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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 Placeholder

ABSTRACT: Asymmetric isotopic labelling 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 non-intrusively labelling 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 labelled organometallic compounds, on the example of charge transfer Pt(II) cis-acetylide compounds. We demonstrate selective ^{13}C labelling of one of two acetylide groups. We further show that such isotopic labelling successfully decouples the two ν(C≡C) in the mid-IR region, permitting independent spectroscopic monitoring of two otherwise identical electron transfer pathways, along the ^{12}C≡^{12}C and the ^{13}C≡^{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 density functional theory 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 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 non-intrusive "contrast agent" for 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 one of otherwise identical pathways would be an ideal method to explore these phenomena. However, this presents a significant challenge, as 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 the most interesting and challenging to understand and control. Donor–bridge-acceptor molecular architectures are ideal platform to study electron transfer. In particular, the square planar coordination environment in Pt(II) complexes provides synthetic versatility and a well-defined directionality of electron transfer.[4–14]

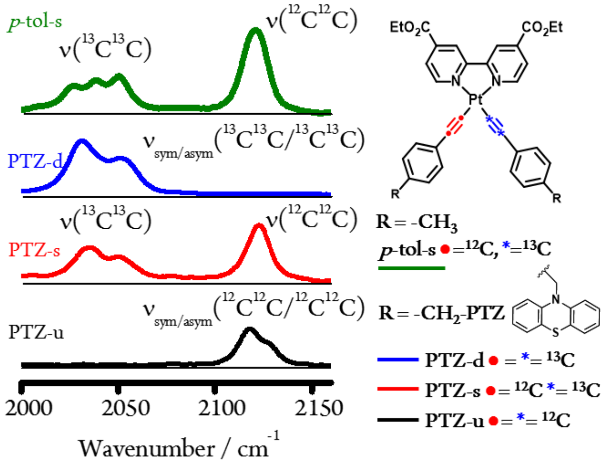


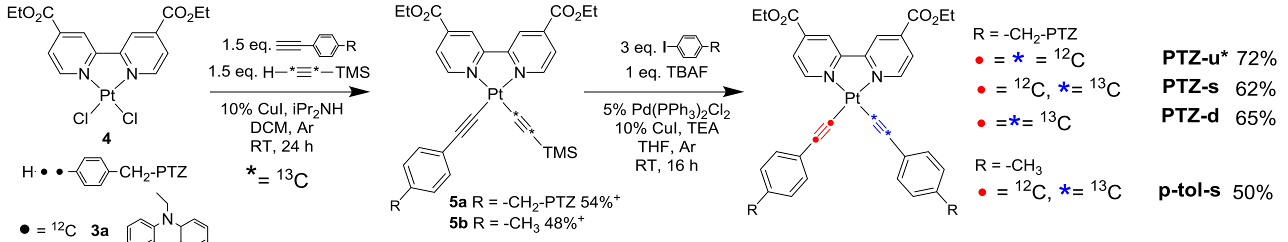
Figure 1. Left - Comparison of the FTIR spectra of all complexes in dichloromethane solution at r.t. Right - Isotopic labeling scheme for Pt((CO$_2$Et)$_2$bpy)(C≡C-p-C$_6$H$_4$-R)$_2$

This framework affords the possibility of having two indistinguishable, parallel electron transfer pathways: an ideal target for asymmetric isotopic labeling. The Pt(II) diimine cis-bis acetylide complex **PTZ-u** (Figure 1)[4] has been specifically chosen as a well-studied, model donor-bridge-acceptor system that has been shown to undergo photoinduced electron transfer.[4,15] In **PTZ-u**, two equivalent phenothiazine (PTZ) electron donors are coordinated to the Pt(II) center via a phenyl-acetylide moiety. Substitution of one acetylide unit for its ^{13}C≡^{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, labelling 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 Pt(II) diimine dichloride.[7,16]

A number of asymmetric complexes, which bear chemically distinct acetylides, have been reported recently.[6,17,18] The general synthesis of these 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, yet cannot be used to obtain complexes possessing isotopically labelled but otherwise chemically identical acetylides. A different synthetic strategy is clearly required.

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



$^{+}$ Expressed in terms of theoretical maximum of 50%

*synthesis of PTZ-u in Supporting Information

Here, we present a controlled synthetic strategy to such asymmetric complexes, proceeding via an asymmetric bis-acetylide intermediate (Scheme 1; **5a & b**).

