# **ORGANOMETALLICS**

# Charge and Spin Confinement to the Amine Site in 3-Connected Triarylamine Vinyl Ruthenium Conjugates

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**Supporting Information** 

**ABSTRACT:** The triarylamine vinyl ruthenium conjugate  $(4-OMeC_6H_4)_2N_{C_6H_4}-3-CH=CH-RuCl(CO)(P^iPr_3)_2$  (m-1) has been prepared and investigated in its neutral and one-electron-oxidized states. Comparison with tris(4-anisylamine), An<sub>3</sub>N, and the related 4-methoxystyryl complex 4-OMeC\_6H\_4-CH=CH-RuCl(CO)(P^iPr\_3)\_2, 2, shows that the intrinsic formal potentials of the two nonidentical redox-active subunits of complex m-1 (triarylamine and vinyl ruthenium) are very similar. Complex m-1 is oxidized in two consecutive one-electron waves with a half-wave potential splitting of 320 mV. Detailed investigations of the one-electron-oxidized radical cation m-1<sup>\*+</sup> by IR and EPR spectroscopy and by quantum chemical calculations as well as comparison to An<sub>3</sub>N<sup>\*+</sup> and 2<sup>\*+</sup> indicate that the charge and the unpaired spin of m-1<sup>\*+</sup> are dominantly located on the triarylamine site. This is in stark contrast to the previously published *para* isomer p-1<sup>\*+</sup>, which, despite the nonidentical



redox sites, is a fully delocalized mixed-valent system of Class III. As a consequence of partial charge localization, the low-energy absorption bands in the near-infrared assume the character of ruthenium or styryl ruthenium to triarylamine intervalence charge-transfer (IVCT) transitions with significantly diminished absorptivities compared to the highly intense charge resonance bands of  $p-1^{\bullet+}$ . Hush analysis of the IVCT bands indicates that  $m-1^{\bullet+}$  is a significantly coupled mixed-valent system of Class II. The crystallographically determined structures of complexes m-1 and 2 and of the amine precursor  $(4-OMeC_6H_4)_2N(C_6H_4Br-3)$  (An<sub>2</sub>N-Br) are also reported.

# ■ INTRODUCTION

Triarylamines combine a convenient synthesis from cheap commercial starting materials<sup>2</sup> with very favorable electrochemical properties. They usually undergo reversible oxidations at well-accessible formal potentials that are easily tuned by the substituents on the aryl rings.<sup>3</sup> Their associated radical cations are generally stable if para substituents on the arenes prevent benzidine-type rearrangements. Owing to these favorable properties, triarylamines have found extensive use as selective one-electron oxidants and electrocatalysts<sup>3a,c,4</sup> or as holeconducting materials in electrooptical devices or in xerography.<sup>5</sup> Moreover, their radical cations display intense absorptions at low energies whose positions can again be tuned by the aryl substituents.<sup>3d</sup> These absorptions are shifted well into the near-infrared (NIR) for the mixed-valent radical cations of bis(triarylamine)s  $[Ar_2N(\mu-arylene)NAr_2]^{\bullet+}$  and move to higher energies into the vis/NIR borderline region upon further oxidation to their dications.<sup>6</sup> Mono- and bis(triarylamine)s hence constitute two- or three-state polyelectrochromic materials whose absorption profiles change reversibly upon the application of a suitable potential,<sup>7</sup> which makes them good candidates for the construction of "smart windows".

Vinyl ruthenium complexes of the type (RCH=CH–)-RuCl(CO)( $P^iPr_3$ )<sub>2</sub> can be viewed as metal–organic analogues

of triarylamines, as is shown by the very similar properties of bis(triarylamine)- and bis(vinylruthenium)-appended styrenes,<sup>6d,8</sup> squaraines,<sup>9</sup> and [2.2]paracyclophanes.<sup>10</sup> We and others have just demonstrated that alkynyl or alkenyl ruthenium triarylamine conjugates  $N(C_6H_5)_n\{-C\equiv C-C_6H_4$ -RuCl- $(dppe)_{2}_{3-n}$   $(n = 1 \text{ or } 3)^{11}$  and  $N(C_{6}H_{4}-4-OMe)_{n} \{(C_{6}H_{4}-4-OMe)_{n}\}$ CH=CH-)RuCl(CO)( $P^iPr_3$ )<sub>2</sub> $_{3-n}$  (n = 1-3) constitute highly electrochromic compounds with as many accessible redox states as electroactive NAr3 and alkynyl or vinyl metal moieties are present. In particular the vinyl systems show massive NIR absorptions ( $\varepsilon$  of up to 90.000 and oscillator strengths f of up to 1.0) for the higher oxidized forms (n = 2: 2+, n = 3: 2+ and 3+). The mixed-valent radical cation of the monoruthenium complex  $(4-OMeC_6H_4)_2N\{C_6H_4-4-CH=$ CH-RuCl(CO)( $P^{i}Pr_{3}$ )<sub>2</sub> (p-1 in Chart 1) exhibits full charge and spin delocalization over the electroactive NAr<sub>3</sub> and vinyl ruthenium subunits, as is indicated by the Ru(CO) band shift of about half the magnitude of that observed in the related styryl complex  $(C_6H_5-4-CH=CH-)RuCl(CO)(P^iPr_3)_2$ .<sup>12</sup> Moreover, hyperfine splittings of the unpaired spin with the amine nitrogen atom of one site and the phosphorus and ruthenium nuclei of the other are half those in the

