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Synthesis, characterization and the thermal isomerization mechanism of a series of *trans*-tetracarbonyl-bis(phosphinite)molybdenum(0) complexes and an evaluation of their potential to form heterobimetallic compounds

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The reactions of coordinated phosphorus-donor ligands have previously been used to prepare bimetallic *trans*-[*cis*-$\mathrm{Mo(CO)_4(PPh_2NHCH_2CH_2NCH(}o\mathrm{\text{-}C_6H_4)O)_2]M}$ (M = Ni(II), Cu(II)) complexes. Similar bimetallic complexes containing *trans*-tetracarbonyl-bis(phosphinite)molybdenum(0) centers could be even more interesting because they could serve as molecular gyroscopes. In an attempt to prepare such complexes, the three intermediate compounds *trans*-$\mathrm{Mo(CO)_4(PPh_2Cl)_2}$ (**1**), *trans*-$\mathrm{Mo(CO)_4(PPh_2NHCH_2CH_2NH_2)_2}$ (**2**), and *trans*-$\mathrm{Mo(CO)_4(PPh_2NHCH_2CH_2NCH(}o\mathrm{\text{-}C_6H_4)OH)_2}$ (**3**) were successfully synthesized and fully characterized by multinuclear NMR spectroscopy, elemental analysis and X-ray crystallography. However, the reaction of **3** with $\mathrm{Ni(OAc)_2(H_2O)_4}$ yielded a mixture of crude products with the previously reported *trans*-[*cis*-$\mathrm{Mo(CO)_4(PPh_2NHCH_2CH_2NCH(}o\mathrm{\text{-}C_6H_4)O)_2]Ni}$ being the only product successfully isolated. The cis product was formed due to facile trans–cis isomerization during the coordination of the Ni(II) to **3**. To gain more insight into such isomerizations, the trans–cis isomerizations of **2** and **3** have been followed by $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy. The reactions follow reversible first order kinetics and appear to display intramolecular mechanisms due to the lack of carbonyl substitutions of the phosphinamidite ligands when the isomerizations are performed under CO atmospheres. Eyring analyses performed on the two complexes show that they have nearly identical activation energies (**2**: $\Delta H = 10 \pm 2$ kJ mol^{-1}, $\Delta S = 39 \pm 5$ J mol^{-1} K^{-1}; **3**: $\Delta H = 11 \pm 2$ kJ mol^{-1}, $\Delta S = 41 \pm 7$ J mol^{-1} K^{-1}).

1. Introduction

Transition metal complexes with ligands that give rise to sterically well-defined coordination environments are useful in homogeneous catalysis and in the design of molecular machines, such as rotors [1–5]. One potential approach to actualize these well-defined environments is to incorporate a second metal center into the complex that would provide a fixed coordination environment in the ligand backbone. We have previously demonstrated that it is possible to accomplish this through functionalization of coordinated phosphinamidite ligands in octahedral *cis*-tetracarbonyl-bis(phosphinamidite)molybdenum(0) complexes with terminal salicylaldiminato moieties that can form trans square planar complexes with Ni(II) [6] and Cu(II) [7]. Similar reaction sequences have also been used to prepare trinuclear complexes with bridging ω-salicylaldiminato-substituted phosphinamidite ligands [8].

In light of the successful syntheses of the bi- and tri-metallic complexes described in the previous paragraph, we were interested in using similar methods to generate isomers of the bimetallic complexes containing *trans*-tetracarbonyl-bis(phosphinamidite) molybdenum(0) centers. Such complexes can be considered ‘molecular gyroscopes’ because they restrict molecular rotation to the equatorial carbonyl ligands about the octahedral metal center. Molecular machines that can perform rotor functions such as these are becoming increasingly popular in the fields of nanofluidics and photonics [1,9]. Additionally, the incorporation of an electric dipole moment in these complexes could be a method to drive unidirectional rotation, which is a necessary feature of functional rotor systems [10].

In this manuscript, we describe our attempts to use the stepwise synthesis shown in Scheme 1 to prepare the *trans*-[*trans*-$\mathrm{Mo(CO)_4(PPh_2NHCH_2CH_2NCH(}o\mathrm{\text{-}C_6H_4)O)_2]Ni}$, **4**, heterobimetallic

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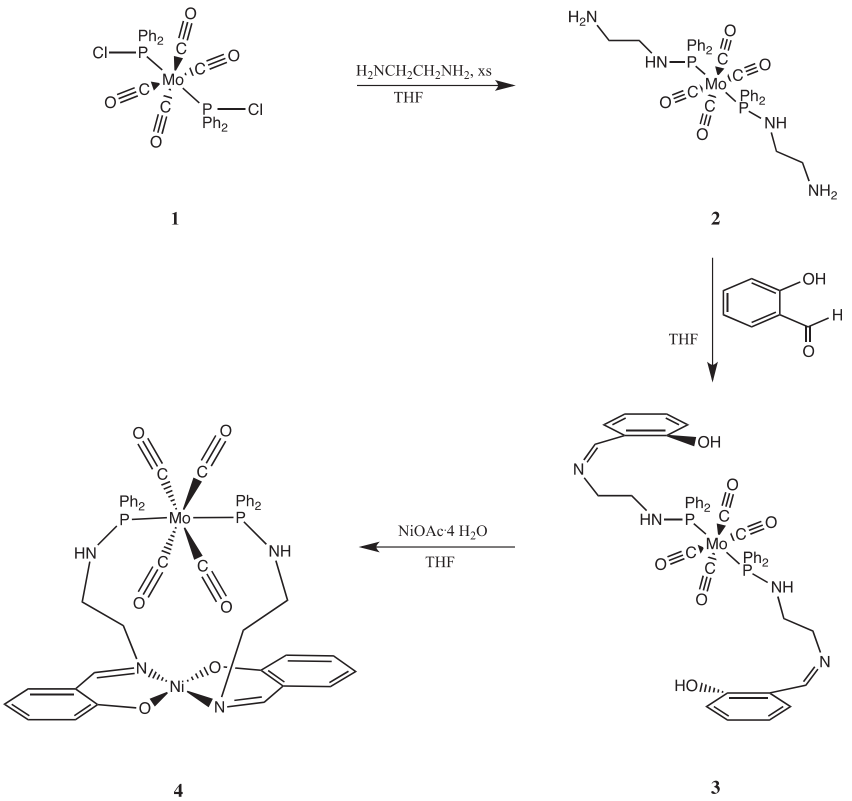

