ABSTRACT: Rigid, conjugated alkyne bridges serve as important components in various transition-metal complexes used for energy conversion, charge separation, sensing, and molecular electronics. Alkyne stretching modes have potential for modulating charge separation in donor−bridge−acceptor compounds. Understanding the rules of energy relaxation and energy transfer across the metal center in such compounds can help optimize their electron transfer switching properties. We used relaxation-assisted two-dimensional infrared spectroscopy to track energy transfer across metal centers in platinum complexes featuring a triazole-terminated alkyne ligand of two or six carbons, a perfluorophenyl ligand, and two tri( p-tolyl)phosphine ligands. Comprehensive analyses of waiting-time dynamics for numerous cross and diagonal peaks were performed, focusing on coherent oscillation, energy transfer, and cooling parameters. These observables augmented with density functional theory computations of vibrational frequencies and anharmonic force constants enabled identification of different functional groups of the compounds. Computations of vibrational relaxation pathways and mode couplings were performed, and two regimes of intramolecular energy redistribution are described. One involves energy transfer between ligands via high-frequency modes; the transfer is efficient only if the modes involved are delocalized over both ligands. The energy transport pathways between the ligands are identified. Another regime involves redistribution via low-frequency delocalized modes, which does not lead to interligand energy transport.

INTRODUCTION

For the past decade, compounds composed of long sp-hybridized carbon chains and transition-metal end groups have received substantial interest, leading to extensive research on the synthesis of transition-metal clusters containing alkynes and their derivatives. These ligands offer versatility in coordination modes with the possibility of donating electrons serving as promising candidates for novel materials for molecular electronics. Additionally, recent studies have indicated that these compounds could be useful as pharmaceuticals, optical wires, and electronic reservoirs.

Linear and rigid alkyne-based molecular wires feature strong covalent bonds with frequencies in the convenient region of ca. 2100 cm\(^{-1}\). As such they can serve as useful infrared (IR) reporters for studying structures via two-dimensional infrared (2DIR) spectroscopy. Recent studies of ballistic transport of vibrational energy via oligomeric chains revealed that electronic conjugation within the chain can lead to higher transport speeds and ballistic transport efficiency. Alkyne-based molecular wires have not yet been tested as energy transporters. Here, we report on energy relaxation and transfer in two square planar Pt complexes featuring alkynyl triazole ligands with alkyne moieties of different lengths, \(C_2\) and \(C_6\), denoted as \(C_2\) and \(C_6\), respectively (Chart 1). These contain the \(F_3\)Ph ligand opposite to the \(C_6\)-Tri ligand and two trans tri( p-tolyl)phosphine ligands.

Transition-metal complexes and organic compounds with polyynes (ligands) are widely used as bridges in donor−bridge−acceptor (DBA) compounds, providing conjugation enhanced electronic coupling of the electron donor and acceptor. Because of their unique properties of supporting conjugation and convenient vibrational frequency, such vibrationally excited bridges are attractive candidates for modulating electron transfer rates in DBA compounds. Vibrational relaxation dynamics of excited alkyne bridges are important for the electron transfer studies but not well understood.

Vibrational relaxation and thermalization in molecules occur via an intramolecular vibrational energy redistribution (IVR)
process, which has been studied using a variety of experimental methods.\textsuperscript{29–33} Energy transfer and thermalization in covalent networks \textsuperscript{34–38} is better understood than the transfer across a metal center in a transition-metal complex for which only a few studies were reported.\textsuperscript{39–42} The coordination bonds at the metal center are often weak resulting in very inefficient energy transfer across the metal. For example, the lifetime of CO stretching modes in some metal carbonyls reaches 1 ns.\textsuperscript{43–47} A similar situation is encountered when an organic compound is attached to a metal or semiconductor surface. The surface binding energy is often small resulting in weak thermal conductivity through the interface.\textsuperscript{48–52} In contrast to surfaces, transition-metal complexes feature high-frequency vibrational modes on each side of the metal atom, which can potentially participate in the exchange of high-frequency quanta across the metal center. Understanding the role of energy transport involving high-frequency modes across the metal center is the objective of this study.

In this study, we use dual-frequency relaxation-assisted 2DIR (RA 2DIR) spectroscopy\textsuperscript{53} to investigate intramolecular energy redistribution and energy transport in the C2 and C6 compounds. This technique uses a pair of short mid-IR pulses to excite a vibrational tag at one end of the molecule, while a third mid-IR pulse probes various reporter modes in regions of the molecule spatially distant from the tag. When the excess energy arrives at the reporter site, it excites low-frequency modes coupled to the reporter thus enhancing the tag-reporter cross peak. The amplitude of the 2DIR cross peak between the tag and reporter changes with the time delay of the third pulse arrival, referred to as a waiting time, \( T \), yielding energy transport kinetics.\textsuperscript{53}

As detailed below, multiple 2DIR cross peaks of C2 and C6 demonstrated coherent oscillations. Vibrational and vibronic coherences have long been observed in polyatomic molecules in the ground\textsuperscript{54,55} and excited\textsuperscript{56–59} electronic states, respectively. In this study, we used coherent oscillations to identify modes located at the same moiety, which appears useful when severe peak overlap occurs in the linear Fourier transform infrared (FTIR) spectrum.

This paper is structured as follows: we start with assigning peaks in the FTIR absorption spectra of the two compounds using density functional theory (DFT)-based normal-mode analysis. Then the RA 2DIR data are discussed, reporting on the energy transport from and toward \( \nu_{\text{cm,CO}} \) as well as between different ligands. The experimental results highlighted include energy transfer times, cooling times, and frequencies of coherent oscillations observed for a range of various cross peaks. A computational section follows that clarifies the nature of energy transport pathways responsible for the observed RA 2DIR data. Special attention is given to identifying the requirements for efficient energy transfer across the Pt center.

\section*{EXPERIMENTAL DETAILS}

\textbf{2DIR Measurements.} A detailed description of a fully automated dual-frequency three-pulse echo 2DIR instrument with heterodyne detection is presented elsewhere.\textsuperscript{50,51} Briefly, a Ti:sapphire laser operating at 1 kHz generates 80 fs pulses at 800 nm (Libra, Coherent) pumps a computer-controlled dual optical parametric amplifier (OPA, Palitra-duo, Quantronix). Each OPA output is directed to a computer-controlled noncollinear difference frequency generation unit (DFG; NIR Quantronix) to generate independently tunable mid-IR pulses used in the fully automated 2DIR instrument that features a sensitivity of better than 10\textsuperscript{-4} cm\textsuperscript{-1} in measured anharmonicities. The automatic frequency tuning to any diagonal or cross peak of choice within the range of 800–4000 cm\textsuperscript{-1} is achieved by using a direction stabilization schematic for each mid-IR beam. The spectral width of the mid-IR pulses was \( \sim 150 \text{cm}^{-1} \), and the instrument response function, measured as a nonresonant signal, was fitted to a Gaussian function with the width \( \delta_{\text{whm}} = 140 \text{ fs} \). 2DIR box-car measurements were achieved by scanning the delay between the first two mid-IR pulses \( t \) at a fixed waiting time \( T \), which is the delay between the second and third pulses, and recording the heterodyned spectrum in the frequency range of interest (\( \lambda \rightarrow \omega_r \)) for every \( t \). Fourier transformation along \( t \) results in the \( \omega_r \) (pump) axis in the 2DIR spectrum. For the RA 2DIR measurements, the 2DIR spectra were recorded for each waiting time, which was scanned with varying delay steps ranging from 100 fs at small waiting times up to 5 ps at large waiting times. It takes 1–2 h to acquire a waiting-time dependence with 40–50 points along \( T \).

We used a dual-frequency RA 2DIR method\textsuperscript{53} to investigate energy relaxation and transport in the compounds. If a cross peak among spatially distant vibrational modes is measured, the cross-peak amplitude rises with the waiting time due to energy transfer from the mode initially excited by the first two laser pulses, the tag, to the vicinity of the reporter, the mode probed by the third laser pulse. The waiting time of the cross-peak maximum, \( T_{\text{max}} \), is referred to as the energy transfer time. A one-dimensional waiting-time trace for any diagonal or cross peak was obtained by integrating each 2DIR spectrum within a rectangular region centered at the peak. The waiting-time dependences were fitted with an asymmetric double sigmoidal function, \( y = y_0 + A \left[ 1 + \exp \left( \frac{T - \overline{T} + \omega_r / 2}{\omega_r} \right) \right]^{-1} \), using Ori-gen software. This function was selected because of its ability to fit the waiting-time data more accurately over longer waiting times than a bi-exponential function, accounting well for peak asymmetry. The reported \( T_{\text{max}} \) values were obtained by averaging five or more independent measurements.

\textbf{Sample Preparation.} Compounds trans-\textsuperscript{-}(C\textsubscript{6}F\textsubscript{5})(p-tolol,P)\textsubscript{3}Pt(C≡C)\textsubscript{1}C≡CCH(\textsubscript{2}CH\textsubscript{2})N≡N with \( n = 1 \) and 3, referred to as C2 and C6 (Chart 1), were synthesized by the Gladysz group, as previously described.\textsuperscript{57} For FTIR and 2DIR measurements, ca. 15 mM CDCl\textsubscript{3} solutions were used. The measurements were performed in a sample cell made of 1 mm-thick CaF\textsubscript{2} windows and a 100 \( \mu \)m Teflon spacer at room temperature, 22 ± 0.5 °C.