Received: July 26, 2013 Published: September 20, 2013 Chart 1



Scheme 1



trianisylaminium radical cation  $[N(C_6H_4-4-OMe)_3]^{\bullet+}$  $(An_3N^{\bullet+})^{13}$  and in  $[(C_6H_5-4-CH=CH-)RuCl(CO)-(P^iPr_3)_2]^{\bullet+,12}$  but very similar to those in the related arylenebridged bis(triarylamine) radical cations<sup>6f,8b,14</sup> and in  $[1,4-C_6H_4\{-CH=CH-RuCl(CO)(P^iPr_3)_2\}_2]^{\bullet+,15}$  The strong electronic coupling in these conjugates and their radical cations is a consequence of significant aryl contributions to the occupied frontier levels (FMOs) of triarylamines and of styryl ruthenium complexes and their close FMO energies. Similar properties have already been reported for neutral triarylamine tris-(perchlorophenyl)methyl radicals, which likewise constitute rare cases of strongly or completely delocalized mixed-valent systems with two dissimilar redox sites.<sup>16</sup>

In all these systems the two redox-active subunits are in direct conjugation through 1,4-disubstituted (oligo)phenylene bridges, often with additional alkynyl or alkenyl spacers. We herein disclose that changing the 1,4- into the 1,3-disubstitution pattern has a dramatic influence on the formal potentials and the degree of electronic coupling in a triarylamine vinyl ruthenium conjugate and leads to charge and spin localization on the NAr<sub>3</sub> unit and only weak NIR electrochromism.

# RESULTS AND DISCUSSION

The synthesis of complex **m-1** was accomplished in the overall four-step procedure of Scheme 1 involving Ullman coupling of 3-bromoaniline with 2 equiv of 4-iodoanisol (49%), Sonoga-

shira coupling of the resulting 3-bromo-N,N-di(4methoxyphenyl)aniline An<sub>2</sub>N-Br with trimethylsilyl acetylene (70%) followed by deprotection (KF, MeOH, 97%), and the subsequent insertion of the ethynyl function of the free alkyne into the Ru–H bond of HRuCl(CO)( $P^{i}Pr_{3}$ )<sub>2</sub> (97%). The first reaction provides a more straightforward access to the brominated precursor than the original three-step synthesis of Bushby et al.<sup>17</sup> A comparison of the <sup>1</sup>H NMR data of precursors An2N-Br, An2N-CCTMS, and An2N-CCH with those of m-1 reveals a continuous downfield shift of the resonance signals of the four unique protons at the 3substituted phenyl ring and, to a smaller degree, of the arene protons at the anisyl groups as the 3-substituent becomes more electron releasing (see Experimental Section). As a point of comparison for the electrochemical and spectroscopic properties of m-1 we also investigated the 4-methoxystyryl ruthenium complex 2 (Chart 1), which was analogously prepared from 4methoxyphenylacetylene (98%).<sup>18</sup> The NMR spectra of styryl complexes m-1 and 2 display all the characteristic features of this class of compounds such as the signals of the vinyl protons and carbon atoms at 8.35 and 151.3 or 8.25 and 146.5 ppm (Ru-CH) and at 5.86 and 134.7 or 5.90 and 133.8 ppm (Ru-CH=CH) for complexes m-1 and 2, respectively, with the  ${}^{3}J_{\rm H,H}$  coupling of 12.8 or 13.4 Hz and resolved  ${}^{2}J_{\rm P,C}$  and  ${}^{4}J_{\rm P,H}$ couplings in the usual range of 11 or 2 Hz, respectively. Other characteristic resonance signals include the Ru(CO) at 203.5 or

209.4 ppm ( ${}^{2}J_{P-C}$  ca. 13 Hz), the proton and carbon signals of the P<sup>*i*</sup>Pr<sub>3</sub> protons, and the singlet resonance in the  ${}^{31}P$  NMR spectrum at 38.2 or 38.3 ppm. Further details can be found in the Experimental Section.

Suitable crystals for an X-ray analysis of  $An_2N-Br$  and complexes m-1 and 2 could be grown from CH<sub>2</sub>Cl<sub>2</sub> by layering with *n*-hexane ( $An_2N-Br$ , m-1) or MeOH (2). Amine  $An_2N-Br$ crystallizes in the monoclinic space group  $P2_1/c$  with four identical molecules in the unit cell. Details of the data collection and refinement are compiled in Table 1 of the Supporting Information. The three arene rings show the usual propellerlike arrangement but with a notably high degree of coplanarity of the acceptor-substituted 3-bromophenyl ring and the plane through the central nitrogen atom and the *ipso* carbon atoms of the attached aryl rings (see Figure 1) with an interplanar angle



Figure 1. ORTEP of a molecule of  $An_2N$ -Br with ellipsoids shown at the 30% probability level. Hydrogen atoms are omitted for clarity reasons. Important bond lengths (in Å) and angles (in deg): N(1)-C(1) 1.436(3), N(1)-C(7) 1.437(4), N(1)-C(13) 1.404(3), C(17)-Br(1) 1.905(3), C(1)-N(1)-C(7) 117.0(2), C(1)-N(1)-C(13) 120.4(2), C(7)-N(1)-C(13) 118.9(2).

of 20.2°. The latter contrasts with the interplanar angles of 54.6° and 61.5° for the two anisyl rings. Preferred conjugation with the nitrogen lone pair is also indicated by the short N(1)–C(13) bond of 1.404(3) Å when compared to the N(1)–C(1) and N(1)–C(7) bonds of 1.436(3) and 1.437(4) Å. Similar trends are observed for other triarylamines bearing two 4-anisyl and a third, acceptor-substituted aryl ring such as (4-OMeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>N(C<sub>6</sub>H<sub>4</sub>-C(O)Me-4)<sup>19</sup> and (4-OMeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>N-{C<sub>6</sub>H<sub>3</sub>-(COOH)<sub>2</sub>-3,5}.<sup>20</sup> In the crystal individual molecules of **An**<sub>2</sub>**N**-**Br** associate through C–Br···C=C interactions of 3.322 (Br(1), C(10)), 3.461 Å (Br(1), C(9)) and several CH··· O contacts of 2.503 and 2.684 Å (for a packing diagram see Figure 1 of the Supporting Information).

