Redox-Active Molecular Wires Incorporating Ruthenium(II) σ-Arylacetylide Complexes for Molecular Electronics

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The preparation and properties of novel ruthenium carbon-rich complexes for molecular electronics are reported. The synthetic procedure used in this work led to the first series of neutral redox-active conjugated molecular wires including mono-, bi-, and trimetallic bis(σ-arylacetylide) complexes (Ru_nNC and $CNRu_nNC$, $n = 1$–3) having 1,4-diethynylbenzene spacers and one or two isocyanide terminal groups for surface binding. An analogous cationic σ-arylacetylide-allenylidene molecule ($AllRuNC^+$) is also reported. These new structurally rigid complexes have lengths ranging from 1.8 to 4.5 nm and are excellent candidates for the building of alternative metal−molecule−metal junctions. Indeed, the molecules uniquely contain up to three metal-redox centers that are efficiently coupled by conjugated ligands to provide significant electronic communication along the molecular backbone, as indicated by the optical and electrochemical properties. Furthermore, the wires offer multiple low potential redox states that can lead to unusual current–voltage behavior and efficient charge conduction. Overall, these molecules will open a route to establish the structure–property relationships of conductive molecular wires and to gain valuable insights into the correlation between charge transport and molecular length.

Introduction

Understanding of charge transport through molecular wires in metal−molecule−metal junctions is a central issue in the field of molecular electronics.[1,2] For example, electron transport across these junctions has been proposed to occur via resonant tunneling, nonresonant tunneling, or hopping mechanisms. However, the establishment of concrete correlations between these mechanisms, the structure of tailored molecules, and the metal contacts is still required. In addition, intriguing transport phenomena including Coulomb blockades or Kondo resonances,[3] current rectification,[2d] switching,[4] and negative differential resistance[5] suggest possible applications in nanoscale electronics and have stimulated continuing studies. So far, much of the progress is based on organic molecules. Wires incorporating metal complexes are particularly interesting, but scarce.[3b,c,6–9] They offer multiple redox and spin states that can lead to unusual current–voltage and efficient charge conduction. Polynuclear complexes bridged with π-conjugated ligands constitute a particularly attractive class of candidates. Indeed, the growing understanding of electronic structures of metal-based wire-like complexes suggests that the tailored design of extended molecules for efficient charge transport over long distances should be now possible.[10–13] However, to our knowledge, electrical measurements involving molecules having multiple redox-active metal units and various lengths have not been reported yet. This type of molecule is of primary interest to

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investigate the charge transport mechanism with respect to the molecular length and electronic structure of the wire, a crucial point that few studies have specifically addressed.[9a,c,14]

Several transition metal complexes of the type $[M]-C\equiv C-R-C\equiv C-[M]$ with direct connection of a carbon-rich bridge with metal centers have shown excellent abilities to provide a strong electronic interaction between the two remote redox-active metal centers.[12,13] This interaction occurs through the organic bridge by matching the energy of the metal-based redox orbitals with those of the bridging ligand orbitals, such that delocalization in the mixed valence state can be optimized by a process involving this ligand.[15] The role of the metallic moieties within the bridge has also been considered,[16,17] and the exceptional ability of ruthenium to operate as a connector allowing electron flow to occur between different elements in *trans*-ditopic carbon-rich systems, in contrast to other metals such as platinum, was demonstrated. Given the proposed relationship between electron delocalization and conductance,[18] these results gave us impetus to design several oligomeric carbon-rich ruthenium molecular wires terminated by surface linking groups and with a rigid rod architecture using $Ru(dppe)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) fragments developed in our group.[13] These molecules would allow the formation of alternative molecular junctions, from which the study of charge transport behavior as a function of molecular length can be achieved.

Herein, we report the synthesis and the optical and electrochemical properties of two unique series of linear ruthenium(II) bis(σ-arylacetylide) complexes, Ru_nNC and $CNRu_nNC$ (n = 1–3), in that (i) they contain up to three metal centers efficiently coupled by conjugated ligands to build a continuous π-system that undergoes easy oxidations and with lengths ranging from 1.8 to 4.5 nm, and (ii) they are terminated by one or two isocyanide (−NC) surface linking groups in order to allow the formation of self-assembled monolayers (SAMs) on metals. The compounds were designed with several parameters in mind. The diethynylbenzene linker to be introduced between the ruthenium centers has been chosen in order to provide a particularly stable π-electron-conjugated structure with a rigid-rod geometry, via an easy synthetic procedure, and also to maintain a high level of electronic coupling.[19] Furthermore, the low oxidation potentials of ruthenium σ-arylacetylides compared to organic molecules and the large separation of the reversible oxidation waves in bimetallic complexes indicate the chemical and thermodynamic stability of easily accessible redox states. Regarding the surface binding groups, two sets of molecules with one or two isocyanide functions were chosen in order to examine conductivity, as well as contact effects in symmetric ("bichemicontacts") or asymmetric ("monochemicontact") junctions,[20] with techniques such as conducting probe atomic force microscopy (CP-AFM) and crossed-wire (X-wire) junctions.[14b,21] In addition, we also targeted a cationic σ-arylacetylide-allenylidene arrangement[13d] with one isocyanide alligator clip ($AllRu_1NC^+$). Because these potential molecular wires should display properties strongly connected to their structure, this latter compound with a cationic charge and an easily accessible reduction state is of special interest. The significance of the molecules we report here was recently highlighted in a preliminary report dealing with the electrical properties of the $CNRu_nNC$ series that shows an exceptional weak dependence of the wire resistance with molecular length and demonstrates the correlation between the charge transport mechanism and molecular length.[22]

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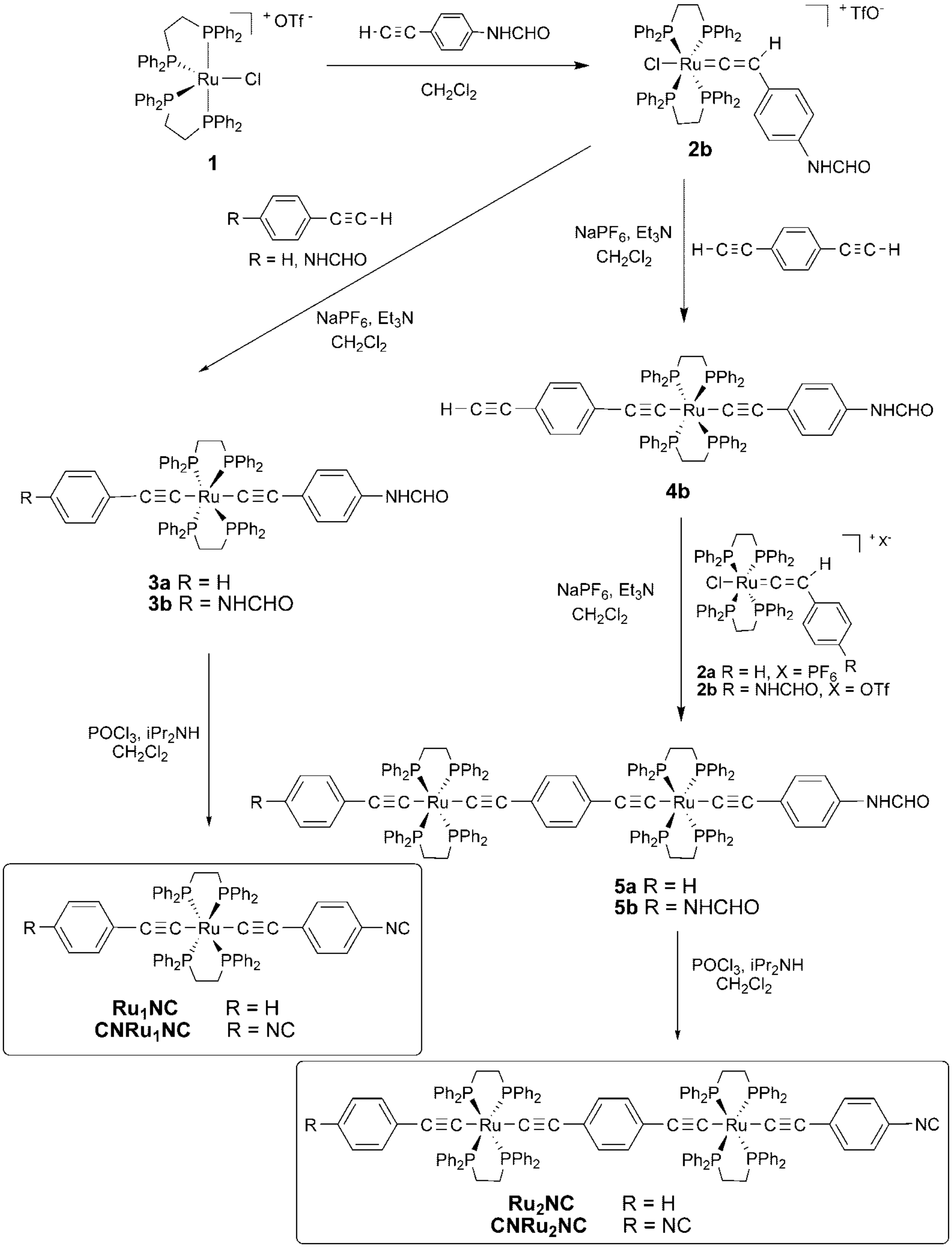
Scheme 1. Synthetic Pathways Yielding Ru$_n$NC and CNRu$_n$NC (n = 1, 2)