Scheme 1. Proposed reaction scheme for the preparation of the *trans*-[*trans*-$Mo(CO)_4(PPh_2NHCH_2CH_2NCH(o\text{-}C_6H_4)O)_2$]Ni, **4**, heterobimetallic molecular gyroscope.

molecular gyroscope. The intermediates have been characterized with elemental analysis, multinuclear NMR spectroscopy and X-ray crystallography. During the course of this work, we discovered that the *trans*-$Mo(CO)_4(Ph_2PNHR)_2$ intermediates undergo relatively rapid trans–cis isomerizations whereas the *trans*-$Mo(CO)_4(Ph_2PCl)_2$ intermediate does not. To gain more insight into the factors that affect the trans–cis isomerizations in these complexes, the manner in which the changes in the P-donor ligands affect the mechanism of the isomerization reaction has been studied, and the results from these studies are presented.

2. Results and discussion

2.1. Synthesis and characterization

The syntheses of the intermediate complexes shown in Scheme 1, **1**, **2** and **3**, were relatively straightforward. Complex **1** was prepared via the thermal substitution reaction of $Mo(CO)_6$ with PPh_2Cl as has been previously reported [11,12]. The consumption of the PPh_2Cl in the substitution reaction was monitored using $^{31}P\{^1H\}$ NMR spectroscopy. After 28 h, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture indicated that both **1** and its cis isomer had formed along with the monosubstituted $Mo(CO)_5(PPh_2Cl)$ complex. The three species were successfully separated by column chromatography followed by recrystallization. The syntheses of **2** and **3** were essentially identical to those of their cis isomers [6,7] and gave the complexes in high yields.

The $^{13}C\{^1H\}$ and ^1H NMR spectra of the intermediate complexes, **2** and **3**, were completely assigned using a combination of $^1H\{^{31}P\}$ NMR, ^1H–^{13}C HSQC and ^1H–^1H COSY experiments. Each complex exhibited a single downfield 1:2:1 triplet ^{13}C NMR resonance for the four carbonyl ligands indicating that both complexes have trans coordination geometries. The trends in the $^{13}C\{^1H\}$ NMR chemical shifts of the carbonyl ligands are quite similar to those previously reported for the carbonyls cis to similar phosphinite ligands in $Mo(CO)_5(Ph_2PX)$ complexes (X = Cl, δ $^{13}C\{^1H\}$ = 208.23 ppm; X = NH^nPr, δ $^{13}C\{^1H\}$ = 211.07 ppm). The more downfield $^{13}C\{^1H\}$ chemical shifts of carbonyl ligands in the complexes with phosphinamidite ligands as compared to those of complexes with chlorodiphenyphosphine ligands are consistent with their lower CO stretching frequencies [13] and demonstrate that they are better electron donors. The other $^{13}C\{^1H\}$ and ^1H NMR assignments were consistent with those previously reported for the cis isomers [7].

The synthesis of **4** was expected to be more difficult than that of the previously reported cis isomer [6,7] due to an increased potential for the formation of oligomeric and/or polymeric products. Such products are more likely with a trans coordination geometry because the two salicylaldiminato groups in **3** are on opposite sides of the molecule and thus could preferentially coordinate to different nickel(II) centers. The reaction is further complicated by the lack of a common solvent for the $Ni(OAc)_2(H_2O)_4$ and **3**. Because of these issues, a stoichiometric amount of $Ni(OAc)_2(H_2O)_4$ was dissolved into a large quantity of a mixture of methanol and THF, and this solution was then added dropwise over a 26 h period to a solution of **3**. However, even under these conditions, multiple resonances were observed in the $^{31}P\{^1H\}$ NMR spectrum of the crude product as shown in Fig. 1. The chemical shifts of the $^{31}P\{^1H\}$ NMR resonances suggested that both the cis and trans isomers of the $Mo(CO)_4(PPh_2NHR)_2$ group were present. Only the cis isomer of the desired product **4**, *trans*-[*cis*-$Mo(CO)_4(PPh_2NHCH_2CH_2NCH(o\text{-}C_6H_4)O)_2$]Ni, subsequently denoted as ***cis*-4**, was isolated by precipitating a dichloromethane solution of the reaction products into a rapidly stirred 1:10 v/v mixture of dichloromethane and hexanes. All complexes except for ***cis*-4** precipitated, and pure ***cis*-4**