3$ and CH_3NO_2 are significantly different.

Therefore we looked in more detail at the behavior of these molecules in solution at low temperatures. However, for this, the solubility of the compounds $[Mo(CO)_3(bipy)X_2]$ is too low. In comparison with the complexes containing the non-substituted bipyridine as a ligand the compounds with tert-butyl groups on the pyridine rings $[Mo(CO)_3(4,4'\text{-}{}^tBu_2bipy)X_2]$ are much more soluble in all tested organic solvents. This increase allows various spectroscopic studies among which the low temperature ^{13}C NMR gave new important information on the fluxional behavior and energetics of these seven-coordinated complexes. The present paper describes our results in the dynamic stereochemistry of the six-coordinated tetracarbonylmolybdenum(0) complex $[Mo(CO)_4(4,4',4''\text{-}{}^tBu_3terpy)]$ and the seven-coordinated tricarbonylmolybdenum(II) compounds $[Mo(CO)_3(4,4'\text{-}{}^tBu_2bipy)X_2]$ (X = Cl, Br or I) and $[Mo(CO)_3(4,4'\text{-}{}^tBu_2bipy)(SnBr_3)Br]$.

2. Results and discussion

2.1. Tetracarbonylmolybdenum(0) complexes

The compound $[Mo(CO)_4(4,4'\text{-}{}^tBu_2bipy)]$ (**1**) has already been reported using $[Mo(CO)_4(norbornadiene)]$ as

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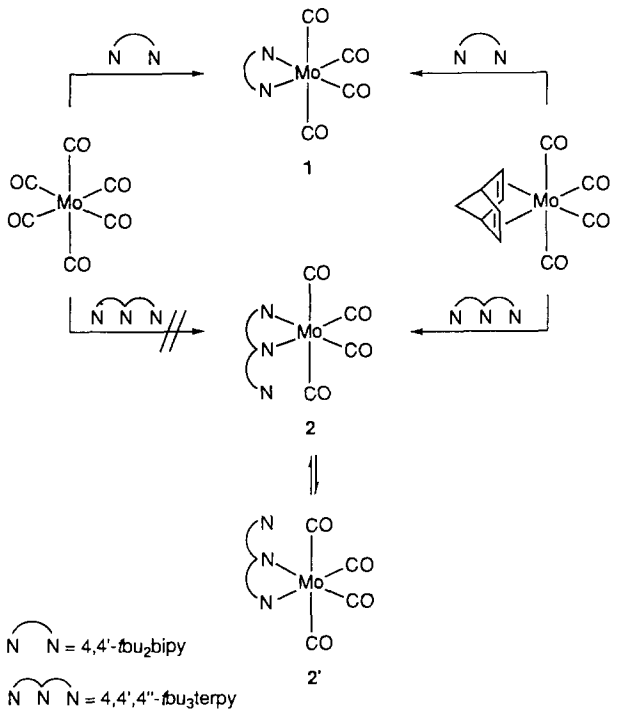


Scheme 1.

the starting material [3]. We have now found that the indirect pathway through the norbornadiene complex is not necessary. After refluxing an 1:1 mixture of $[Mo(CO)_6]$ and 4,4'-di-tert-butyl-2,2'-bipyridine in toluene for 2 h, **1** can be also isolated with a nearly 100% yield. Nevertheless, for the preparation of the analogous 4,4',4''-tri-tert-butyl-2,2' : 6',2''-terpyridyl complex **2** this direct method was not successful. Here the indirect pathway via the norbornadiene complex, which allows ligand substitution under much milder conditions, is necessary. Stirring of equivalent amounts of $[Mo(CO)_4$(norbornadiene)] and 4,4',4''-tri-tert-butyl-2,2' : 6',2''-terpyridine for several hours at room temperature gives the compound $[Mo(CO)_4(4,4',4''\text{-}^tBu_3terpy)]$ (**2**) with an almost quantitative yield (Scheme 1).

Recently it was reported [4] that the complex $[Mo(CO)_4(terpy)]$, which contains the non-substituted terpyridine as a bidentate ligand, shows fluxional behavior in solution with the two outer pyridine rings exchanging between the coordinated and the uncoordinated form. The ^1H NMR spectra of **2** measured in the temperature range from 25 to $-70°C$ illustrate that for the 4,4',4''-tri-tert-butyl-2,2' : 6',2''-terpyridyl complex

