

A stable carbonyl–pyrazine–metal(0) complex: Synthesis and characterization of *cis*-tetracarbonylpyrazinetrimethylphosphitetungsten(0)

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Abstract

Pentacarbonylpyrazinetungsten(0), $(\text{CO})_5\text{W}(\text{pyz})$, is not stable in solution in polar solvents such as acetone or dichloromethane and undergoes conversion to a bimetallic complex, $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$ plus free pyrazine. These three species exist at equilibrium. Using the quantitative ^1H NMR spectroscopy, the equilibrium constant could be determined to be $K_{\text{eq}} = (5.9 \pm 0.8) \times 10^{-2}$ at 25 °C. Introducing a second pyrazine ligand into the molecule does not stabilize the complex, as *cis*- $\text{W}(\text{CO})_4(\text{pyz})_2$ was found to be less stable than $\text{W}(\text{CO})_5(\text{pyz})$ and, therefore, could not be isolated. However, introducing trimethylphosphite as a donor ligand into the complex leads to the stabilization of the carbonyl–pyrazine–metal(0) complexes, as shown by the synthesis of *cis*- $\text{W}(\text{CO})_4[\text{P}(\text{OCH}_3)_3](\text{pyz})$. This complex could be isolated from the reaction of the photogenerated $\text{W}(\text{CO})_4[\text{P}(\text{OCH}_3)_3](\text{tetrahydrofuran})$ with trimethylphosphite upon mixing for 2 h at 10 °C in tetrahydrofuran and characterized by elemental analysis, IR, MS, ^1H , ^{13}C , and ^{31}P NMR spectroscopy.

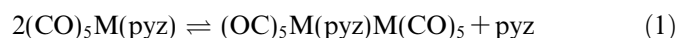
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1. Introduction

Pyrazine, pyz, has two nitrogen donor atoms in *para* positions in the aromatic heterocyclic ring and, therefore, is well known as linking ligand between metal ions generating low dimensional or infinite chain compounds [1]. Pyrazine is expected to be a good π acceptor ligand as its LUMO is the relatively low energy π^* orbitals [2]. The first transition metal pyrazine complex, $[\text{Ru}(\text{NH}_3)_5(\text{pyz})]^{2+}$, is considered as an example for its π accepting ability [3]. However, two factors can contribute to the ruthenium–nitrogen bond strength and, thus, to the stability of this complex: (i) +2 charge of ruthenium leading to a decrease in the demand for π back donation, (ii) the presence of five ammine ligands having no π accepting ability. In fact, the

pyrazine complexes of the zero valent d^6 ions are not stable [4]. Although the pyrazine complexes of low-spin d^6 metal centers have been found to be nonfluxional, in contrast to the stereochemically nonrigid ruthenium complexes exhibiting 1,4-metallotropic shift of the pyrazine ligand, the Group 6 metal pyrazine complexes of the type $\text{M}(\text{CO})_5(\text{pyz})$ readily undergo dissociation of the pyrazine ligand even at ambient temperature [5]. One consequence of this dissociation is the formation of binuclear complexes for $\text{M} = \text{Mo}, \text{W}$ (Eq. (1)) [1h,2,6], similar to the Creutz–Taube binuclear ruthenium complexes [7]



The $(\text{OC})_5\text{M}(\text{pyz})\text{M}(\text{CO})_5$ complexes of the Group 6 metals have been found to be moderately stable in the solid form when kept in the dark at 273 K; storing under argon greatly increased their long-term stability [6]. In solution at 298 K, the complexes exhibit varying degrees of stability,

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with chromium and molybdenum complexes showing the fastest decomposition, and with tungsten complex being sufficiently stable for photochemical study in solution [6]. Instability of the metal(0) pyrazine complexes is obviously due to the weak metal \rightarrow pyrazine back donation.

