Inorganic Chemistry
Communication
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Intramolecular Nucleophilic Addition to the 2 Position of Coordinated 2,2′-Bipyridine by a Deprotonated Dimethyl Sulfide Ligand[†]

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Ⓢ *Supporting Information*

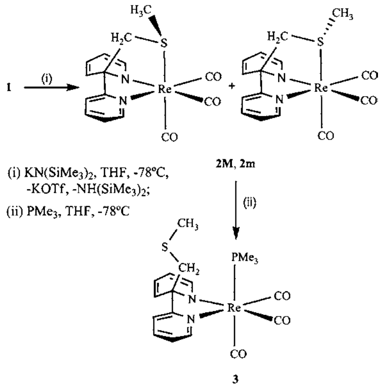
ABSTRACT: Deprotonation of the dimethyl sulfide ligand in [Re(bipy)(CO)$_3$(SMe$_2$)][OTf] (**1**) by KN(SiMe$_3$)$_2$ afforded a mixture of two diastereomers (**2M** and **2m**) in which a C−C bond has been formed between the S-bonded CH$_2$ group and the 2 position of 2,2′-bipyridine. The solid-state structure of the more stable 2,6-^{i}Pr-BIAN analogue could be determined by X-ray diffraction.

Coordination of organic molecules to a Lewis acid through a heteroatom can have two effects on the α groups: an increase in the acidity of the CH groups[1] and an increase in the electrophilicity of C atoms forming multiple bonds to the heteroatom.[2] If the same Lewis acid center could bind in proximal positions a molecule with α-CH groups and a molecule with an electrophilic α-C, deprotonation of the former by an external base could trigger an intramolecular nucleophilic addition.[3] The marked geometrical preferences of some transition-metal centers, along with the relative stability of their coordinative bonds, make them ideal Lewis acid centers for this purpose. Herein we illustrate this approach using the very weak acid dimethyl sulfide[4] and 2,2′-bipyridine (bipy) as the electrophilic counterpart. bipy is a diimine and, therefore, potentially electrophilic; however, throughout its extensive coordination chemistry,[5] it has been found to be a remarkably inert ligand.

Compound [Re(bipy)(CO)$_3$(SMe$_2$)][OTf] (**1**) was prepared by the reaction of [Re(bipy)(CO)$_3$(OTf)][6] with excess dimethyl sulfide in a CH$_2$Cl$_2$ solution and characterized by IR and NMR.[7] The IR ν(CO) bands [2036, 1939, and 1928 cm^{-1} in tetrahydrofuran (THF)] showed that **1** is a *fac*-tricarbonyl, as is typical of rhenium tricarbonyl complexes; therefore, SMe$_2$ must be cis to each 2-pyridyl group. Because attempts to obtain X-ray-quality single crystals of **1** failed, [Re(bipy)(CO)$_3$(SMe$_2$)][BAr′$_4$] [**1′**; Ar′ = 3,5-bis(trifluoromethyl)phenyl] was prepared from **1** and Na[BAr′$_4$][8] and characterized spectroscopically and by X-ray diffraction.[7] Both the solution spectra and the results of the solid-state structure characterization confirmed the composition given above for **1′** and hence support that proposed for **1**.

A freshly prepared THF suspension of **1** cooled to −78 °C reacted with a slight excess of KN(SiMe$_3$)$_2$ to afford a species with IR ν(CO) bands at lower wavenumbers (2012, 1910, and 1893 cm^{-1} in THF). Attempts to crystallize the product under a variety of conditions failed because of limited thermal stability.[9] However, THF-d_8 solutions of the residue, obtained by evaporation of volatiles in vacuo, afforded informative NMR spectra.[7] To aid in the signal assignment, the labeled analogue [Re(bipy)(CO)$_3$(S(^{13}CH$_3$)$_2$)][OTf] (**1***) was similarly prepared, characterized, and deprotonated.[7] The NMR spectra of the deprotonation crudes are consistent with deprotonation of one dimethyl sulfide CH$_3$ group and attack of the resulting methylene onto one of the C atoms of the bipy ligand (see Scheme 1).

Scheme 1. Deprotonation of 1 and Reaction of the Diastereomeric Products (Only One Enantiomer of Each Is Shown) with PMe$_3$



(i) KN(SiMe$_3$)$_2$, THF, -78°C, -KOTf, -NH(SiMe$_3$)$_2$;
(ii) PMe$_3$, THF, -78°C

These spectra show the presence of two species with the same connectivity, which are proposed to be two diastereomers (**2M** and **2m** or **2M*** and **2m*** for the ^{13}C-labeled mixture), resulting from the presence of four stereocenters in the product (Re, S, the attacked C, and its adjacent N), two of which (Re and S) can adopt either configuration (at C and N, the configuration results from the attack being on a given face of bipy). As a result, the methylene H atoms (which do not show coupling with bipy H atoms) are diasterotopic and appear as two doublets ($^2J_{HH}$ = 12.1 Hz). A **2M**/**2m** ratio of 2.2 was consistently found in several