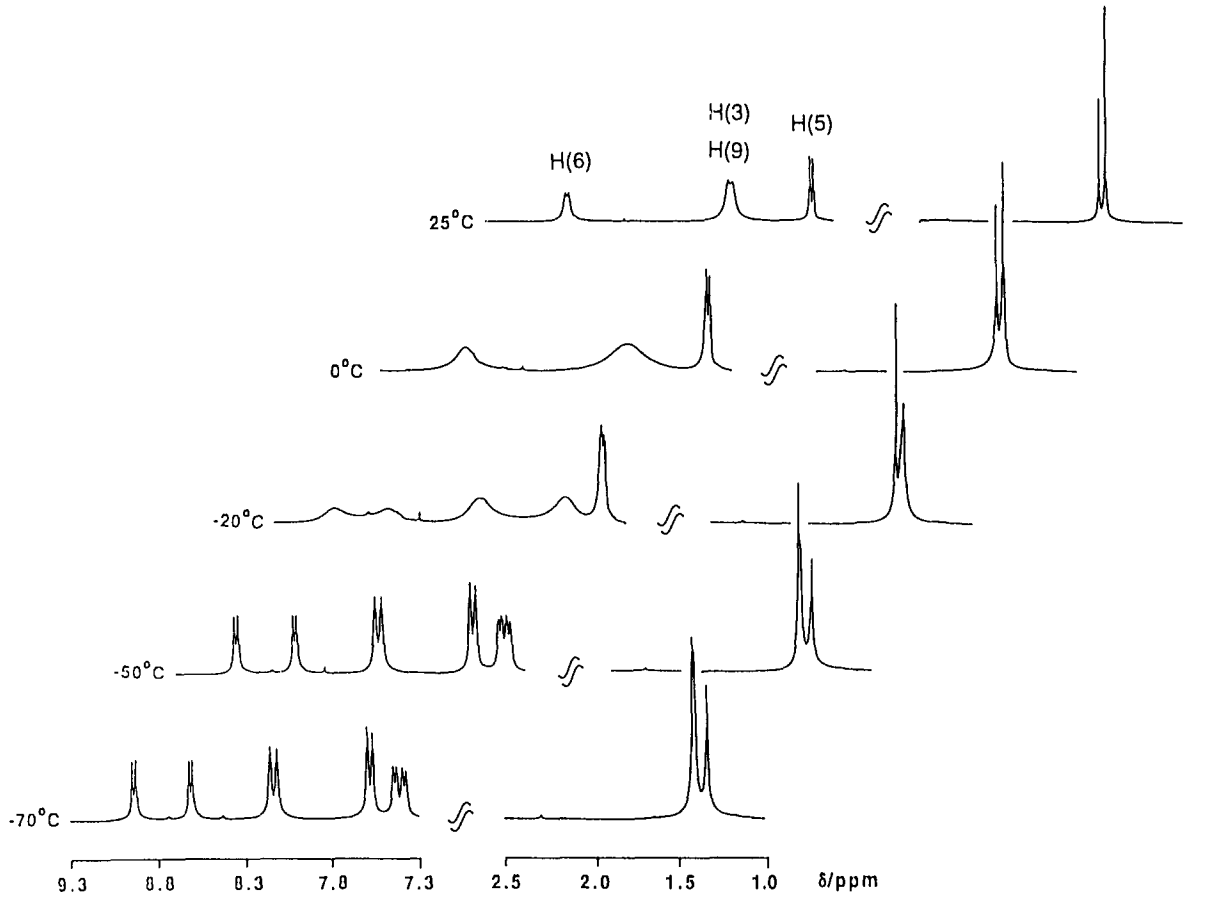


Fig. 1. The ^1H NMR spectra (CD_2Cl_2, 270 MHz) of $[Mo(CO)_4(4,4',4''\text{-}^tBu_3terpy)]$ (**2**) at various temperatures.

the same fluxional process occurs (Fig. 1). At 25°C, only four resonances for the aromatic protons of the terpyridyl ligand are found, which broaden on lowering the temperature and finally all coalesce between −30 and −40°C. In contrast, the spectrum at −70°C shows eight sharp signals since at this temperature the fluxional process is slow on the NMR time scale. It is remarkable that the only signal not changing form with the temperature is that belonging to the tert-butyl group of the middle terpyridine ring.

The use of the tert-butyl-substituted terpyridine instead of the non-substituted terpyridine as ligand allows us to follow the fluxional process by ^{1}H NMR spectroscopy more easily. Better solubility of **2** makes it also possible to measure temperature-dependent ^{13}C NMR spectra within reasonable periods (Fig. 2). While at room temperature in the aryl region of the ^{13}C NMR spectrum only a few signals (most of them rather broadened) are visible, at −70°C every aromatic carbon of the 4,4′,4″-tri-tert-butyl-2,2′ : 6′,2″-terpyridyl ligand has its own sharp resonance. Only the line shape of one of the signals at $\delta \approx 161.7$ ppm, which is assignable to the carbon atom in the 4-position of the middle pyridine ring, is not influenced by the variation in temperature.

Whereas the information coming from the aromatic carbon region of the temperature-dependent ^{13}C NMR spectra strengthens the knowledge already obtained by the ^{1}H NMR spectroscopy, the changes observed for the CO signals at various temperatures are more important to note. The spectrum at −70°C shows four sharp signals above 200 ppm. While the resonances at $\delta =$ 205.56 ppm and $\delta = 203.73$ ppm are assignable to the CO ligands *trans* to each other, the resonances for the two CO in the *trans* position to the terpyridyl ligand are found at $\delta = 224.24$ ppm and $\delta = 217.35$ ppm. On warming the solution, the two sets of signals broaden and finally coalesce at about −35°C and about 0°C. At room temperature, one relatively sharp singlet at $\delta =$ 205.68 ppm and a very broad singlet at $\delta = 221.5$ ppm are observed.

Mainly the resonances found for the CO ligands, but also some aromatic signals both in the ^{13}C NMR spectra and in the ^{1}H NMR spectra, give us the chance to estimate the value of the free enthalpy of activation, even without the application of band shape analysis methods [5]. From the selected resonances which all coalesce in-between 0 and −40°C, $\Delta G^{\ddagger}$ values for the fluxional process from 50.0 to 52.5 kJ mol^{-1} can be calculated. In comparison with [Mo(CO)$_4$(4,4′,4″-^{t}Bu$_3$terpy)] (**2**), for the complex [Mo(CO)$_4$(terpy)] containing the non-substituted terpyridyl ligand a value of 48.4 kJ mol^{-1} was reported for the free enthalpy of

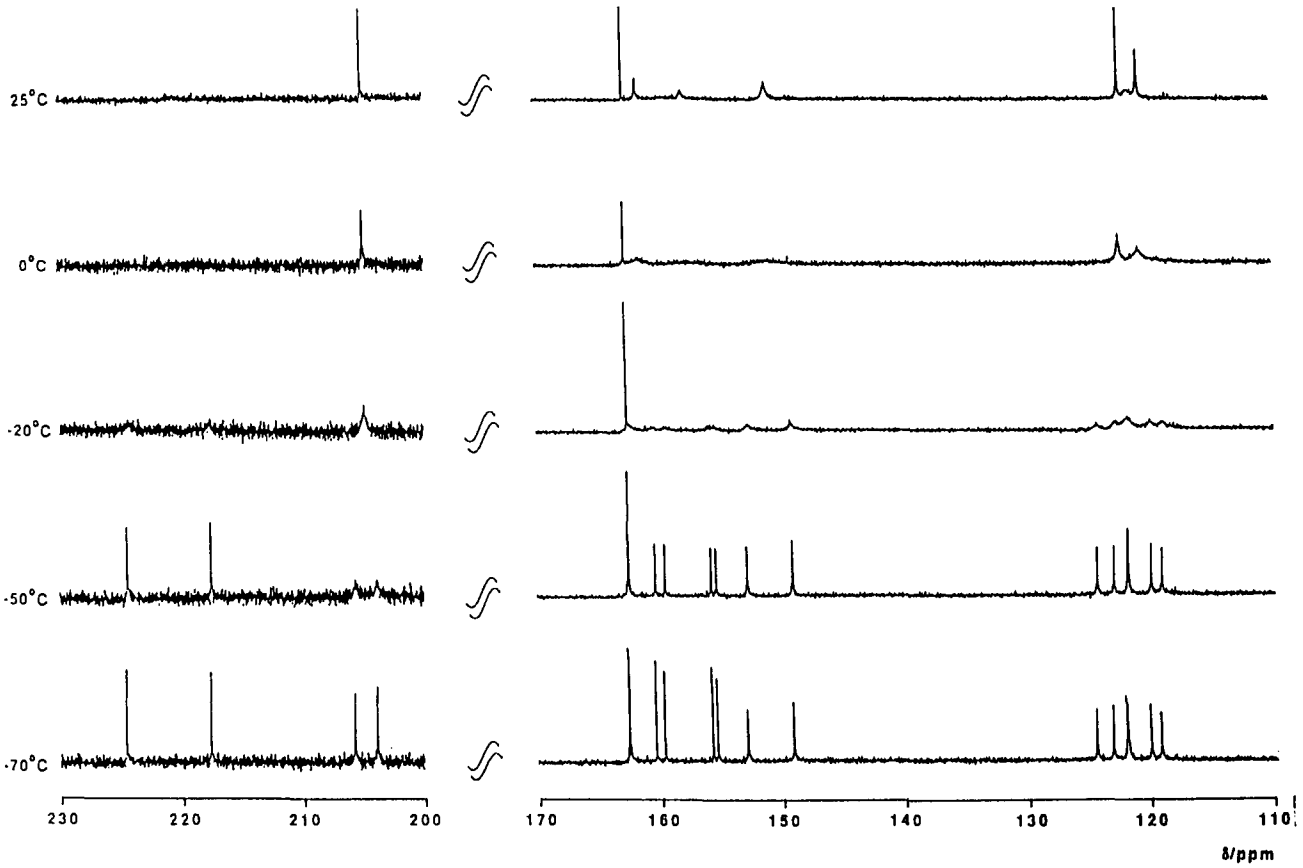
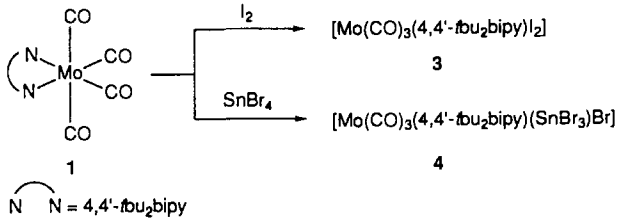