Because of the tendency toward binucleation, $M(\text{CO})_5(\text{pyz})$ complexes have not been isolated in pure form and, therefore, their characterization has been based essentially on the solution IR spectra and elemental analysis [6]. Although the ^1H NMR chemical shifts of the $(\text{CO})_5M(\text{pyz})$ complexes have recently been reported [5], there exists no report on the ^{13}C NMR data which would definitely identify the mononuclear and binuclear complexes. Here, we report the ^{13}C NMR spectroscopic characterization of both the mononuclear and binuclear pyrazine complexes for the case of $M = \text{W}$. The equilibrium between the mononuclear $\text{W}(\text{CO})_5(\text{pyz})$ complex on one side and the binuclear $(\text{OC})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$ complex plus the free pyrazine molecule on the other side was investigated by using NMR spectroscopy. Furthermore, we report here our effort for the synthesis of a stable carbonyl pyrazine complex of Group 6 metals. Replacement of one CO group in the $\text{W}(\text{CO})_5(\text{pyz})$ complex by trimethylphosphite appears to strengthen the metal–pyrazine bond and thus to stabilize the resulting complex. As the first example of stable tungsten–pyrazine complexes containing a donor ligand, *cis*- $\text{W}(\text{CO})_4[\text{P}(\text{OCH}_3)_3](\text{pyz})$ could be isolated and characterized by elemental analysis, IR, NMR, and MS techniques. We also attempted to prepare a metal carbonyl complex containing two pyrazine ligands, *cis*- $\text{W}(\text{CO})_4(\text{pyz})_2$ from the ligand substitution reaction of *cis*- $\text{W}(\text{CO})_4(\text{piperidine})_2$ with excess pyrazine in dichloromethane. However, this complex appears to be unstable in solution and undergoes rapid decomposition at room temperature during the work-up. Therefore, its identification relies solely on the IR spectra taken in solution.

2. Experimental

2.1. General procedure

All reactions and manipulations were carried out either in vacuum or under a dry and oxygen free inert atmosphere (N_2 or Ar). Solvents were distilled after refluxing over metallic sodium or phosphorous pentoxide for 3–4 days and stored under nitrogen until used. Hexacarbonyltungsten(0), trimethylphosphite, and pyrazine were purchased from Merck GmbH, Darmstadt, Germany, and used without further purification.

The synthesis of complexes and substitution reactions were followed by taking IR spectra from tetrahydrofuran, *n*-hexane or dichloromethane solutions using Nicolet 510 FT-IR Spectrometer with OMNIC software. NMR spectra were recorded on a Bruker DPX 400 (400.1 MHz for ^1H ; 100.6 MHz for ^{13}C ; 161.3 MHz for ^{31}P). TMS was used as internal reference for ^1H and ^{13}C NMR chemical shifts. H_3PO_4 (85%, in a glass capil-

lary) was used as reference for ^{31}P NMR chemical shifts. FAB-MS was done on a Fisons VG Autospec with *m*-nitrobenzylalcohol as matrix. Elemental analysis was performed using LECO CHNS-932 instrument.

Photochemical reactions were carried out in an immersion-well apparatus [8] (solidex glass, $\lambda > 280$ nm) by using a Hanau TQ 150 high pressure mercury lamp. $\text{W}(\text{CO})_5[\text{P}(\text{OCH}_3)_3]$ [9], *cis*- $\text{W}(\text{CO})_4(\text{piperidine})_2$ [10], $\text{W}(\text{CO})_4(\eta^{2:2}\text{-norbornadiene})$ [11] and $\text{W}(\text{CO})_4(\eta^{2:2}\text{-1,5-cyclooctadiene})$ [12] were prepared according to the literature procedures.

2.2. Pentacarbonylpyrazinetungsten(0), $\text{W}(\text{CO})_5(\text{pyz})$, (1), and μ -pyrazine-bis(pentacarbonyltungsten(0)), $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$, (2)

Following the procedure [2] pyrazine (pyz, 0.454 g, 5.68 mmol) was added to a solution of $\text{W}(\text{CO})_5(\text{thf})$ photo-generated [13] from $\text{W}(\text{CO})_6$ (1.0 g, 2.84 mmol) in 250 mL tetrahydrofuran (thf) at 10 °C. After mixing for 2 h, the volatiles were removed under vacuum. The residue was washed several times with *n*-hexane and dried under vacuum (10^{-3} bar) (1.06 g, 93% yield for **1**). The complex is soluble in polar solvents such as acetone or dichloromethane. However, it is converted in solution to the bimetallic complex, $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$, plus free pyrazine reaching at an equilibrium. Both complexes could be characterized by IR, NMR and MS. $\text{W}(\text{CO})_5(\text{pyz})$, **1**: IR ($\nu(\text{CO})$, in CH_2Cl_2): 2069, 1941, and 1912 cm^{-1} ; molecular peak (m/z) = 404; ^{13}C NMR (d-acetone, in ppm) $\delta = 202.99$ (CO_{trans}), 197.17 (CO_{cis} , $J(^{183}\text{W}-^{13}\text{C}) = 131$ Hz), 151.40 (s, C(2,6)), 148.3 (s, C(3,5)); ^1H NMR (d-acetone, in ppm) $\delta = 9.07$ (s, H(2,6)), 8.74 (s, H(3,5)). $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$, **2**: ^{13}C NMR (d-acetone, in ppm) $\delta = 203.08$ (CO_{trans}), 198.9 (CO_{cis} , $J(^{183}\text{W}-^{13}\text{C}) = 131$ Hz), 153.27 (s, C2, C3, C5, C6, pyrazine); ^1H NMR (d-acetone, ppm) = 9.10.

