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^{13}C or Not ^{13}C: Selective Synthesis of Asymmetric Carbon-13-Labeled Platinum(II) *cis*-Acetylides

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Supporting Information

ABSTRACT: Asymmetric isotopic labeling of parallel and identical electron- or energy-transfer pathways in symmetrical molecular assemblies is an extremely challenging task owing to the inherent lack of isotopic selectivity in conventional synthetic methods. Yet, it would be a highly valuable tool in the study and control of complex light-matter interactions in molecular systems by exclusively and nonintrusively labeling one of otherwise identical reaction pathways, potentially directing charge and energy transport along a chosen path. Here we describe the first selective synthetic route to asymmetrically labeled organometallic compounds, on the example of charge-transfer platinum(II) *cis*-acetylide complexes. We demonstrate the selective ^{13}C labeling of one of two acetylide groups. We further show that such isotopic labeling successfully decouples the two $\nu(C{\equiv}C)$ in the mid-IR region, permitting independent spectroscopic monitoring of two otherwise identical electron-transfer pathways, along the $^{12}C{\equiv}^{12}C$ and $^{13}C{\equiv}^{13}C$ coordinates. Quantum-mechanical mixing leads to intriguing complex features in the vibrational spectra of such species, which we successfully model by full-dimensional anharmonically corrected DFT calculations, despite the large size of these systems. The synthetic route developed and demonstrated herein should lead to a great diversity of asymmetric organometallic complexes inaccessible otherwise, opening up a plethora of opportunities to advance the fundamental understanding and control of light-matter interactions in molecular systems.

Methods for controlled asymmetric synthesis are a key part of the modern chemist's toolkit. In particular, selective isotopic substitution provides a chemically nonintrusive "contrast agent" for the precise identification of reaction pathways in a broad range of (bio)chemical systems. Many such systems, ranging from light-harvesting complexes to dendritic molecular wires,[1] possess multiple identical parallel electronic energy-transfer pathways. This property is known to give rise to complex interactions, governing the overall efficiency of electron or energy transfer.[2] Isotopic labeling of one of the otherwise identical pathways would be an ideal method to explore these phenomena. However, this presents a significant challenge because conventional synthetic methods do not generally allow isotopic selectivity. Here, we present the first synthetic route to asymmetrically isotopically labeled transition-metal acetylide complexes. Electron transfer, a process ubiquitous in nature,[1,3] is one of the most interesting and challenging to understand and control. Donor−bridge−acceptor molecular architectures are ideal platforms to study electron transfer. In particular, the square-planar coordination environment in platinum(II) complexes provides synthetic versatility and a well-defined directionality of electron transfer.[4−14]

This framework affords the possibility of having two indistinguishable, parallel electron-transfer pathways: an ideal target for asymmetric isotopic labeling. The platinum(II) diimine *cis*-diacetylide complex **PTZ-u** (Figure 1)[4] has been specifically

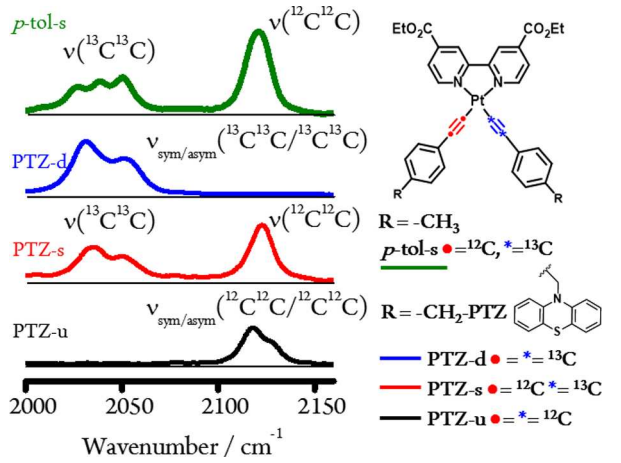

Figure 1. (Left) Comparison of the FTIR spectra of all complexes in a dichloromethane solution at room temperature. (Right) Isotopic labeling scheme for $Pt[(CO_2Et)_2bpy](C{\equiv}C\text{-}p\text{-}C_6H_4\text{-}R)_2$.

chosen as a well-studied model donor−bridge−acceptor system that is known to undergo photoinduced electron transfer.[4,15] In **PTZ-u**, two equivalent phenothiazine (PTZ) electron donors are coordinated to the platinum(II) center via a phenylacetylide moiety. Substitution of one acetylide unit for its $^{13}C{\equiv}^{13}C$ equivalent should decouple the acetylide vibrations, allowing them to be distinguished by IR spectroscopy, without significantly altering the electronic properties of the electron donors.