Fig. 2. The carbonyl and aryl region in the ^{13}C NMR spectra (CD_2Cl_2, 67.8 MHz) of [Mo(CO)$_4$(4,4′,4″-^{t}Bu$_3$terpy)] (**2**) at various temperatures.

activation [4]. This indicates that the presence of the electron-donating tert-butyl group influences the fluxional behavior of the terpyridyl ligand, even if the effect of the substituent is not very significant.

2.2. Tricarbonylmolybdenum(II) complexes

As explained in the introduction, our main interest was in the field of the stereochemical behavior of the compounds $[Mo(CO)_3(4,4'\text{-}^tBu_2bipy)X_2]$ in solution. The diiodo complex $[Mo(CO)_3(4,4'\text{-}^tBu_2bipy)I_2]$ (**3**) can easily be prepared by treating the tetracarbonyl complex $[Mo(CO)_4(4,4'\text{-}^tBu_2bipy)]$ (**1**) with an equivalent amount of iodine at room temperature in either CH_2Cl_2 or toluene (Scheme 2). While under similar conditions **1** also reacts with $SnBr_4$ to give the complex $[Mo(CO)_3(4,4'\text{-}^tBu_2bipy)(SnBr_3)Br]$ (**4**), the oxidative addition of bromine is problematic. After stirring equivalent amounts of $[Mo(CO)_4(4,4'\text{-}^tBu_2bipy)]$ (**1**) and Br_2 in CH_2Cl_2 for 10 min at room temperature, the products were isolated and found to contain, besides the dibromo complex $[Mo(CO)_3(4,4'\text{-}^tBu_2bipy)Br_2]$ (**5**), small amounts of the starting material **1** and an unidentified paramagnetic species. Whereas the separation of the molybdenum(0) complex **1** was successful, the total exclusion of the paramagnetic byproduct, which meant that the NMR spectroscopy analysis of compound **5** was impossible, had failed.



Scheme 2.

In trying to avoid this dilemma, we discovered that copper(II) bromide is a more suitable starting material for the synthesis of the dibromo complex **5**. After stirring a solution of $[Mo(CO)_3(4,4'\text{-}^tBu_2bipy)]$ (**1**) in CH_2Cl_2 in the presence of a double excess of $CuBr_2$ for about 1 h at room temperature separation of the formed copper(I) bromide, the dibromomolybdenum(II) complex $[Mo(CO)_3(4,4'\text{-}^tBu_2bipy)Br_2]$ (**5**) can be isolated as the pure product with a nearly quantitative yield (Scheme 3). In a similar reaction (except that the reaction time has to be prolonged to about 5 h) the dichloro compound $[Mo(CO)_3(4,4'\text{-}^tBu_2bipy)Cl_2]$ (**6**) is available starting from **1** and two equivalent amounts of $CuCl_2 \cdot 2H_2O$.