Results and Discussion

1. Synthesis of Bis(σ-arylacetylide) Wires. The synthetic strategy to achieve complexes terminated with one or two isocyanide (−NC) linking groups involves the preliminary introduction of a formamide function (−NHCHO) on one or both of the terminal phenyl groups. This function can be further dehydrated to give the desired isocyanide groups.[23] This dehydration should be the last synthetic step involved in the building of the mono-, bi-, and trimetallic carbon-rich complexes to avoid any complexation of the isocyanide function to 16-electron ruthenium intermediates.

The synthetic routes to Ru$_n$NC and CNRu$_n$NC (n = 1, 2) are shown in Scheme 1. The synthesis of the vinylidene precursor **2b** was achieved by activation of the *N*-(4-ethynylphenyl)formamide with the 16-electron precursor [(dppe)$_2$RuCl][OTf] (**1**) in good yield (75%). Following the general procedure previously developed in the laboratory to remove the *trans*-chlorine atom and to prepare bis(σ-arylacetylide),[13e] this cationic complex **2b** was further reacted with phenyl acetylene or *N*-(4-ethynylphenyl)formamide, in the presence of a noncoordinating salt (NaPF$_6$) and a base (Et$_3$N), to afford **3a** (86% yield) and the very poorly soluble complex **3b** (66% yield), respectively. These compounds were dehydrated using the phosphoryl chloride method to provide the bis(σ-arylacetylide) monometallic wires Ru$_1$NC and CNRu$_1$NC (60% yields), with one and two surface linking groups.

In order to build the bimetallic analogues, vinylidene **2b** was first reacted with 1,4-diethynylbenzene to achieve the building block **4b** bearing one terminal triple bond for further activation, under the same conditions as described before (60% yield). It should be noted that reaction with a large excess of 1,4-

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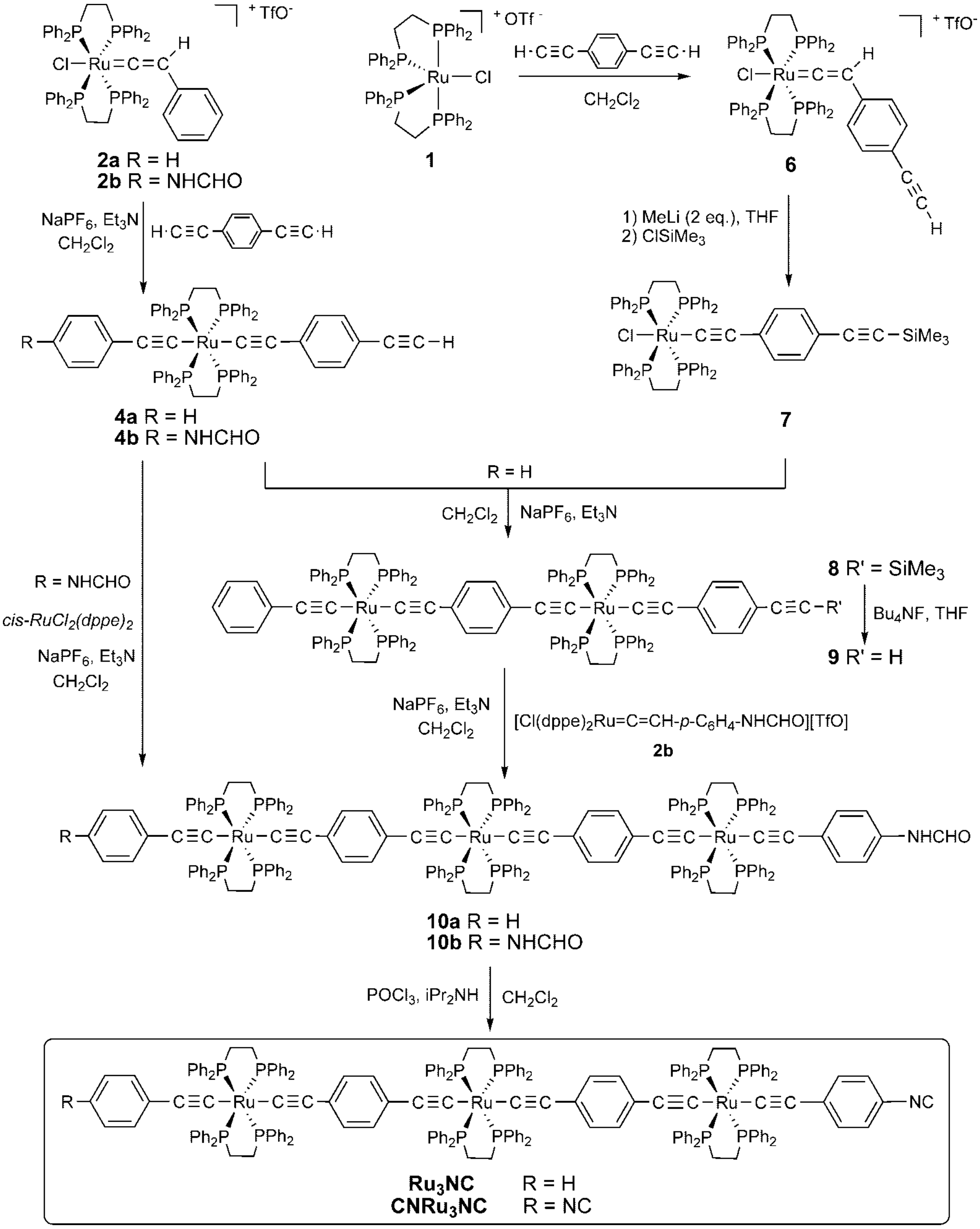
[23] Obrecht, R.; Herrmann, R.; Ugi, I. *Synthesis* **1985**, 400–402.