2.3. Tetracarbonylbis(pyrazine)tungsten(0), *cis*- $\text{W}(\text{CO})_4(\text{pyz})_2$, (3)

A suspension of *cis*-tetracarbonylbis(piperidine)tungsten(0), *cis*- $\text{W}(\text{CO})_4(\text{pip})_2$ [10] (0.30 g, 0.80 mmol) in methylene chloride (25 mL) refluxed with threefold pyrazine (0.190 g, 2.4 mmol) at 38 °C for 6 h. The solution turned its color from yellow to red. After the complete reaction as monitored by taking the IR spectrum, the red solution containing *cis*- $\text{W}(\text{CO})_4(\text{pyz})_2$ complex was filtered. Volume of the solution was reduced to 2 mL by evaporating solvent under vacuum and 2 mL *n*-hexane was added. Cooling the solution to -35 °C for one day yielded red crystalline solid of *cis*- $\text{W}(\text{CO})_4(\text{pyz})_2$. Due to the instability of the complex in solution at room temperature, the complex was identified only by taking the IR spectrum in solution. IR ($\nu(\text{CO})$, in CH_2Cl_2): 2007, 1922, 1875, and 1835 cm^{-1} .

2.4. Tetracarbonylpyrazinetrimethylphosphitetungsten(0), *cis*-W(CO)₄[P(OCH₃)₃](pyz) (**4**)

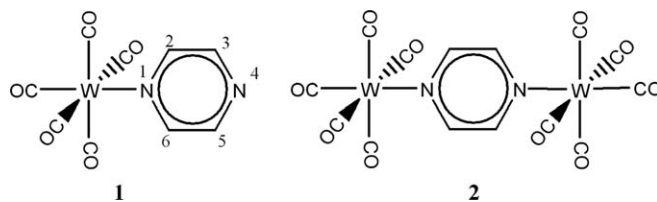
A solution of pentacarbonyltrimethylphosphitetungsten(0), W(CO)₅[P(OCH₃)₃], [9] (0.60 g, 1.34 mmol) in 250 mL tetrahydrofuran (thf) was irradiated to yield the metastable *cis*-W(CO)₄[P(OCH₃)₃](thf) intermediate. Upon addition of pyrazine (0.161 g, 2.01 mmol), the color of the solution was turned from dark-orange to red. After complete removal of volatiles, the residue was dissolved in toluene and transferred to a column (20 cm length, 3 cm diameter) packed with silica gel in toluene. The red complex was eluted with toluene. Then, the solution was brought to dryness in vacuum. The red oil-like residue was dissolved in *n*-hexane and solution was cooled down to -78 °C overnight. The red precipitate was separated from the supernatant solution by decantation, then dried under vacuum (Yield: 10%; 0.062 g). Anal. Calcd for C₁₁H₁₃N₂O₇PW ($M = 500.03$): C, 26.42; H, 2.63; N, 5.60. Found: C, 26.84; H, 2.75; N, 5.71. MS: m/z 500 (M^+). IR ($\nu(\text{CO})$, in *n*-hexane): 2024, 1929, 1901, and 1887 cm^{-1} ; ¹³C NMR (d-chloroform, in ppm): 202.52 (d, CO(1,2), $J(^{31}\text{P}-^{13}\text{C}) = 10.9$ Hz), 206.48 (d, CO(3), $J(^{31}\text{P}-^{13}\text{C}) = 51.2$ Hz), 207.59 (d, CO(4), $J(^{31}\text{P}-^{13}\text{C}) = 7.3$ Hz), 52.25 (d, -OCH₃, $J(^{31}\text{P}-^{13}\text{C}) = 3.1$ Hz), 150.73 (s, C(2,6), $J(^{31}\text{P}-^{13}\text{C}) = 2.2$ Hz), 146.38 (s, C(3,5)); ¹H NMR (d-chloroform, in ppm) = 8.78 (s, H(2,6)), 8.4 (s, H(3,5)), 3.54 ppm (d, -OCH₃, $J(^{31}\text{P}-^1\text{H}) = 11.2$ Hz); ³¹P NMR (d-chloroform, in ppm) = 148.09 (s, P(OCH₃)₃, $J(^{183}\text{W}-^{31}\text{P}) = 392$ Hz).