Figure 2 displays the crystallographic structure of complex **m-1**, which also crystallizes in the  $P2_1/c$  space group (for a listing of the data collection and structure refinement parameters see Table 2 of the Supporting Information). With interplanar angles of 36.1°, 37.1°, and 43.5°, all three donor-substituted aryl rings of complex **m-1** are similarly rotated out of the NC<sub>3</sub> plane of the nitrogen and the three *ipso* carbon atoms. All three N–C(*ipso*) bond lengths are equal within the



Figure 2. ORTEP of a molecule of complex m-1 with ellipsoids shown at the 30% probability level. Hydrogen atoms are omitted for reasons of clarity. Important bond lengths (in Å) and angles (in deg): Ru(1)–Cl(1) 2.4326(11), Ru(1)–P(1) 2.3987(11), Ru(1)–P(2) 2.4066(11), Ru(1)–C(41) 1.817(4), Ru(1)–C(1) 1.999(4), C(1)–C(2) 1.336(5), C(2)–C(3) 1.472(5), C(7)–N 1.419(4), C(9)–N 1.423(5), C(15)–N 1.423(5), Cl(1)–Ru(1)–C(1) 100.47(11), C(41)–Ru(1)–C(1) 89.18(16), P(1)–Ru(1)–C(1) 93.44(11), P(2)–Ru(1)–P(1) 97.24(11), P(1)–Ru(1)–P(2) 169.27(2), Cl(1)–Ru(1)–C(41) 170.21(12), Ru(1)–C(1)–C(2) 133.4(3), C(1)–C(2)–C(3) 124.2(3), C(7)–N(1)–C(15) 119.8(3), C(7)–N(1)–C(15) 120.0(3), C(9)–N(1)–C(15) 119.5(3).

error margins. The vinyl ligand shows an unusual high deviation from coplanarity with the Ru(CO)Cl plane and the attached phenyl ring, as is indicated by torsional angles Cl(1)-Ru(1)-C(1)-C(2) of 167.3(4)°, C(41)-Ru(1)-C(1)-C(2) of  $-16.1(4)^{\circ}$ , Ru(1)-C(1)-C(2)-C(3) of 172.2(3)^{\circ}, C(1)-C(2)-C(3)-C(4) of  $-36.2(6)^{\circ}$ , and C(1)-C(2)-C(3)-C(3)C(8) of 143.5(4)°. Such rotation limits  $\pi$ -conjugation between the redox-active triarylamine and vinyl ruthenium entities. Hydrogen bonding between hydrogen atom H(14) next to the vinyl substituent and O(1) of a neighboring molecule (2.568 Å, 0.152 Å shorter than the sum of the van der Waals radii) might also contribute to the observed torsion in the crystalline state (see Figure 2 of the Supporting Information). We note here that the quantum chemically optimized structure of the slightly truncated PMe3 model complex m-1<sub>Me</sub> has an almost perfectly coplanar arrangement of the vinyl ruthenium fragment and the aryl ring, as is indicated by torsional angles Ru(1)-C(1)-C(2)-C(3) of 178.3° and C(1)-C(2)-C(3)-C(4) of  $-1.5^{\circ}$ . This suggests that the observed deviations might indeed originate from "packing effects". A comparison of the experimental and computed values of relevant structural parameters may be found in Table 3 of the Supporting Information.

The 4-methoxystyryl ruthenium complex 2 crystallizes in the monoclinic space group  $P2_1/n$  (for relevant data see Table 4 of the Supporting Information). As for **m-1**, the immediate environment of the ruthenium atom shows all the characteristic features of styryl ruthenium complexes with this particular ligand set including the distorted square pyramidal geometry with *trans* angles of the basal ligands of ca. 170° and the displacement of the ruthenium atom out of the pyramid base

toward the apical alkenyl ligand (see Figures 2 and 3) and ruthenium ligand bond lengths in the usual range of ca. 2.43 Å



Figure 3. ORTEP of a molecule of complex 2 with ellipsoids shown at the 30% probability level. Hydrogen atoms are omitted for reasons of clarity. Important bond lengths (in Å) and angles (in deg): Ru(1)-Cl(1) 2.4289(5), Ru(1)-P(1) 2.4102(5), Ru(1)-P(2) 2.4116(5), Ru(1)-C(1) 1.808(2), Ru(1)-C(2) 1.992(2), C(1)-O(1) 1.160(3), C(2)-C(3) 1.337(3), C(3)-C(4) 1.473(3), Cl(1)-Ru(1)-C(2) 101.17(7), C(1)-Ru(1)-C(2) 89.57(10), P(1)-Ru(1)-C(2) 93.92(6), P(2)-Ru(1)-C(2) 91.77(6), P(1)-Ru(1)-P(2) 174.26(2), Cl(1)-Ru(1)-C(1) 168.78(7), Ru(1)-C(1)-C(2) 135.2(2), C(2)-C(3)-C(4) 126.2(2).

for Ru–Cl, 2.40 Å for Ru–P, 2.00 Å for Ru–C(alkenyl), and 1.81 Å for Ru–C(CO).<sup>1,8c,12,21</sup> As in the vast majority of such structures, the alkenyl ligand is oriented toward the CO ligand, which has been attributed to secondary bonding interactions between the occupied alkenyl  $\pi$  and unoccupied CO  $\pi^*$  orbitals.<sup>22</sup> There are no particular intermolecular interactions in the packing of **2** apart from very weak CH… $\pi$  contacts just below the sum of the van der Waals radii, which involve protons of the <sup>i</sup>Pr substituents on the phosphine ligands.

