Reviews

Diruthenium *σ*-Alkynyl Compounds: A New Class of Conjugated Organometallics

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Reviewed herein are key aspects of the recent progress in the chemistry of *σ*-alkynyl compounds of $Ru_2(LL)_4$, where LL is an N,N′-bidentate bridging ligand. Synthetic methodologies for both the mono-alkynyl Ru_2(II,III) and bis-alkynyl Ru_2(III,III) compounds have been thoroughly investigated. The basic electronic properties of these Ru_2(II,III) and Ru_2(III,III) compounds were elucidated on the basis of solution voltammetry and absorption spectroscopy, which revealed rich redox characteristics and small energy gaps ranging from 1.2 to 1.6 eV. Facile *electron* transfer across the polyyn-diyl chains was demonstrated on the basis of Ru_2-$(ap)_4$ type compounds (ap is 2-anilinopyridinate), and a very small electronic decay constant (β) of 0.063 Å^{-1} was determined. Also demonstrated was the long-range electronic coupling between Fc−Fc$^+$ termini bridged by a $-(C\equiv C)_m-Ru_2(DMBA)_4-(C\equiv C)_n-$ fragment (DMBA is *N,N′*-dimethylbenzamidinate), and high *hole* mobility across the Ru_2(III,III) unit was inferred. Illustrating the potential of metal−alkynyl compounds in molecular electronics, scanning tunneling microscopy (STM) studies of $Ru_2(ap)_4(\sigma$-OPE) embedded in an alkanethiol matrix revealed significantly improved molecular conductance compared to the OPE of comparable length (OPE is oligo(phenyleneethynylene)). Using the weak-base protocol, several donor−$Ru_2(DMBA)_4$−acceptor type compounds have been obtained, and their voltammetric characteristics are consistent with what are expected for a *molecular diode*. $Ru_2(ap)_4(C_{2n}R)$ type compounds undergo [2 + 2] cycloaddition/insertion reactions with TCNE, which drastically alter the electronic structures of metal−alkynyl compounds. Also described are the covalent modification chemistry both at the *σ*-alkynyl ligands and the periphery of N,N′-bridging ligands and supramolecular chemistry based on the latter modification.

I. Introduction

Organic π-conjugated compounds, especially those in oligomeric form, have found a broad range of applications as electronic and optoelectronic materials.[1−11] Recent years have also witnessed significant progress in utilizing tailored carbon-rich organometallic compounds as NLO chromophores,[12−15] photovoltaic polymers,[16,17] molecular emitters,[18] and prototypes of molecular electronic wires and molecular devices.[19] Many of the endeavors on the latter subject have been based on type **1a** compounds in Chart 1 with [M] as a mononuclear capping unit.[20−26] As expected for the

(1) Mullen, K.; Wegner, G. *Electronic Materials: the Oligomer Approach*; Wiley-VCH: Weinheim, Germany, and New York, 1998.
(2) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.
(3) Dalton, L. R. *J. Phys. Condens. Mater.* **2003**, *15*, R897.
(4) Halpern, J. *Pure Appl. Chem.* **2000**, *73*, 209.
(5) *Acetylene Chemistry: Chemistry, Biology and Materials Science*; Diederich, F., Tykwinski, R. R., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 2004.
(6) Brabec, C. J.; Dyakonov, V.; Parisi, J.; Sariciftci, N. S. *Organic Photovoltaics: Concepts and Realization*; Springer: Berlin, 2003.
(7) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350.
(8) Schwab, P. F. H.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863.
(9) Schwab, P. F. H.; Smith, J. R.; Michl, J. *Chem. Rev.* **2005**, *105*, 1197.
(10) Nielsen, M. B.; Diederich, F. *Chem. Rev.* **2005**, *105*, 1837.
(11) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537.

(12) Long, N. J. *Angew. Chem., Int. Ed.* **1995**, *34*, 21.
(13) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1998**, *42*, 291.
(14) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1999**, *43*, 349.
(15) Coe, B. J.; Curati, N. R. M. *Comments Inorg. Chem.* **2004**, *25*, 147.
(16) Lu, M.; Xie, B. H.; Kang, J. H.; Chen, F. C.; Yang, Y.; Peng, Z. H. *Chem. Mater.* **2005**, *17*, 402.
(17) Peng, Z. H. *Angew. Chem., Int. Ed.* **2004**, *43*, 930.
(18) Yam, V. W.-W. *Acc. Chem. Res.* **2002**, *35*, 555.
(19) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178−180*, 431.
(20) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, *50*, 179.
(21) Low, P. J.; Bruce, M. I. *Adv. Organomet. Chem.* **2001**, *48*, 71.
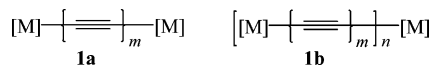(22) Chisholm, M. H. *Angew. Chem., Int. Ed.* **1991**, *30*, 673.
(23) Lang, H. *Angew. Chem., Int. Ed.* **1994**, *33*, 547.
(24) Bunz, U. H. F. *Angew. Chem., Int. Ed.* **1996**, *35*, 969.
(25) Long, N. J.; Williams, C. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2586.
(26) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2003**, *103*, 4175.

Chart 1. Dimeric and Oligomeric Metal−Polyyne-diyls[a]

[M]━┤═══┤ₘ━[M]   [M]━┤═══┤ₘ┤ₙ━[M]
    1a   **1b**

[a] *m, n* = integers.

model compounds of molecular wires, facile charge transfer between two [M] termini mediated by the polyyn-diyl bridge have been demonstrated through voltammetric studies in *bulk* solution with [M] as $CpRuP_2$ and CpRu(P−P), where P and P−P stand respectively for mono- and bidentate phosphines,[27−29] CpFe(P−P),[30−34] CpReP(NO),[35−41] and $Mn(P−P)_2I$.[42] Electronic interactions mediated by carbon-rich bridges can also be gauged from the magnitude of spin−spin couplings among paramagnetic metal centers determined from the temperature dependence of magnetism.[43] In comparison with polyyne-diyl bridged compounds, bimetallic compounds with bridges such as oligoen-diyl $((CH)_{2m})$[44,45] and ene-yne[46,47] are rare but exhibit wire-like behavior as well. More recently, attempts to interrogate the current−voltage (*I*−*V*) characteristics of metal−alkynyl species at both single- and few-molecule levels yielded mixed results: *trans*-Pt-$(PPh_3)_2(C≡CC_6H_4S)_2$ was studied with a mechanically controlled break junction and deemed as a *molecular insulator*,[48] and the series *trans*-Pt(PR₃)₂(C≡CC₆H₄S)₂ (R = Cy, Ph, Bu, OEt, OPh) were shown to be more conductive than OPE (oligo(phenyleneethynylene)) of

comparable lengths through the cross-wire junction measurement.[49] It is noteworthy that both the *trans*-Pt(PR₃)₂(C≡CC₆H₄S)₂ type compounds and the majority of organic molecules investigated as *molecular wires* have HOMO−LUMO gaps (E_g) ranging from 2.40 to 5.0 eV.[50] Clearly, there is still plenty of room for E_g reduction through molecular engineering, which should lead to a smaller tunneling decay parameter β and consequently higher molecular conductivity.[1,8,50] Our contention is that an optimal match in orbital energies between the metal unit and carbon-rich bridges will yield monomers displaying very small E_g's, which form type **1b** oligomers functioning as true molecular wires. It is historically important and prudent to recognize that type **1b** polymers based on both the coinage (Ag^+ and Au^+) and group 10 metal ions (Ni^{2+}, Pd^{2+}, and Pt^{2+}) have been known for over four decades.[51,52] Not surprisingly, these polymers are insulators,[53] due to either the closed-shell nature of Ag^+ and Au^+ or highly stable d^8 configuration of group 10 M^{2+} ions, highlighting the importance of choice of metal units.

Metal−alkynyl chemistry based on a dimetallic paddlewheel motif was first investigated by Cotton et al., where $Ru_2(ap)_4(C≡CPh)$ was obtained from the reaction between $Ru_2(ap)_4Cl$ and $LiC≡CPh$ (ap is 2-anilinopyridinate).[54−56] Subsequently, Bear and Kadish reported the synthesis of both the mono(acetylide) compound $Ru_2(DPhF)_4(C≡CPh)$ and bis(acetylide) compound $Ru_2(DPhF)_4(C≡CPh)_2$ (DPhF is *N,N*′-diphenylformamidinate).[57,58] Structural studies of these compounds clearly revealed the collinear geometry between the acetylide moieties and Ru−Ru vector and, thus, the promise of these types of compounds as the building blocks (monomers) for linear oligomers. However, assembly of oligomers based on these phenylethynyl complexes would necessitate aromatic C−H activation, a reaction that requires harsh conditions. An effective remedy is to replace phenylethynyl with a polyynyl species capped by a silyl group ($-(C≡C)_m SiR_3$), which can be easily converted to a terminal polyyne ($-(C≡C)_m -H$). These $Ru_2-(C≡C)_m -H$ species can be readily assembled into type **1a** and **1b** oligomers through either Glaser oxidative coupling or Sonogashira cross-coupling, both reactions requiring mild conditions.[5,59−61]

For metal σ-polyynyl compounds with one or more sterically unhindered C≡C units, various interesting

(27) Bruce, M. I.; Ellis, B. G.; Gaudio, M.; Lapinte, C.; Melino, G.; Paul, F.; Skelton, B. W.; Smith, M. E.; Toupet, L.; White, A. H. *Dalton Trans.* **2004**, 1601.
(28) Bruce, M. I.; Low, P. J.; Costuas, K.; Halet, J.-F.; Best, S. P.; Heath, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 1949.
(29) Bruce, M. I.; Denisovich, L. I.; Low, P. J.; Peregudova, S. M.; Ustynyuk, N. A. *Mendeleev Commun.* **1996**, 200.
(30) Le Narvor, N.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 357.
(31) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129.
(32) Coat, F.; Lapinte, C. *Organometallics* **1996**, *15*, 477.
(33) Coat, F.; Paul, F.; Lapinte, C.; Toupet, L.; Costuas, K.; Halet, J.-F. *J. Organomet. Chem.* **2003**, *683*, 368.
(34) Jiao, H.; Costuas, K.; Gladysz, J. A.; Halet, J.-F.; Guillemot, M.; Toupet, L.; Paul, F.; Lapinte, C. *J. Am. Chem. Soc.* **2003**, *125*, 9511.
(35) Zhou, Y.; Seyler, J. W.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 8509.
(36) Seyler, J. W.; Weng, W.; Zhou, Y.; Gladysz, J. A. *Organometallics* **1993**, *12*, 3802.
(37) Brady, M.; Weng, W.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2655.
(38) Bartik, T.; Bartik, B.; Brady, M.; Dembinski, R.; Gladysz, J. A. *Angew. Chem., Int. Ed.* **1996**, *35*, 414.
(39) Brady, M.; Weng, W.; Zou, Y.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Bohme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 775.
(40) Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 810.
(41) Meyer, W. E.; Amoroso, A. J.; Horn, C. R.; Jaeger, M.; Gladysz, J. A. *Organometallics* **2001**, *20*, 1115.
(42) Kheradmandan, S.; Heinze, K.; Schmalle, H. W.; Berke, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 2270.
(43) Paul, F.; Lapinte, C. In *Unusual Structures and Physical Properties in Organometallic Chemistry*; Gielen, M., Willem, R., Wrackmeyer, B., Eds.; Wiley: West Sussex, U.K., 2002.
(44) Chung, M. C.; Gu, X. H.; Etzenhouser, B. A.; Spuches, A. M.; Rye, P. T.; Seetharaman, S. K.; Rose, D. J.; Zubieta, J.; Sponsler, M. B. *Organometallics* **2003**, *22*, 3485.
(45) Liu, S. H.; Hu, Q. Y.; Xue, P.; Wen, T. B.; Williams, I. D.; Jia, G. *Organometallics* **2005**, *24*, 769.
(46) Rigaut, S.; Le Pichon, L.; Daran, J. C.; Touchard, D.; Dixneuf, P. H. *Chem. Commun.* **2001**, 1206.
(47) Rigaut, S.; Massue, J.; Touchard, D.; Fillaut, J.-L.; Golhen, S.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4513.
(48) Mayor, M.; Hänisch, C. v.; Weber, H. B.; Reichert, J.; Beckmann, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 1183.

(49) Schull, T. L.; Kushmerick, J. G.; Patterson, C. H.; George, C.; Moore, M. H.; Pollack, S. K.; Shashidhar, R. *J. Am. Chem. Soc.* **2003**, *125*, 3202.
(50) Salomon, A.; Cahen, D.; Lindsay, S.; Tomfohr, J.; Engelkes, V. B.; Frisbie, C. D. *Adv. Mater.* **2003**, *15*, 1881.
(51) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89.
(52) Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1980**, *40*, 149.
(53) Dray, A. E.; Wittmann, F.; Friend, R. H.; Donald, A. M.; Khan, M. S.; Lewis, J.; Johnson, B. F. G. *Synth. Met.* **1991**, *41*, 871.
(54) Chakravarty, A. R.; Cotton, F. A. *Inorg. Chim. Acta* **1986**, *113*, 19.
(55) Ren, T.; Xu, G.-L. *Comments Inorg. Chem.* **2002**, *23*, 355.
(56) Hurst, S. K.; Ren, T. *J. Organomet. Chem.* **2003**, *670*, 188.
(57) Li, Y.; Han, B.; Kadish, K. M.; Bear, J. L. *Inorg. Chem.* **1993**, *32*, 4175.
(58) Bear, J. L.; Han, B.; Huang, S.; Kadish, K. M. *Inorg. Chem.* **1996**, *35*, 3012.
(59) *Metal-catalyzed Cross-coupling Reactions*; Diederich, F.; Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998.
(60) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1988.
(61) *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, Germany, 1995.

Chart 2.   Ru$_2$(LL)$_4$(C$_{2n}$Y)$_x$ Building Blocks

2a   **2b**
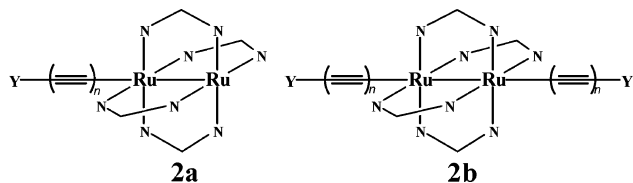
^{a} x = 1, 2; Y = H, SiR$_3$, Ph, Fc.

chemical transformations, typically involving electrophilic reactants, may occur. Both the cycloaddition insertion reaction with TCNE and the Pauson–Khand type addition of Co$_2$(CO)$_6$ fragment and subsequent rearrangement have been extensively examined by Bruce and co-workers.[20] The η^2 adducts between M–C≡C–R and Cu^I/Ag^I, especially the "tweezers" type based on Cp$_2$Ti(C≡C–R)$_2$, have been thoroughly investigated by Lang et al.[62,63] Recently, the η^2 adduct formation has been used to modulate electronic couplings between two Ru centers in [CpRu(P–P)]$_2$(μ-C$_4$) by Chen et al.[64] In a related example, PPEs (poly(phenyleneethynylene)) were cross-linked with both Pt^{II} and Pt^0 centers through η^2 coordination, and the Pt^0 cross-linked polymers exhibit ca. 10-fold enhancement in charge mobility compared with neat PPEs.[65,66] Modifications through η^2 coordination are often reversible and can be modulated with solvent polarity as well and may find broad application in metal–alkynyl chemistry. Two- and three-dimensional supramolecular assembly of metal–σ-alkynyl compounds is a new frontier that may lead to promising materials.[67] Notable examples include the tetra- and octanuclear platinum butadiyne squares,[68–70] Pt– and Ru–acetylide dendrimers,[71–76] and assemblies of chiral macrocycles based on square-planar Pt^{2+} units linked by BINOL-derived bis(alkynes).[77–79] Equally interesting is the use of π complexes bearing ethyne ring substituents as scaffolds for carbon-rich networks that may rival fullerene in both beauty and diversity of properties.[80]

(62) Lang, H.; George, D. S. A.; Rheinwald, G. *Coord. Chem. Rev.* **2000**, *206–207*, 101.
(63) Lang, H.; Kohler, K.; Blau, S. *Coord. Chem. Rev.* **1995**, *143*, 113.
(64) Gao, L.-B.; Zhang, L.-Y.; Shi, L.-X.; Chen, Z.-N. *Organometallics* **2005**, *24*, 1678.
(65) Huber, C.; Bangerter, F.; Caseri, W. R.; Weder, C. *J. Am. Chem. Soc.* **2001**, *123*, 3857.
(66) Kokil, A.; Shiyanovskaya, I.; Singer, K. D.; Weder, C. *J. Am. Chem. Soc.* **2002**, *124*, 9978.
(67) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853.
(68) Al-Qaisi, S. M.; Galat, K. J.; Chai, M.; Ray, D. G.; Rinaldi, P. L.; Tessier, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1998**, *120*, 12149.
(69) Bruce, M. I.; Costuas, K.; Halet, J.-F.; Hall, B. C.; Low, P. J.; Nicholson, B. K.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2002**, 383.
(70) Janka, M.; Anderson, G. K.; Rath, N. P. *Organometallics* **2004**, *23*, 4382.
(71) Leininger, S.; Stang, P. J.; Huang, S. P. *Organometallics* **1998**, *17*, 3981.
(72) Uno, M.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1714.
(73) Onitsuka, K.; Fujimoto, M.; Ohshiro, N.; Takahashi, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 689.
(74) Onitsuka, K.; Shimizu, A.; Takahashi, S. *Chem. Commun.* **2003**, 280.
(75) McDonagh, A. M.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B. *Organometallics* **1999**, *18*, 5195.
(76) Vicente, J.; Chicote, M.-T.; Alvarez-Falcón, M. M.; Jones, P. G. *Organometallics* **2005**, *24*, 2764.
(77) Lee, S. J.; Luman, C. R.; Castellano, F. N.; Lin, W. *Chem. Commun.* **2003**, 2124.
(78) Jiang, H.; Lin, W. *J. Am. Chem. Soc.* **2004**, *126*, 7426.
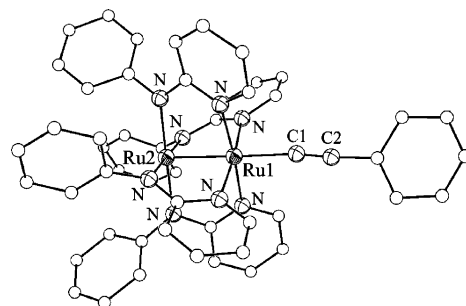

Figure 1. Structural plot of **1** generated from CSD (code DOJMIY).