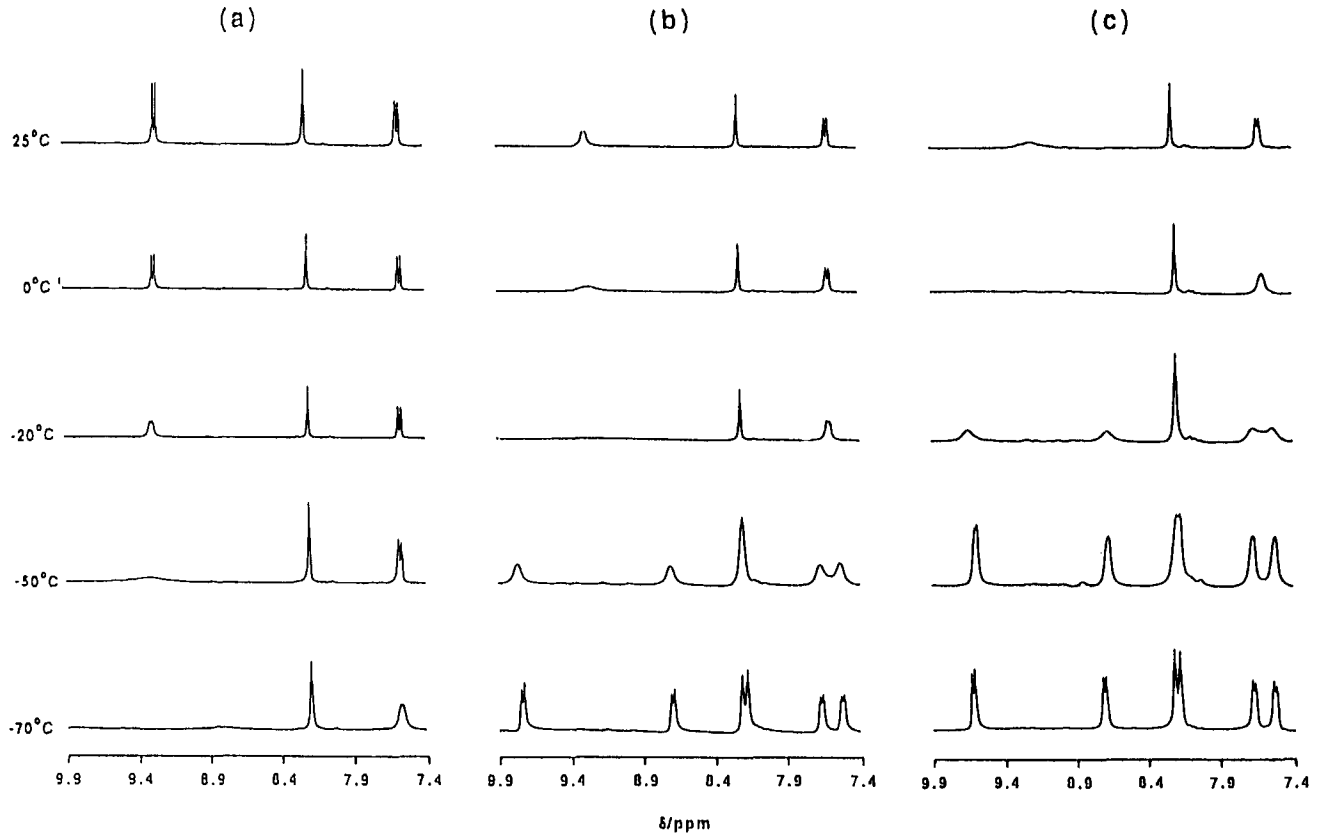
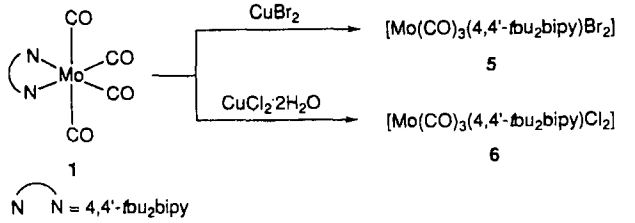


Fig. 3. The aryl region in the ^1H NMR spectra (CD_2Cl_2, 270 MHz) of (a) $[Mo(CO)_3(4,4'\text{-}^tBu_2bipy)I_2]$ (**3**). (b) $[Mo(CO)_3(4,4'\text{-}^tBu_2bipy)Br_2]$ (**5**) and (c) $[Mo(CO)_3(4,4'\text{-}^tBu_2bipy)Cl_2]$ (**6**) at various temperatures.



Scheme 3.

Like the known complexes $[Mo(CO)_3(bipy)X_2]$ (X = Br or I) [2], the 4,4'-di-^{t}Bu-2,2'-bipyridyl analogoues **3**, **5** and **6** are also unstable in solution with the instability growing from the diiodo to the dichloro complex. Their solubilities in all tested organic solvents decrease in the same order. Nevertheless, both the solubility and the stability in solution of all three dihalogeno complexes is sufficient to observe their stereochemical behavior in solution by NMR as well as by IR spectroscopy.

The IR spectra measured in KBr have already shown significant differences. Whereas for the dibromo compound **5** and the dichloro complex **6** only one CO stretching frequency above 2000 cm^{-1} is found, the diiodo complex **3** shows two bands: a medium band at 2033 cm^{-1} and a strong band at 2008 cm^{-1}. Measurements in different organic solvents indicate that the relative intensities of these two bands depends heavily on the polarity of the solvent. While in benzene the CO stretching frequency at lower wavenumbers is more intense, the CO band at higher wavenumbers dominates strongly in CH_3NO_2. It should be noted also that the dibromo complex **5** shows in the less polar solvents $CHCl_3$ and CH_2Cl_2 besides the strong band at about 2050 cm^{-1} a very weak band at about 2015 cm^{-1}, which is absent in the spectra measured in acetone and CH_3NO_2. For the dichloro compound **6** in all tested solvents we were only able to observe one stretching frequency at about 2055 cm^{-1}.

The most reasonable explanation for this observation is that the dihalogeno complexes $[Mo(CO)_3(4,4'\text{-}{}^tBu_2bipy)X_2]$ exist in solution in two isomeric forms, which are in equilibrium at room temperature. For the diiodo compound **3**, real equilibrium is attained with a more apolar isomer dominating in the apolar solvents and a more polar isomer favored in the more polar solvents, whereas in the case of the dibromo compound **5** and the dichloro complex **6** this equilibrium nearly favors the more polar structure but is less influenced by the polarity of the solvent. Similar observations have previously been made by Kummer and Graham [6] for compounds of the general type $[Mo(CO)_3(bipy)(SnX_3)X]$.