\textbf{DFT Calculations and Vibration Relaxation Modeling.} Geometry optimization, normal-mode analysis, and anharmonic force constant calculations were performed using the Gaussian 09 suite. A B3LYP functional and a 6-311G(d,p) basis set were used for all elements except platinum. LANL2DZ basis sets and effective core potential were used for platinum atoms. Vibration relaxation pathways of the endgroup states were computed using a theoretical approach developed in refs 37, 38. The method uses DFT-computed anharmonic force constants of an isolated molecule to compute third-order relaxation pathways while the low-frequency modes of the molecule serve as a bath.\textsuperscript{37,62} The
approach features a single variable parameter, cooling time to the solvent, which was set at 15 ps. 63–65

■ RESULTS AND DISCUSSION

Linear FTIR Spectroscopy Measurements. Linear absorption spectra of compounds C2 and C6 are very similar in the fingerprint region (Figure 1). Alkyne stretching peaks in

![Figure 1](image1)

Figure 1. Solvent-subtracted infrared absorption spectra of compounds C2 and C6 in CDCl₃. The spectrum of C6 was scaled by a factor of ca. 1.2 to match that of C2.

C2 and C6 are different: there is a single peak at 2130 cm⁻¹ for C2, while there are three peaks for C6, located at 2040, 2140, and ca. 2170 cm⁻¹, originating from coupling of three C≡C local modes (Figure S1). The strongest peak for C6, found at 2140 cm⁻¹, is due to in-phase motions of all three C≡C groups; unless stated otherwise, 2DIR measurements for C6 were performed for this peak, referred to as νC≡C.

The spectra of both compounds in the fingerprint region feature intense peaks at 1460 and 1500 cm⁻¹ and medium-strength peaks at 1600, 1435, and 1400 cm⁻¹. The differences between C2 and C6 in the fingerprint region above 1350 cm⁻¹ are minor, involving a peak at 1525 cm⁻¹ for C2, while a similar peak in C6 is slightly weaker and observed at ca. 1539 cm⁻¹, both referred to as a 1530 cm⁻¹ peak (see the next section). Accurate peak assignment is paramount to understanding the results of the following 2DIR studies.

DFT-Based Modeling of Linear Absorption Spectra. To help assign peaks in the fingerprint region, we computed normal modes for both C2 and C6 compounds and constructed theoretical spectra by broadening the line spectra with a Lorentzian line shape of an area equal to the mode IR intensity. The computed line spectrum and theoretical (broadened) spectrum (orange line) for C6 are shown in Figure 2A. The amplitude of the lines in the line spectrum is equal to their computed IR intensities in km/mol, while the color of each bar reflects the location of the normal mode on F₁Ph-, C₅Tri, and Tol moieties (see Table 1 footnote). The resulting frequency-corrected theoretical spectra for C6 and C2 (Figure 2B,C) show a good match with amplitude-scaled experimental spectra. Note that no attempt was made to tweak the correction factors within each group of modes to achieve a better match with the experiment.

The modeling suggests that the peak at 1600 cm⁻¹ is mostly due to Tol motion (Figure 2). The peaks at 1500 and 1460 cm⁻¹ have dominant contributions from modes on F₁Ph (see the SI for the way of computing the contributions). In addition, both peaks have significant (26–33%) contributions from Tol peaks, and the peak at 1460 cm⁻¹ has a significant, 14% (20%) contribution from a single Tri mode for C2 (C6).

The same correction factor was applied to other modes of F₁Ph. Corrections for tolyl groups were based on the peak at 1600 cm⁻¹, which is characteristic of phenyl and Tol groups. A similar κ factor was applied to other modes located on Tol and C₅Tri moieties (see Table 1 footnote). The resulting frequency-corrected theoretical spectra for C6 and C2 (Figure 2B,C) show a good match with amplitude-scaled experimental spectra. Note that no attempt was made to tweak the correction factors within each group of modes to achieve a better match with the experiment.

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The peak at ca. 1435 cm⁻¹ is assigned to a Tri motion. As expected, the peaks at ca. 1530 cm⁻¹ also belong to the alkyn-tri moiety. The peak at 1400 cm⁻¹ is assigned to Tol moieties.

The Tol modes contributing to the peaks at 1500 and 1600 cm⁻¹ involve C=C stretching and C–H bending motions of the phenyl rings (Figure S3A,B), while CH₃ bending modes of Tol moieties (Figure S3C) contribute to the peak at 1460 cm⁻¹ (12 modes). The peak assignment made for C2 and C6 was further corroborated by the results of RA 2DIR measurements (see below).

The mode assignment is crucial for understanding the RA 2DIR data. Numerous cross peaks in 2DIR spectra were used to track the energy relaxation and transfer in the C2 and C6 compounds. The results are arranged into three groups
Computed, Scaled Normal Modes of C2 and C6

Table 1. Main Experimental Absorption Peaks and DFT-Calculated, Scaled Normal Modes of C2 and C6

| experimental peak cm⁻¹ | computed peak cm⁻¹ | IR intensity, km/mol | mode description (number of modes) |
|------------------------|--------------------|----------------------|-----------------------------------|
| C2 1600 1599–1601      | 1599–1601          | 98 (23) b            | Tol (6)                           |
| 1606                   | 4                  | Tri (1)              |
| 1622                   | 3                  | F₃Ph (1)             |
| 1530                   | 1519               | 24Tri (1)            |
| 1500                   | 1499               | 223F₃Ph (1)          |
| 1498–1500              | 94 (22) b          | Tol (6)              |
| 1496                   | 14                 | Tri (1)              |
| 1460                   | 1455               | 211F₃Ph (1)          |
| 1456–1461              | 129 (18) b         | CH₃ of Tol (12)      |
| 1459                   | 55                 | Tri (1)              |
| 1435                   | 1436               | 46Tri (1)            |
| C6 1600                | 1599–1601          | 88 (18) b            | Tol (6)                           |
| 1605                   | 5                  | Tri (1)              |
| 1623                   | 20                 | F₃Ph (1)             |
| 1530                   | 1534               | 20Tri (1)            |
| 1500                   | 1500               | 252F₃Ph (1)          |
| 1498–1500              | 93 (22) b          | Tol (6)              |
| 1496                   | 16                 | Tri (1)              |
| 1460                   | 1458               | 211F₃Ph (1)          |
| 1456–1461              | 135 (17) b         | CH₃ of Tol (12)      |
| 1463                   | 85                 | Tri (1)              |
| 1435                   | 1434               | 73Tri (1)            |

"Frequency correction factors were 0.9885 for all F₃Ph modes and 0.978 and 0.974 for all Tri and Tol modes below and above 1550 cm⁻¹, respectively. A sum of IR intensities of all modes in the range is given; the IR intensity of the mode with the largest IR intensity is given in parentheses. Actual experimental frequencies for the mode denoted as 1530 cm⁻¹ differ for C2 (1525 cm⁻¹) and C6 (1539 cm⁻¹).

Involving energy transfer initiated by $\nu_{C=C}$ energy transfer toward $\nu_{C=C}$ and energy transfer initiated and detected by the modes in the fingerprint region.

Energy Transfer Initiated by $\nu_{C=C}$. The first group of RA 2DIR experiments involves $\nu_{C=C}$ as a tag and a variety of reporters shown with boxes in Figure 3A. The waiting-time dynamics for these cross peaks were recorded, characterizing energy transport from the excited $\nu_{C=C}$ tag toward various reporter modes throughout the molecule. One-dimensional waiting-time traces of the cross-peak amplitude, constructed by integrating the cross-peak area within a respective box, are shown in Figure 3B–F. The $T_{\text{max}}$ values, referred as the energy transport times, were obtained from the fits of the traces (see Experimental Details). Table 2 summarizes the $T_{\text{max}}$ values for the transport initiated by the $\nu_{C=C}$ tag, which vary greatly for different reporters. Note that the $\nu_{C=C}$ mode lifetimes were measured at 0.85 ± 0.1 and 1.9 ± 0.1 ps for C2 and C6, respectively (see Figure S2), which are much shorter than the measured $T_{\text{max}}$ values for each compound.

Most linear absorption peaks for both compounds have contributions of modes located at different moieties, Tri, F₃Ph, and Tol. When such peaks serve as reporters, different contributors may feature different $T_{\text{max}}$ values. Note that the cross-peak amplitude contributions of overlapping reporters scale as squares of their transition dipoles, or as their computed IR intensities (here we neglected the difference in the peak width). For the cross peaks connecting the spatially remote tag and reporter, the cross-peak amplitude also reflects the amount of excess energy delivered to the reporter, which is larger for reporters closer to the tag. As a result, a reporter mode, contributing less to the linear spectrum, can produce a stronger cross peak than a strong but remote reporter.