The PTZ acetylide ligands **3a,b** were synthesized according to a modified literature method[4] from commercially available starting materials (detail in 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 which can be easily modified to attach the desired final substituent. The ideal candidate would be a proton, as 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 Fe(II) mono-acetylide complexes.[19,20] However, in this instance the resultant 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 THF, with one equivalent of tetrabutylammonium fluoride (TBAF) as the deprotection agent, and a 3-fold excess of the appropriate aryliodide, an approach used in 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 centre, and of such coupling to a 3rd row transition metal bis-acetylide.

The "fully labeled" symmetric complex **PTZ-d** bearing ^{13}C as all four acetylide carbons, 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, 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 SI. The 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}, resp.). The fully ^{13}C labeled complex **PTZ-d** shows a similar vibrational pattern, with the expected shift to lower energies, 2052 and 2031 cm^{-1}, and a slightly larger difference between 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 ν(^{12}C≡^{12}C) mode at approx. 2120 cm^{-1} and one ν(^{13}C≡^{13}C) mode at ca. 80 cm^{-1} lower energy to 2040 cm^{-1}. Indeed, DFT calculations within the harmonic approximation predict that the two modes are de-coupled 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 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 similar frequency to that of the symmetric acetylide stretch of the **PTZ-u**. Furthermore, a singly-^{13}C-labelled tolyl analog, **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 in solution and in solid state 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.

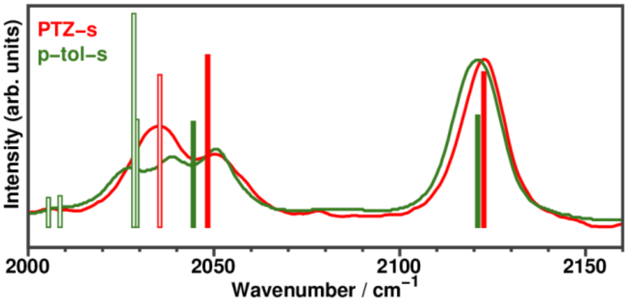


Figure 2. Experimental FTIR spectra (lines) and calculated (B3LYP/SDD[Pt]6-311G(d,p)[H,C,N,O,P,S]/PCM with GVPT2) anharmonic fundamental (filled sticks) and combination (empty sticks, rel. intensity >1%) vibrational modes of **PTZ-s** (red)**, p-tol-s** (green)**.** The calculated peak positions are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

Selected results of the anharmonic calculations are shown in Figure 2; full calculated spectra, diagrams of the vibrational eigenvectors, and animations of all the modes discussed are given in the SI. The 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 the assignment of the experimental IR band at 2033 cm^{-1} to 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 of **p-tol-s**.

In summary, we report the first synthetic route to selectively asymmetrically isotopically labelled transition metal bis-acetylide 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 a TMS-acetylide bound to a transition metal centre. This new strategy has been demonstrated by synthesizing asymmetric Pt^{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

Details regarding the calculations, synthesis, and analysis. These data are available free of charge via the internet at http://pubs.acs.org.

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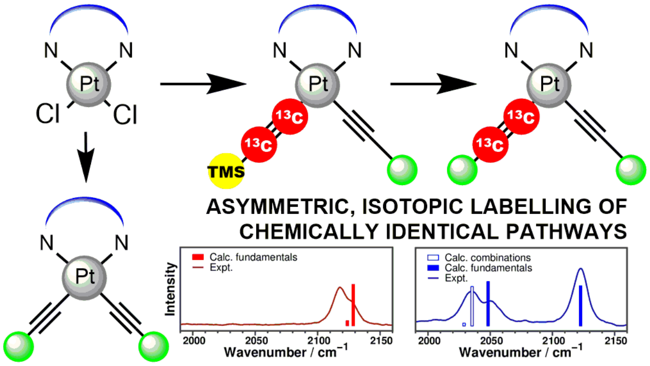

TOC Synopsis:

Asymmetric isotopic labelling of parallel and identical electron or energy transfer pathways in symmetrical molecular assemblies is an extremely challenging task. We describe in this paper the first selective synthetic route to asymmetrically labelled organometallic compounds, using charge transfer Pt(II) cis-acetylide complexes, through selective ^{13}C labelling of one of two acetylide groups. Experimental and computational FTIR is used to elucidate an unusual quantum mechanical mixing phenomena of the decoupled acetylide vibrations.