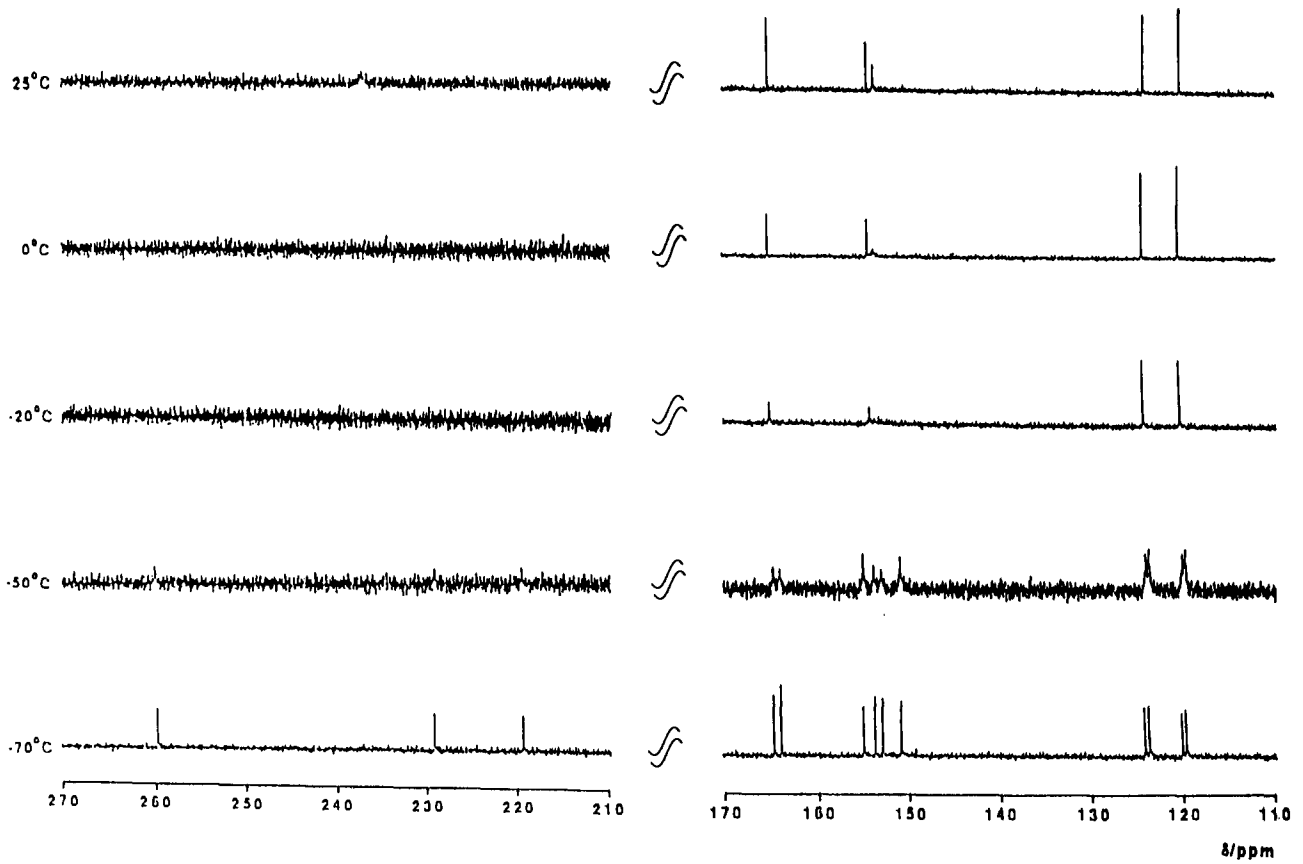


Fig. 4. The carbonyl and aryl region in the ^{13}C NMR spectra (CD_2Cl_2, 67.8 MHz) of $[Mo(CO)_3(4,4'\text{-}{}^tBu_2bipy)Br_2]$ (**5**) at various temperatures.

In order to gain more insight into the structure of these two isomeric forms, we studied the NMR spectra of the dihalogeno complexes **3**, **5** and **6**, which are temperature dependent similar to those of **2** (Figs. 3 and 4). The ^{1}H NMR spectrum of the dibromo complex **5** measured at room temperature shows three relatively sharp signals in the aryl region, which broaden on cooling the solution and finally coalesce. At temperatures lower than −50°C a new set of six signals appeared, illustrating that in the more stable isomer the bipyridyl ligand is asymmetrically bonded to the molybdenum atom. In an analogous manner the changes in the ^{1}H NMR spectra for **3** and **6**, which were also measured in the temperature range from 25 to −70°C, can be explained. It is remarkable that, in comparison with the dibromo complex **5**, for the dichloro compound **6** at temperatures about 25°C higher and for the diiodo complex **3** at temperatures about 45°C lower, nearly the same band shapes for all signals can be found (Fig. 3).

The same phenomena can be observed in the case of the ^{13}C NMR spectroscopy. Because of this (see Fig. 4) only the temperature-dependent spectra of the dibromo complex **5** are shown. Whereas at room temperature in the aryl region five relatively sharp signals are visible, in the spectrum measured at −70°C a double set of these resonances is found. In the carbonyl region at 25°C, only one very broad signal at $\delta = 237$ ppm can be observed. In contrast with this, the spectrum at −70°C shows three rather sharp singlets, one for each CO ligand, and thus indicates that in the more stable isomer not only the bipyridine but also the CO ligands are asymmetrically coordinated (Fig. 5, **A** and **A'**).

The simplicity of the ^{1}H NMR spectra as well as the ^{13}C NMR spectra allows us again to estimate the values for the free enthalpy of activation without the necessity of using band shape analysis methods [5]. For the dichloro complex **6**, a $\Delta G^{\ddagger}$ value of about 53 kJ mol^{-1} can be calculated, whereas a value of about 47 kJ mol^{-1} is obtained from the coalescence of the aryl resonances for the dibromo compound **5**. Unfortunately for the diiodo complex **3** such a quantitative estimation of the free enthalpy of activation is not possible, because the coalescence of all signals occurs at low temperatures.

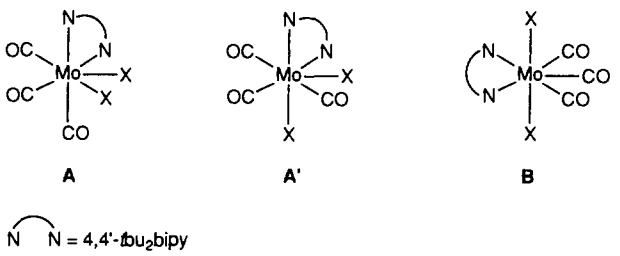


Fig. 5. Possible structures for the two isomeric forms in pentagonal bipyramidal $[Mo(CO)_3(4,4'\text{-}^tBu_2bipy)X_2]$.

Nevertheless, it can be inferred that the fluxional process in the diiodo complex **3** involves an activation energy some kilojoules per mole lower than the value found for the dibromo compound **5** since the process is very fast on the NMR time scale.

This interpretation also corresponds to the information given by the IR spectroscopy. A lower value for the free enthalpy of activation would explain why, in the case of the diiodo complex **3**, both isomers are visible whereas, for the dibromo compound **5**, mainly the more stable isomer and, for the dichloro compound **6**, exclusively only the more stable isomer can be observed.

The question of the manner in which the two isomeric forms the ligands are arranged around the molybdenum atom cannot be answered definitely. Because of the relatively lower stability of the halogeno complexes $[Mo(CO)_3(4,4'\text{-}^tBu_2bipy)X_2]$ in solution, we have so far not been able to grow single crystals for an X-ray structural analysis, which at least would show what the structure of these molecules looks like in the crystal lattice. Only a few molecular structures for seven-coordinated molybdenum(II) complexes containing bipyridine as a ligand are known and these examples also differ in their geometry. While $[Mo(C_2H_5NC)_3(bipy)_2][BF_4]_2$ [7] and $[Mo(CO)_3(bipy)(SnMeCl_2)Cl]$ [8] are reported to be capped octahedral, the compound $[Mo(CO)_3(bipy)(HgCl)Cl]$ [9] has a capped trigonal prism geometry. Recently we found for the complex $[Mo(CO)(norbornadiene)(bipy)Br_2]$ [1] also a nearly perfect pentagonal bipyramidal structure.