Despite severe reporter overlap in the linear spectrum, a good understanding of the energy transport pattern can be obtained from these experiments. For the $\nu_{C=C}$ tag, short

Figure 3. (A) 2DIR magnitude spectrum of C2 at $T = 2.7$ ps (see Figure S4 for C6). The magenta boxes show the integration windows for obtaining the waiting-time traces in panels (B–F). (B–F) Waiting-time traces for indicated cross peaks for C2 (blue lines) and C6 (green lines). The traces were fitted with an asymmetric double sigmoidal function (cyan lines for C2 and red for C6, see Experimental Details). $T_{\text{max}}$ values are shown in the graphs with matching colors.

Table 2. $T_{\text{max}}$ Values Obtained from the Fit of the Waiting-Time Cross-Peak Traces for C2 and C6

| cross peak | $T_{\text{max}}$ (ps) | reporter location |
|------------|-----------------------|-------------------|
| $\nu_{C=C}/1600$ | 14 | 14.2 | Tol |
| $\nu_{C=C}/1530$ | 0 | 4.2 | Tri |
| $\nu_{C=C}/1500$ | 7.4 | 9.7 | F₃Ph, Tri, Tol |
| $\nu_{C=C}/1460$ | 2.7 | 6.6 | F₃Ph, Tri, Tol |
| $\nu_{C=C}/1435$ | 1.5 | 3.3 | Tri |

"Reporters contributing the most to the specific cross peak.

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energy transport times are expected to the reporters at the triazole side as the two moieties are linked directly via a strong covalent bond. Indeed, the reporters with dominant Tri contributions (1435 and 1530 cm$^{-1}$, Figure 3C,F) feature the shortest $T_{\text{max}}$ values for C6 and dominating direct tag-reporter coupling for C2 (strongest cross peak at $T = 0$ ps). Interestingly, the tag-reporter ($\nu_{\text{C=C/Tri}}$) coupling is much weaker for the C$_6$ bridge, despite the tag delocalization over the three C=C=C bonds.

The two strongest IR peaks at 1500 and 1460 cm$^{-1}$, featuring the largest contribution from F$_3$Ph (Table 1), show widely varying $T_{\text{max}}$ values from 2.7 to 9.7 ps (Figure 3D,E). The transport times for the 1460 cm$^{-1}$ peak are smaller than those for the 1500 cm$^{-1}$ peak for both compounds due to a larger Tri contribution at 1460 cm$^{-1}$ (Table 1). At the same time, the Tri mode contribution to the peak at 1500 cm$^{-1}$ is small and does not affect the $T_{\text{max}}$ significantly. Therefore, the F$_3$Ph mode is the strongest contributor to the $\nu_{\text{C=C/C}}$ cross peak. A contribution of Tol peaks to this cross peak could also be sizable but affect the cross peak only at larger delays. Note that the contribution of Tol modes to the $\nu_{\text{C=C/C}}$ cross peak could be smaller than to $\nu_{\text{C=C/C}}$ as the Tol modes within 1460 cm$^{-1}$ peak reside further away at the Tol methyl groups, while the Tol modes at $\sim$1500 cm$^{-1}$ reside at the phenyl rings. Therefore, the $T_{\text{max}}$ for $\nu_{\text{C=C/C}}$ cross peak is likely affected more by the Tol modes, resulting in their larger values. The 1600 cm$^{-1}$ reporter is dominated by the Tol ring stretching modes, featuring the longest $T_{\text{max}}$ values of 11.2 ps (C2) and 14.2 ps (C6), Figure 3B. These quantities are taken as characteristic energy transfer time from $\nu_{\text{C=C}}$ to the Tol groups. To conclude, it takes approximately 1–4 ps to reach the triazole, 4–7 ps to reach F$_3$Ph, and 11–14 ps to reach tolyl. Despite the complexity of the assignment, the transport times correlate with the tag-reporter distance, and all $T_{\text{max}}$ times are longer for the C6 compound by ca. 3 ps, compared to C2.

A range of strongly coupled covalent bonds within the C$_n$Tri ligand offer efficient energy transfer pathways, in agreement with previous studies. Weak coordination bonds typically prevent efficient transfer across the metal atoms. The energy transfer across the Pt center in C2 and C6 is investigated further computationally, vide infra.

Note that not all cross peaks for C2 exhibit a rise in their waiting-time traces. The waiting-time dependences for the $\nu_{\text{C=C/C}}$ and $\nu_{\text{C=C/C}}$ cross peaks show the largest amplitude at $T = 0$, although similar cross peaks for C6 show rises with $T_{\text{max}}$ values of 4.2 and 3.3 ps, respectively (Figure 3C,F). The observation is not surprising as both 1435 and 1530 cm$^{-1}$ modes are assigned to CC and CN stretching motions in the triazole ring, are spatially close to alkyne group, and are strongly coupled. Note that modes at the terminal phenyl ring of the C$_n$Tri ligand are weak and do not contribute much to the waiting time dependences.

**Energy Transfer toward $\nu_{\text{C=C}}$.** Relaxation pathways, resulting in energy transfer to remote moieties, are sensitive to the tag identity and location. Therefore, it is expected that reversing the tag and reporter would lead to different energy transfer dynamics, especially when high-frequency modes are involved in the pathways. Comparing the data for the reversed tag and reporter in each compound, the mechanism of energy transport can be assessed. In this section, we describe experiments where various peaks in the fingerprint region served as tags initiating energy transport while the $\nu_{\text{C=C}}$ mode served as a reporter detecting energy arrival. Several cross peaks were measured (Figure 4A), and their waiting-time dependences were constructed (Figure 4B–D).

![Figure 4](https://example.com/figure4.png)

**Figure 4.** (A) 2DIR magnitude spectrum of C6 at $T = 2.0$ ps (see Figure S5 for C2). The magenta boxes show the integration windows for obtaining the waiting-time traces in panels (B–D). (B–D) Waiting-time traces for indicated cross peaks for C2 (blue lines) and C6 (green lines). The traces were fitted with an asymmetric double sigmoidal function (cyan lines for C2 and red lines for C6, see Experimental Details). $T_{\text{max}}$ values are shown in the graphs with matching colors.

As expected, the two cross peaks with modes at triazole (1530 and 1435 cm$^{-1}$) feature the shortest $T_{\text{max}}$ values of ca. 5–6 ps (Figure 4D, Table 3). The direct coupling between the

| cross peak | $T_{\text{max}}$ (ps) | reporter location |
|------------|----------------------|-------------------|
| 1600/$\nu_{\text{C=C}}$ | weak | Tol |
| 1530/$\nu_{\text{C=C}}$ | NA | $5 \pm 1.5$ | Tri |
| 1530/$\nu_{\text{C=C}}$ | 9.8 $\pm$ 0.2 | 10.5 $\pm$ 0.3 | F, Ph, Tri, Tol |
| 1460/$\nu_{\text{C=C}}$ | 7.2 $\pm$ 0.2 | 7.5 $\pm$ 0.2 | F, Ph, Tri, Tol |
| 1435/$\nu_{\text{C=C}}$ | 5.5 $\pm$ 0.5 | 6.1 $\pm$ 0.5 | Tri |

*Reporters contributing the most to specific cross peak.*

1530 cm$^{-1}$ mode and $\nu_{\text{C=C}}$ is strong in C2 resulting in the highest cross-peak intensity at $T = 0$ (data not shown). The 1600/$\nu_{\text{C=C}}$ cross peaks are too weak to record with confidence, as the excess energy escapes from the Tol moieties very slowly resulting in only a small amount arriving in the alkyne moiety region, see the next section. Similarly, other Tol modes do not contribute much to the 1500/$\nu_{\text{C=C}}$ and 1460/$\nu_{\text{C=C}}$ cross peaks. The 1500/$\nu_{\text{C=C}}$ cross peak (Figure 4B) is dominated by the F$_3$Ph contribution, as the Tri contribution to the 1500 cm$^{-1}$ mode is small (<5%). The $T_{\text{max}}$ values for this cross peak represent energy transfer to the F$_3$Ph moiety. They are found to be only slightly larger (1–2 ps) than the $T_{\text{max}}$ values for the reverse direction, $\nu_{\text{C=C}/1500}$ (Tables 2 and 3). The $T_{\text{max}}$ values for the 1460/$\nu_{\text{C=C}}$ cross peaks are smaller than those for 1500/$\nu_{\text{C=C}}$ explained by a stronger contribution of the Tri mode in the 1460 cm$^{-1}$ peak.
Convolution of two cross peaks, 1460(F,Ph)/ν_{C≡C} and 1460(Tri)/ν_{C≡C}, results in smaller measured $T_{\text{max}}$.

