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Syntheses and material applications of Ru(II)(bisphosphine)$_2$ alkynyls

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ABSTRACT

Described in this review are the synthetic methods to produce both mono- and bis-alkynyl Ru(II)(L-L)$_2$ type complexes, where L-L is dppe, dppm, or dmpe. This synthetic tool kit encompasses reactions utilizing trimethylstannyl capped reagents, Ru-alkyl starting materials, or the 16 e$^-$ [RuCl(dppe)$_2$]$^+$ intermediate to produce the desired Ru(II)(L-L)$_2$ alkynyl complexes. Advantages and drawbacks of each synthetic approach are touched upon. A brief overview of material applications of these complexes is also provided, highlighting their promises as efficient non-linear optical materials, wire-like molecules, molecular wires and switches, and active molecules in dye-sensitized solar cells.

1. Introduction

Chemistry of transition metal alkynyl compounds is a rich and dynamic research area [1–4]. These complexes, ranging from monomeric complexes with single alkynyl ligand to polymeric complexes, can trace their origins of interest back to the homoleptic hexakis-alkynyl [M(C≡C-R)$_6$]$^{n-}$ (M = Cr, Mn, Fe, and Co), tetrakis-alkynyl [M(C≡C-R)$_4$]$^{n-}$ (M = Mn, Ni, Pd, Pt, Zn, Cd, and Hg), and bis-alkynyl [M(C≡C-R)$_2$]$^{n-}$ (M = Cu, Ag, and Au) complexes by Nast and co-workers [5] as well to the dehydrohalogenation reactions that generated polymeric alkynyl complexes containing Ni, Pd, and Pt, reported by Hagihara and co-workers in the 1970s and 1980s [6–8]. Transition metal-alkynyl complexes are promising candidates for a variety of material applications, such as NLO materials [9], photovoltaics [10,11], OLED [12], molecular wires [13–15], and active species for nanoscale devices [16,17].

Given the abundance of sweeping surveys of transition metal alkynyl compounds [1–4,18–20] since the original review by Nast [5], the primary focus of this review will be the synthetic strategy for preparing trans- mono- and bis-alkynyl complexes based on Ru(II)(L-L)$_2$ units with L-L as dppe(bis(diphenylphosphino)ethane) or dppm (bis(diphenylphosphino)methane)), an area with only one other recent review, dedicated to the unconventional reactions with Ru(II)/Os(II) dppm frameworks [21]. The general motifs for both the mono- and bis-alkynyl complexes with explicit ligand structures are provided in Chart 1. This review also provides a brief overview of the material applications of these Ru(II) complexes.

2. Synthetic methods for Ru bis-alkynyl complexes

2.1. Synthesis from trimethylstannyl alkynyl

Prior to 1990s, synthetic methods based on a Cu(I) assisted dehydro-halogenation reaction (Hagihara coupling) [7,8] successfully produced a large number of group 10 metal alkynyl complexes. However, Hagihara coupling cannot be extended to other metal alkynyls as the use of amines as solvents rendered most phosphine-containing starting materials (besides those in Group 10) unstable and prone to ligand substitution [1]. In the mid-1990s, Lewis and co-workers took inspiration from a metathesis reaction first reported by Cetinkaya et al. [22] that utilized the trimethylstannyl alkynyl reagents and metal chlorides, and reported the first copper-catalyzed syntheses of Ru-based alkynyl dimers [23] and polymers [24], while avoiding the use of harsh amine solvents. The approach developed by Lewis and co-workers (Scheme 1) was found to reliably synthesize trans-Ru alkynyl structures of bi- and polymeric complexes with phosphine backbones (L-L)$_2$ (L-L = dppe or dppm), but was not applicable for the preparation of mono-alkynyl complexes [24].

The only products obtained from the reaction between trans-RuCl$_2$(L-L)$_2$ and one equiv of Me$_3$Sn(C≡C-R) were the dichloro starting material and the symmetrical bis-alkynyl complex, implying the second chloride substitution was the faster step of the two. In order to successfully generate mono-alkynyl Ru complexes, Younus and co-workers utilized Dixneuf's alternative synthetic route that generates a vinylidene (see Section 2.2.1 below), followed by deprotonation with a short alumina column or DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) to generate the desired mono-alkynyl complexes as starting materials for further additions onto

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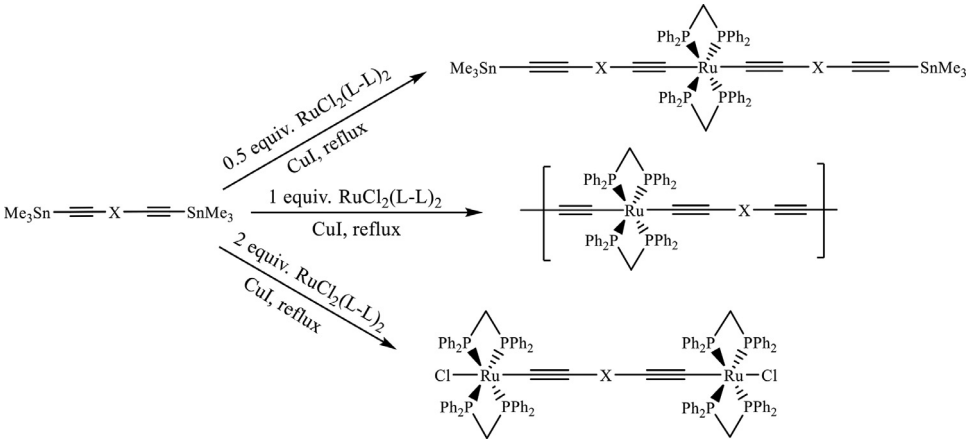
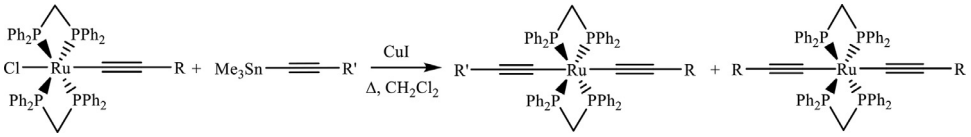


Scheme 1. Synthesis based on trimethylstannyl alkynyls; X = bridge groups.



Scheme 2. Synthesis of Ru bis-alkynyls utilizing trimethylstannyl reagents.

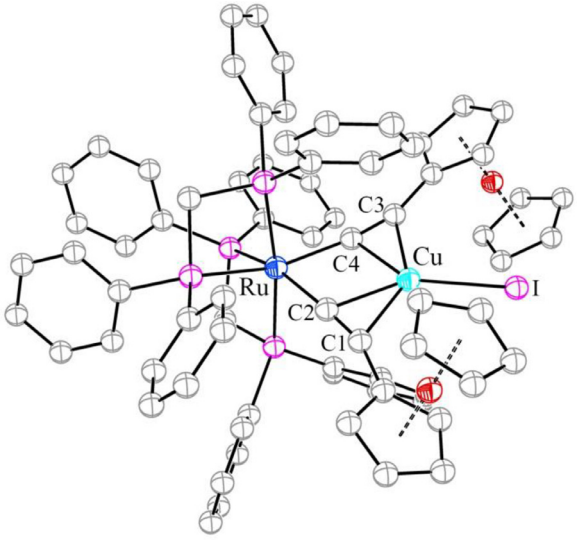


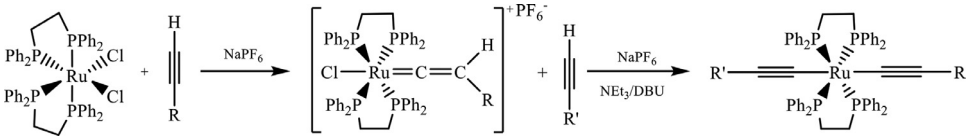
Chart 1. Representative structural motifs of trans- mono and bis-alkynyl complexes based on dppm (left) and dppe (right).

the Ru center (Scheme 2). In most ligand combinations, the second alkynyl addition generated both the desired unsymmetrical bis-alkynyl complex and one of the two possible symmetrical bis-alkynyl complexes [23], presumably through a disproportionation mechanism which has been observed in other synthetic methods [25].

In order to generate soluble polymeric complexes, high purity trans-$RuCl_2(dppm)_2$ starting material and an exact Ru to ligand stoichiometry (1:1) were deemed essential to obtain a high degree of polymerization [24]. Polymers of higher molecular weight (M_W > 55000) were achieved with $Ru(dppm)_2$ unit [24] than those with $Ru(depe)_2$ unit (M_W < 30000; depe = 1,2-bis(diethylphosphino)ethane) [26] using the CuI-catalyzed method. While these polymers were characterized by gel permeation chromatography and ^1H and ^{31}P NMR techniques, there was NO structure-oriented study such as powder X-ray diffraction or electron microscopy.

In the late 1990s, Wolf and co-workers successfully expanded upon Lewis' synthetic method. Through the reaction of tributylstannyl reagents, R-C≡C-Sn(n-Bu)$_3$ (R = Fc, 2-thienyl, 5-(2,2′-bithienyl), and 5-(2,2′:5′,2″- terthienyl)) with cis-$RuCl_2(dppm)_2$, both the symmetric, bis-alkynyl trans- and cis-$Ru(C≡C-R)_2(dppm)_2$ complexes were generated [27–29]. The reactions with R = Fc yielded products in either the cis or trans configuration, depending on both the amount of CuI and the reaction temperature. When a catalytic amount of CuI was utilized (5–25%) and the reaction was heated to reflux in 1,2-dichloroethane, the trans-$Ru(C≡C-Fc)_2(dppm)_2$ was obtained in high yield. However, when a stoichiometric amount of CuI was utilized under reflux conditions, two new products with similar ^1H NMR spectra were obtained, and elemental analysis suggested the presence of both $[Ru(C≡C-Fc)_2(dppm)_2]CuI$ and $[Ru(C≡C-Fc)_2(dppm)_2]CuCl$. After performing metathesis on $[Ru(C≡C-Fc)_2(dppm)_2]CuCl$ with NaI, the [cis-$Ru(C≡C-Fc)_2(dppm)_2$]CuI complex was isolated (see Fig. 1); this complex was also generated through the room temperature reaction of cis-$RuCl_2(dppm)_2$ with Fc-C≡C-Sn(n-Bu)$_3$ in CH_2Cl_2. The CuI unit is bonded in a η^2 fashion to both acetylide bonds, presumably what holds the complex in the cis configuration. Removal of the CuI yielded trans-$Ru(C≡C-Fc)_2(dppm)_2$, and reaction of the trans bis-alkynyl with a stoichiometric amount of CuI successfully regenerated the cis product, demonstrating the stabilization of the cis isomer by CuI η^2 bonds [28]. These Fc-modified complexes exhibit strong orbital interactions (more detail in Section 3.2.2 below) between the Ru center and the ancillary ferrocene ligands. Similar to the work of Lewis, the vinylidene method had to be utilized to generate mono-acetylide complexes (see Section 2.2.1 below) [29].

Although the use of tin-modified alkynyl ligands requires an extra step to prepare tin reagents and raises the concern of toxicity [30,31], Lewis's innovative synthetic method avoids the use of amine solvents, and hence broadens the scope of Ru alkynylation reactions. Davies et al. utilized this method to generate Ni(II), Pd(II), Pt(II), and Rh(I) alkynyl complexes [32]. Viola et al. have adapted this method to generate both mono-alkynyl and bridged alkynyl cyclopentadienyl Ru complexes via a palladium-catalyzed trimethylstannyl synthetic route [33]. Cotton demonstrated the



Scheme 3. Unsymmetric Ru alkynyl synthesis through formation of vinylidene intermediate.

preferential alkynylation of the trimethylstannyl complexes at the Ru-Ru-Cl position, while avoiding alkynylation of the modified anilinopyridinate backbones [34].