Even if there is no chance of describing the absolute positions of the ligands, a statement as to their arrangement around the molybdenum atom relative to each other seems to be possible. The IR and NMR spectroscopic data allow us to argue that in the more stable isomer an "all-*cis* arrangement" of the ligands (analogous to **A** or **A'** in Fig. 5) is probable. With reference to the other isomer the only information is that its structure should be less polar. Whether this means that here the complexes exist in a more symmetrical form with the halogen atoms in mutually *trans* positions (Fig. 5, **B**) cannot be more than a speculation.

In conclusion, it should be mentioned that we also tried to look into the behavior of the complex $[Mo(CO)_3(4,4'\text{-}^tBu_2bipy)(SnBr_3)Br]$ (**4**) in solution (Scheme 2). Like other compounds of the general type $[Mo(CO)_3(bipy)(SnX_3)X]$ [6], this 4,4'-di-^{t}Bu-2,2'-bipyridyl complex shows two bands in the IR spectrum measured in CH_2Cl_2 above 2000 cm^{-1}, which are more visible using acetone as solvent. Unfortunately in the ^{1}H NMR spectra we were not able to observe any interpretable change in the line shape of the three aromatic resonances by lowering the measurement temperature from 25 to −70°C. Also the five singlets found in the aryl region of the ^{13}C NMR spectra measured at 25,

−20, −40, −50 and −70°C show no really conspicuous differences. With regard to a dynamic process for the 4,4′-di-^{t}Bu-2,2′-bipyridyl ligand the only definite observation was that the signal for the CMe_3 carbon atom continuously grows in intensity on lowering the temperature.

The existence of a fluxional behavior for compound **4** could be ensured by the temperature dependence found for the signals of the CO ligands. Whereas no signal in the carbonyl region was observed in the spectra at −40°C and above, a broad signal at $\delta \approx 227$ ppm was visible in the ^{13}C NMR spectrum measured at −50°C. By cooling the solution to −70°C this signal sharpens and a second singlet, of about half the intensity, appeared at $\delta = 219.12$ ppm.

Because of their poor solubility for analogous seven-coordinated molybdenum(II) complexes with a bipyridyl ligand, comparable data have so far not been available in the literature [10], while the reported ^{13}C NMR spectrum of the similar seven-coordinated compound $[Mo(CO)_3(NCMe)_2(SnCl_3)Cl]$ measured in acetone-d_6 at −70°C shows not less than 12 resonances in-between $\delta = 200$ ppm and $\delta = 230$ ppm, indicating that there must be several different isomers in solution [11]. However, even without comparable data it does not seem to be too difficult to interpret the ^{13}C NMR spectroscopy observations for the compound $[Mo(CO)_3$-$(4,4'$-$^t Bu_2bipy)(SnBr_3)Br]$ (**4**). In contrast with the dihalogeno complexes $[Mo(CO)_3(4,4'$-$^t Bu_2bipy)X_2]$, the molecular structure in the crystal is reported for the compound $[Mo(CO)_3(bipy)(SnMeCl_2)Cl]$ [8], which shows a capped octehedral geometry with the $SnMeCl_2$ unit capping an octaeder build by the other ligands (Fig. 6, **C**).

The assignment of this structure to the most stable isomer of **4** in solution must be in agreement with the ^{13}C NMR spectrum observed at −70°C. The two equivalent CO ligands *trans* to the bipyridyl ligand, should be assigned by the signal at $\delta = 227.25$ ppm, whereas the singlet at $\delta = 219.12$ ppm of about only half the intensity, should be assigned to the CO *trans* to the bromo ligand. In the supposed capped octahedral geometry (Fig. 6, **D**) the two pyridine rings of the 4,4′-di-^{t}Bu-2,2′-bipyridyl ligand have to be equivalent. Because of this, even at −70°C, only one set of signals for the aromatic protons and carbon atoms can be observed.

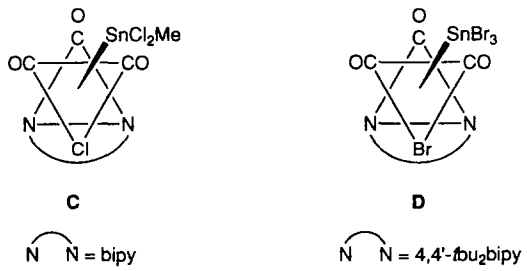


Fig. 6. Molecular structure of $[Mo(CO)_3(bipy)(SnCl_2Me)Cl]$ in capped octahedral geometry and supposed structure of the most stable isomeric form in $[Mo(CO)_3(4,4'$-^{t}Bubipy$)(SnBr_3)Br]$ (**4**).

3. Experimental section

All reactions were carried out under an atmosphere of argon and in carefully dried solvents. The starting materials $[Mo(CO)_4$(norbornadiene)] [12], 4,4′-di-tert-butyl-2,2′-bipyridine [13] and 4,4′,4″-tri-tert-butyl-2,2′ : 6′,2″-terpyridine [14] were prepared by published methods. The spectrometer were as follows: 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 $[Mo(CO)_4(4,4'$-$^t Bu_2bipy)]$ (1) [15]

A suspension of $[Mo(CO)_6]$ (3.0 g, 11.4 mmol) in 30 ml of toluene was treated with 4,4′-di-^{t}Bu-2,2′-bipyridine (3.0 g, 11.2 mmol) and the mixture was heated under reflux for 2 h. The solvent was then removed and the residue was washed twice with 20 ml of pentane to give a red microcrystalline solid (yield, 5.3 g (99%); decomposition temperature, above 250°C). Anal. Found: C, 55.34; H, 5.08; N, 5.83. $C_{22}H_{24}MoN_2O_4$ Calc.: C, 55.47; H, 5.08; N, 5.88%. IR (KBr): ν(CO) 2012(s), 1902(vs), 1873(vs), 1821(vs) cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz): δ 8.97 (d; J(HH) = 5.9 Hz; 2H; H(6)), 8.07 (d; J(HH) = 1.7 Hz; 2H; H(3)), 7.36 (dd; J(HH) = 5.9 and 1.7 Hz; 2H; H(5)), 1.44 (s; 18H; CCH_3) ppm. ^{13}C NMR ($CDCl_3$, 67.8 MHz): δ 223.10, 205.04 (CO), 162.04, 154.77, 152.59, 122.53, 118.60 (C(2)–C(6)), 35.35 (CCH_3), 30.42 (CCH_3) ppm.