Diagonal Peaks and Cross Peaks in the Fingerprint Region. Diagonal Peaks. Diagonal 2DIR peaks were measured for all the main peaks in both compounds, and the waiting time traces were used to determine the lifetimes. Note that the diagonal 2DIR peaks for the absorption peaks with multiple overlapping contributions favor the strongest peak contributor as the diagonal-peak contribution is proportional to the square of the contributions of the two modes that are spatially separated from the alkyne moiety introducing the only primary structure difference of the two compounds. The modes of F,Ph, 1500 and 1460 cm$^{-1}$, show similar but different kinetics. The lifetimes of both modes are ca. 2 ps in both compounds, and the cooling time is ca. 9.4 ps (Table 4). While the fast components for both modes lay within their error bars, the overall traces are systematically different (Figure S9), with longer mean decay times for C6 compared to C2. In addition, for each mode the decays are slower for C6. Nevertheless, the characteristic lifetime and cooling time provide a fingerprint of the F,Ph moiety in such compounds.

The two C$_6$-Tri peaks at 1435 and 1530 cm$^{-1}$ in C2 feature similar lifetimes of 1.7 ps and a similar cooling time of ca. 5 ps (Figures S10, S11). The mean decay times of both diagonal peaks in C2 are characteristically short at ca. 3 ps. The 1435 trace for C6 has a similar mean time of 3.7 ps but is essentially single exponential. The question remains if the 3.7 ps is the true lifetime of the 1435 cm$^{-1}$ mode in C6 or the exponential behavior is a convolution of the lifetime and peculiar cooling dynamics. The diagonal peak at 1530 cm$^{-1}$ for C6 is too weak to detect with confidence, indicating its small diagonal anharmonicity combined with weak IR intensity. Nevertheless, the kinetics of these peaks appear to be characteristic of the C$_6$-Tri moiety.

Table 4. Fit Parameters for Several Diagonal Peaks

|     | freq, cm$^{-1}$ | $t_1$, ps | $t_2$, ps | fast component contribution, % | $\tau_{\text{max}}$, ps | dominant contribution |
|-----|-----------------|-----------|-----------|-------------------------------|--------------------------|----------------------|
| C2  | 1600            | 1.00 ± 0.06 | 25 ± 2   | 56                            | 100%                     | Tol                  |
| C6  | 1600            | 1.06 ± 0.06 | 27 ± 2   | 55                            | 100%                     | Tol                  |
| C2  | 1500            | 2.0 ± 0.1  | 9.1 ± 0.2 | 41                            | 6.2                      | F,Ph                 |
| C6  | 1500            | 2.1 ± 0.1  | 9.5 ± 0.2 | 36                            | 6.8                      | C$_2$-Tri            |
| C2  | 1460            | 1.93 ± 0.07 | 9.2 ± 0.3 | 52                            | 5.4                      | C$_2$-Tri            |
| C6  | 1460            | 2.3 ± 0.2  | 9.6 ± 0.5 | 46                            | 6.2                      | C$_2$-Tri            |
| C2  | 1530            | 1.8 ± 0.2  | 4.8 ± 0.9 | 71                            | 2.6                      | C$_6$-Tri            |
| C6  | 1435            | 1.6 ± 0.2  | 5.9 ± 0.5 | 58                            | 3.4                      | C$_6$-Tri            |

The diagonal-peak traces at 1600 cm$^{-1}$ are very characteristic with the fast components of ca. 1.03 ps and slow components of ca. 26 ps (Figure S5B, Table 4, Figure S9A).

Similar to other diagonal peaks, the slow component is attributed to the relaxation-assisted effect: lower-frequency modes coupled to the tag are excited via vibrational relaxation of the tag, thus perturbing the tag frequency and enhancing the diagonal peak. The slow component of the 1600 peak is slower than a typical cooling time of organic molecules to the solvent of ca. 15 ps, and has a surprisingly larger amplitude $A_2 = 45\%$ (Table 4). The large amplitude of the slow component is supported by the strength of the coupling among the modes of Tol, facilitated by its compactness and electronic conjugation. Slow cooling is caused by relative isolation of the Tol moieties from other functional group types and by closeness of three Tol groups within a single phosphine.

The long cooling time likely occurs due to relative isolation of the Tol moieties separated from the rest of the molecules by three dissimilar bonds involving heavy atoms, C=C, P=P, and Pt−C. The C−P−Pt−C bridge connecting Tol to F,Ph and C$_6$-Tri features a small number of degrees of freedom and different low-frequency modes, so that mode delocalization across the bridge is limited making the energy transport inefficient, trapping the excess energy at toyls. The closeness of three Tol groups within a single phosphine makes the cooling longer as cooling of 1600 cm$^{-1}$ mode in one Tol moiety to another two Tol moieties of a phosphine group still contributes to the 1600 diagonal peak at later times.

Figure 5. Scaled waiting-time traces for indicated diagonal and cross peaks for C6 (see Figure S6 for C2). (A) Results of individual fits of T-traces of diagonal peaks (red lines) are shown in Table 4. The insets in A and B show 2DIR spectra measured at 2.3 ps with color-matching boxes indicating the cross-peak integration regions. (B) 1600/1600 and 1600/1570 peaks were fitted globally with a double-exponential decay function (red lines) resulting in $t_1 = 1.06 ± 0.06$ ps and $t_2 = 27 ± 2$ ps and amplitudes of the fast component of 55% for 1600/1600 and 45% 1600/1570.
Cross Peaks Involving 1600 cm\(^{-1}\) Mode. Two cross peaks involving 1600 cm\(^{-1}\) peak as a reporter (probed mode) and peaks at 1500 and 1460 cm\(^{-1}\) as tags (pumped modes) were also measured (Figure 5B, yellow and gray lines). Note that the main contributors for both tags reside at the F\(_3\)Ph moiety. A rise of the amplitude is expected for a cross-peak between a tag at F\(_3\)Ph and a reporter at Tol at delays exceeding 10 ps due to the significant distance between the moieties. However, no rise was observed. Instead, the waiting-time traces for both cross peaks follow the trace of the 1600 diagonal peak (Figure 5B) suggesting that both cross peaks originate fully from modes at the Tol moieties. Indeed, peaks at 1500 and 1460 cm\(^{-1}\) bear significant contributions from the modes at Tol (Table 2, Figure 2), The coupling of the Tol modes at 1500 and 1460 cm\(^{-1}\) (tags) and the Tol mode at 1600 cm\(^{-1}\) (reporter) is large, computed at ca. \(-3.8\) cm\(^{-1}\), resulting in a significant cross-peak amplitude at \(T = 0\). Relaxation of these tags populates lower-frequency modes in Tol similar to relaxation of the 1600 cm\(^{-1}\) tag, resulting in similar waiting-time traces for three different Tol tags at 1600, 1500, and 1460 cm\(^{-1}\). Apparently, the mode proximity wins over the strength of the transition dipole of the tag.

Interestingly, there is a rather strong cross peak at 1600/1570. The Tol moiety features a mode computed at ca. 1570 cm\(^{-1}\), but it is over 10-fold weaker than that at 1600 cm\(^{-1}\). However, the 1600/1570 cross peak is strong at about a half of the diagonal peak at 1600 cm\(^{-1}\). The strength of the cross peak originates from a large off-diagonal 1600–1570 anharmonicity, computed at 7.4 cm\(^{-1}\), which is much larger than the diagonal anharmonicity of the mode at 1600 cm\(^{-1}\), computed at ca. 1 cm\(^{-1}\). The pair of diagonal and cross peaks can serve for identifying Tol moieties in 2DIR spectra. The waiting-time trace of this cross peak follows the trace of the 1600 diagonal peak (Figure 5B, blue line) and shows no coherent oscillations.

Multiple cross peaks were observed in the fingerprint region (see Figure 6 inset), and their waiting-time dependences were analyzed. Only one of these cross peaks shows a clear rise time, but several cross peaks show coherent oscillations as a function of the waiting time. We first discuss the oscillations, then analyze the cross-peak decay times, and then discuss the cross peak showing a rise.

Coherent Oscillations in Cross Peaks. The presence of oscillations in a cross peak indicates that a coherent superposition of strongly coupled states is excited by a short mid-IR pulse. \(^{34,71,72}\) Therefore, coherent oscillations in 2DIR spectra can help identify modes that belong to the same moiety as their strong coupling requires significant spatial overlap. Several 2DIR cross peaks of C2 and C6 show coherent oscillations. These include the cross peaks between the two strongest peaks, 1500 and 1460 cm\(^{-1}\) (1500/1460 and 1460/1500), as well as the cross peaks among the 1460 and 1435 cm\(^{-1}\) peaks (1435/1460 and 1460/1435), Figure 6. The period of oscillations, \(T_o\) corresponds to the beating frequency as \(\Delta \nu\) (in cm\(^{-1}\)) = 1/(\(cT_o\)), where \(c\) is the speed of light under vacuum. The computed beating frequencies, 43 ± 1 cm\(^{-1}\) for 1500/1460 and 1460/1500 and 21 ± 1 cm\(^{-1}\) for 1435/1460, are expected to match the energy gap between the involved states excited coherently — the two frequencies of the cross peak. Indeed, the frequency difference between the peaks at 1500 and 1460 cm\(^{-1}\) for C6 is 43.2 cm\(^{-1}\) (1500.1–1456.9 cm\(^{-1}\)), which matches well the oscillation frequency. The function used for fitting the data is described in Figure 6 caption, while the fit parameters are given in Table 5.

