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Re(CO)₃-Templated Synthesis of α -Amidino AzaDi(benzopyrro)methenes

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Abstract

α -amidino azadi(benzopyrro)methenes were synthesized using the Re(CO)₃ unit as a templating agent. The products of these template reactions are six-coordinate Re complexes, with a facial arrangement of carbonyls, a non-coordinating anion, and a tridentate α -amidino azadi(benzopyrro)methene ligand. The tridentate ligand shows the conversion of one diiminoisoindoline sp² carbon to a sp³ carbon which has been seen in the “helmet” and bicyclic phthalocyanines. The bidentate diiminoisoindoline fragment tilts out of the plane of coordination. Five examples of α -amidino azadi(benzopyrro)methenes were produced from these reactions using different nitrile solvents, including the nitrile activation of acetonitrile, propionitrile, butyronitrile, cyclohexanecarbonitrile, and benzonitrile were formed.

Summary

The Re(CO)₃ unit was used to template the synthesis of α -amidino azadi(benzopyrro)methene (A³DBM) complexes, which resulted in the activation of nitriles to form rhenium bound amidines. The nitrile can be varied and acetonitrile, propionitrile, butyronitrile, cyclohexanecarbonitrile, and benzonitrile examples have been prepared.

Keywords

α -amidino azadi(benzopyrro)methene; ADBM; isoindoline ligand; template reaction; Re(CO)₃

The unusual chemistry of the Re(I)(CO)₃ fragment continues to attract significant attention in inorganic synthesis.^{1–6} This interest arises from both its notable properties as a non-labile unit with a rigid facial geometry as well as its use as a synthon for a wide variety of functional inorganic complexes.^{7–10} Recently, we have used the Re(CO)₃ moiety as a template to produce isoindoline based chelates that can be considered as half of a phthalocyanine or a hemiporphyrine (a “semihemiporphyrine”).^{11,12} The limited geometry options and inert nature of this metal unit in both cases prevent larger macrocycles

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org> at DOI: _____. X-ray crystallographic data in CIF format, Synthetic procedures, spectroscopic data, and X-ray parameters.

or chelates from forming. In our continuing studies on the templating behavior of the $\text{Re}(\text{CO})_3$ unit, we have uncovered a new nitrile-activating reaction that affords an α -amidino azadi(benzopyrro)methene (A^3DBM) which is a tridentate complex that has similar connectivity to the “helmet” and bicyclic phthalocyanines.^{13–21} In these reactions, two equivalents of diiminoisoindoline (DII) react with $\text{Re}(\text{CO})_5\text{X}$ to produce a bis-isoindoline ligand with an appended amidine; the template reaction adds a nitrile-derived “tail” to the axial position.

The activation of a nitrile to undergo nucleophilic attack at the $\text{Re}(\text{CO})_3$ unit has been previously observed. Recently, Marzilli *et al.* have activated a bound acetonitrile ligand on rhenium(I)(diimine) tricarbonyl complexes with various amines and alcohols.^{22–24} The nucleophiles attack the carbon of the nitrile, forming a new C–N bond followed by an intramolecular proton transfer to complete the reaction. Similarly, Riera *et al.* reacted $\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})_2(\text{ClO}_4)$ with pyrazoles in refluxing acetonitrile affording pyrazolylamidino complexes where the pyrazoles attacked a rhenium-bound acetonitrile.²⁵ Additionally, Bengali *et al.* reacted rhenium(I)(β -diimine) tricarbonyl complexes with nitriles where the diimine ligand attacks the nitrile after it binds to the rhenium. The reaction forms a new C–C bond followed by proton transfer to the cyano nitrogen.²⁶

In addition to the $\text{Re}(\text{CO})_3$ unit, other transition metal containing compounds have been used to activate nitriles at an *sp* carbon position. Kukushkin *et al.* has shown that aryl ketonitrone can activate platinum bound nitriles to form oxadiazoles via 1,3-dipolar cycloaddition;²⁷ Pombeiro and coworkers have shown similar reactions to occur with palladium.²⁸ Additionally, Cho *et al.* has shown that a peroxocobalt(III) complex can activate nitriles to form hydroximatocobalt(III) complexes via oxidation by the peroxy group while Lee and coworkers have activated nitriles using a Ni(II)-(2-mercaptophenyl)phosphine complex to form a thioiminium moiety by nucleophilic attack of a thiol.^{29,30}

In our work, $\text{Re}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) was reacted with two equivalents of DII and an excess of a nitrile (acetonitrile, propionitrile, butyronitrile, cyclohexanecarbonitrile, and benzonitrile) as the solvent. Scheme 1 shows the reactions and the structures of the resultant yellow crystalline $\text{Re}(\text{CO})_3 \text{A}^3\text{DBM}$ products. All compounds were characterized via spectroscopic methods and elucidated by single crystal X-ray diffraction. Characterization revealed that nitrile activation occurred which afforded a neutral tridentate A^3DBM ligand where one DII *sp*² carbon was converted to a *sp*³ carbon interrupting conjugation through the bis-DII fragment. Similar conversions have been seen in the “helmet” and bicyclic phthalocyanines.^{13–21} The structures of compounds **1–3**, **5**, and **9** are shown in Figure 2. In all cases, the rhenium(I) ion adopts an octahedral geometry and is coordinated by a neutral tridentate A^3DBM ligand and the remaining positions are occupied by the expected three facially coordinated carbonyl ligands. The tridentate A^3DBM ligand is neutral, and in all cases charge balance is provided by a non-coordinating anion. The two isoindoline units form a bidentate fragment similar to the systems we observed upon the templated reaction of diiminoisoindoline with $\text{Re}(\text{CO})_5\text{X}$ and BPh_3 .^{11,31} The axial ligand is composed of an amidine produced from activation of the nitrile solvent.