2.2. Synthesis through vinylidene formation

2.2.1. Starting with cis-$RuCl_2$(L-L)$_2$(L-L = dppm/dppe)

Pioneered by Touchard and co-workers, an efficient and stepwise synthetic approach to the synthesis of both mono- and unsymmetric bis-alkynyl Ru species is to use the starting material cis-$RuCl_2(dppe)_2$ to generate a reactive vinylidene intermediate. These vinylidene intermediates are air-stable and insensitive to attack by methanol as has been observed with other $RuCl_2(PR_3)$(arene) derivatives [25]. Their detailed studies demonstrated that the cis-$RuCl_2(dppe)_2$ isomer readily activated terminal alkynes in the presence of a non-coordinating salt, typically $NaPF_6$, to form stable vinylidene complexes as shown in Scheme 3. In contrast, the trans isomer undergoes a much slower reaction that requires 5–7 days to generate vinylidenes [23,35]. Generally, synthesis of mono-alkynyl complexes through vinylidene intermediates solely requires deprotonation of the vinylidene after removal of excess alkynyl ligand. Depending on the nature of second alkynyl ligand, further alkynylation of the vinylidene intermediate in the presence of $NaPF_6$ leads to either symmetric or unsymmetric Ru bis-alkynyl complexes.

As demonstrated above by Touchard et al., use of either a suitable base like NEt_3 or DBU or a short alumina column deprotonate the vinylidene intermediates to yield the desired mono- or bis-alkynyl complexes [36]. The $NaPF_6$ salt is essential for this process because it promotes the formation of a 5-coordinate, 16 e- Ru species after chloride abstraction (generating NaCl), which is extremely reactive towards alkynyl rearrangement and vinylidene formation. Choice of solvent is also important: dichloromethane was the only solvent that gave desired bis-alkynyl products rather than tetrahydrofuran or methanol when staring from cis/trans-$RuCl_2$(L-L)$_2$ [25,36]. Touchard et al. also explored the use of cis-$RuCl_2(dppm)_2$ as a starting material for both mono- and bis-alkynyl complexes. While the conditions to generate an unsymmetric bis-alkynyl Ru complex are similar to those utilized with cis-$RuCl_2(dppe)_2$, the attempts to generate desired trans-Ru(dppm)$_2$(C≡CR)(C≡CR') species were plagued by low yields [36].

While investigating cis-$RuCl_2(dppm)_2$ as a starting material, Marques-Gonzalez et al. have utilized more powerful halide extracting agents, such as thallium tetrafluoroborate ($TlBF_4$), and bases, 1,8-bis-dimethylaminonaphthalene (Proton Sponge), to prepare both trans- mono- and symmetrical bis-alkynyl complexes. These reactions follow the expected mechanistic pathway: formation of a vinylidene in moderate to high yields (63–80%) after reacting with terminal alkynes HC≡C-C_6H_4-R (R = NO_2, CO_2Me, C≡CSiMe_3, Me, OMe and H) for 1–2 h [37], followed by deprotonation with the Proton Sponge to yield the desired products. The authors emphasized that the stoichiometry of the reaction needs to be 1:1:1 (cis-$RuCl_2(dppm)_2$: ligand: $TlBF_4$) to prevent the generation of the symmetrical bis-alkynyl complexes during formation of the trans- mono-alkynyl complexes, for which the separation is challenging.

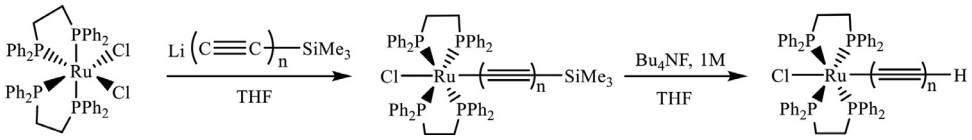
Use of electron-withdrawing or neutral R groups (R = NO_2, CO_2Me and C≡CSiMe_3) and an altered stoichiometric ratio of 1:2.1:2 (cis-$RuCl_2(dppm)_2$: ligand: $TlBF_4$) resulted in the desired symmetrical bis-alkynyl complexes trans-Ru(dppm)$_2$(C≡C-C_6H_4-R)$_2$ [38]. However, use of electron-donating groups (R = Me and OMe) with an identical stoichiometric ratio generated cationic η^3-butenynyl complexes [Ru(η^3-{HC(C_6H_4-4-R)=C-C≡C-C_6H_4-4-R})-(dppm)$_2$][BF_4] (Fig. 2, R = -Me) instead. While ^{1}H NMR recorded during the reaction showed evidence of the formation of a symmetrical bis-alkynyl complex, all attempts to intercept the bis-alkynyl complexes resulted in the isolation of the η^3-butenynyl complexes only, indicating that the bis-alkynyl species underwent further conversion to the η^3-butenynyl species during work-up. The authors proposed a plausible mechanism based on DFT calculations that suggested a higher proportion of protonated alkyne-vinylidene species in solution is achievable with electron-donating alkyne ligands, resulting in favorable transitions to the η3-butenynyl species. This pathway would not be favorable for the cis-$RuCl_2(dppe)_2$ starting material, as the increased bite angle of the phosphines favors trans-arrangement of the alkyne ligands rather than the cis needed for the η3-butenynyl species synthesis [38].

Alternative non-coordinating salts have also been employed during the syntheses of unsymmetric Ru-alkynyl complexes. Akita and co-workers utilized $KB(C_6F_5)_4$ [39] to prevent desilyation of the trimethylsilylbutadiynyl ligand, which was observed during the attachment of the second acetylide in the presence of PF_6^- counteranion.

Synthesis through a vinylidene intermediate is invaluable for generating unsymmetric Ru bis-alkynyl complexes based on both Ru(dppe)$_2$ and Ru(dppm)$_2$ frameworks. The generation of unsymmetric bis-alkynyl complexes from cis-$RuCl_2(dppm)_2$ is difficult, with reactions resulting in symmetric bis-alkynyl products, low yields of the desired products, and difficulty in separation. The vinylidene synthetic method is more beneficial with cis-$RuCl_2(dppe)_2$ as the starting material, and many research groups have taken advantage of this method in generating unsymmetric Ru bis-alkynyl complexes due to the ease of alkyne addition, fast reaction at ambient temperature, and use of inexpensive materials (NEt_3, $NaPF_6$). The most notable drawback is the issue with the order of ligand addition: successful generation of unsymmetric complex was only achieved through the first addition of the electron-withdrawing alkyne then addition of the electron-donating group [40]. The intermediate vinylidene complex was deprotonated before the introduction of the second alkyne in this study [40], potentially impacting the trans influence experienced by the second alkyne during coordination.

2.2.2. Use of lithiated poly-ynyls

To generate an array of possible building blocks for larger bimetallic complexes bridged by poly-ynyl, Dixneuf et al. focused on the synthesis of mono- and bis-complexes with oligoynyls of varying length, namely trans-Ru(dppe)$_2$Cl(C_{2n}R) (n = = 1 - 4) (R = SiMe_3, H) and trans-Ru(dppe)$_2$(C_4R)$_2$ (R = SiMe_3, H) [41], while the dppm framework has not been explored. The mono-complexes, trans-Ru(dppe)$_2$Cl(C_{2n}R), were produced in high yields through the reaction of cis-$RuCl_2(dppe)_2$ with LiC_{2n}SiMe_3, typically occurring overnight with purification achieved through a neutral alumina plug (Scheme 4). Desilylation of these mono-alkynyls utilizing NBu_4F (TBAF) was successful for n = = 2, 3 but the other



Scheme 4. Synthesis of mono-alkynyl complexes using lithiated poly-ynyl.

two lengths either had too low a yield to generate enough useful product ($n = = 4$) or could not be desilylated ($n = = 1$) with any of common agents (Bu_4NF in THF, KOH in CH_3OH, or K_2CO_3 in CH_3OH). This is in contrast to the successful production of trans-$Ru(dppe)_2Cl(C_2H)$ from the reaction of cis-$RuCl_2(dppe)_2$ with HC_2SiMe_3 in the presence of DBU/$NaPF_6$, indicating that desilylation likely occurs before deprotonation to generate the alkyne [25]. Unsuccessful deprotonation of $n = = 1$ was postulated to be due to increased steric hinderance of the $[Ru(dppe)_2]$ fragment, or increased vinylidene-character of the alkyne in this complex [41].

It is noteworthy that bis-complexes were not generated in Scheme 4 even with a large excess of lithiated poly-ynyl. To generate the symmetric complexes, trans-$Ru(dppe)_2(C_{2n}R)_2$, the vinylidenes obtained from the reaction of a terminal alkyne and cis-$RuCl_2(dppe)_2$ were deprotonated in the presence of $NaPF_6$ [25]. As with the mono-alkynyl complexes, this approach was successful for producing the bis-complex with $n = 2$, but not in the case of $n = 1$. To generate bimetallic complex trans-[$Cl(dppe)_2$-Ru-$(C\equiv C)_6$-$Ru(dppe)_2Cl$], Dixneuf and coworkers attempted the Glaser coupling reaction under both Eglinton ($Cu(OAc)_2$/py) and Hay (TMEDA/Cu) conditions using either the protected (trans-$Ru(dppe)_2Cl(C\equiv C)_3SiMe_3$) or deprotected (trans-$Ru(dppe)_2Cl(C\equiv C)_3$-H) complexes. Successful coupling of the alkynes was achieved with the deprotected complex under Eglinton conditions to generate the C_{12}-bridged complex. Though less soluble and difficult to characterize, electronic communication between two Ru centers was observed in the C_{12}-bridged complex (see expanded discussion in Section 3.2.2 below). Echoing issues encountered in the copper-catalyzed trimethylstannyl synthesis [24], the lithiation method was unsuccessful in replacing both chlorides on the starting material to generate the bis-complex. However, this method is a moderate to high yielding and facile synthetic approach for mono-complexes with minimal by-products.

2.2.3. Starting with $[RuCl(dppe)_2]^+$

In the early 2000s, interest grew in the use of the isolated 5-coordinate 16 e^- $[RuCl(dppe)_2]^+$ salt as a starting point to generate either mono- or bis-acetylide Ru complexes [42–47]. From cis-$RuCl_2(dppe)_2$, the reactive $[RuCl(dppe)_2]PF_6$ species can be generated in situ through the ready abstraction of a chloride ligand with either $NaPF_6$ or NH_4PF_6. However, trans-$RuCl_2(dppe)_2$ requires the use of Ag(I) salts (commonly AgOTf or $AgBF_4$) to generate the desired $[RuCl(dppe)_2]OTf$ or $[RuCl(dppe)_2]BF_4$ complexes in a reasonable time scale (<1 h at room temperature). This reaction can be monitored with an almost instantaneous color change from yellow to red. Advantageous as a starting material, $[RuCl(dppe)_2]^+$ is easily isolated in high yield after the removal of AgCl, and stable at room temperature under ambient conditions. Although previously reported with a variety of counterions and phosphines [48–50], the structure of the triflate salt displays a "Y" distortion around the ruthenium center in the equatorial plane and deviates from the optimal trigonal bipyramidal structure [35].