Note that the 1500 and 1460 cm\(^{-1}\) peaks have dominant contributions from the F\(_3\)Ph ligand. Their cross-peak oscillations are expected to be dominated by coherent excitation of the two F\(_3\)Ph modes, but a smaller contribution from coherent excitation of the modes at Tri is also expected. Because of reduced coupling, it is less likely that the Tol modes will be excited coherently as the group of Tol modes at 1500 cm\(^{-1}\) belongs to the Ph ring motion, while those at 1460 cm\(^{-1}\) are due to CH\(_3\) bending, resulting in smaller coupling.

The peak at 1435 cm\(^{-1}\) belongs exclusively to Tri. Therefore, the oscillations of the 1435/1460 cross peak have to be due to coherent excitation of the modes at the Tri moiety. The presence of oscillations proves that both modes of the cross peak originate from the same moiety, Tri, permitting to identify a minor Tri contribution within the 1460 cm\(^{-1}\) peak, predicted by the DFT-based peak assignment (Table 1). How strong is the contribution to the cross peak of the 1460 cm\(^{-1}\) mode of F\(_3\)Ph and the Tri mode of 1435 cm\(^{-1}\)? Such a cross peak is expected to be weak at waiting times close to zero. Indeed, the amplitude of the oscillations is significant, \(A_3/A_1 = 0.33\), so the cross peak is dominated by the Tri peaks, at least at small waiting times.

Cross-Peak and Diagonal-Peak Decay Times. Slow Decay Components for Diagonal Peaks. While the fast component of a diagonal peak is attributed to the lifetime of the largest peak contributor, the slow decay component of the diagonal peak reflects its cooling time, observed via the mode coupling to low and medium frequency modes (Table 6). Therefore, the slow decay components of diagonal-peak traces for the modes residing at the same moiety should be similar. Indeed, both modes of the Tri moiety, 1435 and 1530 cm\(^{-1}\), feature similar cooling times of ca. 7 ps. The cooling times for the diagonal peaks at 1460 and 1500 cm\(^{-1}\) are also similar at 10 ± 1 ps, as both peaks reside predominantly at F\(_3\)Ph.

Tol-Dominated Peaks. The decay time for the diagonal peak at 1600 cm\(^{-1}\), representing Tol moieties, is exceptionally long at 27 ps (Figure 5B, blue). Interestingly, the decay times for two cross peaks with the reporter at 1600 cm\(^{-1}\) (1500/1600 and 1460/1600) are also the same at ca. 27 ps (Figure 6)
Table 5. Fit Parameters* for Several Cross Peaks for C6

| cross peak     | $T_1$, ps | $T_2$, ps | $T_0$, ps | $\varphi$ | $A_1/A_2$ | oscillation freq., cm$^{-1}$ | dominant contribution |
|----------------|-----------|-----------|-----------|-----------|-----------|-----------------------------|----------------------|
| 1460/1500      | 11.3 ± 0.7| 0.79 ± 0.1| 0.78 ± 0.02| 0.05      | 0.47      | 43 ± 1                      | F,Ph/F,Ph           |
| 1500/1460      | 9.8 ± 0.8 | 0.79 ± 0.1| 0.78 ± 0.02| 0.01      | 0.70      | 43 ± 1                      | F,Ph/F,Ph           |
| 1435/1460      | 9.8 ± 0.7 | 1.3 ± 0.4 | 1.6 ± 0.1  | 0.07      | 0.33      | 21 ± 1                      | Tri/Tri             |
| 1460/1435      | 5.1 ± 0.3 | 0.9 ± 0.2 | 1.7 ± 0.2  | −0.05     | 0.51      | 20 ± 1                      | Tri/Tri             |

*See Figure 6 caption.

Table 6. Exponential Decay Parameters for Cross Peaks for C6

| cross peak     | $t_D$, ps | $T_{max}$, ps |
|----------------|-----------|---------------|
| 1500/1435      | 7.5 ± 0.4 | 0             |
| 1435/1500      | 15.7 ± 1  | 7.0           |
| 1530/1500      | 7.6 ± 0.3 | 0             |
| 1500/1530      | 6.3 ± 0.3 | 0             |

*Coherent oscillations observed.

diagonal and cross peak, also reported in Tables 4 and 5B), despite the fact that the strongest contributors to the 1500 and 1460 cm$^{-1}$ peaks reside at F,Ph. This similarity indicates that all three cross peaks are dominated by the Tol/Tol type cross-peak contributions. In other words, for the 1500/1600 cross peak the Tol-localized modes are contributing as tags, not the strongest 1500 peak contributor of F,Ph. At the same time, the cross-peak contribution associated with the energy transfer between the F,Ph and Tol ligands, expected to feature a rise in the waiting time dependence, is fully masked by a much stronger Tol/Tol type cross-peak contribution. Otherwise, either a cross-peak rise would be observed or the decay time would be longer, affected by delayed energy arrival to the reporter site.

**Tri-Dominated Peaks.** The diagonal peaks of Tri modes at 1435 and 1530 cm$^{-1}$ feature the same cooling time of ca. 7 ps. The slow decay components are nearly the same for a range of cross peaks involving Tri modes, such as 1500/1435, 1469/1435, 1530/1500, and 1500/1530 (Figure 7A, cyan color). This match suggests that these four cross peaks are dominated by local Tri modes, while the Tri/F,Ph and F,Ph/Tri type cross peaks, involving energy transfer between the ligands, cannot compete amplitude-wise with the local Tri/Tri type cross peaks.

**F,Ph-Dominated Peaks.** The diagonal peaks for the F,Ph-residing modes at 1500 and 1460 cm$^{-1}$ show a characteristic cooling time of ca. 10 ps. Their cross peaks, 1500/1460 and 1460/1500, show similar cooling times of 10 ± 1 ps, characteristic of cooling of the F,Ph moiety.

**Cross Peaks at 1435/1500 and 1435/1460.** The cross peaks at 1435/1500 and 1435/1460 can have two contributions: one from spatially close Tri/Tri type modes, which may show coherent oscillations, and another of Tri/F,Ph type, which is expected to show an amplitude rise with the waiting time. Only one cross peak in the fingerprint region is showing a characteristic cooling time of ca. 10 ps. Their cooling times are at ca. 7, 10, and 27 ps, respectively. To further understand the vibrational energy transport within these complex molecules, we computed relaxation pathways of various excited modes.

**Computing Vibrational Relaxation Pathways.** The whole molecules were too large to perform anharmonic DFT calculations, so such computations were performed on the fragments of the compounds, where the Tol and CH$_2$C$_2$H$_5$ groups were replaced by hydrogen atoms (labeled as C2F and C6F), as shown in Figures 8 and S7 insets.

Figure 7. (A) Scaled waiting-time traces for indicated cross peaks for C6. The traces were fitted globally with an exponential decay function (red lines), see results in Table 6. The 1435/1500 cross peak was also fitted with an asymmetric double sigmoidal function (cyan, see Table 5). (B) Exponential decay times measured are summarized for each diagonal and cross peak, also reported in Tables 4–6. The vertical and horizontal lines are color coded to indicate FTIR contributions originated from different ligands, F,Ph (red), Tri (blue), and Tol (green).

Figure 8 shows the dominant relaxation channels for the $\nu_{C=C}$ tag in C2F, presented as rate bars populating various daughter states. Each relaxation daughter mode is labeled with a $j$ value, (Figure 8, right of bars) which represents the level of mode delocalization between the F,Ph and C$_2$C$_2$H$_5$ ligands across the Pt center (excluding motions at the PH$_3$ ligands).
The modes with $\chi \sim 1$ reside at the F$_2$Ph ligand, while those with $\chi \sim 0$ reside at the C$_2$-Tri ligand. Clearly, the $\nu_{\text{C=C}}$ relaxation daughter modes are predominantly (99.5%) residing at the Tri ligand with $\chi$ of 0–0.02. The two daughter modes populated the most are at 1492 and 729 cm$^{-1}$ (Figure 8, bars marked with stars). The $\nu_{\text{C=C}}$ relaxation pathways in the C$_6$ compound are richer but similarly populate predominantly the modes of the Tri ligand with $\chi < 0.01$ (see Figure S7). Both compounds show negligible relaxation of the $\nu_{\text{C=C}}$ tag directly into the F$_2$Ph localized modes.

To illustrate the waiting-time dependence on the chain length, we performed a modeling in which the $\nu_{\text{C=C}}$/F$_2$Ph cross-peak amplitude for C$_2$ and C$_6$ was plotted as a function of the waiting time (Figure 13A and 14A). Reasonable shapes of the waiting-time dependences were obtained with the $T_{\text{max}}$ values showing similar trends to the experimental values (7.4 ps in C$_2$ and 9.7 ps in C$_6$). Detailed analysis showed the presence of a very large number of relaxation pathways in the energy relaxation process, *vide infra*. To identify the pathways leading to energy crossing the Pt center, a detailed analysis of the mode couplings and delocalization was performed (Figures 9 and S8).