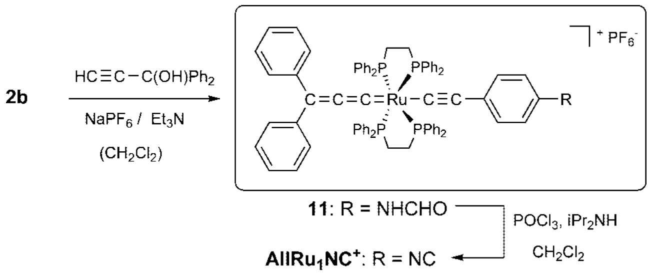
Scheme 2. Synthetic Pathways for Ru_3NC and $CNRU_3NC$



diethynylbenzene in a diluted solution of CH_2Cl_2 and selective precipitation of the product from a trace amount of the poorly soluble bimetallic adducts (CH_2Cl_2/pentane) provides a direct route to **4b**. Indeed, this procedure is advantageous over fastidious protection/deprotection procedures of one of the acetylenic function of 1,4-diethynylbenzene.[19i] Further activation of the terminal acetylenic function of **4b** with vinylidene **2a** or **2b** afforded the two bimetallic bis(σ-arylacetylide) complexes **5a** (58% yield) and **5b** (70% yield), respectively. Finally, dehydration reactions with phosphoryl chloride in the presence of diisopropylamine led to the expected isocyanide complexes Ru_2NC (62% yield) and $CNRu_2NC$ (76% yield).

The synthetic routes to Ru_3NC and $CNRu_3NC$ are shown in Scheme 2. The symmetric trimetallic precursor **10b** bearing two formamide groups was readily obtained from the substitution of the two chlorine atoms of *cis*-[$RuCl_2(dppe)_2$] by reaction with **4b**, followed by careful precipitations to remove unreacted starting materials. Although the solubility of this complex is very poor, preventing ^{13}C NMR analysis, the product was obtained in satisfactory yield (60%). On the other hand, the unsymmetrical trimetallic complex **10a** was more difficult to obtain. The first step followed the guidelines established for complex **4b** to obtain **4a** from vinylidene **2a** without the formamide functional group (76% yield). The building block **7** was achieved with the preliminary synthesis of the vinylidene adduct **6** from the 16-electron species **1**, followed by abstraction of both the vinylidene and acetylenic protons with MeLi. The addition of Me_3SiCl to the reaction mixture then led to the metal acetylide **7**, bearing an acetylenic function protected with the trimethylsilyl group (87% yield). This procedure provided a direct route to **7** in only two steps, with simple precursors. The next step was the coupling reaction between **7** and **4a** to obtain the bimetallic complex **8** (30% yield), followed by subsequent removal of the protecting group with fluoride to afford **9** (85% yield). Further reaction of the terminal acetylenic function with the vinylidene **2b** finally gave **10a**, containing three metal centers (30% yield). In a final step, compounds **10a**,**b** were dehydrated with $POCl_3$ in the presence of a base to afford the

Scheme 3. Synthetic Procedure for AllRu$_1$NC$^+$



trimetallic bis(σ-arylacetylide) wires Ru$_3$NC (65% yield) and CNRu$_3$NC (62% yield).

The cationic metal acetylide-allenylidene complex AllRuNC$^+$ was obtained in identical conditions from the formamide precursor **11**, in 66% yield (Scheme 3). The latter was obtained in moderate yield (40%) from the metal vinylidene **2b**, in the presence of a slight excess of propargylic alcohol, a noncoordinating salt, and a base.

All the wires were characterized by means of ^{31}P, ^{1}H, and ^{13}C (when soluble) NMR, IR, and mass spectroscopies. It is important to note that these large molecules inevitably contain included solvent, precluding any satisfactory elemental analysis.[24] For all final compounds, the success of the formamide dehydration reactions was first established with ^{1}H NMR spectra by the disappearance of the characteristic aldehyde proton signals resulting from the different association forms of the amide group. More direct evidence for the formation of the new functional groups is observed in the IR spectra. In addition to the disappearance of the $\nu_{(C=O)}$ band at 1690 cm^{-1}, a new isocyanide stretching band is observed between 2120 and 2110 cm^{-1}, very close to the $\nu_{(C\equiv C)}$ bands around 2050–2080 cm^{-1} (Figure 1). Furthermore, the intensity ratios of −NC to the −C≡C− stretches are consistent with the number of those bonds in the molecular structures. Finally, the *trans* dispositions of the carbon-rich chains on each of the ruthenium centers were established by the observation of a single resonance peak in the ^{31}P NMR spectra at ca. $\delta = 55$ ppm. On this basis, the molecular lengths were estimated in a range from 1.8 to 4.5 nm (Table 1). It is worth noting that monolayers were formed from the CNRu$_n$NC series.[22] The measured thicknesses were consistent with those estimations and thus fully support the wire structures reported here.

2. UV–Visible Spectra. In addition to the intense short-wavelength absorption bands for transitions involving the dppe ligand and the carbon-rich ligand (intraligand transitions),[25,26] all the bis-acetylide complexes show a broad absorption band with a large extinction coefficient at lower energy around 370–380 nm (Table 1, Figure 2). This low-energy transition ($E_{op} \approx 3.2$ eV) presents a Ru^{II}(dπ)$\rightarrow \pi^*$(L) (MLCT) character admixed with a moderate to strong $\pi \rightarrow \pi^*$ (IL) nature. Indeed, the highest occupied molecular orbital (HOMO) involved in the transition results from a considerable mixing of Ru(dπ) orbitals with alkynyl π-orbitals, leading to an increase of the ligand character with length.[13b,19,25–27] This band is red-shifted by comparison with Ru(dppe)$_2$(−C≡C−Ph)$_2$ ($\lambda_{max} = 322$ nm) owing to the electron-withdrawing effect of the isocyanide group(s), significantly stabilizing the associated unoccupied ligand-centered orbital (LUMO+1 for the former[26]). This MLCT band presents a bathochromic shift when the length of the molecule is increased, and interestingly there is a larger tail on the low-energy side as well. This low-energy tail might be ascribed to forbidden transitions as already suggested,[25,26] showing that the related orbitals are affected by further metal coordination. These observations are thus consistent with an increase of the conjugated path length, as probed by the Franck–Condon absorption event. Consequently, the HOMO–LUMO gap is expected to decrease in the series.[28] For the cumulenic compound AllRu$_1$NC$^+$, the main broad transition in the visible region ($\lambda_{max} = 590$ nm) is expected to arise from the allowed transition from one of the metal-based HOMOs to an unoccupied ligand-based orbital (MLCT), the latter probably being mainly delocalized over the allenylidene ligand.[25] It is worth emphasizing that for all complexes the observed bands are broad and certainly include several transitions close in energy, with a MLCT character, and involving several ligands.

3. Electrochemical Data. The ability of these new conjugated species to act as molecular wires is closely related to their redox properties. Therefore, cyclic voltammetry traces (CVs) were recorded for all compounds to study their nature (CH$_2$Cl$_2$ solutions, 0.1 M Bu$_4$NPF$_6$). The values of the potentials are reported in Table 1, and typical CVs are displayed in Figure 3 as well as in the Supporting Information. The CV traces are slightly distorted because of adsorption of the oxidized species at the electrode. This is not unexpected because of the presence of one or two surface binding groups, related species without isocyanide groups showing usually cleaner behavior. The number of electrochemical processes depends on the number of ruthenium centers present in the molecules. The two monometallic compounds Ru$_1$NC and CNRu$_1$NC undergo a one-electron oxidation followed by an irreversible process consistent with a chemical reaction of the second oxidized species. To a first approximation, the first oxidation step is usually viewed as essentially involving the Ru^{III}/Ru^{II} couple, but is also strongly associated with a carbon-rich ligand character.[26,30] These potentials are consistent with the oxidation potential of Ru(dppe)$_2$(−C≡C−Ph)$_2$ ($E° = -0.05$ V vs FeCp$_2$). However, they are significantly altered by the electron-withdrawing character of the isocyanide group(s), which demonstrates the expected HOMO level shift. The second irreversible oxidation at higher potential is mainly attributed to a ruthenium-based process.

The bimetallic complexes Ru$_2$NC and CNRu$_2$NC display two redox processes in addition to the high potential systems. As

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(24) Importantly, ^{31}P NMR, mass spectroscopy, as well as electrochemical studies (*vide infra*), support the absence of unreacted materials or side-products.