II. Building Blocks

Diruthenium–alkynyl building blocks generally consist of two classes of compounds: mono(alkynyl) and bis(alkynyl) axial adducts as shown in Chart 2. Monoadducts are formally diruthenium(II,III) species, which are *valence-averaged* (i.e. two Ru$^{2.5+}$ centers) due to the Ru–Ru multiple bonding and typically paramagnetic species with an $S = {}^3/_2$ ground state (^{4}B$_2$ in an idealized D_4 symmetry).[81,82] Bis(adducts) are diruthenium(III,III) species that are diamagnetic and contain a Ru–Ru single bond.[81] The N,N'-bidentate bridging ligands (LL) utilized in supporting the Ru$_2$ core include 2-anilinopyridinate (ap) and its anilino-substituted derivatives, N,N'-diarylformamidinates (DArF), and N,N'-dimethylbenzamidinate (DMBA) and its phenyl-substituted derivatives. This section is grouped according to N,N'-bidentate ligands.

Ru$_2$(ap)$_4$-Based Compounds. Ru$_2$(ap)$_4$(C≡CPh) (**1**; Figure 1),[54] the first characterized paddlewheel alkynyl species, is a Ru$_2$(II,III) compound supported by four bridging ap ligands in a so-called (4,0) arrangement, where all pyridine N centers coordinate to the same ruthenium center (Ru1) and all anilino N centers coordinate to the other (Ru2). More recently, several Ru$_2$(ap)$_4$(C≡CY) type compounds were prepared from reactions between Ru$_2$(ap)$_4$Cl and 1 equiv of LiC$_2$Y with Y as SiMe$_3$, Si^{i}Pr$_3$, and CH$_2$OCH$_3$,[83,84] where the (4,0) arrangement was crystallographically established in several cases.

Similar to the aforementioned preparation of Ru$_2$(DPhF)$_4$-containing compounds, the anaerobic reaction between Ru$_2$(ap)$_4$Cl and LiC$_2$Y (Y = Ph, C$_2$SiMe$_3$) in 10–20-fold excess resulted in a solution of burgundy color, which turned dark blue on aerobic quenching. TLC analysis revealed the presence of both Ru$_2$(ap)$_4$-(C≡CY) (brownish green) and Ru$_2$(ap)$_4$(C≡CY)$_2$ (royal blue), and their separation is effected via silica column chromatography.[84–86] The formation of Ru$_2$(ap)$_4$(C≡CY)$_2$ is explained by an equilibrium between Ru$_2$(ap)$_4$(C≡CY) and [Ru$_2$(ap)$_4$(C≡CY)$_2$]$^-$ prior to the quenching, as

(79) Zhang, L.; Niu, Y. H.; Jen, A. K. Y.; Lin, W. B. *Chem. Commun.* **2005**, 1002.
(80) Bunz, U. H. F. *J. Organomet. Chem.* **2003**, *683*, 269.
(81) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Oxford University Press: Oxford, U.K., 1993.
(82) Miskowski, V. M.; Hopkins, M. D.; Winkler, J. R.; Gray, H. B. In *Inorganic Electronic Structure and Spectroscopy*; Solomon, E. I., Lever, A. B. P., Eds.; Wiley: New York, 1999; Vol. 2.
(83) Zou, G.; Alvarez, J. C.; Ren, T. *J. Organomet. Chem.* **2000**, *596*, 152.
(84) Ren, T. *Organometallics* **2002**, *21*, 732.
(85) Xu, G.-L.; Ren, T. *Organometallics* **2001**, *20*, 2400.
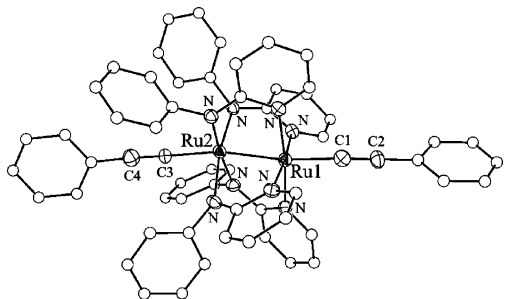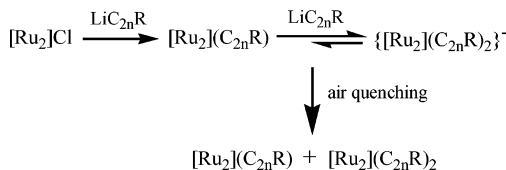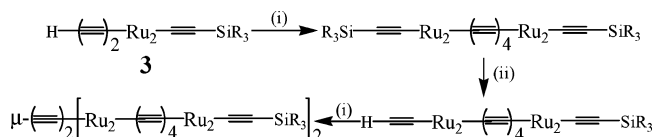(86) Xu, G.-L.; Ren, T. *J. Organomet. Chem.* **2002**, *655*, 239.

Figure 2. Structural plot of compound **2**.

Scheme 1.　Stepwise Formation of Mono- and Bis(alkynyl) Adducts

$$[Ru_2]Cl \xrightarrow{LiC_{2n}R} [Ru_2](C_{2n}R) \underset{\longleftarrow}{\overset{LiC_{2n}R}{\rightleftharpoons}} \{[Ru_2](C_{2n}R)_2\}^-$$

$$\downarrow \text{air quenching}$$

$$[Ru_2](C_{2n}R) + [Ru_2](C_{2n}R)_2$$

Scheme 2.　Iterative Divergent/Convergent Synthesis of Type 1b Monodisperse Oligomers: (i) Glaser Coupling; (ii) Selective Desilylation

shown in Scheme 1. As exemplified by the structural plot of $Ru_2(ap)_4(C\equiv CPh)_2$ (**2**; Figure 2), the second alkynyl ligand occupies the axial position (4-position) opposite to the first alkynyl. However, the 4-position is more crowded than the 0-position due to the bulkness of four anilino groups, which limits the accessibility of the 4-position. This is evident in that $Ru_2(ap)_4(C\equiv CSiR_3)$ with R being methyl or isopropyl remains as the sole product, regardless of the number of equivalents of $LiC\equiv CSiR_3$ used.[84] Such "size" selectivity enables the synthesis of unsymmetric $(YC\equiv C)Ru_2(ap)_4(C\equiv CSiR_3)$ type compounds with Y = C_2SiMe_3, Ph.[84,86] Of particular interest are the compounds $(Me_3SiC_4)Ru_2(ap)_4(C\equiv CSiR_3)$, which can be selectively desilylated using K_2CO_3 to yield $(HC_4)Ru_2(ap)_4(C\equiv CSiR_3)$ (**3**).[84] This type of compound, which is an organometallic version of orthogonal synthons, may be useful in the iterative divergent−convergent synthesis of type **1b** oligomers by analogy to Tour's work on OPEs,[11,87] where the length of oligomer is precisely doubled during each iteration (Scheme 2).

While $Ru_2(ap)_4(C_{2n}SiR_3)$ type compounds with $n = 1-3$ can be readily obtained via the transmetalation reaction between $Ru_2(ap)_4Cl$ and $M'C_{2n}SiR_3$ (M' = Li, SnR'_3),[85,88] preparation of compounds with $n \geq 4$ becomes difficult due to the thermal instability of the corresponding polyynes $HC_{2n}SiR_3$. Effective alternatives to mitigate this difficulty include the Cadiot−Chodkiewicz reaction between {M}−$C_{2m}Cu$ and $BrC_{2n}Y$ to yield {M}−$C_{2(m+n)}Y$,[89−91] the reaction between {M}−C≡

Scheme 3.　Synthesis of $Ru_2(ap)_4(C_{2n}Y)^a$
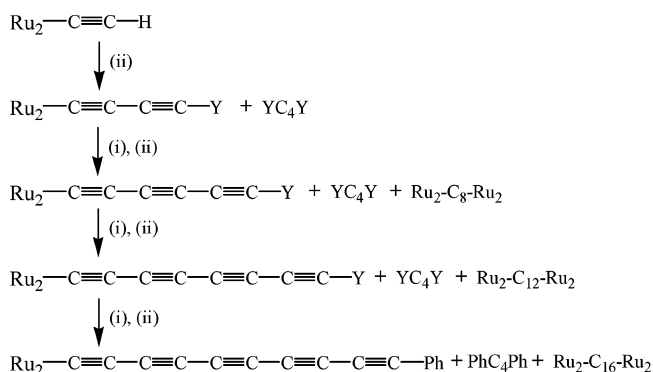
^{a} $Ru_2(ap)_4$ = Ru_2. Legend: (i) Y = Si^iPr_3, Bu_4NF; (ii) HC_2Y (Y = Si^iPr_3, Ph), CuCl, TMEDA, O_2, room temperature.

Chart 3.　Modified ap Ligands: MeOap (Left) and DiMeOap (Right)
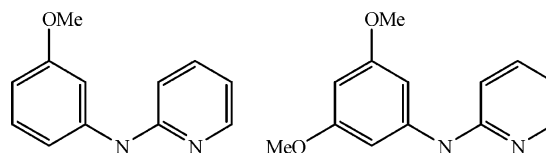
C−$Au(PR_3)$ and $XC\equiv CY$ that is driven by the elimination of $XAu(PR_3)$ (X = halide),[92,93] and the Glaser oxidative coupling reaction between {M}−$C_{2m}H$ and $HC_{2n}Y$.[94−96] Using the last approach, we have prepared two series of $Ru_2(ap)_4(C_{2n}Y)$ with Y = Si^iPr_3 ($n = 1-4$), Ph ($n = 1-5$) according to the sequence outlined in Scheme 3.[97] The main attraction of this approach is its mild reaction conditions. As shown in Scheme 3, the homocoupling of Ru_2−$C_{2n}H$ becomes a competitive reaction path with $n \geq 2$ and can be suppressed partially with the use of organic alkynes in large excess. The difficulty in preparing compounds of $n > 5$ was noted due to the instability of $Ru_2(ap)_4(C_{2n}Si^iPr_3)$ ($n > 4$), which was desilylated in situ under Hay conditions.

$Ru_2(ap)_4$-based compounds can be difficult to handle at times, due to their low solubility in common organic solvents. This problem may be circumvented through the substitution of methoxy group(s) on the anilino group of ap ligands, as shown in Chart 3,[98] which have significantly improved the solubility of $Ru_2(ap)_4$−alkynyls with a minimal alteration of electronic properties. A structural example of metal−alkynyl compounds based on derivatized ap is shown in Figure 3. Ru_2−phenylacetylide compounds based on fluorinated ap ligands (F_xap) were investigated by Bear and Kadish,

(87) Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem., Int. Ed.* **1994**, *33*, 1360.

(88) Cotton, F. A.; Stiriba, S. E.; Yokochi, A. *J. Organomet. Chem.* **2000**, *595*, 300.

(89) Dembinski, R.; Lis, T.; Szafert, S.; Mayne, C. L.; Bartik, T.; Gladysz, J. A. *J. Organomet. Chem.* **1999**, *578*, 229.

(90) Yam, V. W.-W.; Chong, S. H.-F.; Ko, C.-C.; Cheung, K.-K. *Organometallics* **2000**, *19*, 5092.

(91) Bruce, M. I.; Kramarczuk, K. A.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2005**, *690*, 1549.

(92) Bruce, M. I.; Humphrey, P. A.; Melino, G.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *Inorg. Chim. Acta* **2005**, *358*, 1453.

(93) Bruce, M. I.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Organomet. Chem.* **2003**, *683*, 398.

(94) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 2632.

(95) Mohr, W.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Chem. Eur. J.* **2003**, *9*, 3324.

(96) Mohr, W.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Inorg. Chem.* **2001**, *40*, 3263.

(97) Xu, G.-L.; Ni, Y.-H.; Wang, C.-Y.; Goodson, T. G.; Ren, T. *Organometallics* **2005**, *24*, 3247.

(98) Xu, G.-L.; Cordova, A.; Ren, T. *J. Cluster Sci.* **2004**, *15*, 413.

Table 1. Bond Lengths (Å) and Angles (deg) of Selected $Ru_2(ap)_4(C_2Y)_x$ Compounds ($x = 1, 2$)

|	Ru–Ru	Ru–C$_{av}$	Ru–N$_{av}$	C$_\alpha$–C$_\beta$	Ru–Ru–C$_\alpha$
			$x = 1$		
$Ru_2(ap)_4(C_2Ph)$[54]	2.319(3)	2.08(3)	2.066[17]	1.14(3)	178.0(8)
$Ru_2(ap)_4(C_2SiMe_3)$[83]	2.3162(5)	2.077(4)	2.071[2]	1.207(6)	180.0
$Ru_2(ap)_4(C_4SiMe_3)$[85]	2.3303(9)	2.075(9)	2.078[7]	1.207(11)	178.5(3)
$Ru_2(DiMeOap)_4(C_4SiMe_3)$[101]	2.3245(6)	2.089(6)	2.068[5]	1.210(7)	179.2(2)
$Ru_2(ap)_4(C_6H)$[97]	2.3277(6)	2.076(8)	2.063[3]	1.211(11)	180.0
			$x = 2$		
$Ru_2(ap)_4(C_2Ph)_2$[86]	2.4707(3)	1.988[2]	2.0618[18]	1.204[3]	162.99[7]
$Ru_2(ap)_4(C_4SiMe_3)_2$[85]	2.4717(11)	1.947[10]	2.037[8]	1.222[13]	163.5[3]
$(Me_3SiC_4)[Ru_2(ap)_4](C_2Si^iPr_3)$[84]	2.4584(6)	1.966[5]	2.060[4]	1.198[6]	176.43[16]
$(HC_4)[Ru_2(ap)_4](C_2SiMe_3)$[84]	2.4662(3)	1.969[3]	2.056[2]	1.210[4]	165.08[8]
$(PhC_2)[Ru_2(ap)_4](C_4SiMe_3)$[86]	2.4342(8)	1.966[7]	2.061[4]	1.168[10]	180.0

and the coexistence of several regioisomers was prevalent, due to the labile nature of F$_x$ap ligands.[99,100]
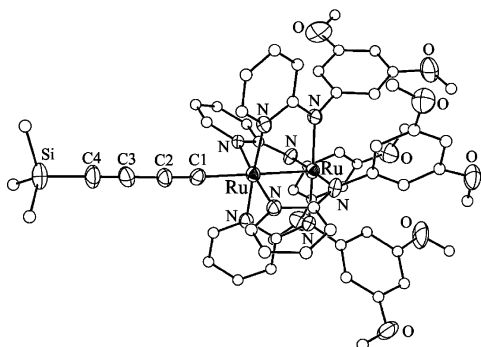

Figure 3. Structural plot of $Ru_2(DiMeOap)_4(C_4SiMe_3)$.