We found that despite some similarities of bond types in the F$_2$Ph or C$_2$-Tri ligands, most of their high-frequency modes are localized on either of the ligands. However, there are a few pairs of normal modes showing significant delocalization. To identify potential delocalization, the coupling strength among the local modes at F$_2$Ph and C$_2$-Tri were computed by varying the masses of the 11 atoms of F$_2$Ph in small increments and computing normal modes for each mass value using the Hessian matrix obtained via DFT normal-mode analysis. As a result of the mass change of the F$_2$Ph moiety, an avoided splitting is observed for the interacting modes which equals $2\beta$, where $\beta$ is the interaction energy (Figure 10). We found that the coupling of local modes across the Pt center does not exceed $\sim 20$ cm$^{-1}$, while typical couplings are less than 2 cm$^{-1}$. Only two pairs of high-frequency modes (>400 cm$^{-1}$) were found to be coupled strongly enough to result in mode delocalization at the actual atomic masses of F$_2$Ph ($\chi = 1$). One pair involves partially delocalized modes at 1355 cm$^{-1}$ ($\chi = 0.14$) and 1362 cm$^{-1}$ ($\chi = 0.84$) with $2\beta = 5$ cm$^{-1}$ (labeled with red circles in Figure 9). Another pair involves modes at 730 cm$^{-1}$ ($\chi = 0.015$) and 790 cm$^{-1}$ ($\chi = 0.94$) with $2\beta = 17$ cm$^{-1}$ (Figure 10B). Relatively small couplings require rather precise match of the site frequencies to result in delocalization, limiting the number of delocalized modes. Interestingly, the low-frequency modes (<400 cm$^{-1}$) are predominantly delocalized across the Pt center (Figure 9).

**Origin of Mode Coupling across the Pt Center.** Two types of coupling mechanisms are possible: through-space electrical coupling and through-bond mechanical coupling. The modes of the two pairs feature IR intensities not exceeding 60 km/mol and the effective distances well exceeding 4 Å (carbon–carbon distance across Pt is ca. 4.1 Å). For such weak modes and distances over 5.3 Å, the electrical dipole–dipole coupling is computed to be smaller than 0.25 cm$^{-1}$ (see the SI). We found that the modes with the largest coupling strength ($2\beta > 5.0$ cm$^{-1}$) are coupled mechanically, involving a change of the C–Pt–C distances, as for modes of a coupled pair at 1350 and 1362 cm$^{-1}$, Figure 11AB. While the Pt atom is heavy and does not move much, both adjacent carbon atoms move in the Pt–C stretching fashion as in-phase and out-of-phase combinations for the modes of the pair. The energy gap of the local modes is larger than the coupling leading to only a partial mixing of the site states. The energy match is somewhat accidental, as the two ligands are different. At the same time, both ligands feature similar bond types, carbon–carbon with a bond order of 1.5, which facilitates the energy match and mixing of the local modes featuring Pt–C stretching motions. Another type of local motion that leads to strong coupling between the local modes of the two ligands involves C–Pt–C angle change (Figure 11C,D). Such motions are present in many local modes with 250–400 cm$^{-1}$ frequencies, ensuring delocalization of normal modes in this frequency region (Figure 9). The lower-frequency modes, <250 cm$^{-1}$, are delocalized over the whole compound, as expected.

Vibrational relaxation is governed by third-order force constants; to be significant they require spatial overlap of the parent and daughter modes. Figure 12 illustrates this statement...
presenting relaxation pathways of the three modes, two modes of the partially delocalized pair at 1361 and 1354 cm$^{-1}$ with a delocalization extent of 0.86 and 0.14, respectively, and a high-frequency mode at 1256 cm$^{-1}$ located at the C$_2$-Tri ligand ($\chi = \ldots$).
The mode at 1354 cm\(^{-1}\) ($\chi = 0.14$) relaxes predominantly to modes within C\(_2\)-Tri (81\%) but also relaxes to modes localized at the F\(_5\)Ph ligand (19\%), thus providing a high-frequency (600–800 cm\(^{-1}\)) pathway to F\(_5\)Ph across the Pt center (Figure 12A). The relaxation pathways of the 1361 cm\(^{-1}\) mode ($\chi = 0.86$) are complementary to those for 1354 cm\(^{-1}\); 19 rate percent of the pathways involve energy passage from F\(_5\)Ph to C\(_2\)-Tri (Figure 12A,B inserts).

The daughters of the 1256 cm\(^{-1}\) mode ($\chi = 0.001$) relaxation located predominantly (>98 rate percent) at the same ligand as the parent mode (Figure 12C). Therefore, to have sizable relaxation rates across the Pt center, the parent mode should be delocalized significantly across the center. If such a delocalized parent mode became excited, it relaxes into modes on both sides of the Pt center. At the same time if a mode is localized at C\(_2\)-Tri, it predominantly relaxes into the modes at C\(_2\)-Tri, resulting in negligible energy transfer across the Pt center (Figure 12C). As the number of delocalized high-frequency modes is small, there are a small number of energy transfer pathways across the Pt center.

Most vibrational modes lower than 400 cm\(^{-1}\) are delocalized (Figure 9). A strong coupling of local modes of F\(_5\)Ph and C\(_2\)-Tri in the 250–400 cm\(^{-1}\) region originates from local modes resulting in a change of the C–Pt–C angle (bending). The low-frequency modes (<250 cm\(^{-1}\)) naturally involve motion of the whole molecule. The delocalized modes (<400 cm\(^{-1}\)) feature a significant coupling to high-frequency modes on each side of the Pt center. If excited, they perturb the reporter at the F\(_5\)Ph moiety causing an increase of the C≡C/reporter cross peak amplitude. It is important to note that excitation of delocalized low-frequency modes does not lead to energy transfer across the Pt center, as the energy excess remains on both sides of the Pt center.

The relaxation dynamics initiated by relaxation of the excited \(\nu_{\text{C=CC}}\) mode was computed, and the excess populations of every mode (Figure 13B) and their contributions to the \(\nu_{\text{C=CC}}/1500\)(F\(_5\)Ph) cross-peak were extracted and analyzed (Figure 13A,C). The IVR process of \(\nu_{\text{C=CC}}\) populates every mode in the compound but to a different extent and at different times. The maximum computed for all modes higher than 15 cm\(^{-1}\) is peaking at ∼6.1 ps (Figure 13A, blue line). To understand which modes are involved in transferring energy from the C\(_2\)-Tri ligand to F\(_5\)Ph, we analyzed contributions from different groups of modes to the cross-peak (Figure 13A).

As expected, we found that the \(\nu_{\text{C=CC}}/1500\)(F\(_5\)Ph) cross-peak is dominated by contributions of the modes at F\(_5\)Ph (those with high \(\chi\), Figure 13A, black) as they are well coupled to the reporter located at F\(_5\)Ph. The high-frequency modes, >400 cm\(^{-1}\), are mostly localized at either ligand so they are easily sorted into the modes at F\(_5\)Ph (large \(\chi\) black line) or C\(_2\)-Tri (small \(\chi\), red line). The modes with \(\chi > 0.96\) contribute the most (black line) with a peak at 7.7 ps. High-frequency modes with \(\chi < 0.1\) (red line) contribute much less, peaking at ca. 3 ps.

Many modes in the 220–400 cm\(^{-1}\) window are delocalized over the two ligands due to the motion involving the C–Pt–C angle change (Figure 11C,D); their contribution is shown in Figure 13A, cyan. Interestingly, the contribution is significant but peaking at earlier delay times of ∼2 ps, thus shortening the \(T_{\text{max}}\) values for the \(\nu_{\text{C=CC}}/\nu_{\text{F=Ph}}\) cross peaks. Low-frequency modes, <220 cm\(^{-1}\) (Figure 13A, green), are not contributing much to the cross peak, mostly because of their small coupling to the high-frequency reporter at F\(_5\)Ph.

Based on the match of the experimental \(T_{\text{max}}\) values for the \(\nu_{\text{C=CC}}/1500\)(F\(_5\)Ph) cross peak (7.4 ps) and the computed \(T_{\text{max}}\) (Figure 13A), we conclude that the high-frequency modes at F\(_5\)Ph (high \(\chi\)) determine the \(T_{\text{max}}\) values.

To understand the pathways populating the high-frequency modes at F\(_5\)Ph, we analyzed the population dynamics of these modes. Figure 13B shows the high-frequency modes with \(\chi > 0.5\) having the highest populations. Importantly, the modes of F\(_5\)Ph that are populated the earliest and to the largest extent contribute the most to the energy transfer process from the C\(_2\)-Tri ligand to F\(_5\)Ph. We found that such modes involve those modes of the coupled pairs: 575.5, 790, and 1362 cm\(^{-1}\) (Figure 13B). The populations for the 790 and 1362 cm\(^{-1}\) modes are rising with no delay, indicating that they are daughter modes of the \(\nu_{\text{C=CC}}\) relaxation. However, their contributions are not very large, even though they carry larger energy. The mode at 575 cm\(^{-1}\) (Figure 13B, magenta) belongs to a coupled pair involving mixing of the CCC bending at C\(_2\)-Tri and F\(_5\)Ph deformation motions (Figure 11). It is not populated directly from \(\nu_{\text{C=CC}}\) as apparent from the presence of the induction period but is still populated very rapidly leading to a maximum at ∼2.3 ps. Another mode of the pair, 574.3 cm\(^{-1}\) (\(\chi = 0.972\), Figure 13B, yellow), follows the trace of the 575.5 mode with some lag, peaking at ∼4.5 ps. Figure 13C shows the largest high-frequency contributors to the cross peak. Note that because of a strong coupling among the modes of F\(_5\)Ph, the...
equilibration among them occurs within a few IVR steps (3–5 ps), so that many F₅Ph modes became populated after 3 ps. The large contribution of the mode at 409 cm⁻¹ (χ = 0.9895) reflects its lower frequency. Nevertheless, the overall contribution of the high-frequency modes (>700 cm⁻¹) is very significant (Figure 13C, green dashed line).