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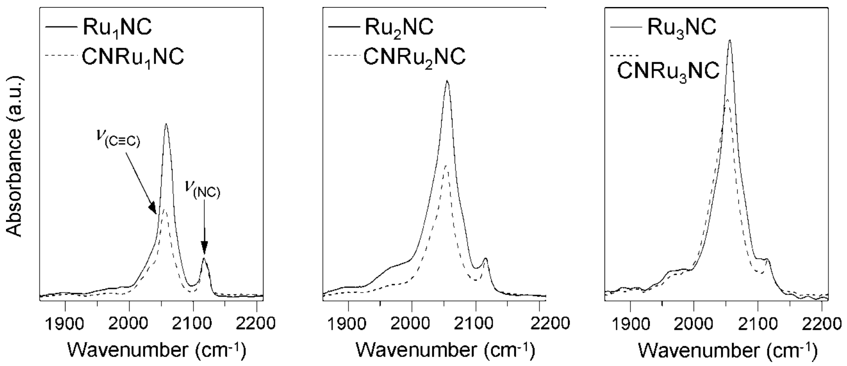

Figure 1. IR vibration stretches observed for $-C\equiv C-$ and $-NC$ bonds in the Ru$_n$NC and CNRu$_n$NC (n = 1–3) series. The spectra are normalized to the $\nu_{(NC)}$ band intensities.

Table 1. Molecular Lengths and Electrochemical (CV) and Uv–Vis Data

		electrochemistry[b]			
	molecular length (Å´)[a]	$E°$/V[c]			UV–vis[h] λ_{max}/nm (ϵ/mol^{-1} L cm^{-1})
Ru$_1$NC	18.6	0.04		0.55[d]	226 (76000), 318 (26600), 368 (32700)
Ru$_2$NC	30.9	−0.24	0.06	0.88[d]	227 (120000), 378 (50000)
Ru$_3$NC	43.7	−0.24	0.03[ef]	0.86[d]	227 (178000), 380 (76600)
CNRu$_1$NC	20.0	0.12		0.87[d]	226 (42200), 374 (29000)
CNRu$_2$NC	32.4	−0.20	0.11	0.94[d]	226 (135300), 382 (83000)
CNRu$_3$NC	45.2	−0.20	0.10[ef]	0.89[d]	231 (180000), 384 (60500)
AllRu$_1$NC$^+$	18.4	−0.94[g]	0.85[e]		232 (47000), 318 (17800), 430 (5800), 590 (12000)

[a] Molecular length was estimated through the MM2 energy minimization using Cambridge Scientific Chem3D software and bond lengths in the literature (see refs 13d and 29). [b] Sample 1 mM, Bu$_4$NPF$_6$ (0.1 M) in CH$_2$Cl$_2$, v = 100 mV s^{-1}, potentials are reported in V vs ferrocene as an internal standard. [c] Reversible oxidation processes, $\Delta E_p \approx$ 60–80 mV. [d] Peak potential of an irreversible process. [e] $\Delta E_p \approx$ 145 mV for Ru$_3$NC, 125 mV for CNRu$_3$NC, and 130 mV for AllRu$_1$NC$^+$. [f] Two overlapping one-electron processes. [g] Reversible reduction process for the allenylidene complex. [h] In CH$_2$Cl$_2$.

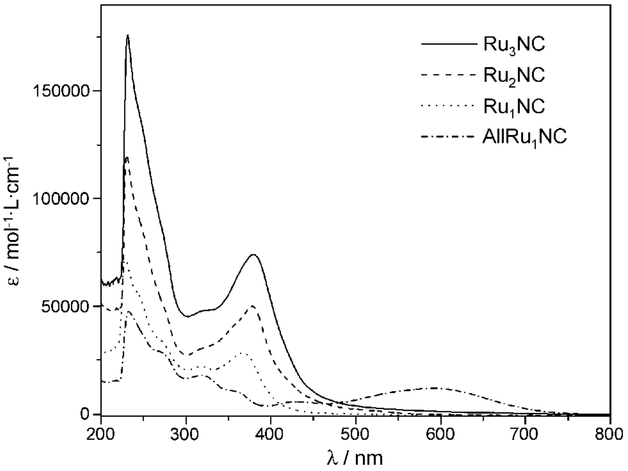

Figure 2. Electronic absorption spectra for AllRu$_1$NC$^+$ and Ru$_n$NC (n = 1–3) in CH$_2$Cl$_2$.

with the monometallic complexes, Ru$_2$NC shows slightly easier processes due to the presence of only one electron-withdrawing surface linking group. The large separation of the first two processes for both compounds ($\Delta E° \approx$ 300 mV, $K_c = \exp(\Delta E°F/RT) = 1.5 \times 10^5$) establishes that all of the mono-oxidized species are stable in solution with respect to disproportionation. Furthermore, the observed first and second oxidation potentials are, respectively, lower and higher than the first oxidation potential of Ru$_1$NC. This fact supports the idea that the first oxidized species gain considerable stabilization due to electron delocalization along the conjugated chain. One can object that it is well-known that other phenomena such as Columbic repulsion, structural distortion through oxidations, and ion pairing besides delocalization also contribute to the redox potential and one must be careful in interpreting the meaning of the K_c trends.[31] However, as such occurrences have been demonstrated as being directly connected to electronic coupling between metal centers and ligands for closely related complexes,[13b,c,19] similar electronic delocalization is expected to occur in the present molecular wires.

The same trend in the positions of the oxidation waves is observed for the trimetallic adducts Ru$_3$NC and CNRu$_3$NC, with the first one-electron oxidation occurring at similar potentials to the bimetallic adducts. On the basis of the intensities of the waves, the second oxidation wave can be considered as a result of two coincident one-electron processes owing to the presence of three ruthenium centers. A closer inspection reveals that this wave is broader than that of the second oxidation for the bimetallic adducts. Added to a potential difference of ca. 145 mV for Ru$_3$NC and 125 mV for CNRu$_3$NC between the anodic and the cathodic peaks, this suggests that the two processes do not occur at exactly the same potential. With the help of the Richardson and Taube protocol[32] and assuming two reversible overlapping systems, their potential difference $\Delta E°$ could be estimated as ca. 105 and 90 mV in Ru$_3$NC and CNRu$_3$NC respectively. Overall, these observations support an electronic communication along the trimetallic wires in the different oxidized states, which is not detected for longer bridging ligands.[19a]

The cationic complex AllRu$_1$NC$^+$ displays a well-defined reversible monoelectronic wave attributed to the reduction of the cumulenic ligand.[33] The oxidation process is observed at

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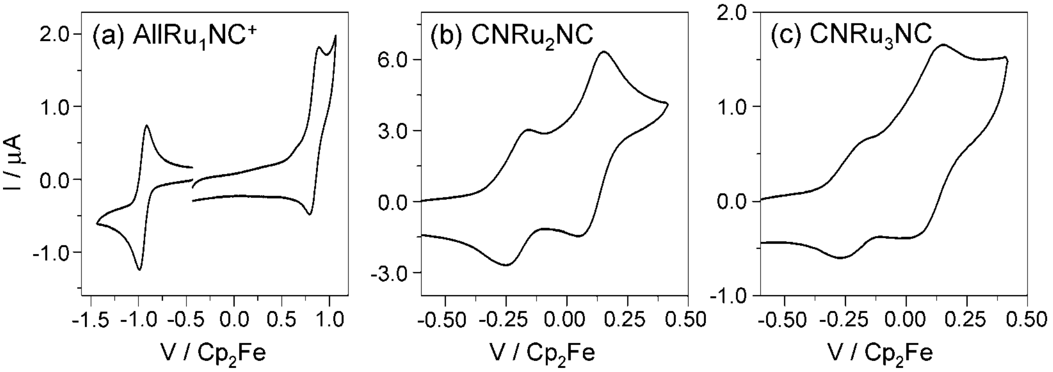