Some key bond lengths and angles of selected $Ru_2(ap)_4(C_2Y)_x$ ($x = 1, 2$) compounds are gathered in Table 1. The Ru–Ru distances of $Ru_2(ap)_4(C_2Y)$ type compounds are within a narrow range of 2.316(1)–2.330(1) Å, which is consistent with a Ru–Ru bond order of 2.5. Ru–C$_\alpha$ distances are about 2.08 Å, and the Ru–Ru–C$_\alpha$ vector is linear or almost linear in all cases. The Ru–Ru distances of $Ru_2(ap)_4(C_2Y)_2$ type compounds range from 2.434(1) to 2.472(1) Å and are significantly longer than those of the mono compounds. The elongation of the Ru–Ru bond is due to the formation of two strong σ(Ru–C$_\alpha$) bonds, which effectively nullifies the σ(Ru–Ru) bond. The first coordination sphere around the Ru$_2$ core in the bis compounds tends to deviate significantly from the idealized D_{4h}, as revealed in Figure 2 and Ru–Ru–C$_\alpha$ angles in Table 1, and the distortion can be attributed to a second-order Jahn–Teller (J-T) effect.[102] Absence of such distortions is noted for both $(Me_3SiC_4)[Ru_2(ap)_4](C_2Si^iPr_3)$ and (PhC_2)-$[Ru_2(ap)_4](C_4SiMe_3)$, which can be attributed to the suppression of J-T effect by the bulkiness of the acetylene substituent Si^iPr_3 and the imposed crystallographic symmetry, respectively.

$Ru_2(DArF)_4$-Based Compounds. Earlier work of Bear and Kadish demonstrated that treating $Ru_2(DPhF)_4$-Cl (DPhF is diphenylformamdinate) with LiC≡CPh in large excess yielded either $Ru_2(DPhF)_4(C≡CPh)$, if the solvent removal was carried out in vacuo, or *trans*-Ru$_2$-$(DPhF)_4(C≡CPh)_2$, if the solution was stirred in air prior to the solvent removal.[57,58,102] The formation of both the mono and bis adducts can be explained by the equilibrium outlined in Scheme 1. The synthesis of butadiynyl compounds follows that of phenylethynyl compounds: $Ru_2(DmAniF)_4Cl$ (DmAniF is bis(*m*-methoxyphenyl)-formamdinate) reacted with 3 equiv of LiC_4SiMe_3, resulting in a mixture of $Ru_2(DmAniF)_4(C_4SiMe_3)$ (42% purified yield) and $Ru_2(DmAniF)_4(C_4SiMe_3)_2$ (28% purified yield), which were separated on silica columns.[103] Similar results were also obtained with Ru$_2$ compounds supported by DArF species with aryl as both *m*-ClC$_6$H$_4$ and *m*-CF$_3$C$_6$H$_4$ ($Ru_2(DmClPhF)_4(C_4SiMe_3)_2$ (**4**) is shown in Figure 4).[101] Kuhn et al. reported that treating
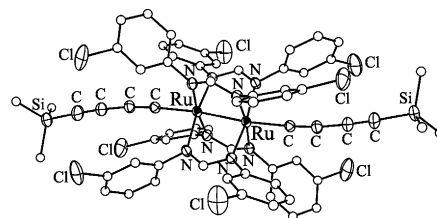
Figure 4. Structural plot of compound **4**.

$Ru_2(DArF)_4Cl$ (Ar = Ph, *p*-tolyl) with an excess of LiC$_2$-4-py resulted in the bis compound *trans*-Ru$_2$-$(DArF)_4(C_2$-4-py$)_2$, which bridges two Re($^tBu_2$bpy)(CO)$_3$ fragments through py-*N* centers to yield an interesting heterometallic supramolecule.[104] Alternatively, the stoichiometric metathesis of the axial chloro ligand by a polyynyl ligand can be achieved with a trimethylstannyl alkynyl agent under Stille coupling conditions,[105] yielding only the mono(polyynyl adduct) (Ru$_2$-$(DmAniF)_4(C_6SiMe_3)$ (**5**), shown in Figure 5).[101]
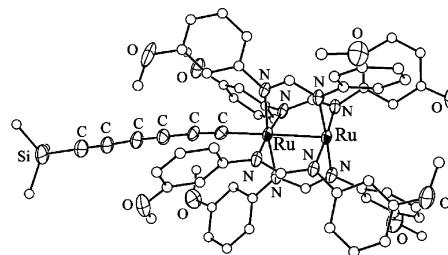
Figure 5. Structural plot of compound **5**.

Some interesting trends can be noted for mono-(alkynyl) compounds in Table 2: the Ru–Ru bond lengths of butadiynyl and hexatriynyl adducts are longer than that of phenylethynyl, while the opposite trend is true for the Ru–C bond lengths. Electron-deficient C$_4$R and C$_6$R ligands form stronger σ(Ru–C)

(99) Kadish, K. M.; Phan, T. D.; Wang, L.-L.; Giribabu, L.; Thuriere, A.; Wellhoff, J.; Huang, S.; Caemelbecke, E. V.; Bear, J. L. *Inorg. Chem.* **2004**, *43*, 4825.

(100) Bear, J. L.; Li, Y.; Han, B.; Caemelbecke, E. V.; Kadish, K. M. *Inorg. Chem.* **2001**, *39*, 182.

(101) Xu, G.-L.; Ren, T. Unpublished results.

(102) Lin, C.; Ren, T.; Valente, E. J.; Zubkowski, J. D. *J. Chem. Soc., Dalton Trans.* **1998**, 571.

Table 2. Bond Lengths (Å) and Angles (deg) of Selected $Ru_2(DArF)_4(C_2Y)_x$ Compounds (x = 1, 2)

|	Ru−Ru	Ru−C_{av}	Ru−N_{av}	C_α−C_β	Ru−Ru−C_α
$Ru_2(DmClPhF)_4(C_2Ph)$[106]	2.3868(10)	2.057(9)	2.082[6]	1.191(11)	180.0
$Ru_2[D(3,5-Cl_2Ph)F]_4(C_2Ph)$[106]	2.4285(11)	2.036(9)	2.058[6]	1.197(12)	180.0
$Ru_2(DmAniF)_4(C_4SiMe_3)$[103]	2.5060(5)	2.027(5)	2.046[3]	1.207(6)	175.34(12)
$Ru_2(DmAniF)_4(C_6SiMe_3)$[101]	2.4936(8)	2.015(7)	2.036[6]	1.228(9)	179.1(2)
$Ru_2(DpClPhF)_4(C_2Ph)_2$[102]	2.5554(12)	1.991[5]	2.054[4]	1.195[7]	158.8[2]
$Ru_2(DmAniF)_4(C_4SiMe_3)_2$[103]	2.5990(3)	1.947[2]	2.056[2]	1.206[3]	164.34[7]
$Ru_2(DmClPhF)_4(C_4SiMe_3)_2$[101]	2.5600(4)	1.970[3]	2.060[2]	1.211[4]	158.29[8]
trans-$Ru_2(DptolF)_4(C_2py$-$Re(CO)_3(^tBubipy))_2$[104]	2.5664(4)	1.961(4)	2.048[3]	1.204(6)	161.12(10)

Chart 4. *N,N′*-Dimethylbenzamidines (Left) HDMBA (X = H), HMeODMBA (X = 3-CH_3O), and HDiMeODMBA (X = 3,5-$(CH_3O)_2$) and *N,N′*-Diethylbenzamidine (HDEBA, Right)
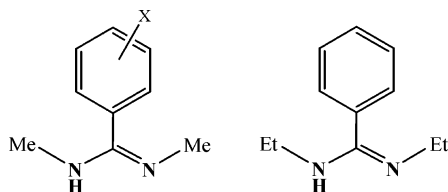
bonds at the expense of the σ(Ru−Ru) bond. The Ru−Ru−C_{2n}R vector is linear or very close to linearity in the mono species. The bis compounds exhibit very pronounced nonlinear Ru−Ru−C linkages, which is clearly the result of the aforementioned second-order Jahn−Teller distortion. The Ru−Ru bond lengths of the bis species are the longest among known Ru_2-paddle-wheel species and are consistent with the absence of the σ(Ru−Ru) bond.

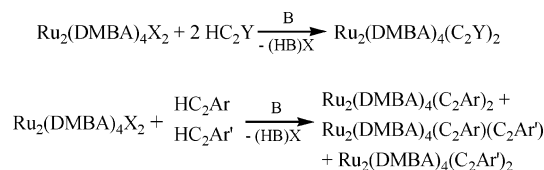**$Ru_2(DMBA)_4$-Based Compounds.** While Ru_2−alky-nyl compounds supported by either DArF or ap ligands exhibit promising electronic properties (see discussion below), both types of ligands have aryls protruding along axial directions, which would necessitate the use of a long polyyn-diyl in forming type **1b** oligomers (Chart 1). Since the electronic coupling generally decays exponentially over distance, it is desirable to shorten the polyyn-diyl bridge via the use of N,N′-bidentate ligands of a minimized steric bulkiness along the axial directions. *N,N′*-Dimethylbenzamidinate (DMBA; Chart 4) and its phenyl-substituted derivatives are particularly suitable.[107−110] The starting diruthenium compound, $Ru_2(DMBA)_4Cl_2$, was readily prepared from $Ru_2(OAc)_4$-Cl and HDMBA in the presence of LiCl and Et_3N, and Ru_2(III,III) compounds supported by the derivatized DMBA ligands were also similarly prepared.

Both $Ru_2(DMBA)_4Cl_2$ and its analogues readily react with 2 equiv of LiC_2Y (Y = Ph, C_6H_4-4-NMe_2, Fc, C_2Fc, SiR_3, C_2SiR_3) to yield the corresponding $Ru_2(DMBA)_4$-$(C_2Y)_2$ type compounds. However, no evidence of the formation of mono(alkynyl) species was found in reactions where the stoichiometry of LiC_2Y was varied between 1 and 2 equiv. The minimized steric crowding

around the axial positions of the Ru_2 unit was confirmed with the successful isolation of the compounds of −C_2Fc and −C_2SiR_3, both bulky ethynyl ligands, and the structure of $Ru_2(DiMeODMBA)_4(C≡CSi^iPr_3)_2$ (**6**) is shown in Figure 6.[108] Unsymmetric bis(alkynyl) compounds *trans*-$(Y'C_2)Ru_2(DMBA)_4(C_2Y)$ (Y, Y′ = Fc, C_2Fc, SiR_3; Y ≠ Y′) were obtained from the reaction between $Ru_2(DMBA)_4Cl_2$ and the mixture of LiC_2Y and LiC_2Y' along with the corresponding symmetric compounds, and they were separated on silica columns.[111]
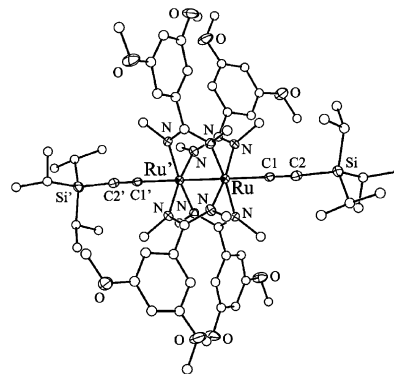
Figure 6. Structural plot of compound **6**.

$Ru_2(DMBA)_4Cl_2$ readily reacts with AgX (X = NO_3^- and BF_4^-) to afford $Ru_2(DMBA)_4X_2$, where the putative counterion X functions as the axial ligand, as revealed by structural studies.[109] Surprisingly, $Ru_2(DMBA)_4X_2$ reacts with *unactivated* terminal alkynes HC_2Y (Y = Ph, Fc, SiR_3, C_2SiR_3) at room temperature in the presence of weak bases such as Et_3N and Et_2NH to furnish the bis(alkynyl) compounds (Scheme 4).[108,110,111]

Scheme 4. Weak-Base Protocol for Symmetric and Unsymmetric Alkynylation[a]

$$Ru_2(DMBA)_4X_2 + 2\ HC_2Y \xrightarrow[-\ (HB)X]{B} Ru_2(DMBA)_4(C_2Y)_2$$

$$Ru_2(DMBA)_4X_2 + \begin{array}{c} HC_2Ar \\ HC_2Ar' \end{array} \xrightarrow[-\ (HB)X]{B} \begin{array}{l} Ru_2(DMBA)_4(C_2Ar)_2 + \\ Ru_2(DMBA)_4(C_2Ar)(C_2Ar') \\ + Ru_2(DMBA)_4(C_2Ar')_2 \end{array}$$

[a] B = Et_3N, Et_2NH

One of the advantages of the weak-base protocol is the facile preparation of compounds containing functional groups sensitive to organolithium agents, which was demonstrated by the high-yield synthesis of $Ru_2(DMBA)_4$-$(C_2C_6H_4$-4-$NO_2)_2$.[110] In addition, the weak-base protocol does not require anaerobic or anhydrous conditions, which permits continuous monitoring of the reaction progress, and the optimization of other reaction

(103) Xu, G.-L.; Ren, T. *Inorg. Chem.* **2001**, *40*, 2925.

(104) Zuo, J.-L.; Herdtweck, E.; Kühn, F. E. *Dalton Trans.* **2002**, 1244.

(105) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

(106) Lin, C.; Ren, T.; Valente, E. J.; Zubkowski, J. D. *J. Organomet. Chem.* **1999**, *579*, 114.

(107) Xu, G.-L.; Campana, C.; Ren, T. *Inorg. Chem.* **2002**, *41*, 3521.

(108) Xu, G.-L.; Jablonski, C. G.; Ren, T. *J. Organomet. Chem.* **2003**, *683*, 388.

(109) Xu, G.-L.; Jablonski, C. G.; Ren, T. *Inorg. Chim. Acta* **2003**, *343*, 387.

(110) Hurst, S. K.; Xu, G.-L.; Ren, T. *Organometallics* **2003**, *22*, 4118.

(111) Ying, J.-W.; Sobransingh, D. R.; Xu, G.-L.; Kaifer, A. E.; Ren, T. *Chem. Commun.* **2005**, 357.