The major advantage in utilizing the $[RuCl(dppe)_2]X$ ($X = PF_6^-$, OTf^-) salt is the avoidance of the unreactive trans isomer commonly present in cis-$RuCl_2(dppe)_2$ starting material. While it is possible to separate the two isomers, it requires careful, fractional crystallization in the dark [35]. Treatment of a mixture of isomers will therefore always give pure $[RuCl(dppe)_2]^+$ as the product, removing the need to separate out the two isomers before alkyne additions, or purification from the unreacted trans isomer after alkyne addition. $[RuCl(dppe)_2]^+$ has been frequently used in the synthesis of a wide variety of mono-alkynyl complexes, due to its expedient reactions with terminal alkynyl ligands (typically under 8 h at room temperature). Purification simply requires the removal of excess ligand and salts generated, with column chromatography only needed to separate out the symmetrical bis-alkynyl byproducts (if present) [35,37,51].

To add the second terminal alkynyl ligand, literature reports commonly follow a mechanistic pathway where the vinylidenes formed from the first addition are deprotonated to give the desired mono-alkynyl complexes (see Scheme 5). Removal of the excess alkyne ligand must be achieved before this deprotonation to prevent the formation of the symmetrical bis-alkynyl complex. The addition of the second ligand is accomplished upon the reaction of the mono-alkynyl and the desired alkynyl ligand in the presence of both $NaPF_6$ and NEt_3 [52,53].

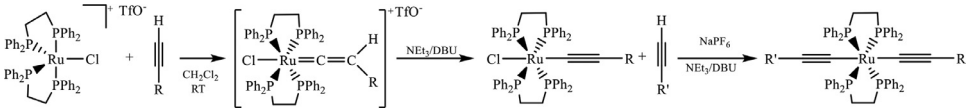
A slightly different approach for trans- bis-alkynyls was advocated by the groups of Rigaut and Olivier (Scheme 6). Rather than adding a step to deprotonate the isolated vinylidene, the second ligand, a base (NEt_3 or DBU) and $NaPF_6$ were added to a one-pot reaction mixture with the vinylidene, which leads to the desired unsymmetric complexes in high yield [43,54–57]. This mechanism is reminiscent of Scheme 3 and is rationalized based on the vinylidene being a better electron-donor to the metal center, which eases chloride abstraction prior to the addition of the second alkynyl ligand [25]. It is interesting to note in such an approach that the first alkynyl addition does not require the presence of an alkali metal salt but does so when the second alkynyl ligand is added. Another feature of interest is that when synthesizing unsymmetric species, the electron-donating alkynyl ligand is added before the electron-withdrawing alkynyl ligand [55,58], but others have noted differently [40] (see discussion above in 2.2.1).

The use of $[RuCl(dppe)_2]^+$ takes advantage of a previously under-utilized compound, trans-$RuCl_2(dppe)_2$, which provides ease of preparation as the $[RuCl(dppe)_2]^+$ salt can be prepared from either isomer. The synthetic routes followed (Scheme 5 vs. Scheme 6) can also be varied, giving flexibility in the order of addition of the desired ligands. A potential drawback is that the triflate counteranion has been documented to produce triflate salt by-products which could react with the desired products. If the triflate interference occurs, the issue can be circumvented with the use of either a different Ag(I) salt or deprotonation with KO^tBu in methanol [35].

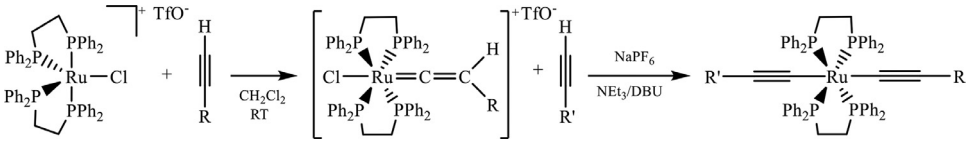
2.2.4. Use of mixed ligand complexes $[Ru(C_2R)(X)(dppe)_2]^+$ ($X = NH_3$, H, CN, N≡C-R)

An alternative intermediate to $[RuCl(dppe)_2]^+$ was first described by Touchard et al. in the seminal vinylidene paper [25]. As shown in Scheme 7, the reaction of trans-$Ru(C_2R)_2(dppe)_2$ (R = Ph, ^{n}Bu, $SiMe_3$) with NH_4PF_6 in dichloromethane resulted in the intermediate complexes trans-$[Ru(C_2R)(NH_3)(dppe)_2]^+$ shown in Fig. 4 (R = Ph).

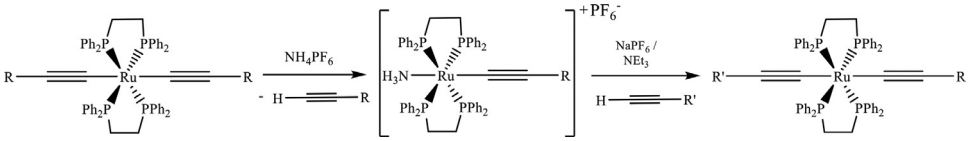
Protonation of symmetrical bis-alkynyl complexes was also demonstrated using strong acids such as HCl, HBF_4, and CF_3CO_2H, but the intermediate complexes were observed to rapidly degrade, presumably due to the lack of a coordinating ligand for the open



Scheme 5. Pathway to generate unsymmetric Ru bis-alkynyls from [RuCl(dppe)$_2$]OTf.



Scheme 6. Alternative pathway to unsymmetric Ru bis-alkynyls from [RuCl(dppe)$_2$][OTf].



Scheme 7. Unsymmetric trans- bis-alkynyl Ru complexes via [trans-Ru(C≡C-R)(NH$_3$)(dppe)$_2$]$^+$.

ruthenium coordination site [25]. The formation of these mixed ammonia-alkynyl ruthenium complexes proceeds with the protonation of one alkynyl ligand at the β carbon (C2 in Fig. 4) with the ammonium ion, NH_4^+. Protonation of the alkynyl ligand leads to the rearrangement to a vinylidene, promoting the release of the newly formed alkyne, and the rapid coordination of the NH_3 to the in situ generated 16 e$^-$ Ru mono-alkynyl complex.

Subsequently, Touchard and co-workers expanded upon this type of reaction in order to synthesize the desired unsymmetric complexes using the mixed ligand complex trans-Ru(C$_2$R)(NH$_3$)(dppe)$_2^+$ as the starting material. Displacement of the labile NH_3 ligand with a different alkynyl ligand in methanol at 50 °C resulted in the desired unsymmetric bis-alkynyl complexes in respectable yields (>75%). The free ammonia ligand is displaced into the solvent and can deprotonate the intermediate vinylidene, regenerating the NH_4PF_6 salt and producing the desired bis-alkynyl complex, although NEt_3 can also be added to deprotonate the vinylidene if the use of NH_3 is unsuccessful (pK_b of NH_3 = 4.75; NEt_3 = 3.75). Expansion of this approach has also led to the generation of other mixed ligand systems such as hydrido-, carbonyl-, and isocyanide-alkynyl ruthenium complexes [59].

Complexes of mixed-ligands, trans-Ru(C$_2$R)(NCR')(dppe)$_2^+$ (NCR' = benzonitrile, cyanoferrocene, and 1,4-dicyanobenzene, and *R* = Ph and Fc), were explored by Fillaut and co-workers [44]. The reaction of trans-RuCl(C$_2$R)(dppe)$_2$ with nitriles in the presence of both NH_4PF_6 and NEt_3 in dichloromethane led to the rapid (< 1 h at room temperature) formation of the mixed nitrile-alkynyl complexes, trans-[Ru(C$_2$R)(NCR')(dppe)$_2$][PF$_6$]. Bimetallic ruthenium complexes with either nitrile or alkynyl bridge were also generated in this study, albeit through differing synthetic methods. To generate the bridging nitrile complex (Fig. 5), the reaction of trans-RuCl(C≡C-R)(dppe)$_2$ with varying equivalents of 1,4-dicyanobenzene led to the isolation of both the mono- (10 equivalents) and bimetallic (0.5 equivalents) complexes. Alternatively, the reaction of [RuCl(dppe)$_2$]$^+$ with 1,4-diethynylbenzene afforded a bis-vinylidene complex, which was converted to a bimetallic complex with bridging alkynyl and terminal benzonitrile in the presence of NEt_3, KPF_6 and 10 equivalents of benzonitrile.

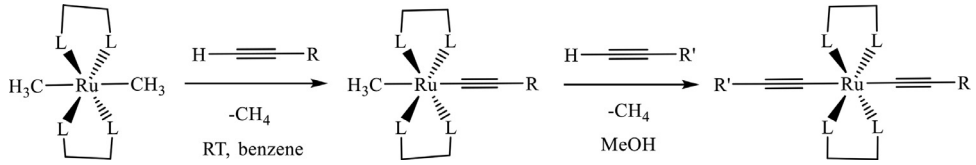
2.3. Single bond metathesis synthesis of mono- and bis- Ru alkynyls

Inspired by work on alkynyl complexes of Pt^{II} [60], Rh^{I} [61] and Co^{I} [62], Field et al. developed a single bond metathesis method to generate alkynyl complexes from alkyl complexes, initially based on a photochemical metathesis utilizing Fe^{II} methyl complexes [63]. Both symmetric and unsymmetric Ru(II) bis-alkynyl complexes have been produced from a thermal metathesis reaction of trans-Ru(L-L)$_2$Me$_2$ (L-L = dmpe (di(methylphosphino)ethane) (Scheme 8) [64]. trans-Ru(dmpe)$_2$Me$_2$ (Fig. 6) is the more reactive isomer that undergoes metathesis with an alkynyl ligand in less than 24 h at room temperature, while the cis-isomer fails to react under the same conditions. As discussed below, the isomer dependence of reactivity Ru(dmpe)$_2$Me$_2$ deviates from that of Ru(dppe)$_2$Cl$_2$.

To generate symmetrical trans-bis-alkynyl complexes, only the presence of excess ligand and reflux are required to promote the metathesis reaction of trans-Ru(dmpe)$_2$Me$_2$ in benzene for solubility considerations. trans-Ru(dmpe)$_2$Me(C$_2$R) was identified as an intermediate through ^{31}P NMR, and isolated after reaction with 1 equiv of alkynyl ligand at room temperature. trans-Ru(dmpe)$_2$Me(C$_2$R), an example shown in Fig. 7, has proved to be a highly important starting point for the generation of symmetric, dissymmetric, and higher order di/tri-metallic alkynyl complexes. Later explorations into the synthesis of these symmetric trans- bis-alkynyl complexes with a wider range of ligands led to the discovery that trans-Ru(dmpe)$_2$Me$_2$ is actually capable of dimerizing terminal alkynes instead of undergoing single bond metathesis [65]. Under refluxing conditions, the di-alkyl starting material (5–8 mol%) was found to head-on dimerize terminal alkynes into either (E)- or (Z)-butenynes, dependent on the solvent and the alkynes utilized.

To prevent ligand scrambling and byproduct (symmetric bis-alkynyls) formation during the synthesis of unsymmetric complexes, replacement of the solvent with methanol (some benzene or toluene added to solubilize the starting materials) resulted in clean generation of the desired products under either thermo or photolytic conditions [64]. Field and co-workers have utilized this synthetic method to generate numerous examples of both bi- and tri-metallic alkynyl bridged complexes [66], and have begun studies to understand how both aromatic [66] and non-aromatic spacers [67] impact the electron transport pathways between the two end-capping Ru centers (see expanded discussion in Section 3.2.2 below).

The advantage of this synthetic method is the limited effort required for work-up and purification after each metathesis reaction. The successful isolation of the mixed mono-alkynyl, mono-alkyl derivatives provides a useful stepping stone for the genera-



Scheme 8. Ru(II) bis-alkynyl from single-bond metathesis.