To summarize, the high-frequency modes of the mode pairs coupled across the Pt center provide pathways to transfer energy between the two ligands. The high-frequency modes, >400 cm⁻¹, are responsible for 66% of the cross-peak amplitude. The modes in the 220–400 cm⁻¹ region also contribute significantly, reaching ca. 40% in amplitude, but interestingly, the maximum is reached much earlier than T_max at 1.9 ps (Figure 13A, cyan). The modes in this range are largely delocalized over the two ligands. This delocalization is caused by the similarity of the groups on each side of the Pt center resulting in similar frequencies of the Pt–C–C bending motion on each ligand. Therefore, the process of energy transfer between the ligands relies on the similarity of the groups at the two ligands in the vicinity of the Pt center and frequencies of their modes.

The relaxation pathways of ν_C=C computed for C₆F revealed a similar behavior to that for C₂F: only high-frequency modes of strongly coupled pairs showed a significant energy transfer from C₅-Tri to F₅Ph (Figure 14B); the populations of those modes and all high-frequency modes of F₅Ph, however, reach much smaller values compared to those in C₂F (Figure 13B). As a result, the overall relative contribution of energy transfer pathways involving high-frequency modes in C₆F (~35%, Figure 14A) is half of that for C₂F. Low-frequency modes, 15–220 cm⁻¹ (green) and especially 220–400 cm⁻¹ (cyan), show a much larger relative contribution to the cross peak in C₆F. Spatial proximity of the centers of the two ligands dictates the outcome of the energy transport process, showing a similar connectivity observed previously for modes within a covalent network.

Detailed analysis of relaxation pathways of high-frequency modes enables us to identify specific modes involved in energy transfer across the molecule in C₂F and C₆F. The efficiency of the energy transfer across the Pt center was found to correlate with the delocalization extent of the parent mode across the center. A negligible energy transport efficiency from the C₅-Tri to F₅Ph moieties was found for the modes with the extent of delocalization at the F₅Ph moiety smaller than 1%. The overall cross-peak waiting-time dynamics in C₂F is dominated by the energy transfer via high-frequency modes (>400 cm⁻¹), while low-frequency modes dominate for C₆F.

The energy transfer time, T_max appears to be different when the tag and reporter are reversed (Tables 2, 3), indicating different contributions of high- and low-frequency energy transfer channels in the two cases. The transport channels associated with high-frequency modes are expected to alter with a change of the tag as the relaxation channels are tag-specific and will not involve the same modes. Such changes are found for C₂, T_max(ν_C=C/1500) = 7.4 ps and T_max(1500/ν_C=C) = 9.7 ps, indicating the importance of the high-frequency mode transport initiated more efficiently by ν_C=C compared to the 1500 cm⁻¹ mode initiation. A similar effect is observed for the ν_C=C/1460 and 1460/ν_C=C peaks, although the Tri contribution to the peak at 1460 cm⁻¹ makes quantitative assessment difficult. On the other hand, the similarity of the transport times for reversed tag and reporters likely points at a dominant contribution of the low-frequency modes in the thermalization process, as, for example, for the ν_C=C/1500 and 1500/ν_C=C cross peaks for C₆ (9.7 and 11 ps, respectively). Note that no strongly coupled high-frequency local modes of Tol and C₅-Tri or Tol and F₅Ph were found. Therefore, we concluded that the thermalization to and from Tol moieties occurs via low-frequency modes.

**CONCLUSIONS**

Rather large compounds, C₂ and C₆, were investigated with 2DIR and RA 2DIR spectroscopy methods, and waiting-time dependences of a large number of cross and diagonal peaks were measured. Comprehensive analysis of their waiting-time traces enabled (i) better assignment of peaks in the FTIR spectrum to different functional groups, (ii) finding delineating kinetic parameters for several functional groups, which include coherent oscillations of specific cross peaks, energy transfer and cooling parameters, and (iii) understanding the mechanism of energy transfer between the ligands.

We deciphered characteristic 2DIR features of several functional groups, which can help identifying these groups using 2DIR spectroscopy. The mode lifetimes and cooling times of several high-frequency modes at F₅Ph, C₅-Tri, and Tol were found to be characteristic of each group. The Tol groups in phosphine ligands are found well isolated from the rest of the compounds showing very slow energy dissipation away from the Tol moieties. The Tol diagonal peak at 1600 cm⁻¹ and cross peaks involving Tol modes show a two-exponential decay with the fast component of ca. 1 ps, corresponding to the excited mode lifetime, and exceptionally slow component of 26 ps corresponding to energy dissipation from the Tol moieties to other parts of the complex and to the solvent. The
amplitude of the slow component is exceptionally high, almost equal to the amplitude of the fast component. It is likely that the excess energy can migrate between different Tol moieties of the same phosphine ligand, but the rate of this process is not known. Note that such energy migration does not change the slow component of the diagonal- and cross-peak kinetics as the excess energy does not leave the Tol moieties. Another interesting feature of the Tol spectra is the presence of a rather strong cross peak at 1600/1570. The anharmonic coupling of the two modes is ca. 7-fold larger than the diagonal strong cross peak at 1600/1570. The anharmonic coupling of excess energy does not leave the Tol moieties. Another known. Note that such energy migration does not change the amplitude of the fast component. It is likely that the excess energy can migrate between different Tol moieties equal to the amplitude of the slow component. It is likely that the excess energy can migrate between different Tol moieties featuring frequencies of 1362/1354, 730/790, and 575.5/574.3 cm\(^{-1}\) and involving C–Pt–C stretching (first two pairs) and bending (last pair) motions (Figure 11). These motions on each ligand are coupled across the Pt center with a coupling strength of 5–20 cm\(^{-1}\), which is sufficient to cause significant delocalization and to provide efficient energy relaxation pathways between the ligands. The similarity of the bond types at the F\(_5\)Ph and C\(_6\_Tri\) ligand helps the frequency match of their local states, thus causing delocalization. However, an accidental frequency match for local states of \(\nu_{Cmax}\) to Tol cross peaks, the delocalized modes <250 cm\(^{-1}\) are contributing the most to the growth of the cross-peak amplitude. A positive correlation between the tag-reporter distance and the \(T_{max}\) time is observed as expected, emphasizing the value of the RA 2DIR method for mode assignment. The distance correlation is clear in comparing the \(T_{max}\) values for C2 and C6 (Figures 3 and 4, Tables 2 and 3).

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.2c02017.

FTIR spectral modeling for acetylide stretching peaks, normal-mode displacements, additional 2DIR spectra and diagonal and cross peak waiting-time traces; additional computational results include relaxation channels of \(\nu_{Cmax}\) for C6F, mode delocalization in C6, and electrical dipole–dipole coupling across the Pt center (PDF)

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REFERENCES

(1) Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J. A. Toward Metal-Capped One-Dimensional Carbon Alloretopes: Wire-like C$_n$–C$_{20}$ Polynediyl Chains That Span Two Redox-Active (η$^5$-C$_{5}$Me$_5$)Re(NO)(PPh$_3$)$_2$ Endgroups. J. Am. Chem. Soc. 2000, 122, 810–822.

(2) Zheng, Q.; Bohling, J. C.; Peters, T. B.; Frisch, A. C.; Hampel, F.; Gladysz, J. A. A Synthetic Breakthrough into an Unanticipated Stability Regime: A Series of Isolable Complexes in which C$_{6}$-C$_{10}$, C$_{12}$, C$_{19}$, C$_{25}$, and C$_{34}$ Polynediyl Chains Span Two Platinum Atoms. Chem. – Eur. J. 2006, 12, 6486–6505.

(3) Gauthier, S.; Weisbach, N.; Bhuvanes, N.; Gladysz, J. A. “Click” Chemistry in Metal Coordination Spheres: Copper(I)-Catalyzed 3+2 Cycloadditions of Benzy1 Azide and Platinum Polyyln Complexes trans-(η$^5$-C$_5$H$_5$)(η-tol,P)$_2$Pt(C≡C≡C≡C≡C≡C≡Pt)$^{5}$ segments; iterative syntheses and functionalization for measurements of single molecule properties. Dalton Trans. 2019, 48, S800–S816.