Table 3. Bond Lengths (Å) and Angles (deg) of Selected $Ru_2(DMBA)_4(C_2Y)_2$ Compounds

	Ru–Ru	Ru–C_{av}	Ru–N_{av}	C_α–C_β	Ru–Ru–C_α
$Ru_2(DMBA)_4(C_2SiMe_3)_2$[107]	2.4501(6)	1.955(4)	2.046[3]	1.207(6)	174.8(1)
$Ru_2(DiMeODMBA)_4(C_2Si^iPr_3)_2$[108]	2.4760(7)	1.991(4)	2.060[3]	1.205(6)	161.0(1)
$Ru_2(DMBA)_4(C_4H)_2$[107]	2.4559(6)	1.952[5]	2.045[4]	1.206[6]	170.5[1]
$Ru_2(DMBA)_4(C_2Fc)_2$[113]	2.4386(9)	1.979[9]	2.042[7]	1.20[1]	169.2[3]
$Ru_2(DMBA)_4(C_4Fc)_2$[114]	2.4453(8)	1.970[8]	2.037[6]	1.18[1]	178.2[3]
$Ru_2(DMBA)_4(C_2Fc)(C_4Fc)$[114]	2.4544(9)	1.969[8]	2.038[7]	1.21[1]	166.2[3]
$Ru_2(MeODMBA)_4(C_2Ph)_2$[108]	2.4478(9)	1.996(7)	2.042[5]	1.20(1)	177.5(6)
$Ru_2(DEBA)_4(C_2Ph)_2$[108]	2.4588(9)	1.984(6)	2.050[5]	1.192(8)	168.3(2)
$Ru_2(DMBA)_4(C_2C_6H_4$-4-$NO_2)_2$[110]	2.459(1)	1.982(7)	2.040[5]	1.190(9)	176.3(7)
$Ru_2(DMBA)_4(C_2C_6H_4$-4-$NO_2)(C_2Ph)$[112]	2.4630(7)	1.994[10]	2.055[11]	1.20[2]	160.5[4]
$Ru_2(DMBA)_4(C_2C_6H_4$-4-$NMe_2)(C_2Ph)$[112]	2.4543(6)	1.990[6]	2.039[5]	1.195[8]	168.2[2]
$Ru_2(DMBA)_4(C_2C_6H_4$-4-$NMe_2)_2$[112]	2.4405(9)	1.981[9]	2.038[7]	1.20[1]	172.6[2]
$Ru_2(DMBA)_4(C_2C_6H_4$-4-$NMe_2)(C_2Ph$-4-$NO_2)$[112]	2.4506(6)	1.992(6)	2.039[4]	1.192[4]	166.9[2]

conditions, such as the nature of bases and stoichiometry of alkynes in leading to the formation of exotic unsymmetric $Ru_2(DMBA)_4(C_2Ar)(C_2Ar')$ type compounds (Scheme 4), where Ar and Ar′ are phenyls bearing donor or acceptor substituents.[112]

Despite great variation in the nature of alkynyl ligands, the Ru–Ru distances of $Ru_2(DMBA)_4(C_2Y)_2$ type compounds are within the narrow range of 2.439(1)– 2.476(1) Å (Table 3), which are about the same as those of the bis compounds based on $Ru_2(ap)_4$ but much shorter than those based on $Ru_2(DArF)_4$. In contrast to the ap- and DArF-based bis adducts, the second-order Jahn–Teller distortion is less pronounced (or suppressed), as reflected by the Ru–Ru–C angles. Also noteworthy is the insensitivity of Ru–Ru bond lengths toward the donor/acceptor substitution on phenylethynyl ligands.[110,112]

Voltammetric and Spectral Properties of the Building Blocks. Redox behaviors of the above-mentioned mono- and bis(alkynyl) compounds have been carefully examined with both cyclic (CV) and differential
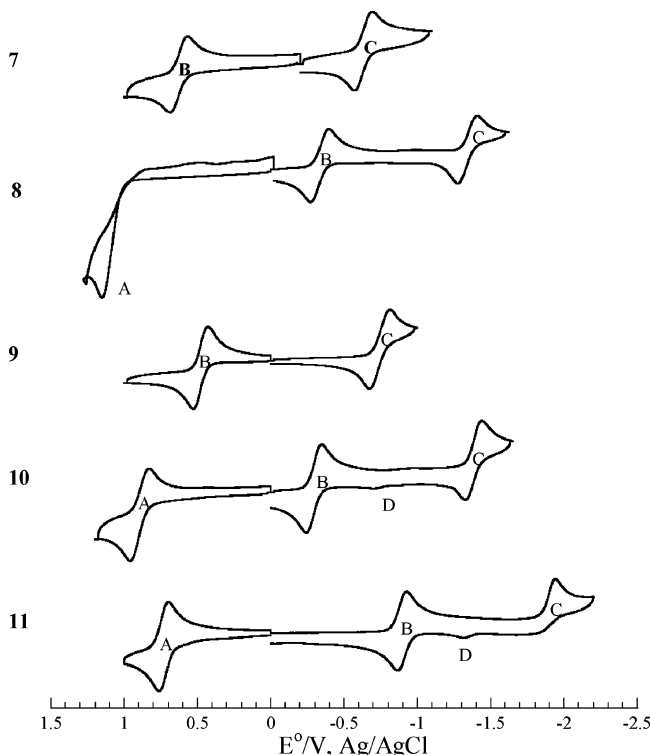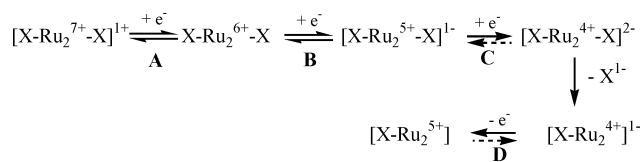
Scheme 5. Redox and Related Chemical Step in $Ru_2(LL)_4X_2^a$

$$[\text{X-Ru}_2^{7+}\text{-X}]^{1+} \xrightleftharpoons{+ e^-}_{A} \text{X-Ru}_2^{6+}\text{-X} \xrightleftharpoons{+ e^-}_{B} [\text{X-Ru}_2^{5+}\text{-X}]^{1-} \xrightarrow{+ e^-}_{C} [\text{X-Ru}_2^{4+}\text{-X}]^{2-}$$
$$\downarrow - X^{1-}$$
$$[\text{X-Ru}_2^{5+}] \xrightleftharpoons{- e^-}_{D} [\text{X-Ru}_2^{4+}]^{1-}$$

^{a} X = butadiynyl.

Table 4. Electrochemical and Spectroscopic Data of Selected Diruthenium–Butadiynyl Modules

	$Ru_2(ap)_4$-$(C_4SiMe_3)_n$		$Ru_2(DmAniF)_4$-$(C_4SiMe_3)_n$		$Ru_2(DMBA)_4$-$(C_4SiMe_3)_2$
	n = 1	n = 2	n = 1	n = 2	
$E(+/0)$, V	0.48	0.90	0.63	1.17^a	0.73
$E(0/-)$, V	−0.74	−0.29	−0.63	−0.32	−0.90
$E(-/2-)$, V	NA^d	−1.38^a	NA	−1.32	−1.94^a
E_g,^{b} V	1.22	1.19	1.26	1.49	1.63
E_{op},^{c} eV	1.63	1.19	1.08	1.35	1.40

^{a} Irreversible couple; $E_{p,a}$ or $E_{p,c}$ is reported. ^{b} $E_g = E(+/0) - E(0/-)$. ^{c} $E_{op} = 10^7/(8065.5\lambda_{max})$. ^{d} NA = not applicable.

pulse voltammetric (DPV) techniques. While the details have been given in original publications,[85,103,107] the CVs obtained for the butadiynyl complexes from all three series are given in Figure 7 along with the assignment of the observed couples in Scheme 5, and the potential data are summarized in Table 4. The mono(butadiynyl) species $Ru_2(DmAniF)_4(C_4SiMe_3)$ (**7**) and $Ru_2(ap)_4$-(C_4SiMe_3) (**9**) both exhibit an oxidation (**B**) and a reduction (**C**), and the electrode potentials ($E_{1/2}$) of the latter compound are cathodically shifted from that of the former by at least 100 mV. The bis(butadiynyl) species $Ru_2(DmAniF)_4(C_4SiMe_3)_2$ (**8**), $Ru_2(ap)_4(C_4SiMe_3)_2$ (**10**), and $Ru_2(DMBA)_4(C_4SiMe_3)_2$ (**11**) all display three one-electron processes: an oxidation (**A**) and two successive reductions (**B** and **C**). The $E_{1/2}$ values for each of three processes are in the following order across the series: DmAniF > ap ≫ DMBA, which reflects the order of donor ability of N,N′-bridging ligands: DmAniF < ap ≪ DMBA. The second reduction at a very negative potential regime leads to the partial (ap) or complete (DMBA) dissociation of an axial butadiynyl ligand and results in a mono(butadiynyl) species that is reoxidized on the backward sweep (**D**).

Since the oxidation and reduction correspond to the removal and addition of an electron to the HOMO and LUMO, respectively, the HOMO–LUMO gap for the solvated species (E_g) can be readily assessed: $E_g =$

Figure 7. Cyclic voltammograms of compounds **7−11** recorded in a 0.20 M THF solution of Bu_4NPF_6 at a scan rate of 0.10 V/s. [Ru_2] ≈ 1 mM.

(112) Ying, J.-W.; Xu, G.-L.; Cordova, A.; Ren, Y. T.; Ren, T. Unpublished results.

Scheme 6
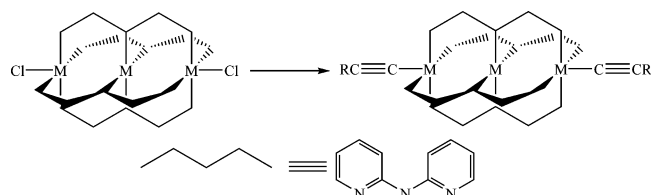
$E(+/0) - E(0/-)$ (see Table 4). Also listed are the optical gaps calculated from the longest λ_{max} values. Both types of gaps range from 1.2 to 1.6 eV, which are much narrower than the optical gaps (the lowest singlet excitation energy) of the monomers for common conjugated organic oligomers, such as thiophene (5.3 eV), styrene (5.1 eV), and phenylethyne (5.2 eV).[115]

Related Di- and Trimetallic Alkynyl Compounds. $M_3(dpa)_4Cl_2$ type compounds shown in Scheme 6, where dpa is the anion of dipyridylamine and M = Cr, Co, Ni, Cu, Ru, Rh, have been studied thoroughly by Cotton et al. In particular, both axial chloro ligands can be displaced by either phenylethynyl in the cases of Ni,[116] Cr, and Co (**12**; shown in Figure 8)[117] or ferrocenylethynyl in the case of Co.[118] With Cl axial liagnds, these compounds often exhibit interesting magnetic properties and sometimes valence tautomerism.[119] Replacing Cl with alkynyl may facilitate the assembly of linear oligomers or polymers based on these trimetallic building blocks. In the case of $Co_3(dpa)_4(C\equiv CFc)_2$, a potential separation of 70 mV was estimated for the sequential Fc oxidations, indicating a very weak coupling between the Fc–Fc$^+$ pair over a C_ω–C_ω' distance of 14.10 Å (C_ω and C_ω' are ferrocenyl carbon centers that are bonded to ethyne units). Extensive studies by Hopkins et al. established a family of bimetallic compounds of equatorial alkynyl ligands: namely, $M_2(PMe_3)_4(C\equiv CY)_4$ with Y = Me, ^iPr, ^tBu, SiMe$_3$, Ph for M = Mo and Y = Me, ^tBu for M = W.[120,121] As shown by Walton and co-workers, multiply bonded dirhenium species also exhibited unique reactivity toward ethyne-containing ligands: $Re_2(\mu-O_2CCH_3)Cl_4(dppm)_2$ promotes the decarbonylation of $HO_2CC\equiv CCO_2H$ and $CH_3C\equiv CCO_2H$,[122] and $Re_2Cl_4(dppm)_2$ facilitates reductive cyclization of 1,7-octadiyne.[123]

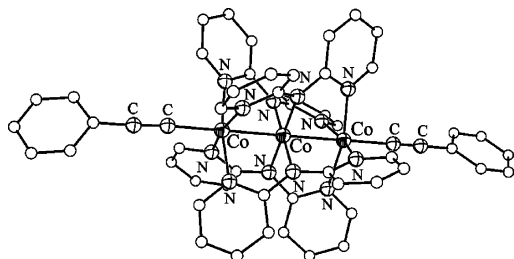**Figure 8.** Structural plot of compound **12** generated from the Supporting Information of ref 117.

A series of $Os_2(ap)_4(C_2Y)_2$ type compounds with Y = Ph, Fc, SiMe$_3$, C$_2$SiMe$_3$ was prepared recently in our

Figure 9. Structural plot of compound **13**.

laboratory.[124] These bis(alkynyl) compounds are diamagnetic, and X-ray diffraction studies of compounds with Y = Ph, SiMe$_3$ revealed features similar to those previously observed for $Ru_2(ap)_4(C_2Y)_2$, and the molecular structure of *cis*-(2,2)-$Os_2(ap)_4(C_2Ph)_2$ (**13**) is shown in Figure 9. However, the Os_2 species is far electron richer than the Ru_2 analogues, and a reversible $Os_2(IV,IV)/Os_2(III,IV)$ couple was observed in the CV of $Os_2(ap)_4(C_2Ph)_2$, implying the possible isolation of a hitherto unknown $Os_2(IV,IV)$ species.

III. Wirelike Molecules and Charge Mobility Therein

The first examples of type **1a** wirelike Ru_2 molecules were reported in 2000, where the reaction between $Ru_2(ap)_4Cl$ and 0.5 equiv of $LiC_{2n}Li$ resulted in [Ru_2-$(ap)_4]_2(\mu-C_{2n})$ (n = 1 (**14**), 2 (**15**)) in high yields.[125] The molecular structure of [$Ru_2(ap)_4]_2(\mu-C_4)$, given in Figure 10, clearly revealed a linear Ru_2–C_4–Ru_2 backbone. Preliminary voltammetric data revealed a significant electronic coupling between two Ru_2 units across the polyyn-diyl bridge, which will be elaborated in more detail below. Shortly after, Lehn et al. reported the synthesis and structural characterization of [(Me$_3$SiC$_4$)-$Ru_2(DPhF)_4]_2(\mu-C_8)$,[126] a remarkable compound that bears much structural analogy to the previously studied $Ru_2(DArF)_4(C_2Ph)_2$ compounds.[58,102] However, voltammetric data obtained for [(Me$_3$SiC$_4$)$Ru_2(DPhF)_4]_2(\mu-C_8)$ were inconclusive as to the degree of electronic coupling between two Ru_2 moieties across the μ-C$_8$ bridge. A related compound, [$Rh_2(ap)_4]_2(\mu-C_4)$, was reported by Bear and Kadish, and a weak coupling between two Rh_2 centers was inferred from voltammetric data.[127]

(116) Berry, J. F.; Cotton, F. A.; Murillo, C. A. *Dalton Trans.* **2003**, 3015.

(117) Berry, J. F.; Cotton, F. A.; Murillo, C. A.; Roberts, B. K. *Inorg. Chem.* **2004**, *43*, 2277.

(118) Berry, J. F.; Cotton, F. A.; Murillo, C. A. *Organometallics* **2004**, *23*, 2503.

(119) Berry, J. F.; Cotton, F. A.; Lu, T. B.; Murillo, C. A.; Roberts, B. K.; Wang, X. P. *J. Am. Chem. Soc.* **2004**, *126*, 7082.

(120) Stoner, T. C.; Schaefer, W. P.; Marsh, R. E.; Hopkins, M. D. *J. Cluster Sci.* **1994**, *5*, 107.

(121) John, K. D.; Miskowski, V. M.; Vance, M. A.; Dallinger, R. F.; Wang, L. C.; Geib, S. J.; Hopkins, M. D. *Inorg. Chem.* **1998**, *37*, 6858.

(122) Bera, J. K.; Fanwick, P. E.; Walton, R. A. *Dalton Trans.* **2001**, 292.

(123) Ganesan, M.; Fanwick, P. E.; Walton, R. A. *Organometallics* **2003**, *22*, 870.

(124) Shi, Y.-H.; Chen, W.-Z.; John, K. D.; Da Re, R. E.; Cohn, J. L.; Xu, G.-L.; Eglin, J. L.; Sattelberger, A. P.; Hare, C. R.; Ren, T. *Inorg. Chem.* **2005**, *44*, 5719.

(125) Ren, T.; Zou, G.; Alvarez, J. C. *Chem. Commun.* **2000**, 1197.

(126) Wong, K.-T.; Lehn, J.-M.; Peng, S.-M.; Lee, G.-H. *Chem. Commun.* **2000**, 2259.

(127) Bear, J. L.; Han, B.; Wu, Z.; Caemelbecke, E. V.; Kadish, K. M. *Inorg. Chem.* **2001**, *40*, 2275.

(113) Xu, G.-L.; DeRosa, M. C.; Crutchley, R. J.; Ren, T. *J. Am. Chem. Soc.* **2004**, *126*, 3728.

(114) Xu, G.-L.; Crutchley, R. J.; DeRosa, M. C.; Zhang, H.-X.; Wang, X.; Ren, T. *J. Am. Chem. Soc.*, in press.