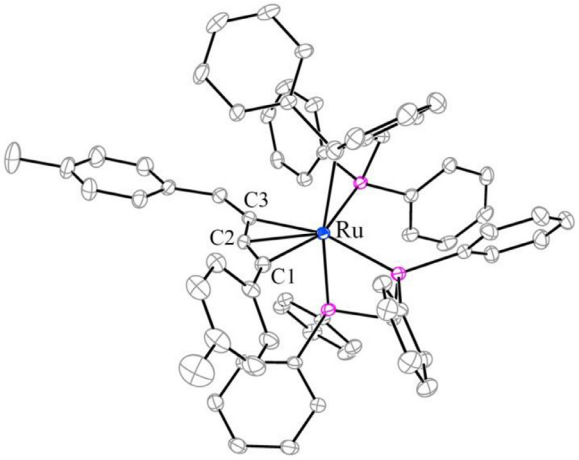


Fig. 1. Molecular structure of [cis-Ru(C≡C-Fc)$_2$(dppm)$_2$]CuI generated from CCDC 1238773.

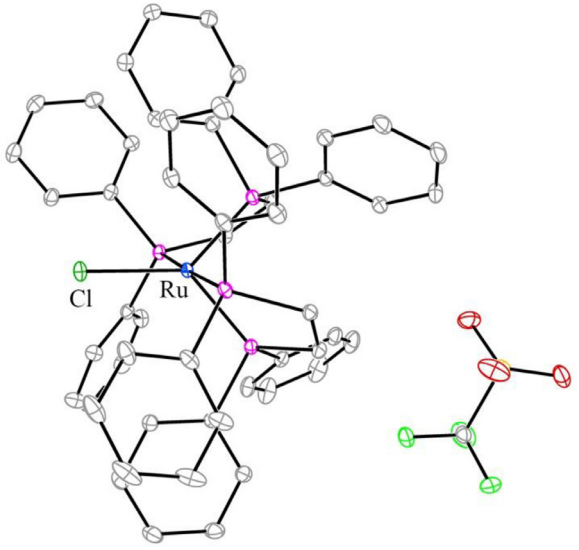


Fig. 2. Molecular structure of [Ru(η^3-{HC(C_6H_4-4-Me)=C-C≡C-C_6H_4-4-Me})-(dppm)$_2$]$^+$ generated from CCDC 1426051.

tion of a wide variety of bis- and polymeric Ru alkynyls. Methanol is noted to impact the solubility of the starting materials but is crucial to this synthetic method for generating products cleanly. As noted by Field et al., this synthetic method provides another controlled route to highly polymerized products but does require the use of MeLi to generate the original starting material trans-Ru(dmpe)$_2$Me$_2$. As observed with the RuCl$_2$(dppe)$_2$ syntheses, trans-Ru(dmpe)$_2$Me$_2$ isomerizes into the kinetically inert cis-Ru(dmpe)$_2$Me$_2$ upon UV irradiation or sublimation, and conversion back to the trans orientation is deemed impossible [64]. Avoiding exposure to UV light is critical to prevent the isomerization of both cis-RuCl$_2$(dppe)$_2$ and trans-Ru(dmpe)$_2$Me$_2$ into their respective kinetically inert isomers.

3. Electronic and opto-electronic materials

Beyond rich synthetic chemistry described above, trans-Ru(L-L)$_2$(C$_{2n}$R)$_2$ type compounds display intriguing electronic and opto-electronic properties owing to their electron-richness and extensively delocalized π-system. Ru(II) center can be easily oxidized and reduced, and therefore serves as an effective 'bridge' for electron/hole to pass through, a highly desirable trait for materials design [1].

3.1. Non-linear optical materials

Non-linear optical (NLOs) materials possess inherent electronic properties that result in modification of the propagation characteristics of light they interact with, including changes to the phase, polarization, frequency, amplitude, or path of the light. The multitude of applications (optical storage, optical signal processing, frequency generation, optical signal switching, etc.) has garnered a long-standing interest in the pursuit of new NLO materials [68]. Studies of ruthenium-based alkynyl complexes have generally focused on the unsymmetric 'donor-bridge-acceptor' (D-B-A) construct. A more in-depth discussion on the theory of NLOs has recently been reviewed elsewhere [68,69].

The key metric for second-order NLO materials is a large hyperpolarizability value (β), classically achieved with (1) a polar charge distribution across the molecule (classically achieved with substituents with electron donating and accepting abilities opposite to each other), (2) a pathway for electron density to move through (π-conjugated electrons), and (3) an optimized conjugation length. Experimentally this is observed as metal-ligand charge transfer transitions, which are desirable at relatively low energies with high intensities. As such, Ru(II) alkynyl's NLOs properties are directly proportional to the amount and degree of effectiveness that electron density is able to be polarized throughout the molecule.

Babgi et al. [51,53] and others [70] have successfully investigated the variation of bridge length, alkyne substituents, and use of the ligated metal unit as the 'donor' in dissymmetric systems to optimize the charge transfer and NLO properties of Ru(II)-based alkyne complexes. All Ru(II)-alkyne complexes have been prepared utilizing either a modification of the vinylidene synthesis (see Section 2.2.1 above) or the use of [RuCl(dppe)$_2$]$^+$ salts (see Section 2.2.3 above), generating the desired products in moderate to high yields.

3.2. Molecular switches and wires

3.2.1. Molecular switches

The push towards molecular electronics necessitates molecules that possess inherent charge transfer properties to help realize the characteristics of operating as a 'wire' and as a 'switch' [16]. To be effective at either (or both), the designed molecules must undergo successful charge transport across the entire molecule [71,72]. A good switch requires a component, typically a substituent of the alkyne ligand, that can be modulated with external stimuli such as light or electrical current to promote a change in the physical properties of the molecule (e.g., breaking or formation of bonds).

These physical changes typically allow for modulation of the inherent electronic properties of the molecules, resulting in a molecule as a potential switch [73]. Ideally these switches would be able to retain the 'information' in the form of electric current for long periods of time, but also be able to revert to the original state upon application of a different stimulus.

To realize a molecular switching system, Meng et al. utilized the vinylidene synthetic method (see Section 2.2.1 above) to construct novel diarylethene-based organometallic complexes. The incorporation of oligo(phenyleneethynylene) (OPE) derivatives such as diethienylethene (DTE) into a Ru(II)-alkynyl framework yielded functional switches: upon either UV/visible irradiation or electrochemical current application, the DTE unit can make or break a bond between the two thiophene rings. These Ru(II)-alkynyl molecules can then be derivatized to allow for immobilization on gold surfaces as SAMs (self-assembled monolayers) for switch testing, and devices realized includes a novel Au-molecule-Au transport junction that exhibits controllable switching of conductivity between two distinct states [74,75], as illustrated in Fig. 8. Oyama and coworkers have recently utilized a similar molecular framework to study the switching capability of the anthrahydroquinone(AHQ) / anthraquinone(AQ) system, as this substituent can achieve reversible switching between AHQ and AQ through both redox stimuli and pH stimuli when attached to the Ru(dppe)$_2$ framework [39].

3.2.2. Wire-like molecules and molecular wires

Realization of molecular wires requires similar characteristics to those of molecular switches, although there is no need for components changing physical properties upon application of external stimuli. Here we draw distinction between the demonstration of "wire-like" features through bulk solution study and nano-junction measurement of conductance for authentic "molecular wires".

The earliest comprehensive demonstration of the wire-like character of Ru(bisphosphine)$_2$alkynyls is the study of trans-Ru(dppm)$_2$(C$_2$Fc)$_2$ by Wolf and coworkers: the sequential Fc center oxidations were determined with a $\Delta E_{1/2}$ of 220 mV, and the [Fc—Fc]$^{+1}$ mixed valent ion was assigned as Robin-Day class II on the basis of spectroelectrochemical investigation of intervalence charge transfer (IVCT) bands [27,28]. Rigaut et al. investigated wire-like molecules based on both the end-capped complex and complexes with multiple ruthenium fragments linked by the alkynyl chains. The end-capped trans-[Cl(dppe)$_2$Ru-(C≡C)$_6$-Ru(dppe)$_2$Cl] complex displayed sequential oxidations but no reductions within the solvent window [41]. When multiple Ru(dppe)$_2$ units were bridged with 1,4-diethynylbenzene, the resultant molecules exhibited Ru-Ru electronic interactions in different oxidation states [43]. Use of other π-conjugated systems such as nitriles and thienyls have also been investigated for their abilities to modulate electron communication between ruthenium centers. Comparing electrochemical behaviors of bridged complexes, trans-[(dppe)$_2$(Ph-C≡C)Ru(1,4-N≡C-C$_6$H$_4$-C≡N)Ru(C≡C-Ph)(dppe)$_2$][PF$_6$]$_2$ and trans-[(dppe)$_2$(Ph-C≡N)Ru(1,4-C≡C-C$_6$H$_4$-C≡C)Ru(N≡C-Ph)(dppe)$_2$][PF$_6$]$_2$, the former displayed a single Ru(+3/+2) oxidation wave while the latter exhibited two Ru(+3/+2) oxidation waves, illustrating the importance of the nature of the bridges [44]. The separation of the two oxidation potentials in trans-[(dppe)$_2$(Ph-C≡N)Ru(1,4-C≡C-C$_6$H$_4$-C≡C)Ru(N≡C-Ph)(dppe)$_2$]$^{2+}$ was noted to be smaller than those of a similar compound, trans-[(dppe)$_2$Cl-Ru(1,4-C≡C-C$_6$H$_4$-C≡C)Ru-Cl(dppe)$_2$] [76], highlighting the effect of the capping ligands on the HOMO level. A series of bimetallic Ru complexes [Cl(dppe)$_2$Ru−C≡C-(3R-C$_4$H$_2$S)-C≡C−Ru(dppe)$_2$Cl] (R = H, C$_2$H$_5$, C$_3$H$_7$, C$_4$H$_9$, C$_6$H$_{13}$, OMe, CN) were prepared using the vinylidene method by Roy et al. [77]. The Ru-Ru interaction is negatively attenuated by the introduction of 3-R substituent of the thienylethynyl group, which was attributed to the adverse substituent effect on thermodynamic stability of the resultant cations by the authors. The potential separations of the stepwise Ru(+3/+2) oxidation waves can be as large as 390 mV (R = H), indicating strong Ru-Ru interactions, while that of R = CN is negligible. Naik et al. have also probed electronic interactions through polycyclic saturated and pseudo-aromatic spacers [67]. The bridging complexes [trans,trans-{Ru(dmpe)$_2$(C≡C^{t}Bu)}$_2$(μ-C≡C–C$_8$H$_{12}$–C≡C)], [trans,trans-{Ru(dmpe)$_2$(C≡C^{t}Bu)}$_2$(μ-C≡C–p-C$_2$B$_{10}$H$_{10}$–C≡C)], and [trans,trans-{Ru(dmpe)$_2$(C≡C^{t}Bu)}$_2$(μ-C≡C–p-C$_6$H$_4$–C≡C)] all displayed two Ru(+3/+2) waves, with separations ranging from the moderate 69 mV (-C$_8$H$_{12}$-) to significant 295 mV (-C$_6$H$_4$-). It should be noted that further comparison of the degree of electron delocalization in the last four examples [44,67,76,77] is challenging due to both the absence of proper analysis of IVCT bands and moderate $\Delta E_{1/2}$ values.