Synthetically, labeling only one of the two donor arms posed a significant challenge, as a consequence of a lack of any known synthetic procedure whereby only a single acetylide can by ligated to platinum(II) diimine dichloride.[7,16]

A number of asymmetric complexes, which bear chemically distinct acetylides, have been reported recently.[6,17,18] Their

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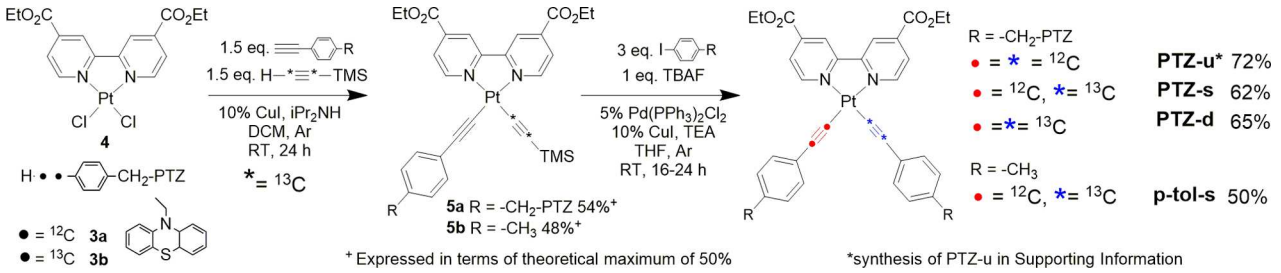
Scheme 1. Synthesis of ^{13}C-Labeled Platinum(II) Complexes



general synthesis uses a molar equivalent of the two different acetylide ligands, resulting in a statistical mixture of the three possible products in a 1:2:1 ratio, with the desired mixed acetylide complex isolated by column chromatography. This approach works well for two chemically distinct acetylides but cannot be used to obtain complexes possessing isotopically labeled but otherwise chemically identical acetylides. A different synthetic strategy is clearly required. Here, we present a controlled synthetic strategy to such asymmetric complexes, proceeding via an asymmetric diacetylide intermediate (Scheme 1; **5a** and **5b**).

The phenothiazine acetylide ligands **3a** and **3b** were synthesized according to a modified literature method[4] from commercially available starting materials (detail in the Supporting Information). The key intermediates, asymmetric complexes **5**, were prepared from **4** (Scheme 1) and isolated from the resulting statistical mixture by column chromatography. The primary requirement for this intermediate is for only one of the acetylide ligands to bear a terminal functional group that can be easily modified to attach the desired final substituent. The ideal candidate would be a proton because it can be coupled directly via Sonogashira coupling and is readily accessible via deprotection of a Me_3Si intermediate. This approach, ubiquitous in organic synthetic methodology, was also successfully employed to synthesize iron(II) monoacetylide complexes.[19,20] However, in this instance, the resulting terminal CC−H complex decomposed rapidly and could not be isolated.

Our alternative route from **5** to the products employs a simultaneous deprotection−cross-coupling in dry tetrahydrofuran, with 1 equivalent of tetrabutylammonium fluoride as the deprotection agent, and a 3-fold excess of the appropriate aryl iodide, an approach used in the synthesis of organic polyacetylides.[21] Purification by column chromatography resulted in analytically pure **PTZ-s** and **p-tol-s** in high yields. To the best of our knowledge, this is the first reported example of a simultaneous deprotection/Sonogashira coupling of an acetylide group bound to a transition-metal center and of such a coupling to a third-row transition-metal diacetylide.

The "fully labeled" symmetric complex **PTZ-d** bearing ^{13}C as all four acetylide carbon atoms and the unlabeled complex **PTZ-u** were prepared according to the standard procedure.[4] The purity of the products was ascertained by ^{1}H and ^{13}C NMR, elemental analysis, and high-resolution mass spectrometry.

Isotopic substitution successfully distinguishes the two acetylide groups, as is evident from IR absorption spectra in solution and in the solid state. The acetylide region (2000−2160 cm^{-1}) of the spectra is shown in Figure 1. The full spectra are available in the Supporting Information (SI). The Fourier transform infrared (FTIR) spectrum of the unlabeled complex **PTZ-u** shows, typical to *cis*-acetylides, two overlapping vibrational bands corresponding to the symmetric and asymmetric combinations of ν(CC) at 2127 and 2117 cm^{-1} respectively, which are in good agreement with previously reported values[15] and with the values obtained from density functional theory (DFT) calculations within the harmonic approximation (2129 and 2116 cm^{-1}, respectively). The fully ^{13}C-labeled complex **PTZ-d** shows a similar vibrational pattern, with the shift to lower energies, 2052 and 2031 cm^{-1}, and a slightly larger difference in the energies of the symmetric/asymmetric combinations.