(115) Pretsch, E.; Simon, W.; Seibl, J.; Clerc, T. *Tables of Spectral Data for Structure Determination of Organic Compounds*; Springer-Verlag: Berlin, 1989.
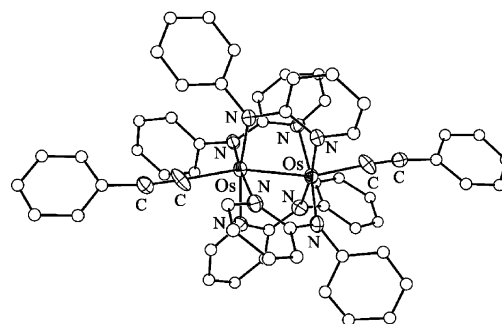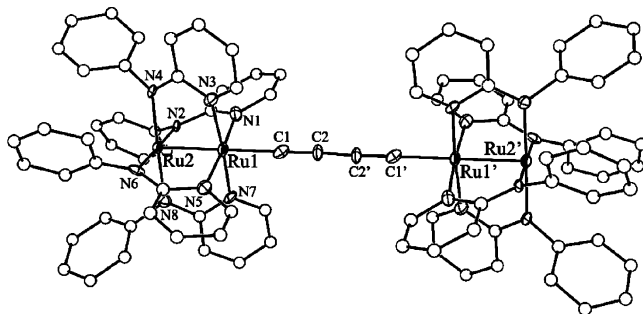
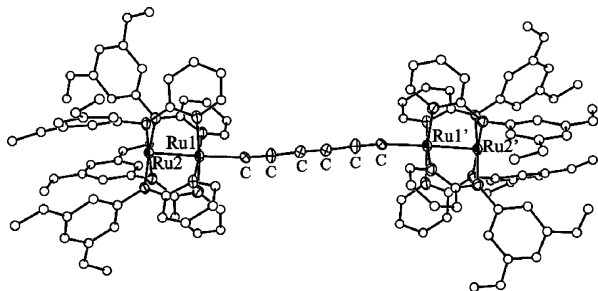**Figure 10.** Structural plot of compound **15**.

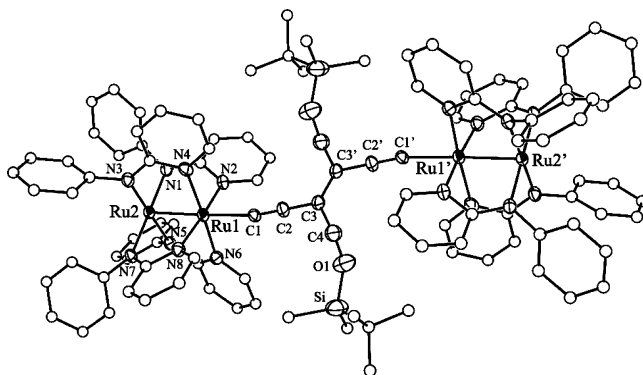**Figure 11.** Structural plot of compound **16′**.

Figure 12. Structural plot of compound **17**.

The anion metathesis reaction used for the preparation of C_2 and C_4 bridging compounds was readily extended to the synthesis of $[Ru_2(ap)_4]_2(\mu\text{-}C_6)$ (**16**), which is unfortunately insoluble in common organic solvents. Recently, the reaction between $Ru_2(DiMeOap)_4Cl$ and LiC_6Li furnished the more soluble analogue $[Ru_2(DiMeOap)_4]_2(\mu\text{-}C_6)$ (**16′**),[101] which was successfully crystallized and is shown in Figure 11. In expanding our scope beyond polyyn-diyl bridges, 2 equiv of $Ru_2(ap)_4Cl$ reacted with the dilithium salt of 3,4-bis(((*tert*-butyldimethylsilyl)oxy)methylene)-(*E*)-hex-3-ene-1,5-diyn-diyl (DEE*)[128,129] to afford $[Ru_2(ap)_4]_2(\mu\text{-}C,C'\text{-}DEE^*)$ (**17**; Figure 12), the first example of a transition-metal compound of DEE*.[130] As mentioned earlier, the use of the anion metathesis technique becomes impractical with longer polyyne ligands, due to the instability of $LiC_{2n}Li$ with $n \geq 4$. Hence, the compounds $[Ru_2(ap)_4]_2(\mu\text{-}C_{2n})$ with $n = 4$ (**18**), 6 (**19**) were prepared from the

(128) Anthony, J. Ph.D. Dissertation, University of California, Los Angeles, 1993.
(129) Schreiber, M.; Anthony, J.; Diederich, F.; Spahr, M. E.; Nesper, R.; Hubrich, M.; Bommeli, F.; Degiorgi, L.; Wachter, P.; Kaatz, P.; Bosshard, C.; Gunter, P.; Coluzzi, M.; Suter, U. W.; Boudon, C.; Gisselbrecht, J. P.; Gross, M. *Adv. Mater.* **1994**, *6*, 786.
(130) Shi, Y.; Yee, G. T.; Wang, G.; Ren, T. *J. Am. Chem. Soc.* **2004**, *126*, 10552.

$$2\ [Ru_2(ap)_4]\!\!-\!\!\left(\!\!\equiv\!\!\right)_{n/2}\!\!\text{H} \xrightarrow[\text{py}]{\text{3 equiv Cu(OAc)}_2} [Ru_2(ap)_4]\!\!-\!\!\left(\!\!\equiv\!\!\right)_{n}\!\!-\![Ru_2(ap)_4]$$
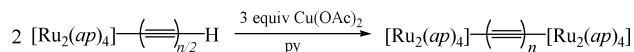
Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[Ru_2(ap)_4]_2(\mu\text{-bridge})$ Type Compounds

	Ru−Ru	Ru−C_α	C_α−C_β	C_β−C_γ	Ru−Ru−C_α	Ru₂- - -Ru₂
14						5.34^a
15	2.331(2)	2.05(1)	1.26(2)	1.33(2)	179.5(4)	7.91
15′	2.3263(4)	2.062(3)	1.239(5)	1.354(7)	177.7(1)	7.95
16′	2.3241(7)	2.107(6)	1.198(8)	1.362(8)	177.9(2)	10.50
17	2.3281(8)	2.137(6)	1.175(8)	1.44(1)	178.1(2)	10.16
18	2.329(1)	2.055(1)	1.20(1)	1.39(2)	177.7(4)	13.05
19						18.19^a

^{a} Crystal structure unavailable; extrapolated from other known structures.

Scheme 8. Polyyn-diyl and Cumulenic Resonance Structures

$$(Ru_2)\!-\!C\!\equiv\!C\!-\!C\!\equiv\!C\!-\!(Ru_2) \longleftrightarrow {}^{+}(Ru_2)\!\!=\!\!\left[C\!=\!C\!=\!C\!=\!C\right]^{2-}\!\!=\!\!(Ru_2)^{+}$$
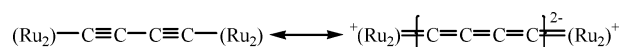
oxidative couplings of the corresponding "half" molecule $Ru_2(ap)_4(C_nH)$ under Eglinton conditions (Scheme 7).[60,94,131]

It is clear from Figures 10−12 that the overall topological feature of the $Ru_2(ap)_4$ unit in $[Ru_2(ap)_4]_2$-(μ-bridge) type compounds is identical with that in Ru_2-$(ap)_4(C_2Y)$. Some selected geometrical parameters about the $Ru_2-C\equiv C-$ linkage are listed in Table 5, which shows (i) the $Ru-Ru-C_\alpha$ backbone deviates from linearity by no more than 3°; (ii) the $C_\alpha-C_\beta$ and $C_\beta-C_\gamma$ distances are fairly close to 1.20 and 1.40 Å, as expected respectively for triple and single bonds in a polyyne backbone.[26] However, the structure of $[Ru_2(ap)_4]_2(\mu\text{-}C_4)$, refined with data of $2\theta \leq 45°$ with Mo Kα, is exceptional in that the $C_\alpha-C_\beta$ bond is elongated to 1.26(2) Å and the $C_\beta-C_{\beta'}$ bond is shortened to 1.33(2) Å, respectively. Recently, a high-resolution data set ($2\theta \leq 56°$) was collected for the analogous compound $[Ru_2(DiMeOap)_4]_2$-(μ-C_4) (**15′**),[101] and the structural refinement revealed similar bond elongation and shortening (Table 5). A structural study of an authentic example of a C_4-cumulene-bridged complex, $[\{Ru(dppe)Cp^*\}_2(\mu\text{-}C_4)][PF_6]_2$, revealed $C_\alpha-C_\beta$ and $C_\beta-C_{\beta'}$ bond lengths of 1.280(7) and 1.294(7) Å, respectively.[132] Hence, the reduced *bond length alternation* (BLA) implies that the cumulenic resonance structure (Scheme 8) contributes significantly to the electronic structure of $[Ru_2(ap)_4]_2(\mu\text{-}C_{2n})$ with shorter polyyn-diyl chains and is responsible for the facile electron mobility within this type of molecule (see discussion below).

Electrochemistry and Spectroelectrochemistry. The degree of electronic coupling between two Ru_2 units across the carbon-rich bridge was initially assessed on the basis of the comparison of their CV/DPVs with that of a "half" molecule. For instance, $Ru_2(ap)_4(C_4SiMe_3)$ (**9**) undergoes an oxidation (**B**) and a reduction (**C**) between -1.5 and $+1.0$ V (Figure 7). The prototype of dimer molecules, i.e., $[Ru_2(ap)_4]_2(\mu\text{-}C_4)$ (**15**), displays four reversible one-electron couples in the same potential window (Figure 13): two oxidations (2+/+ and +/0) at

(131) Xu, G.-L.; Zou, G.; Ni, Y.-H.; DeRosa, M. C.; Crutchley, R. J.; Ren, T. *J. Am. Chem. Soc.* **2003**, *125*, 10057.
(132) Bruce, M. I.; Ellis, B. G.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **2003**, *22*, 3184.
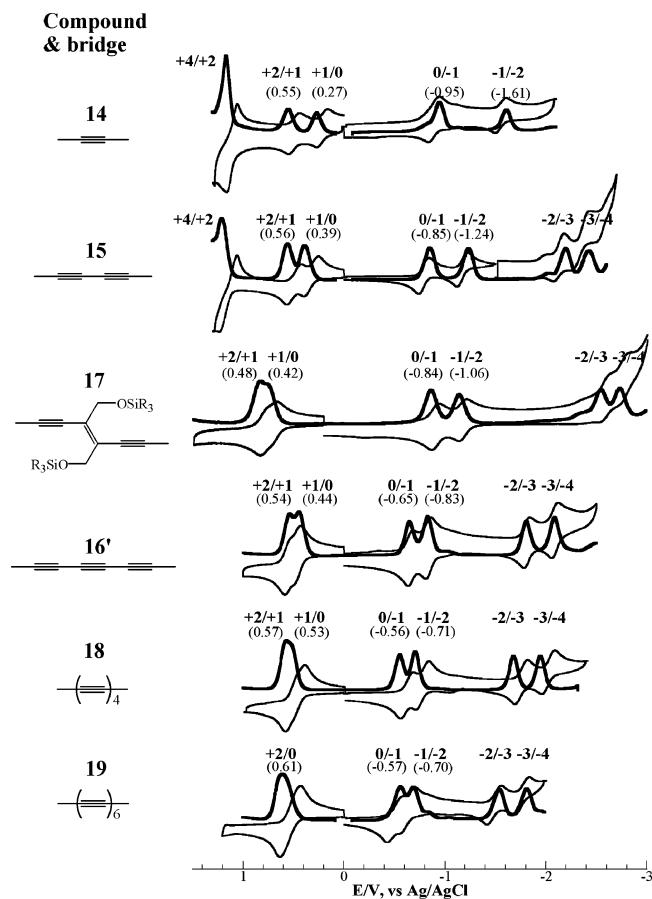
Figure 13. Voltammetric results of [Ru$_2$(ap)$_4$](μ-bridge): (left) bridges; (right) CV (gray line) and DPV (thick solid line).

Figure 14. Visible−near-IR spectra derived from spectroelectrochemical studies of [Ru$_2$(ap)$_4$]$_2$(μ-C$_4$) and Ru$_2$(ap)$_4$-(C$_2$SiMe$_3$): (a) one-electron-oxidation spectra and the deconvoluted IVCT band; (b) one-electron-reduction spectra and the deconvoluted IVCT band.

potentials close to that of **B** and two reductions (0/− and −/2−) at potentials close to that of **C**. The pairwise appearance of one-electron couples in the dimer is indicative of the electronic coupling between two Ru$_2$ centers, and the potential splitting within each pair is proportional to the coupling strength, as is well-known in the chemistry of mixed-valent species.[133−136] It is interesting to note for **15** that the splitting between the oxidative pair (0.17 V) is significantly smaller than that between the reductive pair (0.39 V). The contrast is indicative of the fact that the [Ru$_2$(ap)$_4$]$_2$(μ-bridge) type compounds are much better electron carriers than hole carriers, which can be attributed to the electron-deficient nature of both the Ru$_2$ core and polyyn-diyl bridge.[131]

A quick glance at Figure 13 revealed that other [Ru$_2$-(ap)$_4$]$_2$(μ-bridge) type compounds behave similarly to [Ru$_2$(ap)$_4$]$_2$(μ-C$_4$), and some trends are noteworthy. First, the oxidation couples 2+/+ and +/0 remain resolved up to the C$_6$ bridge but merge into a pseudo two-electron wave with the C$_8$ bridge and become a standard two-electron wave with the C$_{12}$ bridge. A similar trend holds for the pair of 0/− and −/2− couples, where the splitting gradually reduces as the chain elongates, but the pair remains resolved up to the C$_{12}$ bridge. These trends are consistent with the general agreement that the degree of electronic coupling between a pair of donor−

acceptor centers decays exponentially as the distance increases.[133,135,137,138] A quasi-reversible two-electron oxidation (4+/2+) is observed at very positive potential with C$_2$ and C$_4$ bridges, but not with longer bridges, where the increasing electron deficiency has shifted the couple out of the potential window accessible in THF (≤+1.5 V). Also of interest is the emergence of a second pair of one-electron reductions at more negative potentials, marked as 2−/3− and 3−/4−, the assignments of which remain uncertain to date.

While the aforementioned splitting in potentials of oxidation/reduction pairs ($\Delta E_{1/2}$) serves as a *qualitative* indicator of the electronic coupling between two Ru$_2$ centers,[134] the use of $\Delta E_{1/2}$ as a quantitative measure may be inappropriate, since its magnitude and the comproportionation constant K_{com} calculated from $\Delta E_{1/2}$ significantly depend on the nature of solvents and electrolytes.[139] A more direct approach is to examine spectroscopic characteristics of the mixed-valent species, as evidenced by spectroelectrochemical studies of **15** and its reference compound Ru$_2$(ap)$_4$(C$_2$SiMe$_3$) below (Figure 14). Comparison of the spectra of {Ru$_2$(ap)$_4$(C$_2$SiMe$_3$)}$^+$ and {[Ru$_2$(ap)$_4$]$_2$(μ-C$_4$)}$^+$ reveals an intervalence charge

(133) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.
(134) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.
(135) Crutchley, R. J. *Adv. Inorg. Chem.* **1994**, *41*, 273.
(136) Demadis, K. D.; Hartshorn, C. M.; Meyer, T. J. *Chem. Rev.* **2001**, *101*, 2655.
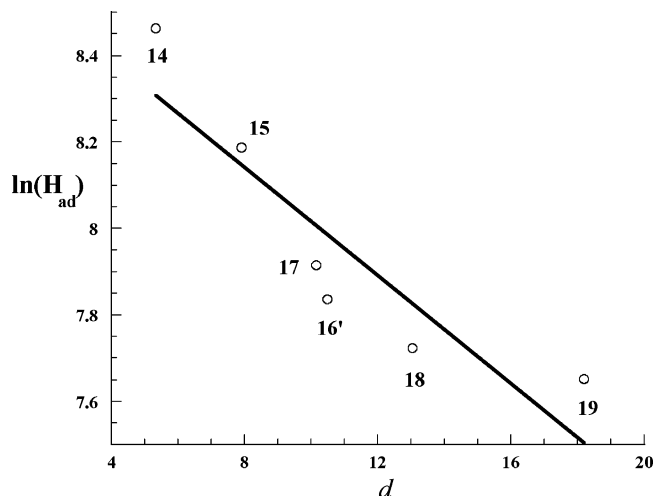
(137) Endicott, J. F. In *Comprehensive Coordination Chemistry II: From Biology to Nanotechnology*; Elsevier/Pergamon: Oxford, U.K., 2004; Vol. 7.
(138) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148.
(139) Barrière, F.; Camire, N.; Geiger, W. E.; Mueller-Westerhoff, U. T.; Sanders, R. *J. Am. Chem. Soc.* **2002**, *124*, 7262.