The electrochemical properties of the triarylamine precursor  $An_2N$ -CCTMS and of complexes 2 and m-1 were investigated by cyclic voltammetry in the CH<sub>2</sub>Cl<sub>2</sub>/NBu<sub>4</sub>PF<sub>6</sub> supporting electrolyte. Relevant data are collected in Table 1 along with those of complex p-1 and An<sub>3</sub>N. An<sub>2</sub>N-CCTMS displays a Nernstian oxidation wave at a formal potential of 0.295 V against the internal ferrocene/ferrocenium standard (see Figure 4 of the Supporting Information for a representative CV). Substitution of one 4-anisyl substituent of N(C<sub>6</sub>H<sub>4</sub>OMe-4)<sub>3</sub> (An<sub>3</sub>N,  $E_{1/2} = 0.109$  V) by the 3-C $\equiv$ CSiMe<sub>3</sub> one thus shifts

Table 1. Cyclic Voltammetry Data of  $An_2N$ -Br and Complexes m-1 and 2 along with Those of the Reference Compounds of Chart  $1^a$ 

	$\begin{array}{c} E_{1/2}^{0/+} \left[ \mathrm{V} \right] \\ \left( \Delta E_{\mathrm{p}} \left[ \mathrm{m} \mathrm{V} \right] \right) \end{array}$	$\begin{array}{c} E_{1/2}^{0/+} \left[ \mathrm{V} \right] \\ \left( \Delta E_{\mathrm{p}} \left[ \mathrm{m} \mathrm{V} \right] \right) \end{array}$	$\Delta E_{1/2}$ [mV]	$K_{c}^{b}$
An <sub>2</sub> N- CCTMS	0.295 (62)			
An <sub>3</sub> N	0.109	0.860	751	$1.7 \times 10^{17} {}^{3d}$
2	0.135 (63)	$0.725^{c}$ (84)	590	$9.5 \times 10^{9}$
m-1	0.170 (64)	0.490 (67)	320	$2.6 \times 10^{5}$
p-1	-0.118 (68)	0.266 (71)	384	$3.1 \times 10^{6}$ <sup>1</sup>
$\mathbf{TADP}^d$	0.245	0.307	62	11 <sup>17</sup>

<sup>*a*</sup>Data in CH<sub>2</sub>Cl<sub>2</sub>/NBu<sub>4</sub>PF<sub>6</sub> (0.1 M) at rt and  $\nu = 0.1$  V/s; potentials are provided against the internal Cp<sub>2</sub>Fe<sup>0/+</sup> standard ( $E_{1/2} = 0.000$  V). <sup>*b*</sup>K<sub>c</sub> is the comproportionation constant given by the equation K<sub>c</sub> = exp[ $nF\Delta E_{1/2}/(RT)$ ]. <sup>*c*</sup>At  $\nu = 1.0$  V/s. <sup>*d*</sup>Data in PhCN, 0.1 M NBu<sub>4</sub>PF<sub>6</sub>. the half-wave potential anodically by 186 mV and to basically the same value as observed in  $N(C_6H_4OMe-4)_2(C_6H_4Cl-4)$  $(E_{1/2} = 0.290 \text{ V})$ .<sup>3d</sup> Under the same conditions complex 2 shows a fully reversible first oxidation at 0.135 V. As for other styryl ruthenium complexes of this type, a second one-electron oxidation is observed at higher potential, here at 0.725 V. The electron-donating methoxy substituent has the effect of shifting the potentials of these oxidations cathodically by 145 and 125 mV, respectively, when compared to the parent styryl complex and of slowing down detrimental chemical processes following the second oxidation to a degree that allows for the observation of the associated cathodic return peak, particularly at higher sweep rates (see Figure 5 of the Supporting Information).

Complex **m-1** features two interlinked, well-behaved electroactive subunits and is hence oxidized in two consecutive, chemically reversible one-electron waves at formal potentials of 0.170 and 0.490 V against the ferrocene/ferrocenium couple (Figure 4). The 320 mV splitting between these processes



**Figure 4.** Cyclic voltammogram of complex m-1 in  $CH_2Cl_2/NBu_4PF_6$  at rt and  $\nu = 0.1$  V/s.

translates into a comproportionation constant (K<sub>c</sub>) of  $2.6 \times 10^5$ and indicates that the radical cation is chemically stable with respect to disproportionation. The comparison of the formal potentials of m-1 to those of An<sub>2</sub>N-CCTMS, An<sub>3</sub>N, complex 2, and the para-substituted analogue, complex p-1 (Chart 1), in Table 1 reveals some interesting details. First, substitution of the mildly electron withdrawing trimethylsilyl-protected ethynyl function by the powerful  $CH=CH-RuCl(CO)(P^{i}Pr_{3})_{2}$ donor shifts the formal potential of the first oxidation to a value that is negative of that of An<sub>2</sub>N-CCTMS but slightly positive of that of complex 2 and that of An<sub>3</sub>N. Second, placement of the vinyl ruthenium moiety in the 3- (m-1) instead of the 4position (p-1) of the attached phenyl ring, i.e., out of the path of direct  $\pi$ -conjugation with the bis(4-anisyl)phenylaniline moiety into a "coextensive" location,<sup>17</sup> increases the oxidation potentials of the first and the second oxidations by ca. 290  $(E_{1/2}^{0/+})$  and 225 mV  $(E_{1/2}^{+/2+})$ , respectively.