2.5. The determination of equilibrium constant by means of ¹H NMR spectroscopy

¹H NMR spectra were used to quantify the relative concentrations of the species at equilibrium and, thus, to determine the equilibrium constant. The equilibrium constant was determined from the ¹H NMR spectra taken from the solution of the complex after addition of various amount of the free pyrazine molecule in dichloromethane-d₂. The areas under the peaks were measured by taking the integral and used to calculate the concentrations of monometallic and bimetallic complexes as well as of the free pyrazine, thus, the equilibrium constant.

3. Results and discussion

Pentacarbonylpyrazinetungsten(0), W(CO)₅(pyz), was prepared starting with hexacarbonyltungsten(0) and pyrazine according to the literature procedure [2]. The complex could be isolated from the reaction solution as crystalline materials and found to be stable in solids. However, it is not stable in solution in polar solvents such as acetone or dichloromethane and slowly converted to the binuclear complex and free pyrazine molecule, ultimately reaching at an equilibrium



Although both complexes in dichloromethane solution give the same IR absorption bands for $\nu(\text{CO})$ stretching at 2069, 1941 and 1912 cm^{-1} as expected for the W(CO)₅ moiety of C_{4v} symmetry [14], they are distinguishable by NMR spectroscopies.

Both ¹³C NMR and ¹H NMR spectra of the sample freshly prepared by dissolving W(CO)₅(pyz) in d₂-dichloromethane show signal for the monometallic and bimetallic complexes as well as for the free pyrazine molecule. The ¹H NMR spectral data are in line with the literature values [5]. In ¹³C-¹H NMR spectrum, W(CO)₅(pyz) gives two signals for the pyrazine ligand at 151.40 and 148.30 ppm (assigned to C2, C6 and C3, C5 carbon atoms, respectively), while only one signal is observed for each of the pyrazine ligand in the bimetallic (CO)₅W-(pyz)W(CO)₅ complex and free pyrazine molecule at 153.27 and 146.09 ppm, respectively. It is noteworthy that the coordination shift [15] is more pronounced for the C2, C6 carbon atoms ($\Delta\delta = 5.3$ ppm) than that for the C3, C5 carbon atoms ($\Delta\delta = 2.2$ ppm). The coordination shift to the lower magnetic field implies on a stronger σ -donor ability of pyrazine rather than π -acceptor character [16].

In ¹³C NMR spectrum, both of the (CO)₅W(pyiz) and (CO)₅W(pyiz)W(CO)₅ complexes give two signals for the carbonyl ligands with an intensity ratio of 1:4. For both complexes, the CO ligand *trans* to the pyrazine gives ¹³C NMR signal at lower magnetic field (202.99 and 203.08 ppm, respectively) than the *cis* ones do (199.17 and 198.86 ppm, respectively). This is a consequence of the known fact that the π -competition for the use of the metal d-orbitals between the two *trans* ligands is stronger than that between the two *cis* ligands [17].

The observation of all the three species in solution implies on the existence of an equilibrium (Eq. (2)). To test this hypothesis, free pyrazine was added to the solution and the behaviour of the solution was followed by taking ¹H and ¹³C NMR spectra. Both NMR spectra show that the concentration of the complex W(CO)₅(pyz) increases while the concentration of the bimetallic complex (CO)₅W(pyiz)W(CO)₅ decreases upon addition of free pyrazine into the solution. When pyrazine is added to the solution more than fivefold, both NMR spectra show essentially the signals of W(CO)₅(pyz) and the free pyrazine molecule, but practically no signals for (CO)₅W(pyiz)W(CO)₅.

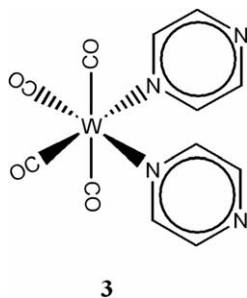
The ¹H NMR spectra could be used for the quantification of the relative concentrations of the species at equilibrium

and, thus, for the determination of the equilibrium constant. The equilibrium constant was determined to be $K_{\text{eq}} = (5.9 \pm 0.8) \times 10^{-2}$ from the ^1H NMR spectra taken from the solution of the complex after addition of various amount of the free pyrazine molecule.