Figure 15. Distance-dependence plot of $\ln(H_{ad})$ (in cm^{-1}) vs $d_{Ru2-Ru2}$ (in Å).

transfer (IVCT) band for the latter at 7700 cm^{-1}, and a half-width ($\Delta\nu_{1/2}$) of 1820 cm^{-1} was estimated from spectral deconvolution assuming a Gaussian profile. In comparison with $\{Ru_2(ap)_4(C_2SiMe_3)\}^-$, $\{[Ru_2(ap)_4]_2(\mu\text{-}C_4)\}^-$ exhibits a very pronounced IVCT band centered at 8450 cm^{-1} with a half-width ($\Delta\nu_{1/2}$) of 1820 cm^{-1}. The Hush model that describes weakly coupled mixed-valent species (Robin−Day class II) predicts $\Delta\nu_{1/2} = (2310\nu_{max})^{1/2}$ [140−142] and numeric values of 4220 and 4420 cm^{-1} for $\{[Ru_2(ap)_4]_2(\mu\text{-}C_4)\}^+$ and $\{[Ru_2(ap)_4]_2(\mu\text{-}C_4)\}^-$, respectively. Hence, the narrowness of the observed IVCT bands indicates that both the mixed-valent cation and anion of compound **15** are strongly coupled.[131,143]

The availability of E_{IVCT} also enables the estimation of H_{ad} (adiabatic electronic coupling element) for the series of $[Ru_2(ap)_4]_2(\mu\text{-bridge})$ compounds through $H_{ad} = (\Delta G_r E_{IVCT})^{1/2}$.[144] It is most often described by an exponential dependence on distance

$$H_{ad} = H_0 \exp(-\beta R)$$

where H_{ad} and H_0 are donor and acceptor wave function resonance exchanges at distance R and van der Waals contact distance, respectively, β is a decay factor measuring the medium's ability to mediate electronic coupling, and R is the separation between the donor and acceptor from van der Waals contacts.[133,135,143] For the reduced mixed-valence ions of $[Ru_2(ap)_4]_2(\mu\text{-bridge})$ compounds, a rough estimate of $\beta = 0.063$ Å^{-1} was derived from a $\ln(H_{ad})$ vs $d_{Ru2-Ru2}$ plot (Figure 15),[144] which is slightly smaller than that found for oligoene-bridged pentaamineruthenium(II,III) donor−acceptor pairs ($\beta \approx 0.070$ Å^{-1})[145] and Fc−Fc$^+$ donor−acceptor pairs ($\beta = 0.087$ Å^{-1}).[146] While the conventional wisdom in the community of conjugated materials scientists is that oligoene is superior to oligoyne,[1,143] our results clearly reveal that oligoyn-diyls are as effective as oligoene-diyls

(140) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.
(141) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.
(142) Nelsen, S. F. *Chem. Eur. J.* **2000**, *6*, 581.
(143) Launay, J. P. *Chem. Soc. Rev.* **2001**, *30*, 386.
(144) Evans, C. E. B.; Naklicki, M. L.; Rezvani, A. R.; White, C. A.; Kondratiev, V. V.; Crutchley, R. J. *J. Am. Chem. Soc.* **1998**, *120*, 13096.
(145) Ribou, A. C.; Launay, J. P.; Takahashi, K.; Nihira, T.; Tarutani, S.; Spangler, C. W. *Inorg. Chem.* **1994**, *33*, 1325.
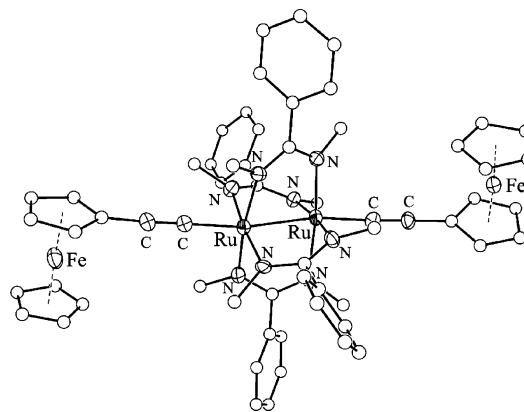
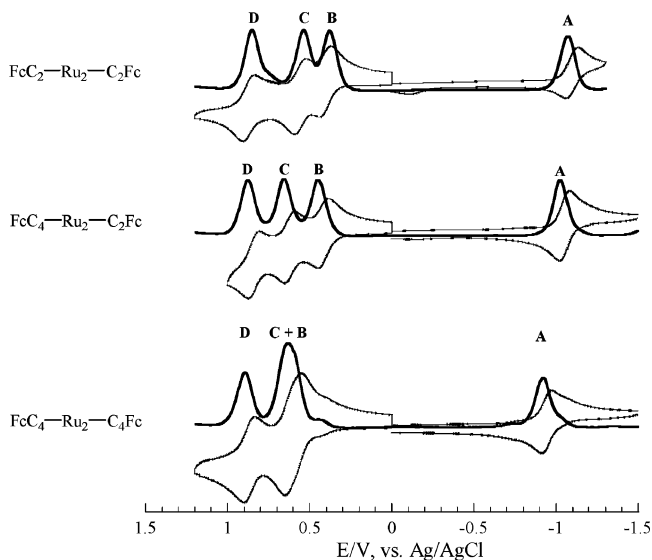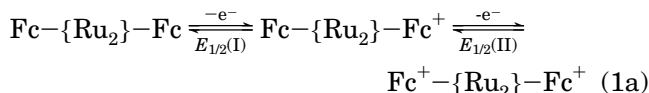**Figure 16.** Structural plot of compound **20**.

Figure 17. DPV (solid) and CV (gray) of FcC$_{2m}$−Ru$_2$-(DMBA)$_4$−C$_{2n}$Fc recorded in a 0.20 M THF solution of Bu$_4$NPF$_6$.

in mediating electronic coupling in the context of bridged organometallic species.

In addition to the above-mentioned charge mobility across carbon-rich bridges, use of the oligomer **1b** outlined in Chart 1 as molecular wires requires facile charge transfer across the Ru$_2$ unit along the axial direction. Synthesis of the series of *trans*-(FcC$_{2m}$−Ru$_2$-(DMBA)$_4$−C$_{2n}$Fc) (m, n = 1, 2) type compounds enables the probe of charge mobility across the Ru$_2$(DMBA)$_4$ unit by monitoring the electronic coupling between two Fc termini.[113,114] The molecular structure of Ru$_2$(DMBA)$_4$-(C$_2$Fc)$_2$ (**20**) is shown in Figure 16.[113] A strongly coupled Fc−bridge−Fc$^+$ pair should exhibit sequential ferrocenyl oxidation (eq 1a), and the free energy of comproportionation ΔG_c ($F\Delta E_c$, and ΔE_c is defined by eq 1b) can be readily calculated from voltammetric data and used as a criterion for the degree of coupling.[147]

$$\text{Fc}-\{\text{Ru}_2\}-\text{Fc} \underset{E_{1/2}(\text{I})}{\overset{-e^-}{\rightleftharpoons}} \text{Fc}-\{\text{Ru}_2\}-\text{Fc}^+ \underset{E_{1/2}(\text{II})}{\overset{-e^-}{\rightleftharpoons}}$$

$$\text{Fc}^+-\{\text{Ru}_2\}-\text{Fc}^+ \quad (1a)$$

$$\Delta E_c = E_{1/2}(\text{II}) - E_{1/2}(\text{I}) \quad (1b)$$

(146) Ribou, A. C.; Launay, J. P.; Sachtleben, M. L.; Li, H.; Spangler, C. W. *Inorg. Chem.* **1996**, *35*, 3735.

Scheme 9[a]
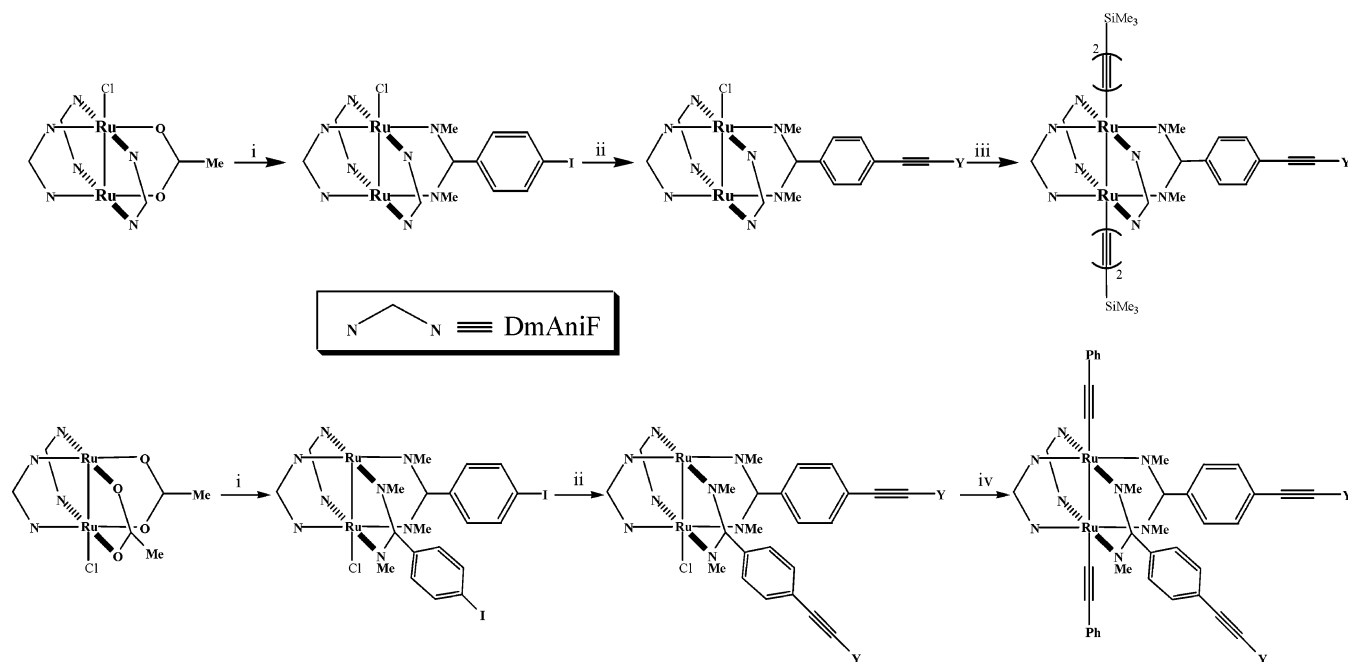
[a] Conditions: (i) N,N′-dimethyl-4-iodobenzamidine, LiCl, Et₃N; (ii) HC₂Y, *trans*-Pd(PPh₃)₂Cl₂, CuI, *i*Pr₂NH, Y = SiMe₃, Fc, Ph; (iii) 3 equiv of LiC₄TMS; (iv) 10 equiv of LiC₂Ph.

Initial CV and DPV studies of $FcC_2-Ru_2(DMBA)_4-C_2Fc$ revealed one one-electron reduction couple (**A**) and three one-electron oxidation couples instead of two in the potential window typical for Fc oxidation, as shown in Figure 17. Subsequent spectroelectrochemical studies identified the first oxidation couple (**B**) as Ru₂ based and the next two (**C** and **D**) as Fc based, which reveals a remarkably large ΔE_c value of 0.31 V.[113,114] The $Fc-Fc^+$ IVCT band observed for $[Fc-Ru_2(III,IV)-Fc]^{2+}$ has a ν_{max} value of 6000 cm⁻¹ and a $\Delta\nu_{1/2}$ value of 800 cm⁻¹,[113] which is much narrower than the value predicted by the Hush model for a weakly coupled system $(\Delta\nu_{1/2} = (2310\nu_{max})^{1/2} = 3720)$.[140]

As shown in Figure 17, the two Fc oxidation couples **C** and **D** remain resolved on sequential insertion of one and two C≡C units into the conjugated backbone, yielding $FcC_2-Ru_2(DMBA)_4-C_4Fc$ and $FcC_4-Ru_2(DMBA)_4-C_4Fc$, respectively. Spectroelectrochemical studies[114] revealed that the $Fc-Fc^+$ states for both compounds are on the borderline of classes II (valence trapped) and III (delocalized) mixed-valent ions by the Robin–Day classification.[141] These results indicated that the $Ru_2(DMBA)_4$ unit is a remarkable mediator of *hole* transfer over a long distance.

IV. Postmetalation Modifications: Supramolecules and Beyond

Since Ru₂–alkynyl compounds are both intense visible–near-infrared chromophores and excellent electrophores with multiple reversible redox couples over a broad potential window, we are keen on exploring their utilities in addition to molecular wires. Areas of particular interest include (i) incorporation into 2- and 3-D supramolecular assemblies for photovoltaic application and (ii) formation of peptide and nucleic acid conjugates for biochemical sensing applications. To achieve these objectives without significant alteration of spectroscopic

and electrochemical characteristics, covalent modification away from the Ru₂–σ-alkynyl backbone is desired.

Key to selective functionalizations is the ability to synthesize Ru₂ compounds of mixed bridging ligands, $Ru_2(DArF)_{4-n}(LL')_nCl$, where LL′ is either a DMBA or DArF ligand that is iodo substituted.[148–150] The presence of an iodo substituent allows $Ru_2(DArF)_{4-n}(LL')_nCl$ to undergo a variety of Pd-catalyzed cross-coupling reactions, including the Suzuki, Heck, and Sonogashira types,[59,151] and the modification sequences based on Sonogashira coupling reactions for $n = 1, 2$ are illustrated in Scheme 9. The bottleneck of both sequences appears to be the cross-coupling step (ii) with typical yields between 40 and 50%, while the first (bridging ligand exchange) and last (axial alkynylation) steps proceed at nearly quantitative yields.[148–150] It was noted that $trans$-(Me₃SiC₄)₂-Ru₂(DmAniF)₃(DMBA-I) decomposed by losing at least one axial alkynyl ligand when subjected to Sonogashira coupling conditions, indicating that the isolation of final products shown in Scheme 9 is very sequence dependent.

Peripherally derivatized Ru₂–alkynyl compounds are highly crystalline, and a structural example, *cis*-Ru₂-(DmAniF)₂(DMBA-4-C₂Fc)₂-*trans*-(σ-C₂Ph)₂ (**21**), is shown in Figure 18. As hoped, the modified compounds exhibit redox and spectroscopic features similar to the corresponding unmodified species.[148,149] A voltammetric study of compound **21** revealed the absence of electronic interaction between two Fc groups, implying the weak coupling nature along the equatorial directions of the Ru₂-paddlewheel.

A natural extension of peripheral modification methodology is the supramolecular assemblies based on Ru₂ units. For instance, $Ru_2(DArF)_3(DMBA-4-C_2H)Cl$ (**22**)

(147) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637.
(148) Chen, W.-Z.; Ren, T. *Organometallics* **2004**, *23*, 3766.
(149) Chen, W.-Z.; Ren, T. *Organometallics* **2005**, *24*, 2660.
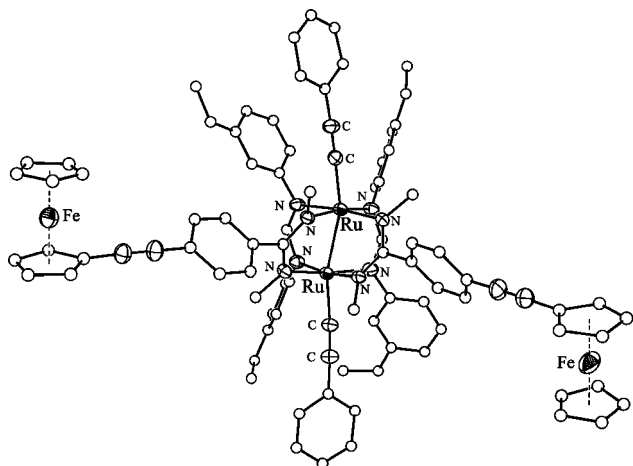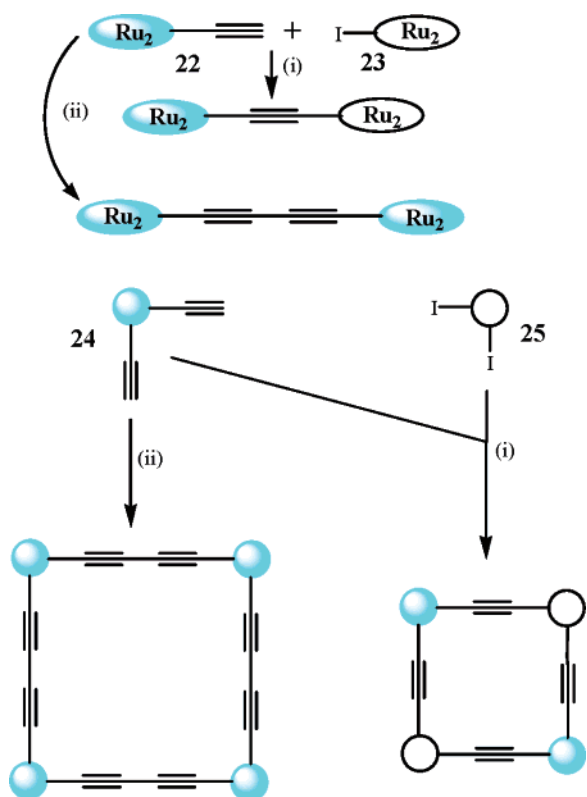(150) Xu, G.-L.; Ren, T. *Organometallics* **2005**, *24*, 2564.