*N*,*N*,*N'*,*N'*-Tetra-4-anisyl-3,4'-diaminobiphenyl (**TADP**, see Chart 1) provides another interesting point of comparison with **m-1**. Here, a small splitting of half-wave potentials  $\Delta E_{1/2}$  of 62 mV and formal potentials of 0.245 and 0.307 V have been observed under comparable conditions.<sup>17</sup> **TADP**, **m-1**, and **p-1** all feature inequivalent redox sites such that the difference in half-wave potentials also includes the intrinsic energy difference between the two hypothetical valence tautomers resulting from the primary oxidation of one site or the other. This factor adds

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to the statistical, inductive, Coulombic, and resonance contributions that are operative in compounds with two interlinked and potentially interacting redox sites.<sup>23</sup> Only the resonance contribution, however, relates to the strength of the electronic coupling between the interlinked redox sites. Experimental and quantum chemical investigations on p-1 and its mono- and dioxidized forms have shown that the positive charge (hole) and the unpaired spin in the radical cation are equally shared between the vinyl ruthenium and the triarylamine moieties. This extensive conjugation also gives rise to intense absorption in the NIR.<sup>1</sup> TAPD<sup>•+</sup>, with the same topological placement of the redox sites as in m-1, has its spin localized on just one triarylamine subunit.<sup>17</sup> This raises questions about the extent to which the hole and the unpaired spin in m-1<sup>•+</sup> are delocalized over both subunits or whether they are confined to just one of these sites (and, if so, to which) and how this affects the NIR (poly)electrochromism of m-1.

These questions can be addressed by monitoring the spectroscopic changes on one-electron oxidation in IR and UV/vis/NIR spectroscopies as well as by analysis of the hyperfine splitting patterns in the EPR spectrum of  $m-1^{\bullet+}$ . IR spectroelectrochemistry of complexes m-1 and 2 was therefore conducted, and the results are collected in Table 2 along with

Table 2. IR Data of Complexes m-1, p-1, and 2 in Their Various Oxidation States<sup>a</sup>

complex	$\nu(\text{CO}) [\text{cm}^{-1}]$	$\nu$ (C=C <sub>vinyb</sub> C=C <sub>aryl</sub> ) [cm <sup>-1</sup> ]
m-1	1910(s)	1592(w), 1583(w), 1576(w), 1555(m), 1507(s)
m-1•+	1922(m)	1603(m), 1577(m), 1560(m), 1507(s)
p-1	1910(s)	1503(s)
p-1•+	1944(vs)	1608(s), 1503(vs)
p-1 <sup>2+</sup>	1985(s)	1605(m), 1591(m), 1503(w)
2	1909(s)	1604(w), 1582(w), 1554(w), 1506(m)
2 <sup>•+</sup>	1966(s)	1585(vs), 1506(w)
<sup><i>a</i></sup> Data in	1,2-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> , 0.	2 M NBu <sub>4</sub> PF <sub>6</sub> at rt.

those of p-1. The 12 cm<sup>-1</sup> blue shift of the Ru(CO) tag from 1910 to  $1922 \text{ cm}^{-1}$  during the first oxidation of m-1 is much smaller than that of 34 cm<sup>-1</sup> observed for the **p-1**<sup>0/+</sup> process and that of 57 cm<sup>-1</sup> that accompanies the first oxidation of complex 2 (see Figure 6 of the Supporting Information). Radical cation  $2^{\bullet+}$  may be seen as a model of  $m-1^{\bullet+}$  with hypothetical charge confinement to just the styryl ruthenium site. Overall, our observations indicate that the vinyl ruthenium subunit is rather little affected by the first oxidation of m-1 and that the hole is largely confined to the triarylamine entity. Also of note is the parallel growth of a broad absorption band of electronic origin at ca. 5800 cm<sup>-1</sup> (1720 nm) (see inset of Figure 5). While a more detailed discussion of this band is deferred to a later section of this paper, we note here that its position and shape already suggest that it originates from an intervalence charge-transfer (IVCT) transition within an asymmetric mixed-valent system.

Further oxidation of  $\mathbf{m} \cdot \mathbf{1}^{\bullet+}$  at an applied potential sufficiently anodic of the half-wave potential of the  $\mathbf{m} \cdot \mathbf{1}^{+/2+}$  couple resulted in the initial growth of a new Ru(CO) band at 1965 cm<sup>-1</sup> and then the parallel growth of a new band at 1952 cm<sup>-1</sup> that was not present during the initial stages of this process. The assignment of the 1965 cm<sup>-1</sup> band to  $\mathbf{m} \cdot \mathbf{1}^{2+}$  is therefore only tentative. Despite this coupled chemical process, an isosbestic point was maintained until the final stages when the intensity of the 1965 cm<sup>-1</sup> band decreased at the expense of an additional



Figure 5. Spectroscopic changes during the first oxidation of complex m-1 in a transparent thin-layer electrolysis cell at rt in the 1,2- $C_2H_4Cl_2/NBu_4PF_6$  (0.2 M) supporting electrolyte. The asterisk marks a region of strong supporting electrolyte background absorption.

band at 2025 cm<sup>-1</sup> (see Figure 7 of the Supporting Information). This behavior suggests that dication  $m-1^{2+}$  and the species giving rise to the band at 1952 cm<sup>-1</sup> are related by a chemical process. All attempts to identify this electrogenerated product and to clarify the nature of the underlying chemical process were so far in vain. We also note that the second oxidation is accompanied by a decrease of the intensity of the low-energy electronic band. This latter transition is therefore specific to the radical cation.