The first study of authentic "molecular wires" was the conductance study of Ru(II) alkynyls from the cross-wire junction measurement of the SAMs formed by trans-Ru(dppe)$_2$(C$_2$Ar)$_2$ and its dimeric / trimeric analogues with nitrile capping groups by Kim and coworkers [78], and noteworthy among many interesting findings is a very weak distance dependence of the wire resistance. Similar conclusions were drawn from the subsequent CP-AFM (conducting probe atomic force microscopy) measurement of the same group of Ru(II) σ-acetylides with thiol-caps by Luo et al. [79]. In the more recent years, Mulas and coworkers examined the dynamics of the electron transfers within the monolayers of the afore-mentioned Ru(II) acetylides with high-speed voltammetry, and speculated the relevance of the rates determined to the possibility of charge storage and redox switchable devices [80,81]. Sugimoto and co-workers demonstrated that single-molecule conductance of mono-Ru-molecular wires with pyridine termini is better than their organic counterparts, despite the increased length [82]. The enhancement of the single molecule conductance over the pure organic analogue is attributed the improved energy alignment between the high-lying HOMO that is distributed across the entire Ru-alkynyl molecule and the Fermi level of Au electrodes. Using the Au(I) capped trans-(C$_{2n}$)Ru(dppe)$_2$(C$_{2n}$) complexes (n = 2 – 4), Akita and coworkers achieved the direct insertion of -(C$_{2n}$)Ru(dppe)$_2$(C$_{2n}$)- fragment between Au nanojunction, and remarkably high conductance (10^{-3} – 10^{-2} G$_0$; G$_0$ is the conductance quantum) was determined using the STM-break junction technique [83], as shown in Fig. 9. trans-Ru(C$_2$-3-C$_4$H$_3$S)$_2$(dppe)$_2$ was studied using scanning tunnelling microscope break-junction technique by Martin, Lambert, Low and coworkers, which yielded a modest conductance range of 1 to 3 × 10^{-4} G$_0$ [84]. Elegantly designed by Ezquerra and coworkers, the SAM of trans-Ru(C$_2$-3-C$_4$H$_3$S)(C$_2$-1,4-C$_6$H$_4$C$_2$-Au(PPh$_3$))(dppe)$_2$ was formed on an Au substrate, and the removal of PPh$_3$ via mild thermal treatment resulted in the formation of Au nanoparticles atop the SAM [85]. The CP-AFM measurement of the said junction gave an estimated conductance of 1.6 × 10^{-4} G$_0$ [85].

Overall, many research groups have successfully modulated ligand design of Ru(II) alkynyl complexes and demonstrated their "wire-like" properties. However, device implementation of switches and wires remains a significant challenge [16,73].

3.3. Dye-sensitized solar cells

Over the past decade, dye-sensitized solar cells (DSSCs) have been viewed as a promising technology due to the high theoretical efficiencies and potential low cost [86]. Again, Ru(II)-acetylide complexes are highly advantageous for this application due to their well-documented π-conjugation between the d orbitals with the π^* system of the alkynyl ligands that produces intense, low energy MLCT excitations. These excitations can be utilized to inject holes

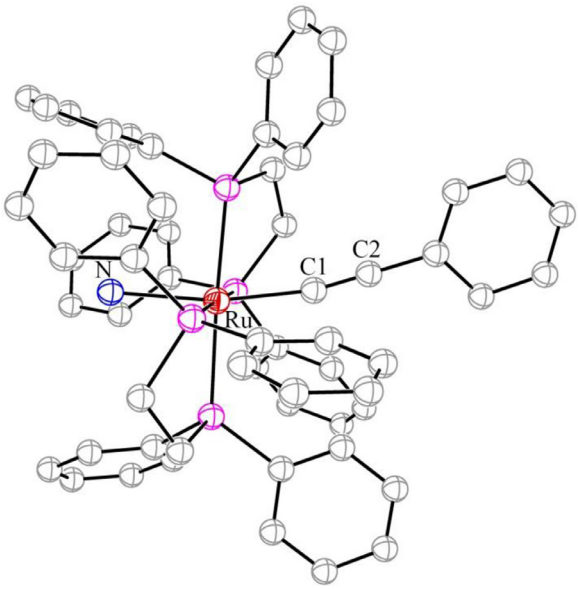


Fig. 3. Molecular structure of $[RuCl(dppe)_2][OTf]$, generated from CCDC 719111.

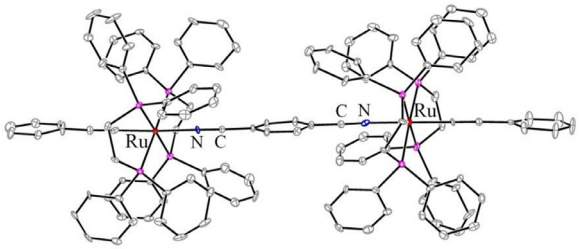


Fig. 4. Molecular structure of trans-$[Ru(C_2Ph)(NH_3)(dppe)_2]^+$ generated from CCDC 1234388.

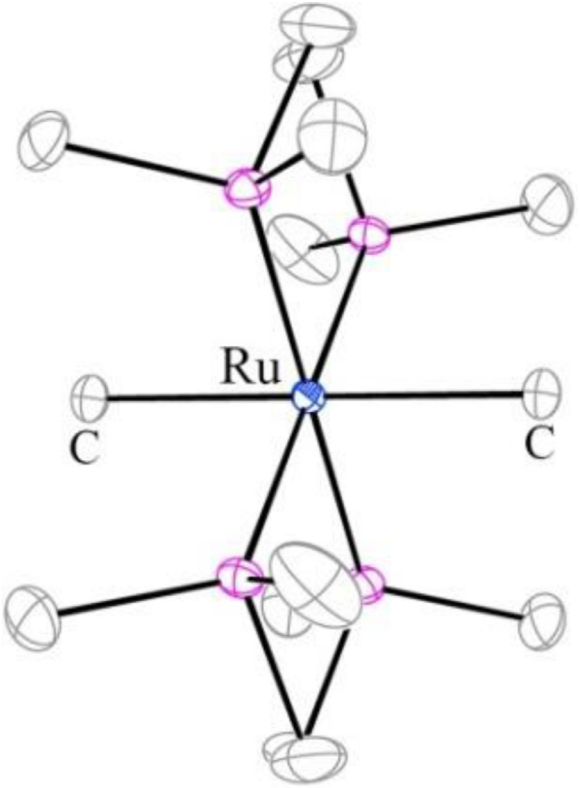


Fig. 5. Molecular structure of $[(dppe)_2(Ph\text{-}C{\equiv}C)Ru(N{\equiv}CC_6H_4C{\equiv}N)Ru(C{\equiv}C\text{-}Ph)(dppe)_2][PF_6]_2$ generated from CCDC 211235.

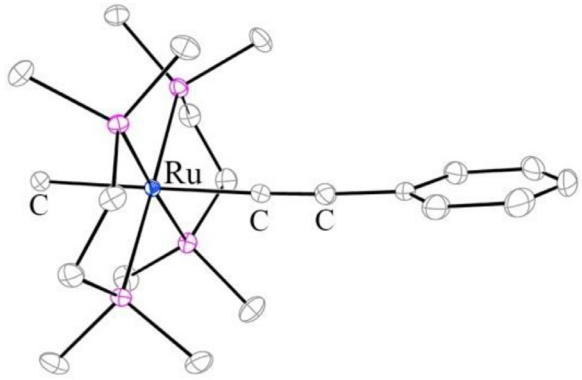


Fig. 6. Molecular structure of trans-$Ru(dmpe)_2Me_2$ generated from CCDC 665447.

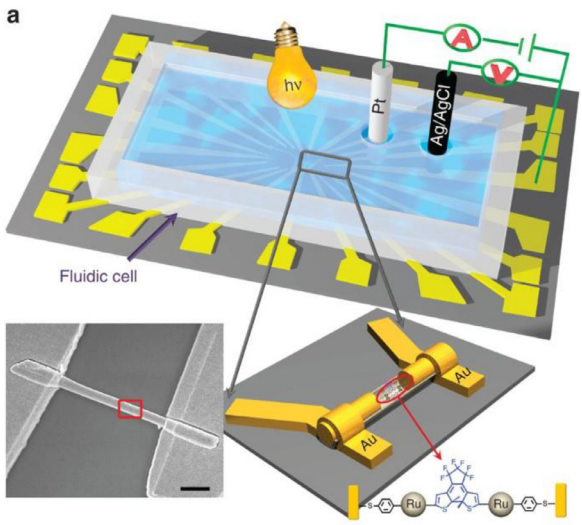


Fig. 7. Molecular structure of trans-$Ru(dmpe)_2Me(C_2Ph)$ generated from CCDC 665448.

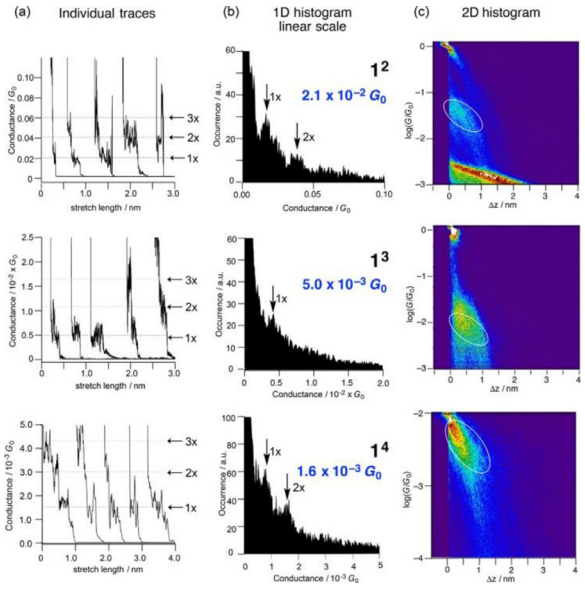


Fig. 8. Schematics of the functionalized nanogap devices based on -Ru-(C_2-DTE-C_2)-Ru- complex. Inset: SEM image of a device fabricated by OWL-generated nanowire. Taken from Ref. [74]

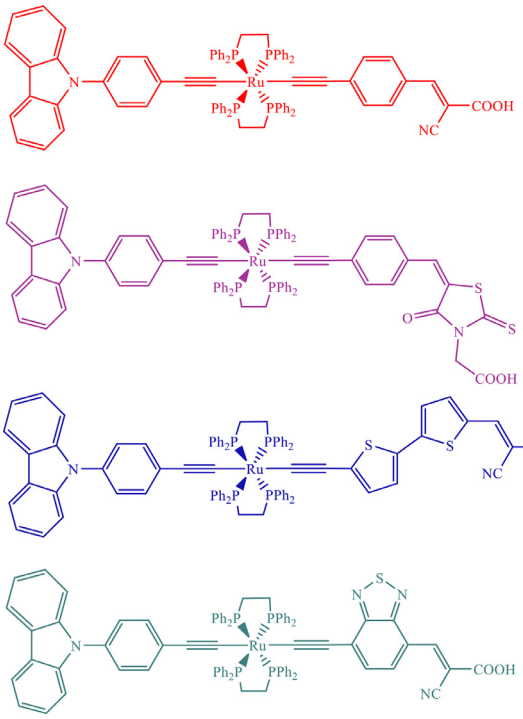


Fig. 9. Molecular conductance of -(C_{2n})Ru(dppe)$_2$(C_{2n})- measured with the STM-break junction technique; n = 2 (1^2), 3 (1^3) and 4 (1^4). Taken from Ref. [83]