Figure 3. CV traces obtained for (a) AllRu$_1$NC$^+$, (b) CNRu$_2$NC, and (c) CNRu$_3$NC in CH_2Cl_2 (Bu_4NPF_6, 0.1 M); $v = 200$ mV s^{-1}.

higher potential than those of the neutral metal acetylides and is ascribed to the Ru^{III}/Ru^{II} couple with some ligand participation as well.[25]

For several years, it has been well-recognized that the structure of mixed-valence compounds is highly dependent on the bridging ligand and on the nature of the metallic building block.[10–13] The oxidations are less involved in the metal centers with ruthenium complexes relative to iron species, as an example, and thus involve a significant participation of the noninnocent ligands in redox events.[12,13b,c,19,27,34] For this reason, the electronic communication is difficult to quantify with the usual Robin and Day or Hush parameters.[13c,19a,34a] Nevertheless, with the present molecules, the optical and electrochemical properties support significant electronic coupling along the backbone, especially between two adjacent metals through the bridging ligand. Another important parameter is the HOMO–LUMO gap, estimated to be only 2 eV for $Ru(PH_3)_4(-C{\equiv}C-Ph)_2$, due to the large amount of orbital mixing between the ruthenium and ligand orbitals.[26] This value is expected to be even lower for our isocyanide complexes, particularly for the polymetallic ones (vide supra). Such a low gap, relevant for conductance efficiency, makes the Fermi level of the electrodes closer in energy to the frontier orbitals by comparison with usual organic molecules ($E_g \approx 3$–8 eV). Therefore, taking into account the overall properties described above, these new ruthenium wires that include one or more metal centers are especially suitable candidates for molecular electronics. In particular, the low oxidation potentials and the electronic delocalization are properties expected to enhance efficiency of tunnelling and/or direct charge injection (hopping), as well as to promote low length dependence of resistance in molecular junctions.[22]

Conclusion

In this work, we have synthesized and studied ruthenium carbon-rich complexes to achieve a unique series of molecular wires for molecular electronics. These ruthenium(II) σ-arylacetylide complexes with structural rigidity and surface linking groups will allow for the building of alternative molecular junctions bearing one, two, or three metal centers. The electrochemical and optical properties are intricate functions of the metal and conjugated ligand orbitals leading to extended electronic delocalization in different oxidation states. In particular, cyclic voltammetry reveals the presence of low oxidation potentials that should enhance the efficiency of tunneling, and also of direct charge injection into the molecular wires. Therefore, these compounds are expected to show improved molecular conductance over pure OPE (oligo(phenylene-ethylene)s) of comparable length. Moreover, the different molecular lengths (from 1.8 to 4.5 nm) and structures (neutral acetylide/cationic allenylidene) are expected to give valuable insights into the structure–property relationships, with emphasis on the transport mechanisms.

This area is likely to undergo further developments in the future with the possibility to modulate the properties of molecules with design. We believe that carbon-rich organometallics are an attractive basis for a device toolbox in which a spectrum of device properties can be achieved by changing the nature of the spacer group and/or metal. Further experiments to build related and longer organometallic wires are underway.

Experimental Section

General Comments. The reactions were carried out under an inert atmosphere using Schlenk techniques. Solvents were dried and distilled under argon using standard procedures. Electrochemical studies were carried out under argon using an Eco Chemie Autolab PGSTAT 30 potentiostat (CH_2Cl_2, 0.1 M Bu_4NPF_6), the working electrode was a Pt disk, and ferrocene the internal reference. High-resolution mass spectra (HRMS) were recorded in Rennes at the CRMPO (Centre Régional de Mesures Physiques de l'Ouest) on a ZabSpecTOF (LSIMS at 4 kV) spectrometer. The ruthenium complexes [RuCl(dppe)$_2$][TfO] (1),[35] *trans*-[Cl(dppe)$_2$Ru=C=C-HPh][PF$_6$] (**2a**),[13e] *cis*-RuCl$_2$(dppe)$_2$,[36] H−C≡C−*p*-C$_6$H$_4$−NHCHO[37] and H−C≡C-*p*-C$_6$H$_4$−C≡C−H[37] have been obtained as previously reported.

***trans*-[Cl(dppe)$_2$Ru=C=CH(*p*-C$_6$H$_4$)−NHCHO][TfO] (2b).** A Schlenk flask was charged with [RuCl(dppe)$_2$][TfO] (**1**) (541 mg, 0.5 mmol), H−C≡C−(*p*-C$_6$H$_4$)-NHCHO (72 mg, 0.5 mmol), and CH_2Cl_2 (40 mL). The mixture was stirred at room temperature for 24 h. The solvent was removed under vacuum, and the residue was washed with Et_2O (3 × 30 mL). A brown powder was isolated after drying under vacuum (400 mg, 75% yield). $^{31}P\{^1H\}$ NMR (81 MHz, CDCl$_3$): δ 41.49 (s, PPh$_2$). ^1H NMR (300 MHz, CDCl$_3$): δ 9.30 (s, 1H), 8.34 (s, 1H), 7.37−5.60 (m, 44H, Ph), 2.99 (s, 1H),

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2.83 (m, 8 H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 356.3 (quint., $^2J_{PC}$ = 13 Hz, Ru=C), 159.7 (C=O), 136.5–119.8 (Ph), 108.9 (Ru=C=$\underline{C}$−), 28.6 (m, CH_2, $|^1J_{PC}+^3J_{PC}|$ = 24 Hz). IR (KBr): 1687 cm^{-1} ($\nu_{C=O}$), 1636 cm^{-1} ($\nu_{=C=C}$). HR-MS ES$^+$ (*m/z*): 1042.2236 ([M]$^+$, calcd: 1042.2199).

***trans*-[Ph-C≡C−Ru(dppe)$_2$−C≡C-*p*-C_6H_4-NHCHO] (3a).** A Schlenk flask was charged with **2b** (500 mg, 0.4 mmol) and $NaPF_6$ (136 mg, 0.8 mmol). After addition of CH_2Cl_2 (20 mL), phenylacetylene (88 μL, 0.8 mmol), and Et_3N (0.225 mL, 1.6 mmol), the mixture was stirred for 20 h at room temperature. The solution was filtered, washed with water (3 × 30 mL), and dried with $MgSO_4$, and the solvent was removed under vacuum. After washing of the residue with pentane (2 × 20 mL), a yellow powder was recovered (400 mg, 86% yield). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 55.09 (s, PPh_2). ^1H NMR (200 MHz, $CDCl_3$): δ 8.60 (d, J_{HH} = 11.3 Hz, 0.5H), 8.37 (s, 0.5H), 7.57−6.70 (m, 48H, Ph), 2.64 (m, 8 H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 161.2 (C=O), 157.7–122.1 (Ph), 118.4 and 117.7 (Ru−C≡$\underline{C}$−), 30.6 (m, CH_2, $|^1J_{PC}+^3J_{PC}|$ = 24 Hz). IR (KBr): 2065 cm^{-1} ($\nu_{C≡C}$), 1695 cm^{-1} ($\nu_{C=O}$). HR-MS ES$^+$ (*m/z*): 1166.2516 ([M + Na]$^+$, calcd: 1166.2508).

***trans*-[OHCHN-*p*-C_6H_4−C≡C−Ru(dppe)$_2$−C≡C−*p*-C_6H_4−NHCHO] (3b).** The same procedure as that used to obtain **3a** was carried out with **2b** (490 mg, 0.4 mmol), H−C≡C−(*p*-C_6H_4)−NHCHO (174 mg, 1.2 mmol), $NaPF_6$ (135 mg, 0.8 mmol), and Et_3N (0.230 mL, 1.6 mmol). After treatment, a poorly soluble brown powder was isolated (312 mg, 66% yield). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 55.05 (s, PPh_2). ^1H NMR (200 MHz, $CDCl_3$): δ 8.63 (d, J_{HH} = 11.3 Hz, 1H), 8.38 (s, 1H), 7.51− 6.70 (m, 48H, Ph), 2.62 (m, 8 H, CH_2). IR (KBr): 2062 cm^{-1} ($\nu_{C≡C}$), 1694 cm^{-1} ($\nu_{C=O}$). HR-MS ES$^+$ (*m/z*): 1186.2677 ([M]$^+$, calcd: 1186.2649).