Received: April 29, 2013
Published: May 28, 2013

deprotonation reactions. For both **2M** and **2m**, the presence of eight ^{1}H NMR signals indicates desymmetrization of the bipy ligand. For each compound, half of these signals occur at chemical shifts within the 4−7 ppm range, diagnostic of dearomatization of one of the 2-pyridyl rings.[3a,7] The same features are apparent in the ^{13}C NMR spectrum of the **2M**/**2m** mixture, consisting of 10 signals for each species, 5 of which occur in the 70−130 ppm range. The NMR spectra demonstrate that the methylene C atom is bonded to the bipy C2 atom. Thus, in the ^{1}H NMR spectra of the **2M***/**2m*** mixture, the signals at 2.96, 2.41, 2.15, and 1.50 ppm were assigned to the methylene groups and those at 2.67 and 1.48 ppm to the methyl groups on the grounds of their couplings with ^{13}C ($^{1}J_{CH}$ = 144.1 Hz and $^{3}J_{CH}$ = 5.2 Hz). On the basis of their higher intensity and opposite phase in the DEPT-135 spectrum, the ^{13}C NMR signals at 33.8 and 32.4 ppm were assigned to the CH_2 groups and those at 25.0 and 18.4 ppm to the CH_3 groups. A 2D HMBC NMR spectrum of the **2M**/**2m** mixture showed a two-bond correlation between the methylene H atom at 2.96 ppm and the ^{13}C NMR signal at 78.0 ppm, assigned (DEPT-135) to a bipy quaternary C atom and a three-bond correlation to the other quaternary C NMR signal at 165.5 ppm. The ^{13}C NMR spectrum of the **2M***/**2m*** mixture showed the quaternary C atom bipy signals at 78.0 and 76.1 ppm as doublets because of coupling with the $^{13}CH_2$ groups ($^{1}J_{CC}$ = 31.5 Hz).

The **2M**/**2m** mixture reacts with 1 equiv of trimethylphosphine to afford a single *fac*-tricarbonyl compound **3** with a PMe_3 ligand (^{31}P NMR singlet at −25.7 ppm) and with NMR signals corresponding to a single diastereomer (see Scheme 1). This indicates that the Re-bonded S atom in **2M** and **2m** was displaced by PMe_3, leading to the loss of the S stereocenter and hence to the formation of a single diastereomer. ^{13}C NMR of the analogous ^{13}C-labeled compound, **3***, confirmed that the methylene group remains bonded to the quaternary C atom because its signal is a doublet at 72.6 ppm ($^{1}J_{CC}$ = 35.0 Hz). Analogously, the mixture **2M**/**2m** reacted with the diphosphine bis(dimethylphosphino)methane (dmpm) to afford a single product (**4**) similar to **3**, i.e., containing a monodentate dmpm ligand. The ^{31}P NMR spectrum of **4** displays two doublets ($^{2}J_{PP}$ = 32.3 Hz) for the coordinated (−18.7 ppm) and uncoordinated (−59.0 ppm) P atoms. Complexes **3** and **4** are, like their precursors, thermally unstable. No product with a chelating dmpm ligand could be detected by NMR despite the high nucleophilicity of this diphosphine, showing that the instability of **2M**, **2m**, and **3** was not due to the lability of the ligands (e.g., decarbonylation).

These results are remarkable in that (a) a bipy ligand is dearomatized, (b) the site of nucleophilic attack is the bipy 2 position, for which there is no precedent, and (c) the employed fragment, *fac*-{Re(bipy)$(CO)_3$}, which has been widely employed in the areas of bioinorganic chemistry,[10] supramolecular chemistry,[11] and catalysis of CO_2 reduction,[12] is notoriously inert.

Analogous results were obtained with complexes of other diimines, but the products suffered also from low stability. Therefore, we turned our attention to the bulky nonaromatic diimine bis{2,8-(2,6-diisopropylphenylimino)acenaphthene (2,6-^{i}Pr-BIAN; Figure 1).[13] Compound [Re(2,6-^{i}Pr-BIAN)-$(CO)_3(SMe_2)$][BAr'_4] (**5**) was prepared similarly to **1** and characterized spectroscopically and by X-ray diffraction (see Figure 2a).[7] The reaction of **5** with $KN(SiMe_3)_2$ afforded the neutral complex **6**, which was found to consist of a single diastereomer and to be quite thermally stable in solution. Slow solvent diffusion furnished crystals of **6**, which was characterized spectroscopically and by single-crystal X-ray diffraction (see Figure 2b).

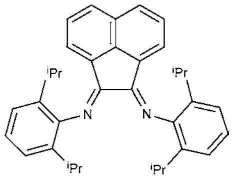


Figure 1. 2,6-^{i}Pr-BIAN.