The spin distribution in the m-1<sup>•+</sup> radical cation is conveniently probed by EPR spectroscopy. Radical cations of ruthenium styryl complexes [(4-R-C<sub>6</sub>H<sub>4</sub>)CH=CH-RuCl- $(CO)(P^{i}Pr_{3})_{2}$ <sup>•+</sup> usually show an isotropic signal in fluid solution at g = 2.04 to 2.05, often with resolved hyperfine splittings to the <sup>31</sup>P nuclei of the phosphine coligands of ca. 22 G.<sup>10c,12</sup> This is a token of the large contribution of the styryl ligand to the HOMO of the neutral complexes and the SOMO of their associated radical cations. Oxidized 2 is no exception and shows a resolved triplet signal at g = 2.033 with hyperfine couplings of 26.5 G to <sup>31</sup>P and of 15.4 G to the <sup>99/101</sup>Ru nuclei as well as additional hyperfine splittings to the alkenyl protons of 11.5 and 3.2 G (see Table 3 and Figure 8 of the Supporting Information).<sup>24</sup> Triarylaminium ions, on the other hand, are characterized by a nonbinomial triplet with hyperfine coupling to the <sup>14</sup>N nucleus (I = 1) of ca. 7–10 G at a g-value even closer to the free-electron one  $(g_e = 2.0023)$ .<sup>3c,10b,17</sup> Consistent with complete spin delocalization in **p-1**<sup>•+</sup>, hyperfine splittings to <sup>14</sup>N, <sup>31</sup>P, and <sup>99/101</sup>Ru are half those in simple triarylaminium ions<sup>13</sup> and the radical cations of aryl-substituted vinyl ruthenium complexes,<sup>12</sup> but very similar to those in the related arylene-bridged bis(triarylamine) radical cations<sup>6f,8b,14</sup> and in  $[1,4-C_6H_4\{-CH=CH-RuCl(CO)(P^iPr_3)_2\}_2]^{\bullet+.15} Chemically$ generated m-1<sup>++</sup> (oxidation with acetylferrocenium hexafluorophosphate) displays a structured EPR signal at g = 2.0048(Figure 6, Table 3). By simulation of the experimental spectrum, hyperfine coupling constants  $A(^{14}N)$  of 10.0 G,  $A^{(31P)}$  of 3.9 G, and  $A^{(99/101Ru)}$  of 4.3 G were extracted.<sup>24</sup> We have to concede, though, that the rather low resolution of the experimental spectrum induces a higher level of uncertainty than usual, but the trend, in particular the <sup>14</sup>N hyperfine splitting, is nevertheless clear. The EPR signature is thus fully consistent with the results of IR spectroelectrochemistry in indicating an only moderate delocalization of the SOMO with



**Figure 6.** Comparison of the simulated (top) and experimental (bottom) EPR spectrum of chemically generated (oxidation with  $[(\eta^5-C_5H_4C(=O)Me)(\eta^5-C_5H_5)Fe]^+PF_6^-)$  m1<sup>++</sup> (CH<sub>2</sub>Cl<sub>2</sub>) at rt.

Table 3. EPR Data of Radical Cations m-1<sup>•+</sup>, p-1<sup>•+</sup>, and 2<sup>•+</sup> and of Some Triarylaminium Ions

	g	hyperfine splittings
$m-1^{\bullet+a}$	2.0048	$A(^{14}N) = 10.0 \text{ G}, A(^{31}P) = 3.9 \text{ G}, A(^{99/101}Ru) = 4.3 \text{ G}$
p-1•+ <i>a</i>	2.015	$A(^{14}N) = 5.1 \text{ G}, A(^{31}P) = 6.6 \text{ G}, A(^{99/101}Ru) = 5.1 \text{ G}^{1}$
$2^{\bullet + a}$	2.0342	$A(^{31}P) = 26.5 \text{ G}, A(^{99/101}Ru) = 15.4 \text{ G}, A(^{1}H_{alkenyl}) =$
		11.5, 3.2 G
NAn3 <sup>•+</sup>		$A(^{14}N) = 9.05 \text{ G}^{13}$
TAPD <sup>•+</sup>		$A(^{14}N) = 9.1 G^{17}$
<sup><i>a</i></sup> Data for	chemically	oxidized compounds (p-1: [Cp <sub>2</sub> Fe] <sup>+</sup> PF <sub>6</sub> <sup>-</sup> ; m-1,

2:  $[(\eta^5 - C_5H_4C(=O)Me)(\eta^5 - C_5H_5)Fe]^+PF_6^-$  in CH<sub>2</sub>Cl<sub>2</sub> at rt).

major contributions from the triarylamine entity and smaller ones from the vinyl ruthenium one.