(4) Weisbach, N.; Kuhn, H.; Amini, H.; Ebnhom, A.; Hampel, F.; Reibenspies, J. H.; Hall, M. B.; Gladysz, J. A. Triposroarylpyl (TIPS) Alkenes as Building Blocks for Syntheses of Platinum Triposroarylpylpolynyl and Diplatinum Polynediyl Complexes. Organometallics 2019, 38, 3229–3310.

(5) Amini, H.; Baranowicz, Z.; Weisbach, N.; Gauthier, S.; Bhuvanes, N.; Reibenspies, J. H.; Gladysz, J. A. Syntheses, Structures, and Spectroscopic Properties of 1,0-Phenanthroline-Based Macrocycles Threaded by PtC$_2$Pt, PtC$_3$Pt, and PtC$_4$Pt Axles: Metal-Capped Rotaxanes as Insulated Molecular Wires. Chem. – Eur. J. 2019, 25, 15896–15914.

(6) Amini, H.; Weisbach, N.; Gauthier, S.; Kuhn, H.; Bhuvanes, N.; Hampel, F.; Reibenspies, J. H.; Gladysz, J. A. Trapping of Terminal Platinapolyynes by Copper(I)-Catalyzed Click Cycloadditions; Probes of Labile Intermediates in Syntheses of Complexes with Extended sp Carbon Chains, and Crystallographic Studies. Chem. – Eur. J. 2021, 27, 12619–12634.

(7) Bruce, M. I.; Zaitseva, N. N.; Nicholson, B. K.; Skelton, B. W.; White, A. H. Syntheses and molecular structures of some compounds containing many-atom chains end-capped by tricobalt carbonyl clusters. J. Organomet. Chem. 2008, 693, 2887–2897.

(8) Cao, Z.; Xi, B.; Jodoin, D. S.; Zhang, L.; Cummings, S. P.; Gao, Y.; Tyler, S. F.; Fanwick, P. E.; Crutchley, R. J.; Ren, T. Diruthened–Polyyl–Diruthened Wires: Electronic Coupling in the Long Distance Regime. J. Am. Chem. Soc. 2014, 136, 12174–12183.

(9) Bruce, M. I.; Cole, M. L.; Ellis, B. G.; Gaudio, M.; Nicholson, B. K.; Parker, C. R.; Skelton, B. W.; White, A. H. The series of carbon-chain complexes [Ru(pdpe)$_2$C$_n$]$_{1/2}$($μ$-CC)$_x$] ($x = 4$–8, 11): Synthesis, structures, properties and some reactions. Polyhedron 2015, 86, 43–56.

(10) Sappa, E.; Tiripicchio, A.; Braunstein, P. Alkyne-substituted homo- and heterometallic carbonyl clusters of the iron, cobalt and nickel triads. Chem. Rev. 1983, 83, 203–239.

(11) Conole, G. The bonding modes adopted by organo-fragments on metal cluster surfaces. Mater. Chem. Phys. 1991, 29, 307–322.

(12) Falloon, S. B.; Szafer, S.; Arif, A. M.; Gladysz, J. A. Attaching Metal-Capped sp Carbon Chains to Metal Clusters: Synthesis, Structure, and Reactivity of Rhodium/Triosmium Complexes of Formula [(η$^5$-C$_{5}$Me$_5$)Re(NO)(PPh$_3$)](CC)$_x$(OS$_2$(CO)$_y$(X)$_z$)$^{m}$, Including Carbon Geometries More Distorted than Planar Tetracoordinate. Chem. – Eur. J. 1998, 4, 1033–1042.
The Journal of Physical Chemistry A

Ruzhansky, V. M.; Kuryshina, D. O.; Burin, A. L. Theoretical study of internal vibrational relaxation and population lifetimes of metal donors in a small helical molecule. J. Phys. Chem. C 2010, 114, 20510–20517.

(36) Backus, E. H. G.; Bloem, R.; Pieterse, R.; Moreetto, A.; Crisma, M.; Toniolet, C.; Hamm, P. Dynamical Transition in a Small Helical Peptide and Its Implication for Vibrational Energy Transport. J. Phys. Chem. A 2009, 113, 13405–13409.

(37) Tesar, S. L.; Kasyanenko, V. M.; Rubtsov, I. V.; Rubtsov, G. I. Semiclassical model for vibrational dynamics of polyatomic molecules: Investigation of Internal Vibrational Relaxation. J. Phys. Chem. C 2010, 114, 20510–20517.

(38) Burin, A. L.; Tesar, S. L.; Kasyanenko, V. M.; Rubtsov, I. V.; Rubtsov, G. I. Self-consistent method for 2DIR photocatalysis. Spectroscopy of coordination complexes: From solvent dynamics to relaxation-assisted 2D IR spectroscopy method. J. Phys. Chem. A 2015, 119, 10025–10034.

(39) Yang, X.; Keane, T.; Delor, M.; Meijer, A. J. H. M.; Weinstein, J.; Bittner, R. E. Identifying electron transfer coordinates in donor-bridge-acceptor systems using mode projection analysis. Nat. Commun. 2017, 8, 14554.

(40) Kasyanenko, V. M.; Lin, Z.; Rubtsov, G. I.; Donahue, J. P.; Rubtsov, I. V. Energy transport via coordination bonds. J. Chem. Phys. 2009, 131, 145508.

(41) Sazanovich, I. V.; Best, J.; Scattagredi, P. A.; Toviere, M.; Tikhomirov, S. A.; Bougnot, O. V.; Meier, A. J. H. M.; Weinstein, J. A. Ultrafast photoinduced charge transport in Pt(II) donor–acceptor assembly bearing naphthalimide electron acceptor and phenothiazine electron donor. Phys. Chem. Chem. Phys. 2014, 16, 25775–25788.

(42) Fedoseeva, M.; Delor, M.; Parker, S. C.; Sazanovich, I. V.; Toviere, M.; Rubtsov, I. V. Vibrational energy transfer dynamics in ruthenium polypyridyl transition metal complexes. Phys. Chem. Chem. Phys. 2015, 17, 1688–1696.

(43) Heilweil, E. J.; Cavanagh, R. S.; Stephenson, J. C. CO(v=1) population lifetimes of metal–carbonyl cluster compounds in dilute CHCl3 solution. J. Chem. Phys. 1988, 89, 230–239.

(44) Crum, V. F.; Kiefert, L. M.; Rubtsov, I. V. Solvent-Dependent Dynamics of a Series of Rhenium Photoactivated Catalysts Measured with Ultrafast 2DIR. J. Phys. Chem. A 2015, 119, 959–965.

(45) Eckert, P. A.; Rubtsov, I. V. Solvent Quality Controls Macromolecular Structural Dynamics of a Dendrimeric Hydrogenase Model. J. Phys. Chem. B 2018, 122, 12154–12163.

(46) Kiefert, L. M.; Rubtsov, I. V. Two-dimensional infrared spectroscopy of coordination complexes: From solvent dynamics to photocatalysis. Coord. Chem. Rev. 2018, 372, 153–178.

(47) Kiefert, L. M.; Rubtsov, I. V. Solvent-Dependent Dynamics of a Series of Rhenium Photoactivated Catalysts Measured with Ultrafast 2DIR. J. Phys. Chem. A 2015, 119, 959–965.

(48) Segal, D.; Agarwalla, B. K. Vibrational Heat Transport in Molecular Junctions. Annu. Rev. Phys. Chem. 2016, 67, 185–209.

(49) Galperin, M.; Ratner, M.; Nitzan, A. Molecular transport junctions: vibrational effects. J. Phys.: Condens. Matter 2007, 19, No. 103201.

(50) Leitner, D. M.; Pandey, H. D.; Reid, K. M. Energy Transport across Interfaces in Biomolecular Systems. J. Phys. Chem. B 2019, 123, 9507–9524.

(51) Pandey, H. D.; Leitner, D. M. Influence of thermalization on thermal conduction through molecular junctions: Computational study of PEG oligomers. J. Phys. Chem. 2017, 117, No. 084701.

(52) Chen, R.; Sharonoy, L.; Nitzan, A. Local Atomic Heat Currents and Classical Interference in Single-Molecule Heat Conduction. J. Phys. Chem. Lett. 2020, 11, 4261–4268.

(53) Kurochkin, D. V.; Nataraissetty, S. R.; Rubtsov, I. V. A relaxation-assisted 2D IR spectroscopy method. Proc. Natl. Acad. Sci. U. S. A. 2007, 104, 14209–14214.

(54) Khalil, M.; Demirdoven, N.; Tokmakoff, A. Vibrational coherence transfer characterized with Fourier-transform 2D IR spectroscopy. J. Chem. Phys. 2004, 121, 362–373.

(55) Chensov, J.; Mokhtari, A. Resonant impulse-stimulated Raman scattering on malachite green. Phys. Rev. A 1988, 38, 3566–3576.
Infrared Spectra based on Vibrational Energy Transfer. Angew. Chem., Int. Ed. 2013, 52, 6214–6217.

(75) Hamm, P.; Lim, M.; Hochstrasser, R. M. Structure of the amide I band of peptides measured by femtosecond non-linear infrared spectroscopy. J. Phys. Chem. B 1998, 102, 6123–6138.