***trans*-[Ph−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C_6H_4)−C≡C−H] (4a).** The same procedure as that used to obtain **3a** was carried out with **2a** (592 mg, 0.5 mmol), 1,4-diethynylbenzene (190 mg, 1.5 mmol), $NaPF_6$ (168 mg, 1.0 mmol), and Et_3N (0.280 mL, 2.0 mmol). After treatment, a selective precipitation by slow addition of pentane in a CH_2Cl_2 solution of the residue was achieved to remove traces of the less soluble bimetallic adduct. Following drying, a brown powder was isolated (430 mg, 76% yield). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 54.94 (s, PPh_2). ^1H NMR (200 MHz, $CDCl_3$): δ 7.71−6.62 (m, 49H), 3.13 (s, 1 H, C≡C−H), 2.65 (m, 8 H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 138.2 (quint., $^2J_{CP}$ = 15 Hz, Ru−$\underline{C}$≡C−), 136.3–114.7 (Ph), 116.2 and 115.9 (Ru−C≡$\underline{C}$), 83.8 ($\underline{C}$≡C−H), 76.0 (C≡$\underline{C}$−H), 30.6 (m, CH_2, $|^1J_{PC}+^3J_{PC}|$ = 24 Hz). IR: 3289 cm^{-1} ($\nu_{≡C\text{-}H}$), 2055 cm^{-1} ($\nu_{C≡C}$). HR-MS ES$^+$ (*m/z*): 1124.2576 ([M]$^+$, calcd: 1124.2533).

***trans*-[OHCHN−C≡C−*p*-C_6H_4−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C_6H_4)−C≡C−H] (4b).** The same procedure that was used to obtain **3a** was carried out with **2b** (500 mg, 0.4 mmol), H−C≡C−*p*-C_6H_4−C≡C−H (152 mg, 1.20 mmol), $NaPF_6$ (135 mg, 0.8 mmol), and Et_3N (0.230 mL, 1.6 mmol) in 60 mL of CH_2Cl_2. After treatment, a selective precipitation by slow addition of pentane in a CH_2Cl_2 solution of the residue was achieved to remove traces of the less soluble bimetallic adduct. Further drying led to a brown powder (430 mg, 60% yield). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 54.88 (s, PPh_2). ^1H NMR (200 MHz, $CDCl_3$): δ 8.63 (d, J_{HH} = 11.8 Hz, 0.5 H), 8.38 (s, 0.5H), 7.71−6.91 (m, 48H, Ph), 3.13 (s, 1 H, C≡C−H), 2.63 (m, 8 H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 162.2 (C=O), 158.7–122.1 (Ph), 119.6 and 118.9 (Ru−C≡$\underline{C}$), 84.9 ($\underline{C}$≡C−H), 77.1 (C≡$\underline{C}$−H), 31.7 (m, CH_2, $|^1J_{PC}+^3J_{PC}|$ = 25 Hz). IR (KBr): 3291 cm^{-1} ($\nu_{≡C\text{-}H}$), 2055 cm^{-1} ($\nu_{C≡C}$), 1695 cm^{-1} ($\nu_{C=O}$). HR-MS ES$^+$ (*m/z*): 1168.2687 ([M]$^+$, calcd: 1168.2689).

***trans*-[Ph−C≡C−Ru(dppe)$_2$-C≡C−*p*-C_6H_4−C≡C−Ru(dppe)$_2$−C≡C−*p*-C_6H_4−NHCHO] (5a).** The same procedure that was used to obtain **3a** was carried out with **2a** (236 mg, 0.2 mmol), bis(σ-arylacetylide) complex **4b** (233 mg, 0.2 mmol), $NaPF_6$ (68 mg, 0.4 mmol), and Et_3N (0.120 mL, 0.8 mmol). After treatment, a brown powder was isolated (250 mg, 58% yield). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 55.09 (s, PPh_2). ^1H NMR (200 MHz, $CDCl_3$): δ 8.66 (d, J_{HH} = 11.8 Hz, 0.5H), 8.34 (s, 0.5H), 7.69-6.53 (m, 93H, Ph), 2.64 (m, 16 H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 161.9 (C=O), 158.4–122.8 (Ph), 119.2, 119,1 118.5, and 118.4 (Ru−C≡$\underline{C}$−), 31.5 and 31.44 (m, CH_2, $|^1J_{PC}+^3J_{PC}|$ = 24 Hz). IR (KBr): 2054 cm^{-1} ($\nu_{C≡C}$), 1690 cm^{-1} ($\nu_{C=O}$). HR-MS ES$^+$ (*m/z*): 2166.4810 ([M + H]$^+$, calcd: 2166.4787).

***trans*-[OHCHN−*p*-C_6H_4−Ru(dppe)$_2$−C≡C−*p*-C_6H_4−C≡C−Ru(dppe)$_2$−C≡C−*p*-C_6H_4−NHCHO] (5b).** The same procedure as that used to obtain **3a** was carried out with **2b** (88 mg, 0.07 mmol), bis(σ-arylacetylide) complex **4b** (84 mg, 0.07 mmol), $NaPF_6$ (24 mg, 0.14 mmol), and Et_3N (60 μL, 0.42 mmol). After treatment, a poorly soluble brown powder was isolated (111 mg, 70% yield). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 55.04 (s, PPh_2). ^1H NMR (200 MHz, $CDCl_3$): δ 8.66 (d, J_{HH} = 11.8 Hz, 1H), 8.34 (s, 1H), 7.69−6.53 (m, 92H, Ph), 2.64 (m, 16 H, CH_2). IR: 2054 cm^{-1} ($\nu_{C≡C}$), 1694 cm^{-1} ($\nu_{C=O}$). HR-MS ES$^+$ (*m/z*): 2208.4780 ([M]$^+$, calcd: 2208.4711).

***trans*-[Cl(dppe)$_2$Ru=C=CH−(*p*-C_6H_4)−C≡C−H][TfO] (6).** The same procedure for the preparation of **2a** was used with [RuCl(dppe)$_2$][TfO] (**1**) (541 mg, 0.5 mmol) and 1,4-diethynylbenzene (252 mg, 2.0 mmol). After treatment, 400 mg of a brown powder was obtained (90% yield), rapidly used in the next step. $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 37.24 (s, PPh_2). ^1H NMR (200 MHz, $CDCl_3$): δ 7.51–7.08 (m, 40H, Ph), 6.65 (d, $^3J_{HH}$ = 7 Hz, 2H, Ph on carbon-rich chain), 5.61 (d, $^3J_{HH}$ = 7 Hz, 2H, Ph on carbon-rich chain), 4.59 (quint., $^4J_{PH}$ = 3 Hz, 1H, H vinylidene), 2.97 (s, 1H, C≡C−H), 2.95 (m, 8H, CH_2). IR (KBr): 3283 cm^{-1} ($\nu_{≡C-H}$), 2102 cm^{-1} ($\nu_{C≡C}$), 1595 cm^{-1} ($\nu_{=C=C}$).