Complexes containing two pyrazine ligands are of interest for testing whether the introduction of a second pyrazine molecule may affect the stability of carbonyl–pyrazine–tungsten(0) complexes. Therefore, many attempts were made for preparation of the tetracarbonylbis(pyrazine)tungsten(0) complex. For this purpose, the known $\text{W}(\text{CO})_4$ -transfer reagents were employed. Neither $\text{W}(\text{CO})_4(\eta^{2:2}\text{-norbornadiene})$ [11] nor $\text{W}(\text{CO})_4(\eta^{2:2}\text{-1,5-cyclooctadiene})$ [12] gives any substitution with pyrazine in toluene or dichloromethane. Tetracarbonylbis(piperidine)tungsten(0), $\text{W}(\text{CO})_4(\text{pip})_2$, known to be a good $\text{W}(\text{CO})_4$ -transfer reagent [10], appears to be a suitable starting material for the preparation of tetracarbonylbis(pyrazine)tungsten(0). A suspension of $\text{W}(\text{CO})_4(\text{pip})_2$ in dichloromethane reacts with pyrazine, whereby the piperidine ligands are replaced by pyrazine forming $\text{W}(\text{CO})_4(\text{pyz})_2$ according to

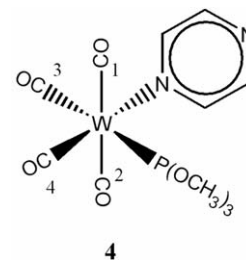
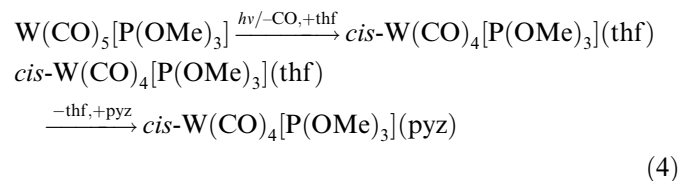


Since tetracarbonylbis(pyrazine)tungsten(0) is soluble in dichloromethane, the yellow suspension turns to a red solution when the reaction is completed as monitored by taking the IR spectra which show four absorption bands at 2007, 1922, 1875, and 1835 cm^{-1} for CO-stretching. The observation of four absorption bands indicates that the tetracarbonylbis(pyrazine)tungsten(0) complex has a *cis* arrangement of the $\text{W}(\text{CO})_4$ moiety, thus, the complex has the *cis-}\text{W}(\text{CO})_4(\text{pyz})_2 formula (3)*



The complex 3 could not be isolated from the reaction solution. Both the chromatographic separation and the crystallization failed in obtaining the complex in solid form. The IR spectra taken at various stages of the manipulation show that the complex is not stable and decomposes. The instability of *cis-}\text{W}(\text{CO})_4(\text{pyz})_2 is found to be much higher compared to $\text{W}(\text{CO})_5(\text{pyz})$. This obviously shows the weak π accepting ability of pyrazine ligand compared to carbonyl ligand.*

With the anticipation that introducing a donor ligand into the carbonyl–pyrazine–metal complex may strengthen the metal–pyrazine bond, *cis-}\text{W}(\text{CO})_4[\text{P}(\text{OCH}_3)_3](\text{pyz}) was synthesized. Irradiation of $\text{W}(\text{CO})_5[\text{P}(\text{OCH}_3)_3]$ [10] in tetrahydrofuran (thf) generates the *cis-}\text{W}(\text{CO})_4[\text{P}(\text{OMe})_3](\text{thf}) intermediate which then reacts with pyrazine to yield the *cis-}\text{W}(\text{CO})_4[\text{P}(\text{OMe})_3](\text{pyz}) complex (4):***



The *cis-}\text{W}(\text{CO})_4[\text{P}(\text{OMe})_3](\text{pyz}) complex (4) could be isolated from reaction solution on a silica gel column followed by crystallization as crystalline solids and characterized by means of IR, MS, ^1H , ^{13}C , and ^{31}P NMR spectroscopy.*

The IR spectrum of 4 taken in *n*-hexane exhibits four strong absorption bands at 2024, 1929, 1901, and 1887 cm^{-1} for CO stretching. The observation of four bands indicates a *cis* arrangement for the $\text{W}(\text{CO})_4$ moiety, which has then a C_s local symmetry with $3A' + A''$ CO stretching modes [14]. *cis-}\text{W}(\text{CO})_4[\text{P}(\text{OCH}_3)_3](\text{pyz}) has, in general, higher CO stretching frequencies than *cis-}\text{W}(\text{CO})_4(\text{pyz})_2, indicating that the pyrazine is a good σ -donor, but a poor π -acceptor ligand [18].**

^{31}P NMR spectrum of 4 recorded from *d*-chloroform solution shows only one signal at 148.09 ppm accompanied by tungsten satellites, $J(^{183}\text{W}-^{31}\text{P}) = 392$ Hz. The coordination shift to lower magnetic field ($\Delta\delta = 7.1$ ppm) is indicative of high σ -donor ability of trimethylphosphite [19].