3.2. Preparation of $[Mo(CO)_4(4,4',4''$-$^t Bu_3terpy)]$ (2)

A solution of $[Mo(CO)_4$(norbornadiene)] (962 mg, 2.40 mmol) in 20 ml of toluene was treated with 4,4′,4″-tri-^{t}Bu-2,2′ : 6′,2″-terpyridine (720 mg, 2.40 mmol) and the mixture was stirred for 4 h at room temperature. The solution was concentrated to about 10 ml in vacuum, and 50 ml of pentane was added. The solution was cooled to 0°C and the red solid that separated was filtered off, washed with pentane and dried in vacuum (yield, 1.37 g (94%); decomposition temperature, 142°C). Anal. Found: C, 61.43; H, 5.71; N, 6.90. $C_{31}H_{35}MoN_3O_4$ Calc.: C, 61.08; H, 5.13; N, 6.89%. IR (KBr): ν(CO) 2011(s), 1893(vs), 1874(vs), 1839(vs) cm^{-1}. ^1H NMR (CD_2Cl_2, 270 MHz, 25°C): δ 8.84 (d, br; J(HH) = 5.6 Hz; 2H; H(6)), 7.92, 7.89 (both s, br; both 2H; H(3) and H(9)), 7.44 (dd; J(HH) = 5.6 and 2.0 Hz; 2H; H(5)), 1.47 (s; 9H; C(10)CCH_3), 1.43 (s; 18H; C(4)CCH_3) ppm, ^1H NMR (CD_2Cl_2, 270 MHz, −70°C): δ 8.93 (d; J(HH) = 5.6 Hz; 1H) and

8.61 (d; J(HH) = 5.3 Hz; 1H; H(6) and H(6)′), 8.15, 8.11, 7.60, 7.57 (all s; all 1H; H(3), H(3)′, H(9) and H(9)′), 7.44 (d; J(HH) = 5.3 Hz; 1H) and 7.39 (d; J(HH = 5.6 Hz; 1H; H(5) and H(5)′). 1.40 (s; 9H; C(10)CCH_3), 1.39, 1.32 (both s; both 9H; C(4)CCH_3 and C(4)′CCH_3) ppm. ^{13}C NMR (CD_2Cl_2, 67.8 MHz, 25°C): δ 221.5 (br; CO), 205.68 (CO), 162.71, 161.6 (br), 157.8 (vbr), 151.1 (vbr), 122.33, 121.5 (vbr) and 120.72 (C(2)–C(10)), 35.70 (C(10)$CCH3$), 35.45 (C(4)CCH_3), 30.54 (C(4)CCH_3), 30.51 (C(10)CCH_3) ppm. ^{13}C NMR (CD_2Cl_2, 67.8 MHz, −70°C): δ 224.24, 217.35, 205.56, 203.73 (CO), 161.78, 161.75, 161.65, 159.55, 158.87, 154.97, 154.57, 152.12, 148.40, 123.76, 122.44, 121.35, 121.22, 119.41, 118.57 (C(2)–C(10)), 35.10 (C(10)CCH_3), 35.04, 34.63 (C(4)CCH_3 and C(4)′CCH_3), 29.74 ($CCCH3$) ppm.

3.3. Preparation of [Mo(CO)$_3$(4,4′-^{t}Bu$_2$bipy)I$_2$] (3)

A solution of **1** (420 mg, 0.88 mmol) in 5 ml of CH_2Cl_2 or 10 ml of toluene was treated with I_2 (244 mg, 0.88 mmol) and the mixture was stirred for 15 min at room temperature. The solvent was removed in vacuum and the residue recrystallized from CH_2Cl_2–pentane to give a yellow–brown solid (yield, 596 mg (96%); decomposition temperature, 147°C). Anal. Found: C, 35.50; H, 3.39; N, 4.03. $C_{21}H_{24}I_2MoN_2O_3$ calc.: C, 35.92; H, 3.44; N, 3.99%. IR (KBr): ν(CO) 2033(m), 2008(s) 1966(m), 1921(vs), 1914(vs) cm^{-1}. IR (CH_2Cl_2): ν(CO) 2038(s), 2018(m), 1972(vs), 1928(vs) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 270 MHz, 25°C): δ 9.26 (d; J(HH) = 5.9 Hz; 2H; H(6)), 8.23 (d; J(HH) = 1.7 Hz; 2H; H(3)), 7.58 (dd; J(HH) = 5.9 and 1.7 Hz; 2H; H(5)), 1.45 (s; 18H; CCH_3) ppm. ^{1}H NMR (CD_2Cl_2, 270 MHz, −70°C): δ 9.8, 8.8 (both s, vbr; both 1H; H(6) and H(6)′), 8.20 (s, br; 2H; H(3)), 7.58 (s, br; 2H; H(5)), 1.38 (s; 18H; CCH_3) ppm. ^{13}C NMR (CD_2Cl_2, 67.8 MHz, 25°C): δ 233.2 (br; CO), 165.11 154.58, 154.31, 124.32, 120.63 (C(2)–C(6)), 35.98 (CCH_3), 30.41 (CCH_3) ppm. ^{13}C NMR (CD_2Cl_2, 67.8 MHz, −70°C): δ 163.96, 155 (vbr), 153.3 (br), 124.05 and 120.29 (C(2)–C(6)), 35.33 (CCH_3), 29.58 (CCH_3) ppm, signal for CO not identified.

3.4. Preparation of [Mo(CO)$_3$(4,4′-^{t}Bu$_2$bipy)(SnBr$_3$)Br] (4)

A solution of **1** (155 mg, 0.33 mmol) in 5 ml of CH_2Cl_2 was treated with $SnBr_4$ (143 mg, 0.33 mmol) and the mixture was stirred for 20 min at room temperature. A yellow microcrystalline solid precipitated which was filtered off, washed with pentane and dried in vacuum, (yield, 221 mg (77%); decomposition temperature, 189°C). Anal. Found: C, 28.43; H, 2.80; N, 3.19. $C_{21}H_{24}Br_4MoN_2O_3Sn$ calc.: C, 28.45; H, 2.73; N, 3.16%. IR (KBr): ν(CO) 2022(vs), 1983(m), 1894(s) cm^{-1}. IR (CH_2Cl_2): ν(CO) 2035(m, sh), 2023(vs), 1977(w), 1953(m, sh), 1928(s) cm^{-1}. IR (acetone): ν(CO) 2045(w), 2022(vs), 1974(m), 1945(m, sh), 1923(s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 270 MHz, 25°C): δ 8.91 (d; J(HH) = 5.9 Hz; 2H; H(6)), 8.22 (d; J(HH) = 2.0 Hz; 2H; H(3)), 7.68 (dd; J(HH) = 5.9 and 2.0 Hz; 2H; H(5)), 1.46 (s; 18H; CCH_3) ppm. ^{1}H NMR ($CDCl_2$, 270 MHz, −70°C): δ 8.61 (d; J(HH) = 5.9 Hz; 2H; H(6)), 8.18 (s; 2H; H(3)), 7.66 (d; J(HH) = 5.9 Hz; 2H; H(5)), 1.40 (s; 18H; CCH_3) ppm. ^{13}C NMR (CD_2Cl_2, 67.8 MHz, 25°C): δ 166.39, 154.12, 153.43, 125.30, 120.83 (C(2)–C(6)), 36.18 ($CCH3$), 30.36 (CCH_3) ppm, signal for CO not found. ^{13}C NMR (CD_2Cl_2, 67.8 MHz, −70°C): δ 227.25 and 219.12 (ratio 2:1; CO), 165.34, 152.81, 152.58, 124.95, 120.43 (C(2)–C(6)), 35.53 (CCH_3), 29.57 (CCH_3) ppm.