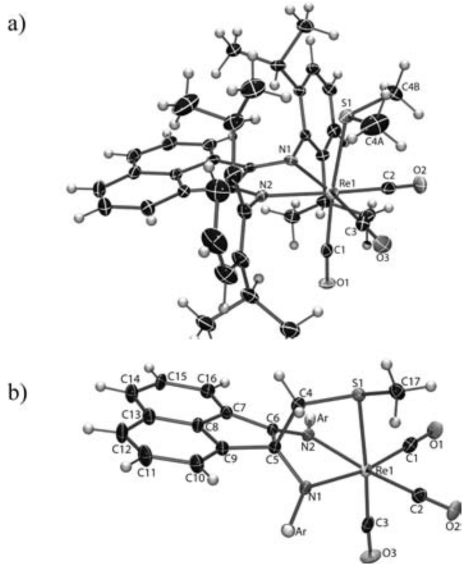


Figure 2. Molecular structures of compounds **5** (a) and **6** (b). 2,6-Bis(isopropyl)phenyl (Ar) groups have been omitted for clarity in **6**.

The ^{1}H and ^{13}C NMR spectra reflected the loss of a molecular mirror plane in the formation of **6**. The ^{13}C NMR featured a signal at 192.8 ppm attributable to the imine C atom, whereas the signal at 91.2 ppm was assigned to the sp^3 C atom formed as a result of the nucleophilic addition. Two- and three-bond correlations like those encountered for **2M** and **2m** (see above) were observed in the 2D HMBC spectrum of **6**.[7]

These results demonstrated that a reaction like that proposed above for the bipy analogue **1** had occurred. Thus, the methylene C atom of a $S(CH_3)CH_2$ moiety (resulting from deprotonation of coordinated dimethyl sulfide) is bonded to the C atom of one of the N-coordinated C−N groups. As a consequence, the C−N distance in that group [1.446(4) Å,[14] consistent with a single bond] is longer than the C−N distance at the intact imine group [1.288(4) Å], and the Re−N distance [2.149(3) Å, consistent with a rhenium amido moiety[15]] is shorter than that at the intact imine donor [2.247(3) Å]. The sum of the angles about the amido N atom is 359.9°, indicating a planar geometry and, therefore, delocalization of the N lone electron pair, a feature previously encountered in most amido complexes.[16] In an organometallic compound like **6**, a dative component in the Re−N bond would lead to a high-energy 20 electron metal center. In some such species, N lone-pair delocalization is made possible through aryl substituents at the N atom.[15] Amido complexes with a localized N lone pair and pyramidal geometry about the N atom are highly reactive species.[17] The instability of the **2M** and **2m** compounds could be due, at least in part, to the presence of this sort of ligand. The full characterization of **6** demonstrates deprotonation of the SMe_2 ligand, and the similarity in the spectral changes supports the structure assignment of the unstable bipy analogue.

Squires et al. found that gas-phase deprotonation of the $Me_2S{-}BH_3$ adduct afforded a stable carbanion that does not rearrange to the B−C species.[17] Gladysz et al. found that deprotonation of cationic rhenium dialkyl sulfide complexes yielded the corresponding alkylthioalkyl products via a [2,3]-sigmatropic rearrangement.[18] However, in the case of dimethyl sulfide, a multitude of noncharacterized products were formed.[18b] To our knowledge, no product of the deprotonation of transition-metal-coordinated dimethyl sulfide has been characterized. Nucleophilic attack on coordinated bipy has been a matter of controversy for a long time,[2,19] and in the very few cases where products have been unambiguously characterized, the attack took place at the 6 position.[3a,20]

In summary, we have demonstrated that the coordination of dimethyl sulfide to the Lewis acid $Re(bipy)(CO)_3^+$ makes deprotonation with the commercially available solution of potassium bis(trimethylsilyl)amide in toluene possible. Moreover, the deprotonated SMe_2 ligand is nucleophilic enough to add to a proximal bipy ligand, which undergoes dearomatization of one of the 2-pyridyl rings. The product is a mixture of two diastereomers due to the creation of four stereocenters in the reaction. The addition of a phosphine, either PMe_3 or dmpm, to this mixture yields a single diastereomer due to substitution of the S-donor atom by the P atom. Deprotonation of a similar 2,6-^{i}Pr-BIAN complex affords a stable product, which could be crystallized and fully characterized, including an X-ray diffraction structural determination.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information of compounds **1′**, **5**, and **6** and full experimental details for **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Dr. Eva Hevia (University of Strathclyde) for the preparation of compound **1** and preliminary studies. Financial support from Ministerio de Ciencia e Innovación (Grant CTQ2009-12366) and Ministerio de Economía y Competitividad (Grants CTQ2012-37379-C02-01 and CTQ2012-37379-C02-02) is gratefully acknowledged. R.A. thanks the Universidad de Oviedo (Beca de Excelencia del Campus de Excelencia Internacional), Principado de Asturias (Beca Severo Ochoa), and Ministerio de Educación, Cultura y Deporte (Beca FPU), for graduate studentships.

■ DEDICATION

[†]Dedicated to Professor Antonio Laguna on the occasion of his 65th birthday.

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