^{13}C NMR spectrum of 4 exhibits three doublets for the carbonyl groups with the relative intensities 2:1:1, indicating a *cis* arrangement of the four CO groups, consistent with the IR result. The signal of the relative intensity 2 at 202.52 ppm with a small coupling is readily assigned to the CO groups *trans* to each other (CO-1 and CO-2). Since these two carbonyls are *cis* to the trimethylphosphite ligands, the $^{31}\text{P}-^{13}\text{C}$ coupling constant has a small value of 10.9 Hz, as expected [20]. One of the other two doublets of relative intensities 1:1 at 206.48 ppm has a large $^{31}\text{P}-^{13}\text{C}$ coupling constant (51.2 Hz) and, therefore, can be assigned to the CO group *trans* to trimethylphosphite (CO-3). The other doublet at 207.59 ppm with a small $^{31}\text{P}-^{13}\text{C}$ coupling constant of 7.3 Hz is assigned to the CO group *trans* to the pyrazine ligand (CO-4).

The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of **4** also shows two signals for the pyrazine ligand, one doublet at 150.73 ppm with a $^{31}\text{P}\text{-}^{13}\text{C}$ coupling of 2.2 Hz and one singlet at 146.38 ppm. The doublet is assigned to the C2 and C6 carbon atoms of the pyrazine ligand, while the singlet is assigned to the C3 and C5 carbon atoms. The doublet at 52.25 ppm with a $^{31}\text{P}\text{-}^{13}\text{C}$ coupling constant of 3.1 Hz is due to the $\text{P}(\text{OMe})_3$ ligand.

The ^1H NMR spectrum of **4** in *d*-chloroform gives two signals at 8.78 ppm (H2, H6) and 8.41 ppm (H3, H5) for the pyrazine ligand and one doublet at 3.54 ppm with a $^{31}\text{P}\text{-}^1\text{H}$ coupling constant of 11.2 Hz for the trimethylphosphite ligand. It is noteworthy that introducing a good σ -donor ligand like trimethylphosphite strengthens the metal–pyrazine bond and, hence, stabilizes the pyrazine containing metal carbonyl complexes.

4. Conclusion

Our study on the stabilization of the pyrazine–carbonyl–tungsten(0) complexes reveals the following conclusions.

Pentacarbonylpyrazinetungsten(0) can be formed and isolated as solid. However, it is not stable in solution in polar solvents such as acetone or dichloromethane. The instability of the complex in solution is attributed to the poor π -accepting ability of the pyrazine ligand. As a consequence of this instability, the mononuclear $\text{W}(\text{CO})_5(\text{pyz})$ complex is converted to the dinuclear $(\text{CO})_5\text{W}(\text{pyz})\text{W}(\text{CO})_5$ complex plus free pyrazine. These three exist at equilibrium. The equilibrium constant was determined to be $K_{\text{eq}} = (5.9 \pm 0.8) \times 10^{-2}$ at 25 °C in *d*₂-dichloromethane by using quantitative ^1H NMR spectroscopy.

Introducing a second pyrazine ligand into the molecule does not stabilize it. *cis*- $\text{W}(\text{CO})_2(\text{pyz})_2$ was found to be less stable than $\text{W}(\text{CO})_5(\text{pyz})$ and, therefore, could not be isolated from the reaction solution.

Introducing a donor ligand into the complex leads to the stabilization of the carbonyl–pyrazine–metal(0) complexes, as shown by synthesis and isolation of a stable complex containing trimethylphosphite as donor ligand, *cis*- $\text{W}(\text{CO})_4[\text{P}(\text{OCH}_3)_3](\text{pyz})$. The procedure developed here for the synthesis of this complex starting with hexacarbonyltungsten(0) can also be used for the preparation of other carbonyl–metal(0) complexes containing two ligands with different σ -donor and π -acceptor abilities.

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