Our experimental results are nicely backed by quantum chemical calculations on the slightly truncated model complex  $m-1_{Me}$  with the P'Pr<sub>3</sub> ligands of the real complex replaced by PMe<sub>3</sub>. The HOMO of  $m-1_{Me}$  is delocalized over the nitrogen atom and the three appended aryl rings and represents an antibonding interaction between the nitrogen lone pair and the  $\pi_2$  orbitals of the three phenyl rings with one nodal plane on each ring and one additional nodal plane between the arenes and their 4- or 3-substituents. There is only little contribution from the alkenyl substituent and practically none from the ruthenium atom and the other coligands (see Figure 9 of the Supporting Information). The HOMO-1, on the other hand, is delocalized over the styryl ruthenium moiety with little contribution from the amine lone pair and practically none from the anisyl rings. This level ordering is also maintained in the associated radical cation, as shown by the calculated spin density distribution in Figure 7. The trends in the experimental EPR parameters are also reproduced by our calculations, which gave a larger g-value and a smaller  $A(^{14}N)$  value of 2.013 and 6.9 G for  $\mathbf{p} \cdot \mathbf{1}_{Me}^{\bullet+}$  compared to those of  $\mathbf{m} \cdot \mathbf{1}_{Me}^{\bullet+}$  (g = 2.0030 and 9.6 G), in satisfactory agreement with the experimental values (Table 3). We also note that our calculations predict only minor structural changes at the vinyl ruthenium site on one-electron oxidation, in internal consistency with all other results (see Table 3 of the Supporting Information).

Shifting the site of vinyl ruthenium attachment from direct conjugation with the amine nitrogen at the 4-position of p-1 to the less well coupled 3-position of m-1 thus has the effect of partially decoupling the unlike redox sites and shifting the hole and the unpaired spin of one-electron-oxidized  $m-1^{\bullet+}$  toward the triarylamine unit. As it will be shown in brief, such hole



Figure 7. Calculated spin densities of the radical cation of model complex  $m-l_{Me}^{\bullet+}$ .

confinement has rather dramatic consequences for the electronic absorption spectrum of  $m-1^{\bullet+}$ .

The UV/vis spectrum of neutral **m-1** is dominated by an intense, asymmetric, and structured band with a main peak at 305 nm ( $\varepsilon = 44400 \text{ M}^{-1} \text{ cm}^{-1}$ , Figure 8, Table 4), which can



Figure 8. Spectroscopic changes during the first oxidation of complex m-1 in a transparent thin-layer electrolysis cell at rt in the 1,2- $C_2H_4Cl_2/NBu_4PF_6$  (0.2 M) supporting electrolyte.

be assigned to  $\pi \to \pi^*$  transitions within the extended metal– organic chromophore. A splitting of the NAr<sub>3</sub>  $\pi \rightarrow \pi^*$  band is the expected result of lowering the ideal  $C_3$  symmetry due to the different substitution patterns and torsions of the appended aryl rings.<sup>3d</sup> TD-DFT calculations on  $m-1_{Me}$  provide several intense transitions at close energies (see Table 5). All transitions that originate from the HOMO are due to excitations that are confined within the NAr<sub>3</sub> subunit. The most intense band, however, involves a transition from the styryl ruthenium-based HOMO-1 to the LUMO+1. The latter orbital is centered on the triarylamine subunit and has major contributions from the phenyl ring that is common to both. Some transfer of charge density from the styryl ruthenium to the triarylamine site may hence accompany this excitation. We note that the more intense bands are markedly blue-shifted with respect to the ones of p-1 at 322 and 343 nm. This is another token of the lower degree of conjugation within the meta isomer m-1. Like for p-1, the additional, weaker band at 511 nm ( $\varepsilon$  = 565) is due to a weakly allowed excitation from

# Table 4. UV/Vis/NIR Data of Complexes m-1, p-1, and 2 and of An<sub>2</sub>N-CCTMS in Their Various Oxidation States

	$\lambda_{ m max}~(arepsilon_{ m max})$
m-1	305 (44 400), 387 (sh, 3200), 512 (565)
m-1*+	298 (28 700), 360 (26 750), 584 (9600), 739 (20 900), 1075 (3100), 1666 (2300)
p-1	322 (sh, 26 000), 343 (30 000), 553 (300)
p-1**	365 (7500), 487 (27000), 516 (sh, 20000), 575 (sh, 3000), 870 (sh, 10000), 1030 (19600), 1160 (22000)
2	301 (11 800), 379 (835), 519 (250)
2 <sup>•+</sup>	298 (4200), 333 (2800), 433 (10 400), 692 (5900)
An <sub>2</sub> N-CCTMS <sup>+</sup>	300 (20 000), 360 (sh, 1900)
An <sub>2</sub> N-CCTMS <sup>•+</sup>	304 (10 000), 322 (9300), 356 (sh, 7500), 368 (7700), 568 (3450), 776 (20 200)

Table 5. Calculated El	lectronic Transition	ns of m-1 <sub>Me</sub> •+ with	1 Oscillator	Strengths <i>f</i> a	and Major	Contributions and	Comparison
with the Experimental	Data						