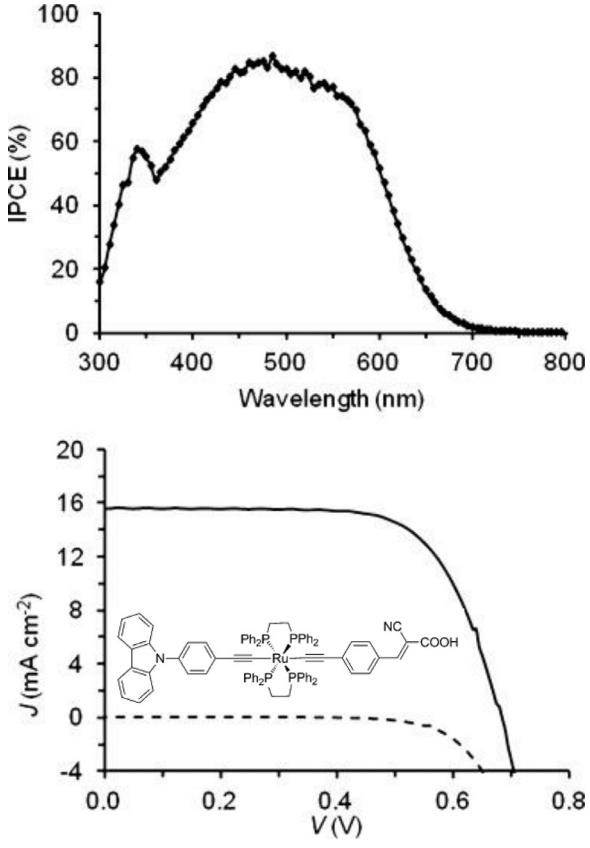


Fig. 10. Representative 'D-B-A' molecules with varying anchors and 'acceptor' ligands for DSSCs from Ref. [87], colored as they appear in CH_2Cl_2 solution. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.).

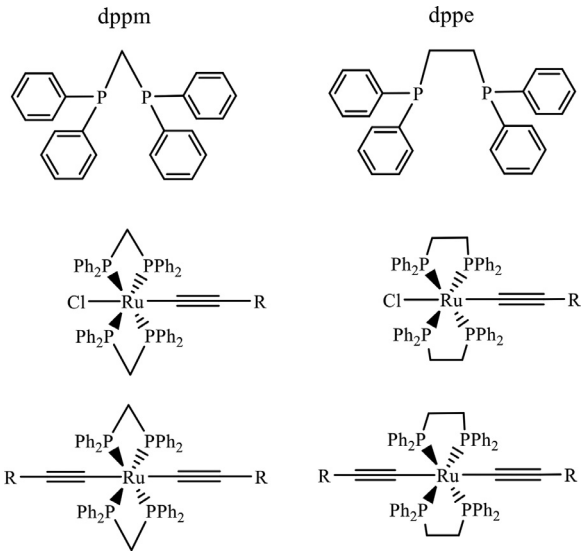


Fig. 11. (top) Incident photon-to-current conversion efficiency (IPCE) and (bottom) current density–voltage profiles of a DSC with a representative Ru dye (insert), under 100 mW cm^{-2} illumination (solid line) and in the dark (dashed line). Modified from Ref. [56]. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

(p-type DSSC) or electrons (n-type DSSC) into the conduction band of the corresponding electrode (NiO or TiO_2) upon photoexcitation of the dye. The other advantage of Ru(II)-acetylide complexes for models of dyes in DSSCs is their facile and high-yielding syntheses, as described above, easily producing a wide variety of model complexes for the study of charge transport through dissymmetric alkynyl complexes.

The dye molecules, classically Ru-based organometallic molecules with high charge transport capabilities and the ability to efficiently absorb the solar spectrum, exhibit a 'D-B-A' framework that produces chromophores based on MLCT bands ranging from 520 to 660 nm (see Fig. 10 above) [87]. These unsymmetrical Ru alkynyl complexes were some of the first examples of efficient blue dyes with overall power conversion efficiencies (PCEs) ranging from 6.10 to 7.08%. The device's PCE was slightly improved (7.49%) when two dyes were co-deposited in a 4:1 ratio onto TiO_2, a result of panchromatic spectral absorption [87]. Representative incident photon-to-current conversion efficiency and current density–voltage profiles of a Ru based DSC [56] are provided in Fig. 11. Green dyes, desirable for low-energy photon absorption in the 500–800 nm range, have also been generated using the Ru unsymmetrical framework with a PCE of 5.23%. Competitive back electron-transfer was attributed to the lower PCE in the green dye when compared to the related purple-blue dye (PCE of 6.45%) [54].

Modification of the dyes' anchoring groups also impact PCEs of DSSCs. Use of cyanoacrylic acid as the TiO_2 anchor resulted in both higher dye loading and increased dye stability, generating higher PCEs (6.45 and 5.23%) when compared to dyes utilizing carboxylic acid anchors (PCE of 3.11%) [54]. For n-type DSSCs, these anchoring groups are typically located off the 'acceptor' substituent to facilitate injection of the electron into the TiO_2 support [54,56,87]. For p-type DSSCs, these anchoring groups are located off the 'donating' substituent to facilitate injection of the hole into the NiO support. Olivier et al. have also investigated unsymmetrical Ru organometallic complexes as p-type DSSCs. Low overall PCEs were noted for their two complexes (0.079% and 0.038%) but are on par for dyes with the same anchoring group for this application [88]. The low PCEs were attributed to low dye-loading, and future optimization will be based on varying

anchoring groups and alkynyl substituents [55]. Of note is how features that help improve DSSCs capabilities also improve NLO characteristics, a possibility investigated by Nisic and coworkers [58].

4. Conclusions, future outlooks

This review focuses on common synthetic schemes to generate mono- and bis-alkynyl complexes based on $Ru(dppe)_2$ and $Ru(dppm)_2$ units. These complexes exhibit rich spectroscopic and electronic features that lead to a wide variety of materials applications. These studies clearly demonstrate the importance of incorporating the $Ru(L\text{-}L)_2$ framework into a π-conjugated alkyne-based system to afford electronically / optically active molecules with tunable properties. A broad comparison between synthetic methods has been attempted to aid in the readers own synthetic design. The alkynylation of $Ru(dppe/m)_2$ often occurs at very mild conditions that are tolerant towards sensitive functional groups, which is highly desirable for the incorporation of chromophores and electron acceptors, as demonstrated in the above mentioned DSSC work. Additionally, facile preparation of $Ru(dppe/m)_2$ oligoynyl compounds allows for further exotic covalent transformation, such as the end capping with Au-carbene demonstrated by Tanaka and co-workers [83]. Other possible but unexplored transformations for $Ru(dppe/m)_2$ alkynyls include the click reaction to form 1,2,3-triazole derivatives [89], the [2+2] cycloaddition reaction between two C≡C bonds (demonstrated for CpRu(dppe) alkynyls [90]), and the CA-RE ([2+2] cyclcoaddition and retroelectrocyclization) reaction with electrophilic olefins [91,92]. Since a rich variety of chromophores and electrophores can be introduced using these transformations, sky is the limit for $Ru(dppe/m)_2$ alkynyls as synthons for opto-electronic materials.(Fig. 3).