3.5. Preparation of [Mo(CO)$_3$(4,4′-^{t}Bu$_2$bipy)Br$_2$)] (5)

(i) A solution of **1** (219 mg, 0.46 mmol) in 10 ml of CH_2Cl_2 was treated with 1.3 ml of a 0.35 M solution of Br_2 in CCl_4 and the mixture was stirred for 10 min at room temperature. The solvent was removed in vacuum and the residue recrystallized from CH_2Cl_2/pentane to give an orange–yellow solid (yield, 207 mg (74%)).

(ii) A solution of **1** (481 mg, 1.01 mmol) in 10 ml of CH_2Cl_2 was treated with $CuBr_2$ (451 mg, 2.02 mmol) and the mixture was stirred for 1 h at room temperature then filtered through cellulose. The filtrate was taken to dryness in vacuum, and the residue recrystallized from CH_2Cl_2–pentane to give an orange–yellow solid (yield, 533 mg (87%); decomposition temperature, 163°C). Anal. Found: C, 41.05; H, 3.89; N, 4.55. $C_{21}H_{24}Br_2MoN_2O_3$ Calc.: C, 41.47; H, 3.98; N, 4.61%. IR (KBr): ν(CO) 2057(vs), 1967(vs), 1919(vs) cm^{-1}. IR (CH_2Cl_2): ν(CO) 2052(vs), 2016(w), 1979(vs), 1925(s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 270 MHz, 25°C): δ 9.29 (d, br; J(HH) = 5.9 Hz; 2H; H(6)), 8.23 (d; J(HH) = 1.7 Hz; 2H; H(3)), 7.57 (dd; J(HH) = 5.9 and 1.7 Hz; 2H; H(5)), 1.45 (s; 18H; CCH_3) ppm. ^{1}H NMR (CD_2Cl_2, 270 MHz, −70°C): δ 9.74 (d; J(HH) = 5.6 Hz; 1H) and 8.70 (d; J(HH) = 5.6 Hz; 1H; H(6) and H(6)′), 8.22 and 8.18 (both s; both 1H; H(3) and H(3)′), 7.67 (d; J(HH) = 5.6 Hz; 1H) and 7.52 (d, J(HH) = 5.6 Hz; 1H; H(5) and H(5)′), 1.39, 1.37 (both s; both 9H; C(4)CCH_3 and C(4)′CCH_3) ppm. ^{13}C NMR (CD_2Cl_2, 67.8 MHz, 25°C): δ 237 (vbr; CO), 165.05, 154.36, 153.63, 124.33, 120.40 (C(2)–C(6)), 35.89 ($CCH3$), 30.33 (CCH_3) ppm. ^{13}C NMR (CD_2Cl_2, 67.8 MHz, −70°C): δ 259.47, 229.30, 219.65 (CO), 164.31, 163.54, 154.66, 153.43, 152.62, 150.60, 124.24, 123.77, 120.26, 119.82 (C(2)–C(6)), 35.25, 35.14 (C(4)CCH_3 and C(4)′CCH_3), 29.49 ($CCH3$) ppm.

3.6. Preparation of [Mo(CO)$_3$(4,4′-^{t}Bu$_2$bipy)Cl$_2$)] (6)

A solution of **1** (390 mg, 0.82 mmol) in 10 ml of CH_2Cl_2 was treated with $CuCl_2$–$2H_2O$ (279 mg, 1.64

mmol) and the mixture was stirred for 5 h at room temperature then filtered through cellulose. The filtrate was taken to dryness in vacuum, and the residue recrystallized from CH_2Cl_2–pentane to give a yellow microcrystalline solid (yield, 367 mg (86%); decomposition temperature 156°C). Anal. Found: C, 47.90; H, 4.55; N, 5.36. $C_{21}H_{24}Cl_2MoN_2O_3$ Calc.: C, 48.57; H, 4.66; N, 5.39%. IR (KBr): ν(CO) 2062(vs), 1968(vs), 1919(vs) cm^{-1}. IR (CH_2Cl_2): ν(CO) 2057(vs), 1979(vs), 1922(s) cm^{-1}. ^1H NMR (CD_2Cl_2, 270 MHz, 25°C): δ 9.2 (s, vbr; 2H; H(6)), 8.22 (s; 2H; H(3)), 7.62 (d; J(HH) = 5.3 Hz; 2H; H(5)), 1.45 (s; 18H; CCH_3) ppm. ^1H NMR (CD_2Cl_2, 270 MHz, −70°C): δ 9.62 (d; J(HH) = 5.0 Hz; 1H) and 8.68 (d; J(HH) = 4.3 Hz; 1H; H(6) and H(6)′), 8.22 and 8.19 (both s; both 1H; H(3) and H(3)′), 7.69 (d; J(HH) = 5.0 Hz; 1H) and 7.53 (d; J(HH) = 4.3 Hz; 1H; H(5) and H(5)′), 1.41, 1.38 (both s; both 9H; C(4)CCH_3 and C(4)′CCH_3) ppm. ^{13}C NMR (CD_2Cl_2, 67.8 MHz, 25°C): δ 164.90, 154.11, 153 (vbr), 124.17 and 120.16 (C(2)–C(6)), 35.71 (CCH3), 30.22 (CCH_3) ppm, signal for CO not assigned. ^{13}C NMR (CD_2Cl_2, 67.8 MHz, −70°C): δ 264.56, 230.99, 220.23 (CO), 164.15, 163.29, 154.19, 153.09, 152.35, 149.27, 124.19, 123.42, 120.01, 119.51 (C(2)–C(6)), 35.02, 34.88 (C(4)CCH_3 and C(4)′CCH_3), 29.30 (CCH_3) ppm.

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[15] Compound **1** has already been reported to be prepared starting from [$Mo(CO)_4$(norbornadiene)]; see [3].