Reduced mass analysis predicts the singly labeled complex, **PTZ-s**, to exhibit two separate bands in the acetylide region of the IR spectrum: one $\nu(^{12}C{\equiv}^{12}C)$ mode at approximately 2120 cm^{-1} and one $\nu(^{13}C{\equiv}^{13}C)$ mode at ca. 80 cm^{-1} lower energy DFT calculations within the harmonic approximation predict that the two modes are decoupled and that 2123 and 2040 cm^{-1} are the expected frequencies when appropriate scaling factors are used to correct for anharmonicity. However, IR spectra in the solid state and solution phase reveal three clear bands in this same region, at 2122, 2051, and 2033 cm^{-1}. The two lower-energy bands appear at *almost* the same frequencies as the two bands for **PTZ-d**, and the single higher-energy band appears at a frequency similar to that of the symmetric acetylide stretch of **PTZ-u**. Furthermore, a singly ^{13}C-labeled tolyl analogue, **p-tol-s**, synthesized via the same route shows an even more complex *four*-band structure in the acetylide region (Figure 1) with maxima at 2121, 2050, 2030, and 2027 cm^{-1}. The precise origin of the multiple band structure in the IR spectra of the singly labeled complexes observed is not clear a priori. One possible cause may be higher-order anharmonic couplings between intramolecular fundamental modes.[22]

To account for anharmonic effects, calculations were performed using full-dimensional generalized vibrational perturbation theory to second order (GVPT2), which includes vibrational anharmonic coupling.[23] The GVPT2 method in combination with the B3LYP functional has been found to reproduce the IR spectra of organometallic complexes with a very high degree of accuracy.[24] Calculations were performed for both the full complex **PTZ-s** (113 atoms, 333 modes) and for a *truncated* version (ester groups removed) of the **p-tol-s** complex (53 atoms, 153 modes) in *Gaussian 09*.[25] To our knowledge, these represent the largest such calculations presently documented in the literature.

Selected results of the anharmonic calculations are shown in Figure 2; full calculated spectra, diagrams of the vibrational eigenvectors, and animations of all of the modes discussed are given in the SI. Calculations of **PTZ-s** predict the presence of a combination mode of significant intensity that involves two fundamental modes centered on the ring and PTZ parts of the labeled ligand, calculated to be only 12 cm^{-1} lower in energy than the $\nu(^{13}C{\equiv}^{13}C)$ fundamental. The calculated intensity of the corresponding combination mode centered on the unlabeled acetylide ligand is almost 0. The calculations unambiguously support assignment of the experimental IR band at 2033 cm^{-1} to

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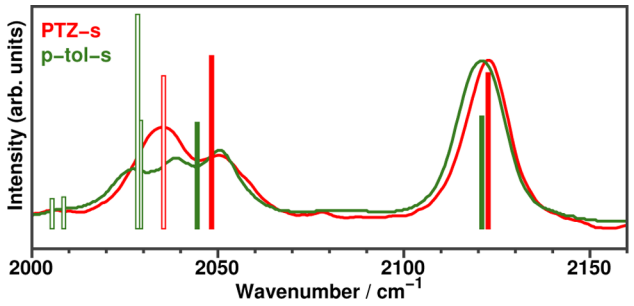

Figure 2. Experimental FTIR spectra (lines) and calculated (B3LYP/SDD[Pt]6-311G(d,p)[H,C,N,O,P,S]/PCM with GVPT2) anharmonic fundamental (filled sticks) and combination (empty sticks; relative intensity >1%) vibrational modes of **PTZ-s** (red) and **p-tol-s** (green). The calculated peak positions are shifted to match the experimental frequency $\nu(^{12}C{\equiv}^{12}C)$.

a near-resonant combination mode that borrows intensity from the $\nu(^{13}C{\equiv}^{13}C)$ fundamental at 2051 cm^{-1} through quantum-mechanical mixing.

For **p-tol-s**, the calculations are marginally less computationally intensive, but the band structure is significantly more complicated. In this case, a total of four combination bands, spanning both acetylide ligands, and the $\nu(^{13}C{\equiv}^{13}C)$ fundamental contribute to the band shape in the 2000−2070 cm^{-1} region. The combination modes couple to and borrow intensity from the $\nu(^{13}C{\equiv}^{13}C)$ fundamental vibration, leading to the four-peak pattern seen in the FTIR spectrum of **p-tol-s**.

In summary, we report the first synthetic route to selectively asymmetrically isotopically labeled transition-metal diacetylide complexes bearing ^{13}C labels on a single acetylide moiety. The key feature of the method is implementation of a simultaneous deprotection/Sonogashira coupling of (trimethylsilyl)acetylide bound to a transition-metal center. This new strategy has been demonstrated by the synthesis of asymmetric platinum(II) *cis*-acetylides in a controlled manner and in high yields. Asymmetric substitution led to a complex vibrational spectral pattern, which has been assigned unambiguously by using state-of-the-art DFT calculations taking into account anharmonic coupling at a scale attempted never before.

Lifting the spectroscopic degeneracy of this system in the mid-IR through isotopic labeling affords precise structural selectivity over two otherwise identical electron-transfer pathways. This feature could enable unprecedented insight into the factors that govern electronic energy transfer in complex molecular systems and allows one to explore new quantum control strategies over molecular function. Furthermore, this synthetic method should be applicable to a broad range of systems through the judicious choice of synthetic intermediates, providing a new approach to asymmetric organometallic complexes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b01287.

Details regarding the calculations, synthesis, and analysis (PDF)

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Notes

The authors declare no competing financial interest.

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