Declaration of Competing Interest

The authors declare no conflicts of interest

Acknowledgment

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References

[1] A. Haque, R.A. Al-Balushi, I.J. Al-Busaidi, Muhammad S. Khan, P.R. Raithby, Rise of Conjugated Poly-ynes and Poly(Metalla-ynes): From Design Through Synthesis to Structure–Property Relationships and Applications, Chem. Rev. 118 (2018) 8474.
[2] N.J. Long, C.K. Williams, Metal Alkynyl Complexes: Synthesis and Materials, Angew. Chem. Int. Ed. 42 (2003) 2586.
[3] M.I. Bruce, Organometallic Chemistry of Vinylidene and Related Unsaturated Carbenes, Chem. Rev. 91 (1991) 197.
[4] M.I. Bruce, Transition Metal Complexes Containing Allenylidene, Cumulenylidene, and Related Ligands, Chem. Rev. 98 (1998) 2797.
[5] R. Nast, Coordination Chemistry of Metal Alkynyl Compounds, Coord. Chem. Rev. 47 (1982) 89.
[6] N. Hagihara, K. Sonogashira, S. Takahashi, Linear Polymers Containing Transition Metals in the Main Chain, Adv. Polym. Sci. 40 (1981) 149.
[7] K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi, N. Hagihara, J. Organomet, Syntheses and Properties of Cis-Dialkynyl and Trans-Dialkynyl Complexes of Platinum(II), Chem. 145 (1978) 101.
[8] K. Sonogashira, K. Ohga, S. Takahashi, N. Hagihara, Studies of Poly-yne polymers containing transition metals in the main chain; VI, J. Organomet. Chem. 188 (1980) 237.
[9] J.P. Morrall, G.T. Dalton, M.G. Humphrey, M. Samoc, Organotransition metal complexes for nonlinear optics, Adv. Organomet. Chem. 55 (2008) 61.
[10] W.-Y. Wong, C.-L. Ho, Organometallic Photovoltaics: A New and Versatile Approach for Harvesting Solar Energy Using Conjugated Polymetallaynes, Acc. Chem. Res. 43 (2010) 1246.
[11] C.-L. Ho, Z.-Q. Yu, W.-Y. Wong, Multifunctional polymetallaynes: properties, functions and applications, Chem. Soc. Rev. 45 (2016) 5264.
[12] A. Haque, L.L. Xu, R.A. Al-Balushi, M.K. Al-Suti, R. Ilmi, Z.L. Guo, M.S. Khan, W.Y. Wong, P.R. Raithby, Cyclometallated tridentate platinum(II) arylacetylide complexes: old wine in new bottles, Chem. Soc. Rev 48 (2019) 5547.
[13] P.J. Low, Metal complexes in molecular electronics: progress and possibilities, Dalton Trans (2005) 2821.
[14] T. Ren, Diruthenium s-Alkynyl Compounds: A New Class of Conjugated Organometallics, Organometallics 24 (2005) 4854.
[15] F. Gendron, T. Groizard, B.Le Guennic, J.F. Halet, Electronic Properties of Poly-Yne Carbon Chains and Derivatives with Transition Metal End-Groups, Eur. J. Inorg. Chem. 2020 (2020) 667.
[16] D. Xiang, X. Wang, C. Jia, T. Lee, X. Guo, Molecular-Scale Electronics: From Concept to Function, Chem. Rev. 116 (2016) 4318.
[17] H. Zhu, S.J. Pookpanratana, J.E. Bonevich, S.N. Natoli, C.A. Hacker, T. Ren, J.S. Suehle, C.A. Richter, Q. Li, Redox-Active Molecular Nanowire Flash Memory for High-Endurance and High-Density Non-Volatile Memory Applications, ACS Appl. Mater. Interfaces 7 (2015) 27306.
[18] J. Manna, K.D. John, M.D. Hopkins, The Bonding of Metal-Alkynyl Complexes, Adv. Organomet. Chem. 38 (1995) 79.
[19] S. Szafert, J.A. Gladysz, Update 1 of: Carbon in One Dimension: Structural Analysis of the Higher Conjugated Polyynes, Chem. Rev. 106 (2006) PR1.
[20] S. Szafert, J.A. Gladysz, Carbon in One Dimension: Structural Analysis of the Higher Conjugated Polyynes, Chem. Rev. 103 (2003) 4175.
[21] H.-L. Shek, C.-F. Yeung, L.-H. Chung, C.-Y. Wong, A focused review on the unconventional alkyne activations by ruthenium(II) and osmium(II) complexes supported by 1,2-bis(diphenylphosphino)methane (dppm), Polyhedron 197 (2021) 115023.
[22] B. Cetinkaya, M.F. Lappert, J. McMeeking, D.E. Palmer, Unsaturated -Hydrocarbyl Transition Metal Complexes. Part 1. Trimethyltin Acetylides as Sources of Late Transition-Metal Derivatives: Metathesis, Oxidative Addition, and Oxidative Cleavage, J. Chem. Soc., Dalton Trans. (1973) 1202.
[23] M. Younus, N.J. Long, P.R. Raithby, J. Lewis, N.A. Page, A.J.P. White, D.J. Williams, M.C.B. Colbert, A.J. Hodge, M.S. Khan, D.G. Parker, Synthesis and characterisation of mono-acetylide and unsymmetrical bis-acetylide complexes of ruthenium and osmium: X-ray structure determinations on [(dppe)(2)Ru(Cl)(C C-C6H4-p- NO2)], [(dppe)(2)Ru(Cl)(C C-C6H3-o-CH3-p-NO2)] and [(dppm)(2)Os(C C-C6H4-p-CH3)(C C-C6H4-p-NO2)], J. Organomet. Chem. 578 (1999) 198.
[24] C.W. Faulkner, S.L. Ingham, M.S. Khan, J. Lewis, N.J. Long, P.R. Raithby, Ruthenium(II) s-acetylide complexes monomers, dimers, and polymers, J. Organomet. Chem. 482 (1994) 139.
[25] D. Touchard, P. Haquette, S. Guesmi, L. Le Pichon, A. Daridor, L. Toupet, P.H. Dixneuf, Vinylidene-, Alkynyl-, and trans-Bis(alkynyl)ruthenium Complexes. Crystal Structure of trans-$[Ru(NH_3)(CC\text{-}Ph)(dppe)_2]PF_6$, Organometallics 16 (1997) 3640.
[26] Z. Atherton, C.W. Faulkner, S.L. Ingham, A.K. Kakkar, M.S. Khan, J. Lewis, N.J. Long, P.R. Raithby, Rigid-Rod Sigma-Acetylide Complexes of Iron, Ruthenium and Osmium, J. Organomet. Chem. 462 (1993) 265.
[27] N.D. Jones, M.O. Wolf, D.M. Giaquinta, Synthesis of a Ferrocenyl-Capped Ruthenium(II) Bis(acetylide) Complex: A Model for Organometallic Molecular Wires, Organometallics 16 (1997) 1352.
[28] Y. Zhu, O. Clot, M.O. Wolf, G.P.A. Yap, Effect of Ancillary Ligands on Ru(II) on Electronic Delocalization in Ruthenium(II) Bisferrocenylacetylide Complexes, J. Am. Chem. Soc. 120 (1998) 1812.
[29] Y. Zhu, D.B. Millet, M.O. Wolf, S.J. Rettig, Models for Conjugated Metal Acetylide Polymers: Ruthenium Oligothienylacetylide Complexes, Organometallics 18 (1999) 1930.
[30] M.E. Wright, Synthesis of Conjugated Polymers using an (n6-arene)Cr(CO)3 Monomer, Macromolecules 22 (1989) 3256.
[31] A.W. Brown, R.D. Verschoyle, B.W. Street, W.N. Aidridge, H. Grindley, The neurotoxicity of trimethyltin chloride in hamsters, gerbils and marmosets, J. Appl. Toxicol. 4 (1984) 12.
[32] S.J. Davies, B.F.G. Johnson, M.S. Khan, J. Lewis, Synthesis of monomeric and oligomeric Bis(acetylide) Complexes of Platinum and Rhodium, J. Chem. Soc., Chem. Commun. (1991) 187.
[33] E. Viola, C. Lo Sterzo, R. Crescenzi, G. Frachey, Formation of metal sigma-acetylides of Mo, W, and Ru via palladium-catalyzed metal-carbon coupling, J. Organomet. Chem. 493 (1995) 55.
[34] F.A. Cotton, S.E. Stiriba, A. Yokochi, Selectivity in alkynylation: the reaction between Ru-2(LL)(4)Cl and Me3SnC CR (LL=2-anilinopyridine, 2-chloro- and 2-bromo-oxypyridine), J. Organomet. Chem. 595 (2000) 300.
[35] M.A. Fox, J.E. Harris, S. Heider, V. Perez-Gregorio, M.E. Zakrzewska, J.D. Farmer, D.S. Yufit, J.A.K. Howard, P.J. Low, A simple synthesis of trans-RuCl(C CR)(dppe)(2) complexes and representative molecular structures, J. Organomet. Chem. 694 (2009) 2350.
[36] D. Touchard, P. Haquette, N. Pirio, L. Toupet, P.H. Dixneuf, New Ruthenium Vinylidene Complexes As Intermediates For the Access to Sigma-Acetylide and Unsymmetrical Trans-Diynyl, Alkynyl Metal-Complexes - Crystal-Structures of [(Ph2pch2pph2)2(Cl)Ru=C=Ch2]Pf6 and [(Ph2pch2pph2)2(Cl)Ruc=Ch] Complexes, Organometallics 12 (1993) 3132.
[37] S. Marques-Gonzalez, M. Parthey, D.S. Yufit, J.A.K. Howard, M. Kaupp, P.J. Low, Combined Spectroscopic and Quantum Chemical Study of trans-Ru(C -CC6H4R1-4)(2)(dppe)(2) (n+) and trans-Ru(C CC6H4R1-4)(C CC6H4R2-4)(dppe)(2) (n+) (n=0, 1) Complexes: Interpretations beyond the Lowest Energy Conformer Paradigm, Organometallics 33 (2014) 4947.