***trans*-[Cl(dppe)$_2$Ru−C≡C−(*p*-C_6H_4)−C≡C−$SiMe_3$] (7).** A Schlenk flask was charged with vinylidene **6** (483 mg, 0.40 mmol) and dry THF (45 mL). The solution was cooled to −78 °C, and MeLi (0.5 mL, 0.80 mmol, 1.6 M in THF) was added dropwise. The mixture was stirred for 1 h at −78 °C. With a syringe, $ClSiMe_3$ (0.5 mL, 4 mmol) was further added, and stirring was continued until warming at room temperature. The solution was evaporated, and the residue dissolved in dichloromethane. After filtration through a short neutral alumina plug, the solvent was removed and the residue was washed by pentane. Drying led to 390 mg of a yellow powder (87% yield). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 50.29 (s, PPh_2). ^1H NMR (200 MHz, $CDCl_3$): δ 7.42−6.49 (m, 44H, Ph), 2.71 (m, 8 H, CH_2), 0.28 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 136.3–124.5 (Ph), 116.4 (Ru−C≡$\underline{C}$−), 106.2 ($\underline{C}$≡C−$SiMe_3$), 93.5 (C≡$\underline{C}$−$SiMe_3$), 30.5 (m, CH_2, $|^1J_{PC}+^3J_{PC}|$ = 23 Hz), −0.2 (s, $SiMe_3$). IR (KBr): 2149 cm^{-1} ($\nu_{C≡C}$), 2062 cm^{-1} ($\nu_{C≡C}$); HR-MS ES$^+$ (*m/z*): 1130.2244 ([M]$^+$, calcd: 1130.2225).

***trans*-[Ph−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C_6H_4)−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C_6H_4)−C≡C−$SiMe_3$] (8).** The same procedure for the preparation of **3a** was used with the acetylide complex **7** (226 mg, 0.2 mmol), the diacetylide complex **4a** (225 mg, 0.2 mmol), $NaPF_6$ (67 mg, 0.4 mmol), and Et_3N (0.120 mL, 0.8 mmol). Following 24 h of stirring at room temperature and usual workup, the residue was dissolved back in dichloromethane and filtered through a short neutral alumina plug. After solvent concentration, precipitation by slow addition of pentane, filtration, and drying, a pale yellow powder was isolated (130 mg, 30% yield). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 54.38 and 54.17 (s, PPh_2). ^1H NMR (200 MHz, $CDCl_3$): δ 7.72−6.49 (m, 93H, Ph), 2.68 (m, 16 H, CH_2), 0.29 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2): δ 137.7–123.2 (Ph), 118.5, 117.8, 117.2, 116.9 (Ru−C≡$\underline{C}$−), 106.8 ($\underline{C}$≡C−$SiMe_3$), 95.5 (C≡$\underline{C}$−$SiMe_3$), 31.9 (m, CH_2, $|^1J_{PC}+^3J_{PC}|$ = 24 Hz), 0.2 (s, $SiMe_3$). IR (KBr): 2146 cm^{-1} ($\nu_{C≡C}$), 2054 cm^{-1} ($\nu_{C≡C}$). HR-MS ES$^+$ (*m/z*): 2257.4652 ([M + K]$^+$ calcd: 2257.4682).

***trans*-[Ph−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−C≡C−H] (9).** The desylilation reaction of **8** (150 mg, 0.07 mmol) was achieved with Bu$_4$NF (0.08 mmol) in THF (10 mL). Stirring was maintained for 1 h at room temperature. After solvent evaporation, the crude material was dissolved in CH$_2$Cl$_2$, washed with water, and dried with MgSO$_4$, and the solvent was removed. Drying led to 107 mg of a pale yellow powder (124 mg, 85% yield) rapidly used in the next step. ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ 54.98 and 54,79 (s, PPh$_2$). ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.66–6.58 (m, 93H, Ph), 3.13 (s, 1 H, C≡C−H), 2.69 (m, 16 H, CH$_2$). IR (KBr): 2055 cm^{-1} ($\nu_{\mathrm{C\equiv C}}$).

***trans*-[Ph−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−NHCHO] (10a).** The same procedure as that used to obtain **3a** was carried out with vinylidene **2b** (61 mg, 0.05 mmol), bimetallic complex **9** (107 mg, 0.05 mmol), NaPF$_6$ (17 mg, 0.1 mmol), and Et$_3$N (0.04 mL, 0.3 mmol). After treatment, precipitation by slow addition of pentane in a CH$_2$Cl$_2$ solution of the residue led to 48 mg of a brown powder (30% yield). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ 55.09 (s, PPh$_2$). ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.65 (d, J_{HH} = 11.8 Hz, 0.5H), 8.35 (s, 0.5H), 7.70−6.70 (m, 137H, Ph), 2.69 (m, 24 H, CH$_2$). ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 161.9 (C=O), 158.4–126.9 (Ph), 118.6 and 118.4 (Ru−C≡$\underline{\mathrm{C}}$−), 31.5 (m, CH$_2$, $|^1J_{PC}+^3J_{PC}|$ = 24 Hz). IR (KBr): 2055 cm^{-1} ($\nu_{\mathrm{C\equiv C}}$), 1698 cm^{-1} ($\nu_{\mathrm{C=O}}$). HR-MS ES$^+$ (*m/z*): 3187.7149 ([M]$^+$calcd: 3187.6716).

***trans*-[OHCHN−*p*-C$_6$H$_4$−Ru(dppe)$_2$−C≡C−*p*-C$_6$H$_4$−C≡C−Ru(dppe)$_2$−C≡C−*p*-C$_6$H$_4$-C≡C−Ru(dppe)$_2$−C≡C−*p*-C$_6$H$_4$−NHCHO] (10b).** The same procedure for the preparation of **3a** was carried out with the diacetylide complex **4b** (170 mg, 0.14 mmol), *cis*-RuCl$_2$(dppe)$_2$ (70 mg, 0.07 mmol), NaPF$_6$ (47 mg, 0.28 mmol), and Et$_3$N (0.085 mL, 0.60 mmol) in 20 mL of CH$_2$Cl$_2$. After treatment, precipitation by slow addition of pentane in a CH$_2$Cl$_2$ solution of the residue led to a poorly soluble brown powder (130 mg, 60% yield). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ 54.93 (s, PPh$_2$). ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.62 (d, J_{HH} = 11.6 Hz, 1H), 8.35 (s, 1H), 7.66−6.69 (m, 136H, Ph), 2.69 (m, 24H, CH$_2$). IR (KBr): 2054 cm^{-1} ($\nu_{\mathrm{C\equiv C}}$), 1696 cm^{-1} ($\nu_{\mathrm{C=O}}$). HR-MS ES$^+$ (*m/z*): 3230.7076 ([M + H]$^+$, calcd: 3230.6863).

***trans*-[Ph$_2$C=C=C=Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−NHCHO][PF$_6$] (11).** A Schlenk flask was charged with vinylidene **2b** (800 mg, 0.65 mmol), Ph$_2$C(OH)−C≡CH (208 mg, 1 mmol), and NaPF$_6$ (440 mg, 2.6 mmol). Then, dry dichloromethane (60 mL) and Et$_3$N (0.360 mL, 2.6 mmol) were added with a syringe. The mixture was stirred for 3 days at room temperature. The solution was washed with water, dried with MgSO$_4$, and filtered, and the solvent was removed under vacuum. The residue was washed with Et$_2$O (2 × 20 mL). Crystallization in a CH$_2$Cl$_2$−C$_5$H$_{12}$ (30/70) mixture led to 350 mg of a blue compound (40% yield). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ 43.34 (s, PPh$_2$). ^{1}H NMR (200 MHz, CDCl$_3$): δ 9.30 (d, J_{HH} = 11.3 Hz, 0.5H), 8.42 (s, 1H), 7.88−6.82 (m, 54H, Ph), 2.96 (m, 8 H, CH$_2$). ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 315.7 (quint., $^2J_{PC}$ = 13.6 Hz, Ru=C), 213.5 (Ru=C=$\underline{\mathrm{C}}$), 161.7 (Ru=C=C=$\underline{\mathrm{C}}$), 161.4 (C=O), 159.2–119.3 (Ph), 118.2 (Ru−C≡$\underline{\mathrm{C}}$−), 29.1 (m, CH$_2$, $|^1J_{PC}+^3\mathrm{J}_{\mathrm{PC}}|$ = 24 Hz). IR (KBr): 2072 cm^{-1} ($\nu_{\mathrm{C\equiv C}}$), 1917 cm^{-1} ($\nu_{\mathrm{C=C=C}}$), 1684 cm^{-1} ($\nu_{\mathrm{C=O}}$), 837 cm^{-1} (ν_{PF}). HR-MS ES$^+$ (*m/z*): 1232.2982 ([M]$^+$, calcd: 1232.2982).