Figure 18. Structural plot of *cis*-Ru$_2$(DmAniF)$_2$(DMBA-4-C$_2$Fc)$_2$-*trans*-(σ-C$_2$Ph)$_2$.

Scheme 10. Hetero- and Homosupramolecules of Diruthenium Units through (i) Sonogashira Coupling and (ii) Glaser Coupling

can either undergo the Hay coupling to yield a butadiyne-bridged symmetric dimer (Scheme 10) or cross-couple with Ru$_2$(DArF′)$_3$(DMBA-4-I)Cl (**23**) under Sonogashira conditions to yield an ethyne-bridged dimer. While a homodimer is produced from the latter reaction with DArF′ ≡ DArF, a heterodimer is produced with DArF′ ≠ DArF. The electronic structures of the heterodimers can be very interesting, given the potential tuning range of electron-donor/electron-acceptor ability of the DArF ligands,[152] which may result in some interesting donor–bridge–acceptor type supramolecules with proper selection of DArF′ and DArF. Difunctionalized molecules,

(151) Negishi, E.-I.; Anastasia, L. *Chem. Rev.* **2003**, *103*, 1979.
(152) Ren, T. *Coord. Chem. Rev.* **1998**, *175*, 43.
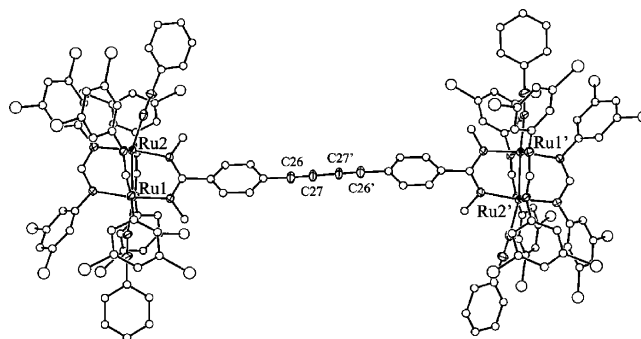
Figure 19. Structural plot of compound **26**.

namely *cis*-Ru$_2$(DArF)$_2$(DMBA-4-C$_2$H)$_2$Cl (**24**) and *cis*-Ru$_2$(DArF′)$_2$(DMBA-4-I)$_2$Cl (**25**), may be similarly cross-coupled or homocoupled (**24** only) to yield molecular squares (Scheme 10). Since the coupling conditions do not exclude the formation of linear zigzag polymers, fine tuning of reaction conditions is necessary and is being investigated in our laboratory. We note that Pt–polyyne squares were previously assembled from the cross-coupling reactions between *cis*-Pt(P–P)(C$_4$H)$_2$ and *cis*-Pt(P–P)Cl$_2$,[68] *cis*-PtP$_2$(C$_4$H)$_2$ and *cis*-PtP$_2$(OTf)$_2$,[69] and PtP$_2$(C$_4$H)$_2$ and *cis*-PtP$_2$Cl$_2$.[70] The molecular structure of [*trans*-(PhC$_2$)$_2$–Ru$_2$(D(3,5-Cl$_2$)PhF)$_3$]$_2$(μ-DMBA–C$_4$–DMBA) (**26**), a symmetric dimer derived from the Glaser coupling method, is shown in Figure 19.[153]

The presence of peripheral ethyne group(s) renders access to the Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction with an organic azide,[154] a *click* reaction that has found broad applications from biological science to materials science, owing to its exclusive regioselectivity, expansive substrate scope, mild reaction conditions, and very high yields.[155] As exemplified by the reaction sequence shown in Scheme 11, diruthenium compounds bearing a formamidinate ligand modified with ethyne substituents readily undergoes 1,3-dipolar cycloaddition with benzyl azide. The resultant 1,2,3-triazole-substituted diruthenium compounds can be readily alkynylated at axial positions, and a structural example is shown in Figure 20.[150] Ru$_2$(DArF)$_3$(DMBA-4-C$_2$H)Cl underwent a similar Cu(I)-promoted alkyne–azide addition reaction. Electrochemical and spectroscopic studies revealed that the peripheral 1,2,3-triazole modification has resulted in a minimal perturbation on the electronic structures of diruthenium–alkynyl compounds. Extension of our *click* strategy to the formation of bioconjugates is being studied.

While the aforementioned peripheral modification leaves the main electronic features of Ru$_2$–σ-alkynyl compounds intact, covalent modification on the Ru$_2$–σ-alkynyl backbone may alter the electronic structure significantly and bring about some novel physical properties. A facile modification is the [2 + 2] cycloaddition insertion of TCNE into an oligoyne backbone, as shown in Scheme 12, and the versatility of TCNE insertion reactions with metal–alkynyl compounds has been demonstrated in the excellent work of Bruce et
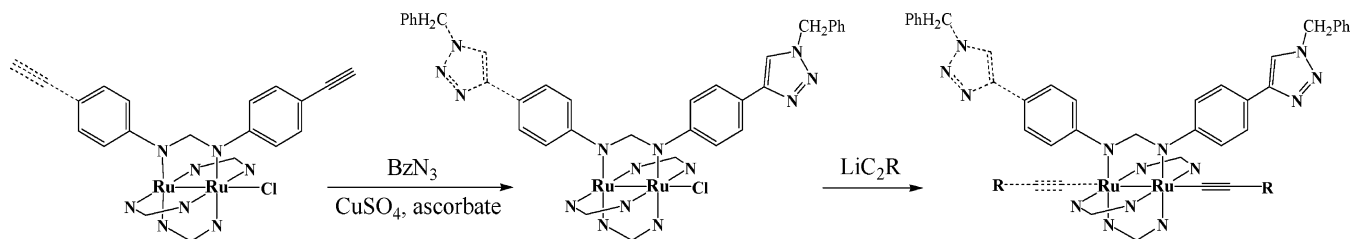
(153) Chen, W.-Z.; Ren, T. Unpublished results.
(154) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596.
(155) Kolb, H. C.; Sharpless, K. B. *Drug Discovery Today* **2003**, *8*, 1128.

[a] Dashed portions of the molecules indicate either the second peripheral ethyne or second axial acetylide that is optional.

al.[156−158] In a few cases explored in our laboratory, $Ru_2(ap)_4(C_4Ph)$ reacted with 1 equiv of TCNE at room temperature to yield $Ru_2(ap)_4−C≡CC\{=C(CN)_2\}$-$C\{=C(CN)_2\}Ph$, and $[Ru_2(ap)_4]_2(\mu-C_6)$ reacted similarly to yield $[Ru_2(ap)_4]_2[\mu-C≡CC\{=C(CN)_2\}C\{=C(CN)_2\}$-$C≡C]$ (**27**; shown in Figure 21).[159] Some interesting features observed from this structure include the formation of a C3−C4 double bond (1.35(1) Å) and C3−C3′ single bond (1.49(1) Å) that are consistent with Scheme 12.

Scheme 12. [2 + 2] Cycloaddition/Insertion Reaction between TCNE and Ethyne
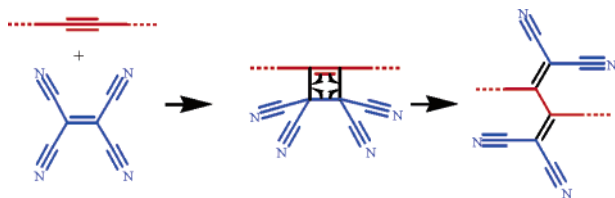
The conversion of the middle C≡C bond in $[Ru_2(ap)_4]_2$-$(\mu-C_6)$ to a C−C single bond on TCNE insertion implies a possible disruption of electronic coupling between two $Ru_2(ap)_4$ termini. Significant contrasts in differential pulse voltammograms of the more soluble pair $[Ru_2$-$(DiMeOap)_4]_2(\mu-C_6)$ (**16′**) and $[Ru_2(DiMeOap)_4]_2[\mu-C≡$$CC\{=C(CN)_2\}C\{=C(CN)_2\}C≡C]$ (**27′**) is clearly shown in Figure 22. With the aid of a spectroelectrochemical study, it is possible to assign the first two 1e reductions to the $=C(CN)_2$ fragments, which leads to unambiguous assignment of both the 2e oxidation at 0.67 V and 2e reduction at −1.32 V as Ru_2 based.[159] The absence of the pairwise feature that is apparent for the parent compound **16′** is a clear indication that the insertion of TCNE converted a "wire" molecule to an "insulator" molecule. Previously, the incorporation of CH_2 units into the backbone of oligo(phenyleneethynylene) resulted in molecules exhibiting negative differential resistance (NDR).[160,161] It would be interesting to see if NDR can be detected in type **27** compounds with further attachment of thiol termini.

(156) Bruce, M. I.; Hall, B. C.; Low, P. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1999**, *592*, 74.
(157) Bruce, M. I.; Ke, M.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **1998**, *17*, 3539.
(158) Bruce, M. I.; Low, P. J.; Skelton, B. W.; White, A. H. *New J. Chem.* **1998**, 419.
(159) Xu, G.-L.; DeRosa, M. C.; Crutchley, R. J.; Ren, T. Manuscript in preparation.
(160) Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y. X.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C. W.; Chen, J.; Wang, W. Y.; Campbell, I. *Chem.-Eur. J.* **2001**, *7*, 5118.
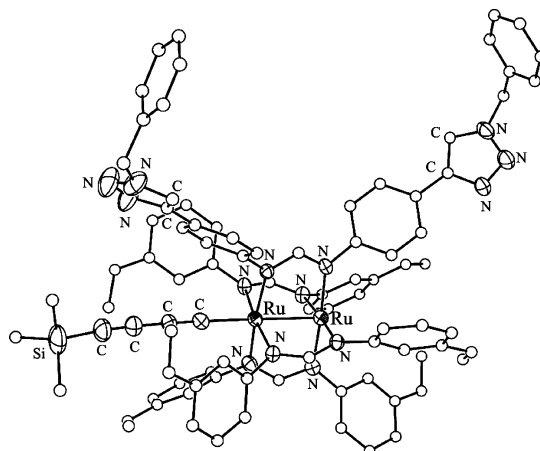(161) Reed, M. A. *Proc. IEEE* **1999**, *87*, 652.

Figure 20. Structural plot of a double *click* Ru_2−butadiynyl compound.
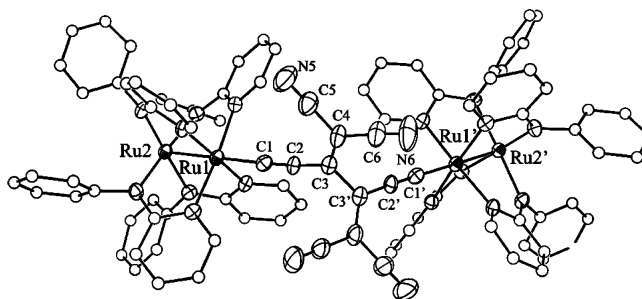

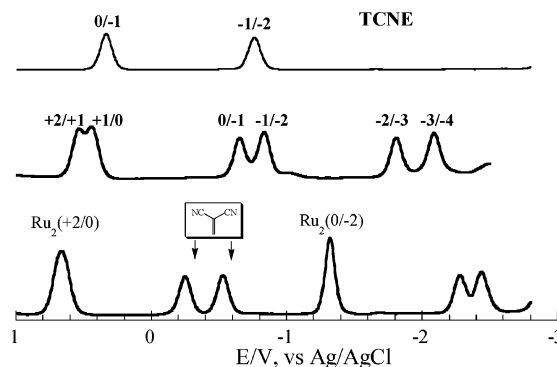**Figure 21.** Structural plot of compound **27**.

Figure 22. DPVs of TCNE (top), compound **16′** (middle), and compound **27′** (bottom) recorded in a 0.20 M THF solution of Bu_4NPF_6.

V. Synthesis and Characterization of Molecular Wires and Diodes

The term "*molecular wires*" is reserved for molecules for which the transport properties can be measured in

a conductor−molecule−conductor junction.[50] Due to the prevalent use of gold as the metal conductor, thiol has become the most popular capping group, or "molecular alligator clip" as coined by Tour,[162] for both attaching molecules to the conductor surface and establishing structural order through the formation of self-assembled monolayers (SAM).[50] Since our chemistry evolves around Ru$_2$−alkynyl compounds, recent efforts in realizing molecular wires have focused on the following thiol-capped phenylethynyl ligands. The tendency for dimerization of free thiols by aerobic oxidation necessitates the use of protecting groups, including acetyl, benzoyl, and trimethylsilylethylene (TMSE) in the order of ascending stability (Chart 5).

Chart 5. Typical Molecular Alligator Clips
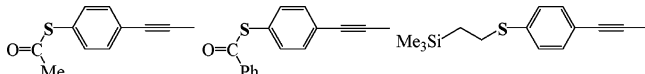
Initially, Ru$_2$(DMBA)$_4$(C$_2$C$_6$H$_4$-4-SC(O)Ph)$_2$ (**28**) was prepared from the reaction between Ru$_2$(DMBA)$_4$(NO$_3$)$_2$ and HC$_2$C$_6$H$_4$-4-SC(O)Ph in the presence of Et$_3$N.[101] Unfortunately, Ru$_2$(DMBA)$_4$(C$_2$C$_6$H$_4$-4-SH)$_2$ forms a multilayer on the Au surface instead of a SAM desired for nano-junction measurements. The failure to form SAM is attributed to the poor aspect ratio caused by the bulkiness of the Ru$_2$(DMBA)$_4$ fragment, as shown in the space-filling model of compound **28** (Figure 23).
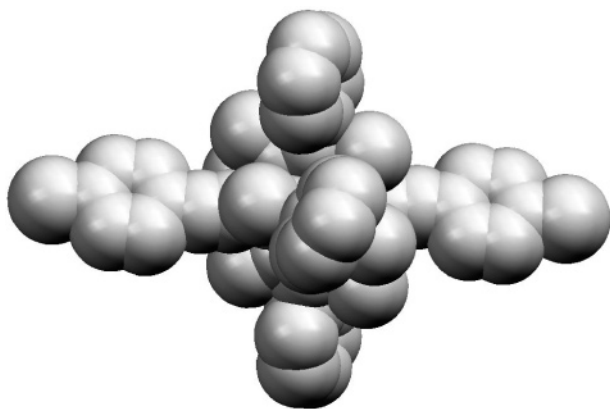
Figure 23. Space-filling model of compound **28** generated from its crystal structure. Benzoyl groups are removed for clarity.