[38] S.G. Eaves, D.S. Yufit, B.W. Skelton, J.M. Lynam, P.J. Low, Reactions of alkynes with cis-RuCl2(dppm)2: exploring the interplay of vinylidene, alkynyl and eta 3-butenynyl complexes, Dalton Trans 44 (2015) 21016.
[39] Y. Oyama, R. Kawano, Y. Tanaka, M. Akita, Dinuclear ruthenium acetylide complexes with diethynylated anthrahydroquinone and anthraquinone frameworks: a multi-stimuli-responsive organometallic switch, Dalton Trans 48 (2019) 7432.
[40] F. Malvolti, C. Rouxel, G. Grelaud, L. Toupet, T. Roisnel, A. Barlow, X.W. Yang, G.M. Wang, F.I.A. Razak, R. Stranger, M.P. Cifuentes, M.G. Humphrey, O. Mongin, M. Blanchard-Desce, C.O. Paul-Roth, F. Paul, Iron and Ruthenium Alkynyl Complexes with 2-Fluorenyl Groups: Some Linear and Nonlinear Optical Absorption Properties, Eur. J. Inorg. Chem. (2016) 3868.
[41] S. Rigaut, J. Perruchon, L.L. Pichon, D. Touchard, P.H. Dixneuf, Synthesis of ruthenium acetylides: new building blocks for molecular electronics, J. Organomet. Chem. 670 (2003) 37.
[42] S. Rigaut, J. Perruchon, S. Guesmi, C. Fave, D. Touchard, P.H. Dixneuf, Carbon-Rich Ruthenium Complexes Containing Bis(allenylidene) and Mixed Alkynyl-Allenylidene Bridges, Eur. J. Inorg. Chem. (2005) 447.
[43] C. Olivier, B. Kim, D. Touchard, S. Rigaut, Redox-Active Molecular Wires Incorporating Ruthenium(II) s-Arylacetylide Complexes for Molecular Electronics, Organometallics 27 (2008) 509.
[44] J.-L. Fillaut, N.N. Dua, F. Geneste, L. Toupet, S. Sinbandhit, Nitrile ligands for controlled synthesis of alkynyl-ruthenium based homo and hetero bimetallic systems, J. Organomet. Chem. 691 (2006) 5610.
[45] J.-L. Fillaut, J. Andries, R.D. Marwaha, P.-H. Lanoe, O. Lohio, L. Toupet, J.A.G. Williams, Flavonal based ruthenium acetylides as fluorescent chemosensors for lead ions, J. Organomet. Chem. 693 (2008) 228.
[46] N. Gauthier, C. Olivier, S. Rigaut, D. Touchard, T. Roisnel, M.G. Humphrey, F. Paul, Intramolecular optical electron transfer in mixed-valent dinuclear iron-ruthenium complexes featuring a 1,4-diethynylaryl spacer, Organometallics 27 (2008) 1063.
[47] D. Weiss, P.H. Dixneuf, Novel Polymetallic Vinylidene- and Allenylideneruthenium(II) Complexes, Organometallics 22 (2003) 2209.
[48] B. Chin, A.J. Lough, R.H. Morris, C.T. Schweitzer, C. D'Agostino, Influence of Chloride versus Hydride on H-H Bonding and Acidity of the Trans Dihydrogen Ligand in the Complexes trans-[Ru(H2)X(PR2CH2CH2PR2)2]+, X = Cl, H, R = Ph, Et. Crystal Structure Determinations of [RuCl(dppe)2]PF6 and trans-[Ru(H2)Cl(dppe)2]PF6, Inorg. Chem. 33 (1994) 6278.
[49] J.R. Polam, L.C. Porter, Ru(II) COMPLEXES CONTAINING CHELATING PHOSPHINE LIGANDS. SYNTHESIS, CHARACTERIZATION, AND X-RAY CRYSTAL STRUCTURES OF DICHLOROBIS(1,2- BIS(DIPHENYLPHOSPHINO)ETHANE)Ru(II)AND THE COORDINATIVELY UNSATURATED TRIGONAL-BIPYRAMIDAL CATION, CHLOROBIS-(1,2- BIS(DIPHENYLPHOSPHINO)ETHANE)Ru(II)., J. Coord. Chem. 29 (1993) 109.
[50] D.N. Cheredilin, F.M. Dolgushin, E.V. Balagurova, I.A. Godovikov, I.T. Chizhevsky, Synthesis of cationic ruthenium diphosphine complexes with nido-dicarbaundecaborate anions. Molecular structure of [RuCl(dppe)2]+[7,8-nido-C2B9H12]–, Russ. Chem. Bull. 53 (2004) 2086.
[51] J. Du, M.S. Kodikara, G.J. Moxey, M. Morshedi, A. Barlow, C. Quintana, G.M. Wang, R. Stranger, C. Zhang, M.P. Cifuentes, M.G. Humphrey, Quadratic and cubic hyperpolarizabilities of nitro-phenyl/-naphthalenyl/-anthracenyl alkynyl complexes, Dalton Trans 47 (2018) 4560.
[52] A. Triadon, G. Grelaud, N. Richy, O. Mongin, G.J. Moxey, I.M. Dixon, X. Yang, G. Wang, A. Barlow, J. Rault-Berthelot, M.P. Cifuentes, M.G. Humphrey, F. Paul, Linear and Third-Order Nonlinear Optical Properties of Fe(?5-C5Me5)(?2-dppe)- and trans-Ru(?2-dppe)2-Alkynyl Complexes Containing 2-Fluorenyl End Groups, Organometallics 37 (2018) 2245.
[53] B.A. Babgi, M.S. Kodikara, M. Morshedi, H. Wang, C. Quintana, T. Schwich, G.J. Moxey, N. Van Steerteghem, K. Clays, R. Stranger, M.P. Cifuentes, M.G. Humphrey, Linear Optical, Quadratic and Cubic Nonlinear Optical, Electrochemical, and Theoretical Studies of "Rigid-Rod" Bis-Alkynyl Ruthenium Complexes, ChemPlusChem 83 (2018) 630.
[54] S. Lyu, C. Bertrand, T. Hamamura, L. Ducasse, T. Toupance, C. Olivier, Molecular engineering of ruthenium-diacetylide organometallic complexes towards efficient green dye for DSSC, Dyes Pigm 158 (2018) 326.
[55] S. Lyu, Y. Farre, L. Ducasse, Y. Pellegrin, T. Toupance, C. Olivier, F. Odobel, Push–pull ruthenium diacetylide complexes: new dyes for p-type dye-sensitized solar cells, RSC Adv 6 (2016) 19928.
[56] S. De Sousa, L. Ducasse, B. Kauffmann, T. Toupance, C. Olivier, Functionalization of a Ruthenium-Diacetylide Organometallic Complex as a Next-Generation Push-Pull Chromophore, Chem. Eur J. 20 (2014) 7017.
[57] Y. Liu, C.M. Ndiaye, C. Lagrost, K. Costuas, S. Choua, P. Turek, L. Norel, S. Rigaut, Diarylethene-Containing Carbon-Rich Ruthenium Organometallics: Tuning of Electrochromism, Inorg. Chem. 53 (2014) 8172.
[58] F. Nisic, A. Colombo, C. Dragonetti, E. Garoni, D. Marinotto, S. Righetto, F.D. Angelis, M.G. Lobello, P. Salvatori, P. Biagini, F. Melchiorre, Functionalized Ruthenium Dialkynyl Complexes with High Second-Order Nonlinear Optical Properties and Good Potential as Dye Sensitizers for Solar Cells, Organometallics 34 (2015) 94.
[59] D. Touchard, S. Guesmi, L.L. Pichon, A. Daridor, P.H. Dixneuf, Ammonia ruthenium complexes for the access to new hydrido, carbonyl and isocyanide ruthenium-alkynyl derivatives, Inorg. Chim. Acta 280 (1998) 118.
[60] F. Ozawa, T. Mori, Preparation and C-Si Reductive Elimination Behavior of cis-Alkynyl(silyl)platinum(II) Complexes, Organometallics 22 (2003) 3593.
[61] D. Zargarian, P. Chow, N.J. Taylor, T.B. Marder, Synthesis of RhI-s-acetylide complexes in aqueous and non-aqueous solutions: molecular structures of [(PMe3)4Rh(CC-Ph)] and [(PMe3)3Rh(CC-SiMe3)], J. Chem. Soc., Chem. Commun. (1989) 540.
[62] H.-F. Klein, H.H. Karsch, Methyl cobalt compounds with non-chelating ligands, I. Methyltetrakis (trimethylphosphine) cobalt and its derivatives, Chem. Ber. 108 (1975) 944.
[63] L.D. Field, A.J. Turnbull, P. Turner, Acetylide-Bridged Organometallic Oligomers via the Photochemical Metathesis of Methyl-Iron(II) Complexes, J. Am. Chem. Soc. 124 (2002) 3692.
[64] L.D. Field, A.M. Magill, Timothy K. Shearer, S.J. Dalgarno, P. Turner, Mono- and Bis-acetylidoruthenium(II) Complexes by Controlled Metathesis of Methylruthenium Complexes with Acetylenes, Organometallics 26 (2007) 4776.
[65] L.D. Field, A.M. Magill, T.K. Shearer, S.J. Dalgarno, M.M. Bhadbhade, Symmetrical Bis(acetylido)ruthenium(II) Complexes, Eur. J. Inorg. Chem. (2011) 3503.
[66] L.D. Field, A.M. Magill, T.K. Shearer, S.B. Colbran, S.T. Lee, S.J. Dalgarno, M.M. Bhadbhade, Controlled Synthesis of Dinuclear Acetylide-Bridged Ruthenium Complexes, Organometallics 29 (2010) 957–965.
[67] S. Naik, S.O. Scottwell, H.L. Li, C.F. Leong, D.M. D'Alessandro, L.D. Field, Dinuclear acetylide-bridged ruthenium(ii) complexes with rigid non-aromatic spacers, Dalton Trans 49 (2020) 2687.
[68] G. Grelaud, M.P. Cifuentes, F. Paul, M.G. Humphrey, Group 8 metal alkynyl complexes for nonlinear optics, J. Organomet. Chem. 751 (2014) 181.
[69] M.G. Humphrey, Ruthenium Alkynyl Complexes in non-linear optics, Aust. J. Chem. 71 (2018) 731.
[70] R.J. Durand, S. Gauthier, S. Achelle, T. Groizard, S. Kahlal, J.Y. Saillard, A. Barsella, N.Le Poul, F.R. Le Guen, Push-pull D-pi-Ru-pi-A chromophores: synthesis and electrochemical, photophysical and second-order nonlinear optical properties, Dalton Trans 47 (2018) 3965.
[71] J.-P. Launay, Long-distance intervalence electron transfer, Chem. Soc. Rev. 30 (2001) 386.
[72] J.P. Launay, Mixed-Valent Compounds and their Properties - Recent Developments, Eur. J. Inorg. Chem. 2020 (2020) 329.
[73] X. He, C. Lagrost, L. Norel, S. Rigaut, Ruthenium(II) sigma-arylacetylide complexes as redox active units for (multi-)functional molecular devices, Polyhedron 140 (2018) 169.
[74] F.B. Meng, Y.M. Hervault, Q. Shao, B.H. Hu, L. Norel, S. Rigaut, X.D. Chen, Orthogonally modulated molecular transport junctions for resettable electronic logic gates, Nature Commun 5 (2014) Art. 3023.
[75] F.B. Meng, Y.M. Hervault, L. Norel, K. Costuas, C. Van Dyck, V. Geskin, J. Cornil, H.H. Hng, S. Rigaut, X.D. Chen, Photo-modulable molecular transport junctions based on organometallic molecular wires, Chem. Sci. 3 (2012) 3113.
[76] O. Lavastre, J. Plass, P. Bachmann, S. Guesmi, C. Moinet, P.H. Dixneuf, Ruthenium or ferrocenyl homobimetallic and RuPdRu and FePdFe heterotrimetallic complexes connected by unsaturated, carbon- rich -C CC6H4C C- bridges, Organometallics 16 (1997) 184.
[77] S.S. Roy, S.R. Chowdhury, S. Mishra, S.K. Patra, Role of Substituents at the 3-position of Thienylethynyl Spacer on Electronic Properties in Diruthenium(II) Organometallic Wire-Like Complexes, Chem. Asian J. 15 (2020) 3304.
[78] B. Kim, J.M. Beebe, C. Olivier, S. Rigaut, D. Touchard, J.G. Kushmerick, X.-Y. Zhu, C.D. Frisbie, Temperature and Length Dependence of Charge Transport in Redox-Active Molecular Wires Incorporating Ruthenium(II) Bis(-arylacetylide) Complexes, J. Phys. Chem. C 111 (2007) 7521.
[79] L. Luo, A. Benameur, P. Brignou, S.H. Choi, S. Rigaut, C.D. Frisbie, Length and Temperature Dependent Conduction of Ruthenium-Containing Redox-Active Molecular Wires, J. Phys. Chem. C 115 (2011) 19955.
[80] A. Mulas, Y.M. Hervault, L. Norel, S. Rigaut, C. Lagrost, Electron-Transfer Kinetics in Polymetallic Carbon-Rich Ruthenium(II) Bis(sigma-arylacetylides) Wires Connected to Gold, ChemElectroChem 2 (2015) 1799.
[81] A. Mulas, Y.-M. Hervault, X. He, E. Di Piazza, L. Norel, S. Rigaut, C. Lagrost, Fast Electron Transfer Exchange at Self-Assembled Monolayers of Organometallic Ruthenium(II) sigma-Arylacetylide Complexes, Langmuir 31 (2015) 7138.
[82] K. Sugimoto, Y. Tanaka, S. Fujii, T. Tada, M. Kiguchi, M. Akita, Organometallic molecular wires as versatile modules for energy-level alignment of the metal–molecule-metal junction, Chem. Commun. 52 (2016) 5796.
[83] Y. Tanaka, Y. Kato, T. Tada, S. Fujii, M. Kiguchi, M. Akita, Doping" of Polyyne with an Organometallic Fragment Leads to Highly Conductive Metallapolyyne Molecular Wire, J. Am. Chem. Soc. 140 (2018) 10080.
[84] S. Bock, O.A. Al-Owaedi, S.G. Eaves, D.C. Milan, M. Lemmer, B.W. Skelton, H.M. Osorio, R.J. Nichols, S.J. Higgins, P. Cea, N.J. Long, T. Albrecht, S. Martin, C.J. Lambert, P.J. Low, Single-Molecule Conductance Studies of Organometallic Complexes Bearing 3-Thienyl Contacting Groups, Chem. Eur. J. 23 (2017) 2133.
[85] R. Ezquerra, S.G. Eaves, S. Bock, B.W. Skelton, F. Perez-Murano, P. Cea, S. Martin, P.J. Low, New routes to organometallic molecular junctions via a simple thermal processing protocol, J. Mater.Chem. C 7 (2019) 6630.
[86] S. Almosni, A. Delamarre, Z. Jehl, D. Suchet, L. Cojocaru, M. Giteau, B. Behaghel, A. Julian, C. Ibrahim, L. Tatry, H. Wang, T. Kubo, S. Uchida, H. Segawa, N. Miyashita, R. Tamaki, Y. Shoji, K. Yoshida, N. Ahsan, K. Watanabe, T. Inoue, M. Sugiyama, Y. Nakano, T. Hamamura, T. Toupance, C. Olivier, S. Chambon, L. Vignau, C. Geffroy, E. Cloutet, G. Hadziioannou, N. Cavassilas, P. Rale, A. Cattoni, S. Collin, F. Gibelli, M. Paire, L. Lombez, D. Aureau, M. Bouttemy, A. Etcheberry, Y. Okada, J.-F. Guillemoles, Material challenges for solar cells in the twenty-first century: directions in emerging technologies, Sci. Tech. Adv. Mater. 19 (2018) 336.
[87] S. De Sousa, S. Lyu, L. Ducasse, T. Toupance, C. Olivier, Tuning visible-light absorption properties of Ru-diacetylide complexes: simple access to colorful efficient dyes for DSSCs, J. Mater. Chem. A. 3 (2015) 18256.

[88] Z. Liu, W. Li, S. Topa, X. Xu, X. Zeng, Z. Zhao, M. Wang, W. Chen, F. Wang, Y.-B. Cheng, H. He, Fine-Tuning of Fluorene-Based Dye Structures for High Efficiency p-Type Dye-Sensitized Solar Cells, ACS Appl. Mater. Interfaces 6 (2014) 10614.
[89] M. Meldal, C.W. Tornøe, Cu-Catalyzed Azide-Alkyne Cycloaddition, Chem. Rev. 108 (2008) 2952.
[90] A. Burgun, F. Gendron, P.A. Schauer, B.W. Skelton, P.J. Low, K. Costuas, J.-F. Halet, M.I. Bruce, C. Lapinte, Straightforward Access to Tetrametallic Complexes with a Square Array by Oxidative Dimerization of Organometallic Wires, Organometallics 32 (2013) 5015–5025.
[91] M.I. Bruce, Some Organometallic Chemistry of Tetracyanoethene: CN-displacement and Cycloaddition Reactions with Alkynyl-Transition Metal Complexes and Related Chemistry, Aust. J. Chem. 64 (2011) 77.
[92] M.I. Bruce, Reactions of polycyano-alkenes with alkynyl- and poly-ynyl-Group 8 metal complexes, J. Organomet. Chem. 730 (2013) 3.