General Procedure for Formation of Isocyanide Complexes. To a solution of the formamide complex in dry dichloromethane were added diisopropylamine (3.0 equiv per function) and phosphoryl chloride (1.2 equiv per function) were added dropwise, while stirring at 0 °C. Stirring was continued for 1 h at 0 °C, then at room temperature from 3 to 5 h, depending on solubility. A saturated aqueous solution of sodium carbonate was added, and stirring was continued for 1 h. After extractions with dichloromethane, the organic layer was washed with water and dried on sodium sulfate, and the solution was concentrated. Slow addition of pentane led to the precipitation of the isocyanide complex, which was dried under vacuum, after filtration of the solution with a canula.

***trans*-[Ph−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−NC](Ru$_1$NC).** The general procedure was used with the formamide complex **3a** (150 mg, 0.13 mmol). The final isocyanide complex Ru$_1$NC was obtained as a pale yellow powder (60% yield). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ 54.91 (s, PPh$_2$). ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.61−6.54 (m, 49H, Ph), 2.63 (m, 8 H, CH$_2$). ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 163.6 (NC), 141.5 and 132.5 (quint., $^2J_{PC}$ = 17 Hz, Ru−$\underline{\mathrm{C}}$≡C−), 137.2–123.0 (Ph), 117.2 and 115.8 (Ru−C≡$\underline{\mathrm{C}}$−), 31.4 (m, CH$_2$, $|^1J_{PC}+^3J_{PC}|$ = 24 Hz). IR (KBr): 2059 cm^{-1} ($\nu_{\mathrm{C\equiv C}}$), 2118 cm^{-1} (ν_{NC}). HR-MS ES$^+$ (*m/z*): 1126.2588 ([M + H]$^+$, calcd: 1126.2563).

***trans*-[CN−(*p*-C$_6$H$_4$)−C≡C−Ru(dppe)$_2$-C≡C−(*p*-C$_6$H$_4$)−NC](CNRu$_1$NC).** The general procedure was used with the formamide complex **3b** (150 mg, 0.126 mmol). The final isocyanide complex CNRu$_1$NC (60% yield) was obtained as a pale yellow powder. ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ 54.66 (s, PPh$_2$). ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.46−6.61 (m, 48H, Ph), 2.62 (m, 8 H, CH$_2$). ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 163.5 (NC), 140.1 (Ru−$\underline{\mathrm{C}}$≡C−), 136.6–125.6 (Ph), 116.6 (Ru−C≡$\underline{\mathrm{C}}$−), 31.3 (m, CH$_2$). IR (KBr): 2054 cm^{-1} ($\nu_{\mathrm{C\equiv C}}$), 2117 cm^{-1} (ν_{NC}). HR-MS ES$^+$ (*m/z*): 1173.2374 ([M + Na]$^+$, calcd: 1173.2374).

***trans*-[Ph−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−NC] (Ru$_2$NC).** The general procedure was used with the formamide complex **5a** (150 mg, 0.07 mmol). The final isocyanide complex Ru$_2$NC was obtained as a pale brown powder (62% yield). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ 54.97 (s, PPh$_2$). ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.65−6.52 (m, 93H, Ph), 2.69 (m, 16 H, CH$_2$). ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 168.9 (NC), 134.3−127.0 (Ph), 118.4 (Ru−C≡$\underline{\mathrm{C}}$−), 31.5 (br, CH$_2$). IR (KBr): 2053 cm^{-1} ($\nu_{\mathrm{C\equiv C}}$), 2114 cm^{-1} (ν_{NC}). HR-MS ES$^+$ (*m/z*): 2147.4579 ([M]$^+$, calcd: 2147.4603).

***trans*-[CN−(*p*-C$_6$H$_4$)−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−NC] (CNRu$_2$NC).** The general procedure was used with the formamide complex **5b** (110 mg, 0.05 mmol). The final isocyanide complex CNRu$_2$NC was obtained as a pale brown powder (76% yield). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ 54.7 (s, PPh$_2$). ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.70−6.52 (m, 92H, Ph), 2.68 (m, 16 H, CH$_2$). ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 169.5 (NC), 136.5–124.8 (Ph), 117.4 and 115,1 (Ru−C≡$\underline{\mathrm{C}}$−), 30.7 (m, CH$_2$, $|^1J_{PC}+^3J_{PC}|$ = 24 Hz). IR (KBr): 2052 cm^{-1} ($\nu_{\mathrm{C\equiv C}}$), 2115 cm^{-1} (ν_{NC}). HR-MS ES$^+$ (*m/z*): 2174.4776 ([M + 2H]$^+$, calcd: 2174.4712).

***trans*-[Ph−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−NC](Ru$_3$NC).** The general procedure was used with the formamide complex **10a** (150 mg, 0.07 mmol). The final isocyanide complex Ru$_3$NC was obtained as a pale brown powder (65% yield). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ 54.93 (s, PPh$_2$). ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.71−6.52 (m, 137H, Ph), 2.68 (m, 24 H, CH$_2$). IR (KBr): 2053 cm^{-1} ($\nu_{\mathrm{C\equiv C}}$), 2113 cm^{-1} (ν_{NC}). HR-MS ES$^+$ (*m/z*): 3170.6795 ([M]$^+$, calcd: 3170.6777).

***trans*-[CN−(*p*-C$_6$H$_4$)−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−C≡C−Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−NC] (CNRu$_3$NC).** The general procedure was used with the formamide complex **10b** (150 mg, 0.07 mmol). The final isocyanide complex CNRu$_3$NC was obtained as a pale brown powder (62% yield). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ 54.7 (s, PPh$_2$). ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.65−6.52 (m, 136H, Ph), 2.69 (m, 24 H, CH$_2$). ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ 169.4 (NC), 136.4–124.8 (Ph), 30.67 (m, CH$_2$). IR (KBr): 2049 cm^{-1} ($\nu_{\mathrm{C\equiv C}}$), 2115 cm^{-1} (ν_{NC}). HR-MS ES$^+$ (*m/z*): 3194.7228 ([M]$^+$, calcd: 3194.6652).

***trans*-[Ph$_2$C=C=C=Ru(dppe)$_2$−C≡C−(*p*-C$_6$H$_4$)−NC][PF$_6$] (AllRuNC$^+$).**The general procedure was used with the formamide complex **11** (138 mg, 0.10 mmol). The final isocyanide complex AllRuNC$^+$ was obtained as a blue powder (66% yield). $^{31}P\{^1H\}$ NMR (81.01 MHz, $CDCl_3$): δ 44.56 (s, PPh_2). ^1H NMR (200 MHz, $CDCl_3$): δ 7.67−6.77 (m, 54H, Ph), 2.94 (m, 8 H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 316.1 (quint., $^2J_{PC} = 13.6$ Hz, Ru═C), 210.8 (Ru═C═$\underline{C}$), 170.2 (NC), 162.6 (Ru═C═C═$\underline{C}$), 144.1–126.2 (Ph), 28.9 (m, CH_2, $|^1J_{PC+}{}^3J_{PC}| = 24$ Hz). IR (KBr): 2117 cm^{-1} (ν_{NC}), 2073 cm^{-1} ($\nu_{C\equiv C}$), 1918 cm^{-1} ($\nu_{C=C=C}$), 837 cm^{-1} (ν_{PF}). HR-MS ES$^+$ (*m*/*z*): 1214.2909 ([M]$^+$, calcd: 1214.2876).

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