To circumvent the failure of SAM formation from pure Ru$_2$−alkynyl compounds, an alternative is to dope Ru$_2$ species into the SAM formed by alkanethiols.[163] Taking advantage of the robustness of TMSE protection group, Ru$_2$(ap)$_4$(C≡CC$_6$H$_4$)$_n$-4-S(CH$_2$)$_2$SiMe$_3$ (n = 1 (**29**), 2 (**30**)) were prepared from Ru$_2$(ap)$_4$Cl and the lithium salt of the corresponding OPE ligands.[164,165] Compound **29** was crystallized, and its structure (Figure 24) bears great similarity to that of Ru$_2$(ap)$_4$(C$_2$Ph).[54] The conjugated backbone defined by the Ru2−Ru1 bond and thiol-capped phenyl−ethynyl group is linear. On the basis of
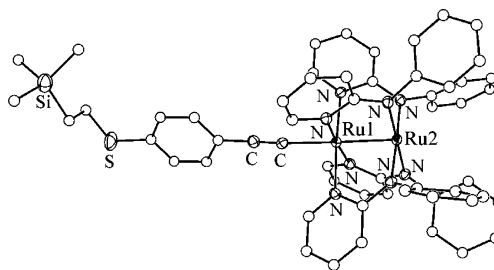
Figure 24. Structural plot of compound **29**.
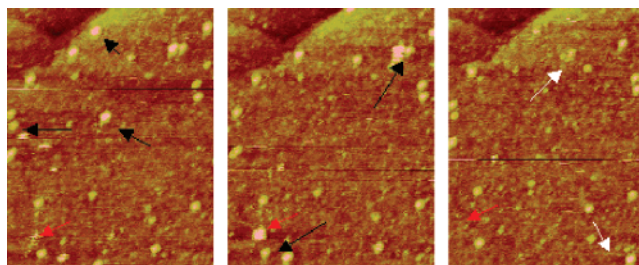
Figure 25. Consecutive scans showing molecule **30′** (bright spots) inserted into C11 undergoing stochastic switching. Black arrows point to molecules turning off, and white arrows point to molecules turning on. Red arrows point to molecules turning off−on−off in the three images.

this structure, both the Ru1···S distance in Ru$_2$(ap)$_4$-(C≡CC$_6$H$_4$)$_2$-4-SH (**30′**) and the overall length of the molecule are estimated to be 16.3 Å, which is sufficiently long to warrant insertion into the SAM of undecanethiol (C11), and 22.4 Å, respectively.

Successful doping of Ru$_2$(ap)$_4$(C≡CC$_6$H$_4$)$_2$-4-SH (**30′**) into the SAM was confirmed by the CV study. The embedded **30′** molecules were further investigated using the STM technique, and interesting findings include (i) stochastic switching (Figure 25) that is characteristic of molecular wires is observed[166−168] and (ii) the decay constant (β) of molecular conductance ($G_{mol} = G_0$ exp-($-\beta h_{mol}$); G_0 is the contact conductance of the conductor−molecule coupling) is at least 15% smaller than that of the OPE molecule of comparable length ($-$SC$_6$H$_4$C≡CC$_6$H$_4$C≡CC$_6$H$_4$S$-$; 20.2 Å).[169−171] The enhancement of conductance clearly demonstrated that the insertion of the Ru$_2$(ap)$_4$ unit with a small energy gap (ca. 1.28 eV from CV measurement) into an organic conjugated backbone brings about a substantial improvement of wire characteristics.

The results obtained for compound **30′** are very encouraging, especially considering it is only a *half* wire.

(162) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791.
(163) Blum, A. S.; Ren, T.; Parish, D. A.; Trammell, S. A.; Moore, M. H.; Kushmerick, J. G.; Xu, G.-L.; Deschamps, J. R.; Pollack, S. K.; Shashidhar, R. *J. Am. Chem. Soc.* **2005**, *127*, 10010.
(164) Yu, C. J.; Chong, Y. C.; Kayyem, J. F.; Gozin, M. *J. Org. Chem.* **1999**, *64*, 2070.
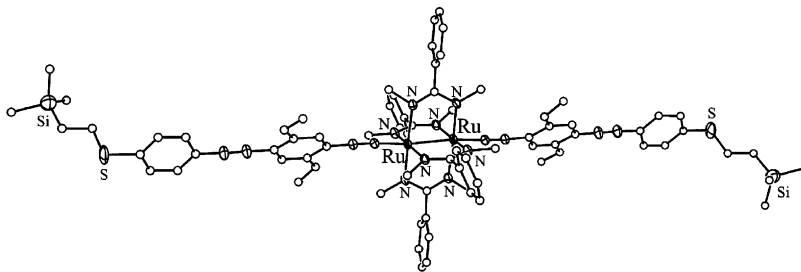(165) Pollack, S. K.; Naciri, J.; Mastrangelo, J.; Patterson, C. H.; Torres, J.; Moore, M.; Shashidhar, R.; Kushmerick, J. G. *Langmuir* **2004**, *20*, 1838.
(166) Blum, A. S.; Kushmerick, J. G.; Long, D. P.; Patterson, C. H.; Yang, J. C.; Henderson, J. C.; Yao, Y.; Tour, J. M.; Shashidhar, R.; Ratna, B. R. *Nat. Mater.* **2005**, *5*, 167.
(167) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **2001**, *292*, 2303.
(168) Ramachandran, G. K.; Hopson, T. J.; Rawlett, A. M.; Nagahara, L. A.; Primak, A.; Lindsay, S. M. *Science* **2003**, *300*, 1413.
(169) Blum, A. S.; Yang, J. C.; Shashidhar, R.; Ratna, B. R. *Appl. Phys. Lett.* **2003**, *82*, 3322.
(170) Moth-Poulsen, K.; Patrone, L.; Stuhr-Hansen, N.; Christensen, J. B.; Bourgoin, J.-P.; Bjørnholm, T. *Nano Lett.* **2005**, *5*, 783.
(171) Kushmerick, J. G.; Holt, D. B.; Pollack, S. K.; Ratner, M. A.; Yang, J. C.; Schull, T. L.; Naciri, J.; Moore, M. H.; Shashidhar, R. *J. Am. Chem. Soc.* **2002**, *124*, 10654.

Figure 26. Structural plot of compound **32**.

A series of complete wires based on *trans*-Ru$_2$(X-DMBA)$_4$-[(C≡CC$_6$H$_4$)$_n$−S(CH$_2$)$_2$SiMe$_3$]$_2$ with n = 1 (**31**), 2 (**32**), 3 (**33**) were prepared, and structural studies of compounds **31** and **32** (shown in Figure 26) revealed the coplanar nature of all phenyleneethyne units and hence extensive conjugation.[111] The S···S distances with n = 1−3 are 21, 35, and 49 Å, respectively. The molecule **33** is much longer than the longest molecular wires studied so far (32 Å),[50] and the measurement of its transport property may yield some interesting results.

Beyond molecular wires that exhibit a linear (ohmic) *I−V* curve, molecular systems exhibiting reproducible nonlinear *I−V* characteristics are more attractive, due to their potential use as memory devices.[172] The molecular rectifier based on the donor−(saturated bridge)−acceptor (D−σ−A) assembly put forth by Aviram and Ratner three decades ago would be a nonlinear device.[173] While this seminal proposal ushered in the era of molecular electronics, demonstration of rectification in a D−σ−A construct at a single molecule level remains elusive.[174] Recently, both D−σ−D and A−σ−A type compounds were produced, based on the Ru$_2$(DMBA)$_4$ core, with D and A being 4-Me$_2$NC$_6$H$_4$C≡C and 4-O$_2$-NC$_6$H$_4$C≡C, respectively,[110] where it was noted that the D−σ−D type compound is less stable. Taking advantage of the instability of such a electron-rich system, we succeeded in isolating the first Ru$_2$−alkynyl-based D−σ−A molecule, *trans*-(4-Me$_2$NC$_6$H$_4$C≡C)Ru$_2$(DMBA)$_4$-(C≡CC$_6$H$_4$-2,5-(OMe)$_2$-4-NO$_2$) (**34**; Figure 27), in substan-
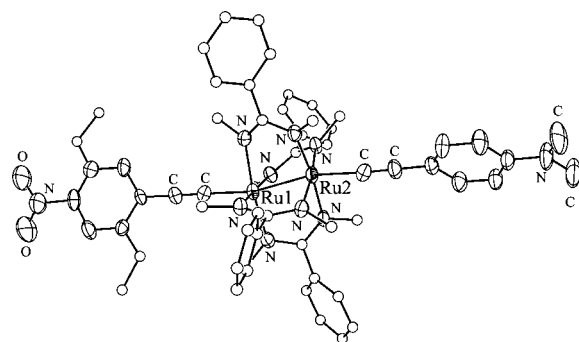

Figure 27. Structural plot of compound **34**.

tial yield. Subsequent optimization using a "high throughput" screening technique revealed conditions to produce unsymmetric compounds directly from Ru$_2$(DMBA)$_4$-(NO$_3$)$_2$ and a mixture of the alkynes (Scheme 4).[112]

Does the Ru$_2$-based prototype of D−σ−A assembly possess the necessary electronic structure to function as a molecular diode? A partial answer, we believe, can
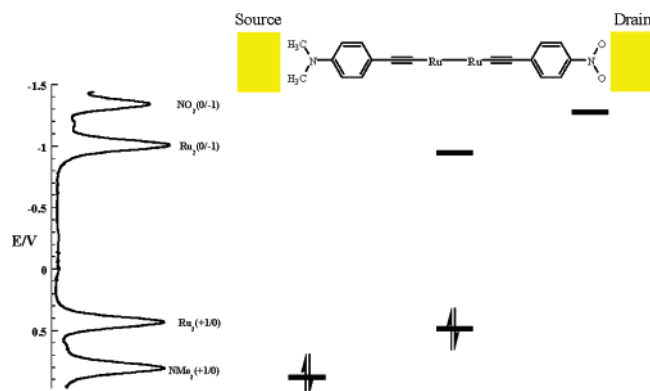

Figure 28. Distribution of frontier orbitals in a D−Ru$_2$−A molecule based on the DPV measurement of compound **34**.

be found from the DPV of **34**, which is shown vertically on the left of Figure 28 so that the order of redox couples conforms to the convention of the MO energy diagram. With the proper match with the Fermi level of a drain electrode, the injected electron will first "land" on the NO$_2$-based LUMO + 1 and subsequently cascade to LUMO, HOMO, and HOMO − 1 before reaching the source electrode, and the entire process is energetically downhill. Conversely, when the potential bias is reversed and the orientation of D−σ−A remains the same, the injected electron would "land" on the NMe$_2$ based HOMO − 1 and travel across the molecule "uphill" all the way, implying a disfavored transport process. A necessary prerequisite to test this naive intuition is the proper alignment of D−σ−A in a nanojunction, which may be realized with the molecule envisioned in Chart 6. The use of different "molecular alligator clips" will ensure the proper orientation as demonstrated by Kushmerick et al.[165]

VI. Conclusions and Outlook

Efforts from our laboratory during the last 6 years have resulted in an appreciable understanding of the synthesis and physical properties of diruthenium alkynyl building blocks. Further exploration of the reactivity of axial alkynyl ligands revealed the possible modification through the addition of electrophiles, and Glaser type homo-/cross-couplings of terminal alkynes, the latter of which is critical to both the extension of polyynyl chains and dimerization of building blocks along the axial direction. A subtle but important feature shared by all three sets of building blocks is their extraordinary stability toward oxygen and moisture, a

(172) *Molecular Nanoelectronics*; Reed, M. A., Lee, T., Eds.; American Scientific Publishers: Stevenson Ranch, CA, 2003.

(173) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277.
(174) Ho, G.; Heath, J. R.; Kondratenko, M.; Perepichka, D. F.; Arseneault, K.; Pézolet, M.; Bryce, M. R. *Chem. Eur. J.* **2005**, *11*, 2914.

Chart 6.   Donor−Ru$_2$−Acceptor Type Diode Molecule with Differently Masked Thiol Termini
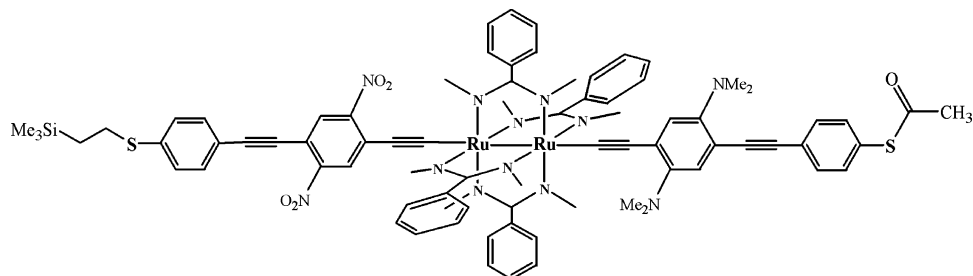
necessary criterion for practical materials that is often unmet by organometallics. Reflecting the minimized E_g values in all three sets of building blocks, facile electron and hole transfer have been demonstrated through bulk solution voltammetry and spectroelectrochemistry, while significant enhancement in molecular conductance over the pure organic molecules has been demonstrated through the STM study.

Our successes with diruthenium−alkynyl compounds not only point to the opportunities and potentials in this area but also bring out more challenging and open-ended questions that we wish to address soon.

(1) The use of type **1b** oligomers as molecular wires beyond a 10 nm length scale may face two potential roadblocks: (i) Peierls transition (metallic state to insulating state) that is well documented for 1-D metals such as polyacetylenes and (ii) the high threshold for bond percolation in a linear oligomer/polymer—a single defect along the conjugated backbone would result in the complete loss of conductivity.[175] A possible solution is to form "bundles" of wires through η^2 coordination of Pt^0 centers, similar to the cross-linking of PPEs by Weder et al.[65,66]

(2) While the methodologies for peripheral modification are becoming sophisticated in our laboratory,[148−150] those leading to the conjugates with peptides and nucleic acids remain unexplored, where the aqueous insolubility of Ru$_2$−alkynyl species is a potential stumbling block.

(3) Little is known about the photophysical properties of Ru$_2$−alkynyl species, such as their emissive properties, the ability to mediate energy transfer (photonic wires),[176] and their possible function as second- or third-order NLO chromophores. We are particularly interested in attaching both the conjugated dendrons (OPVs and OPEs) and nonconjugated dendrons (Fréchet type) to the Ru$_2$ core and using the hybrid dendrimer for photovoltaic application.[177]

(4) Aiming at better organic electronic materials, many interesting carbon-rich scaffolds have been developed in recent years, such as tetraethynylethene (TEE) and (*E*)- and (*Z*)-diethynylethene (DEE) by Diederich,[10] *gem*-DEE by Tykwinski,[178] and ethynyl-functionalized acenes by Anthony.[179,180] Combination of these small energy gap scaffolds and transition metals may

Chart 7

E-DEE   *Z*-DEE   *gem*-DEE   TEE
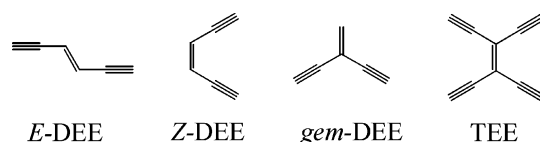
lead to materials with novel properties, although few metal complexes have been synthesized. It is certainly feasible to integrate a Ru$_2$ unit with these ene-yne ligands, as demonstrated by our recent report of [Ru$_2$-(ap)$_4$]$_2$-(μ-*E*-DEE)[130] (Chart 7).

(5) Our preliminary results of dimer and chain formation of Au nanoparticles aided with Ru$_2$−alkynyl linkers[111] revealed the possibility of hierarchical assemblies of nanoparticles in two and three dimensions with Ru$_2$−alkynyl "glues". These molecule−nanoparticle hybrid assemblies are promising new electronic materials, as indicated by the recent examples of coherent spin transfer between quantum dots with a 1,4-dithiolbenzene bridge[181] and NanoCell memories constructed from *disordered* metallic Au islands and sulfide-capped OPEs.[182]

All being said, it is appropriate to conclude by quoting Winston Churchill: *"Now this is not the end, it is not even the beginning of the end. But it is, perhaps, the end of the beginning"*.

(175) Roth, S.; Carroll, D. *One-dimensional Metals: Physics and Materials Science*; Wiley-VCH: Weinheim, Germany, 2004.

(176) Holten, D.; Bocian, D. F.; Lindsey, J. S. *Acc. Chem. Res.* **2002**, *35*, 57.

(177) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons: Concepts, Syntheses, Applications*; Wiley-VCH: Weinheim, Germany, 2001.

(178) Tykwinski, R. R.; Zhao, Y. M. *Synlett* **2002**, 1939.

(179) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C.-C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127*, 4986.

(180) Payne, M. M.; Parkin, S. R.; Anthony, J. E. *J. Am. Chem. Soc.* **2005**, *127*, 8028.

(181) Ouyang, M.; Awschalom, D. D. *Science* **2003**, *301*, 1074.

(182) Tour, J. M.; Cheng, L.; Nackashi, D. P.; Yao, Y. X.; Flatt, A. K.; St. Angelo, S. K.; Mallouk, T. E.; Franzon, P. D. *J. Am. Chem. Soc.* **2003**, *125*, 13279.