From the reactions with $\text{Re}(\text{CO})_5\text{X}$ and from additional chemical methodologies (*vide infra*), nine products (**1–3** and **5–10**) were elucidated by X-ray crystallography (Figure S32–S40). The metal-nitrogen_{DII} bond lengths are ~ 2.15 Å while the metal nitrogen_{amidino} bond lengths are also ~ 2.15 Å. Rhenium-carbonyl bond lengths are ~ 1.92 Å which are similar to those seen in rhenium(I)(diimine) tricarbonyl complexes.^{32,33} The mean plane of the DII moieties in the A^3DBM ligand tilts in relation to the $\text{C}_{\text{CO}}\text{-Re-C}_{\text{CO}}$ plane by $\sim 36^\circ$ which is similar to the tilts seen in the semihemiporphyrzines and other transition metal containing azadipyrromethene complexes.^{12,34–37} The terminal amine and carbonyl oxygen distances are ~ 3.5 Å or longer, indicating hydrogen bonding is not present and the tilt is due to other effects. The terminal amine carbon-nitrogen bond lengths are ~ 1.31 Å which is longer than the carbon-nitrogen double bonds in the $\text{Re}(\text{CO})_3$ -templated aza(dibenzopyrro)methenes and are comparable to the single bond terminal amine carbon-nitrogen bond lengths in the semihemiporphyrzines.^{11,12} Additionally, the double bonds of the axial amidines are ~ 1.29 Å, whereas the single bonds of these groups are ~ 1.35 Å. The bond lengths of the amidines are consistent with those observed in the work of Marzilli *et al.* and Riera *et al.*^{22–25}

As in other rhenium tricarbonyl complexes, the $\text{Re}(\text{CO})_3 \text{A}^3\text{DBM}$ complexes are diamagnetic and were characterized by NMR even though their solubilities are very limited (Figures S1–S21). In the ^1H spectrum, we observed complex splitting of the DII moieties, one DII moiety had resonances similar to that which Kleeberg and Bröring noted with the asymmetric BPI-type chelates, while the other DII moiety differed due to the presence of the amidine group.³⁸ Additionally, we observed four broad resonances for the terminal amines at ~ 10.20 , ~ 9.10 , ~ 8.45 , and ~ 7.25 ppm while we typically observed two strong resonances for the amidine at ~ 9.20 and ~ 8.10 ppm except for **4** and **9** which only had one amidine resonance. In the IR spectra, the $\text{Re}(\text{CO})_3$ unit shows *a*_g- and *e*-type CO stretches produced by the pseudo- C_{3v} environment of the facial carbonyl units with frequencies that range from ~ 2006 to 2011 cm^{-1} and from ~ 1872 to 1912 cm^{-1} , respectively. Furthermore, the amidine shows a strong stretch with frequencies that range from $\sim 1634 \text{ cm}^{-1}$ to 1653 cm^{-1} .

Even though the chloride analogs were synthesized without complication, only the straight chain alkyls (**6–8**) of the bromides could be isolated without a subsequent reaction. The cyclohexyl and phenyl derivatives could not be synthesized as pure materials with the bromide as the halide. We surmised that this was due to the reduced lability of the bromide complex relative to that of the chloride.³⁹ To remove the halide from the metal and drive the reaction to completion, we employed AgNO_3 as a halide metathesis agent. The addition of 1.2 equivalents of AgNO_3 in DMF to the initial reaction product from $\text{Re}(\text{CO})_5\text{Br}$ for these two compounds (Scheme 2) afforded the cyclohexyl and phenyl derivatives (compounds **9–10**) as pure materials as the nitrate salts. The bromide and nitrate compounds **6–10** exhibited identical spectroscopic features as the chloride analogues. Compound **9** was elucidated by single crystal X-ray methods (Figure 2) and the structure of this compound reveals similar structural parameters as seen in **1–3** and **5**. We can hypothesize on the sequence of ligand formation based on the observed bromide effect, shown in Scheme S1. Upon the dissolution of $\text{Re}(\text{CO})_5\text{X}$, the nitrile replaces two equivalents of carbonyl and is subsequently activated by an equivalent of DII. A second DII then forms an additional linkage at the α -carbon position to produce the bis-DII chelate. Halide loss can then occur to allow the final chelate

to form, which can be promoted via the use of silver nitrate at the last step. Support for this possible mechanism could be established through isolation of the mono-DII intermediate.

In conclusion, we have shown that yellow crystalline α -amidino azadi(benzopyrro)methenes can be produced by condensing two equivalents of DII and a nitrile with $\text{Re}(\text{CO})_3$ as a templating agent. In the reaction, one DII sp^2 carbon is converted to a sp^3 carbon interrupting conjugation through the bis-DII fragment. Similar conversions have been seen in the “helmet” and bicyclic phthalocyanines.^{13–21} The elucidated X-ray crystal structures of the α -amidino azadi(benzopyrro)methenes show that the bidentate DII fragment tilts out of the plane of coordination and that the carbon-nitrogen bond lengths are longer than the $\text{Re}(\text{CO})_3$ -templated azadi(benzopyrro)methenes but comparable to the semihemiporphyrazines.^{11,12} We are continuing our work on rhenium-based templating reactions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1:
 $\text{Re(CO)}_3 \text{ A}^3\text{DBM}$ and related compounds.

Figure 2:
Elucidated X-ray structures of (left to right) compounds **1–3**, **9**, and **5** with 35% thermal ellipsoids. Anions, solvent molecules, and hydrogen atoms except on nitrogen atom positions have been omitted for clarity.

Scheme 1:
Synthesis of $\text{Re(CO)}_3 \text{A}^3\text{DBM}$ complexes.

Scheme 2:
Synthesis of the nitrate salts.