calculated data for $m-1_{Me}^{\bullet+}$		experimental da		
$\lambda_{ m max} \; [ m nm] \; ( ilde{ u} \; [ m in \;  m cm^{-1}])$	f	$\lambda_{ m max} \; [ m nm] \; ( ilde{ u} \; [ m in \;  m cm^{-1}])$	$\varepsilon_{\max} \left[ \mathrm{M}^{-1} \mathrm{~cm}^{-1} \right] (f)^a$	major contributors
1694 (5902)	0.031	1666 (6000) 1075 (9300)	2350 (0.030) 3000 (0.039)	$\beta$ -HOMO $\rightarrow \beta$ -LUMO
679 (14733)	0.3105	739 (13 475)	20 900 (0.152)	$\beta$ -HOMO $-3 \rightarrow \beta$ -LUMO
553 (18 100)	0.1805	587 (17 020)	5600 (0.071)	$\beta$ -HOMO-5 $\rightarrow \beta$ -LUMO
489 (20 460)	0.0099			$\beta$ -HOMO $-8 \rightarrow \beta$ -LUMO
472 (21 202)	0.0078			$\alpha$ -HOMO $\rightarrow \alpha$ -LUMO;
		540 (18 500)	4700 (0.137)	$\beta$ -HOMO $\rightarrow \beta$ -LUMO+1
463 (21 595)	0.0318			$\alpha$ -HOMO $\rightarrow \alpha$ -LUMO+1;
				$\beta$ -HOMO $\rightarrow \beta$ -LUMO+2
445 (22 472)	0.0097			$\beta$ -HOMO-6 $\rightarrow \beta$ -LUMO;
				$\beta$ -HOMO-9 $\rightarrow \beta$ -LUMO
_		_		

<sup>*a*</sup>Oscillator strength calculated by the equation  $f = (4.6 \times 10^{-9}) \varepsilon_{\max} \Delta \nu_{1/2}$ , where  $\Delta \nu_{1/2}$  is the bandwidth at half-height.

the mixed  $d(Ru)/\pi(arylamine)$  HOMO-1 to the largely metalbased LUMO that points toward the vacant coordination site.

On oxidation in an optically transparent thin-layer electrolysis (OTTLE) cell,<sup>25</sup> the electronic spectrum of m-1 changes to a pattern of two intense absorptions in the UV at  $\lambda_{\text{max}}$  = 298 and 360 nm, two moderately intense visible bands at 584 and 739 nm, the former with a distinct tail to higher energies, and two weak NIR bands at 1075 ( $\varepsilon$  = 3000 M<sup>-1</sup> cm<sup>-1</sup>) and 1666 nm ( $\varepsilon$  = 2350 M<sup>-1</sup> cm<sup>-1</sup>, see Figure 8 and Table 4). The latter band matches with the NIR band that was already observed in the IR spectroelectrochemical experiment. The band pattern of  $m-1^{++}$  is clearly different from that of p-1<sup>•+</sup>, which showed two much more intense absorptions at 1003 and 1169 nm with extinction coefficients of ca. 20 000 M<sup>-1</sup> cm<sup>-1</sup> and just one major absorption in the visible at 485 nm.<sup>1</sup> We note that the radical cations of amine precursor An<sub>2</sub>N-CCTMS and of complex 2 both present strong absorptions in the visible, as shown in Figures 10 and 11 in the Supporting Information. These transitions are located at 433 and at 692 nm for  $2^{\bullet+}$  or at 568 and 776 nm for  $An_2N$ -CCTMS $^{\bullet+}$ . None of these absorption bands, however, extend deeper into the NIR. The low-energy transitions in  $p-1^{\bullet+}$  and  $m-1^{\bullet+}$  are thus a consequence of extending the conjugated  $\pi$ -system through coupling of the vinyl ruthenium and the triarylamine entities. In p-1<sup>•+</sup>, this coupling is so strong that a very weakly polarized, highly delocalized chromophore results. As a consequence, the NIR bands are best described as  $\pi \to \pi^*$  transitions within an extended, open-shell, metal-organic  $\pi$ -system with no net transfer of charge from one component to the other, i.e., as charge resonance bands. In m-1 and its associated radical cation, however, the two chromophoric and electroactive subunits are only weakly coupled to one another such that a less delocalized metal-organic  $\pi$ -system results. This is already

apparent on inspection of the frontier molecular orbitals (see Figure 9 of the Supporting Information), which are localized on either the styryl ruthenium moiety (HOMO-1, HOMO-3), the metal atom (LUMO), or the triarylamine (HOMO-2, HOMO, LUMO+1, LUMO+2, LUMO+4 to LUMO+6).

TD-DFT calculations on  $m\text{-}{\mathbf{1}_{Me}}^{\bullet+}$  were conducted with the aim of determining the origins of the low-energy transitions and of the two more intense transitions in the visible. Despite the problems associated with performing such calculations on open-shell systems, they reproduce most features of the experimental spectrum rather well, most notably the weak low-energy band, which is calculated at 1694 nm, and the series of three neighboring absorptions in the visible at 679, 553, and 450 nm with decreasing oscillator strengths, but fail to reproduce the experimental band at 1075 nm (see Figure 12 of the Supporting Information). Based on our TD-DFT results, the low-energy NIR band of  $m-1^{\bullet+}$  can be assigned as the  $\beta$ -HOMO  $\rightarrow \beta$ -LUMO transition. The two more prominent transitions in the visible are due to excitations from the lowerlying  $\beta$ -HOMO-3 and  $\beta$ -HOMO-5 to the same acceptor orbital, while the unresolved shoulder at higher energy involves several weak transitions that are highly mixed in character. We note that the level ordering of closed-shell m-1 carries over to that of the  $\beta$ -manifold of its radical cation; that is, the former HOMO resembles the  $\beta$ -LUMO, the former HOMO-1 the  $\beta$ -HOMO, and so forth, while for the  $\alpha$ -manifold the ordering of the HOMO and the HOMO-1 are inverted with respect to the neutral state. The stronger visible bands hence emanate from MOs that are delocalized over the triarylamine subunit and can thus be assigned as  $\pi \to \pi^*$  transitions within that moiety. We also note that these bands closely resemble those observed for An<sub>2</sub>N-CCTMS<sup>•+</sup> (see Figure 9 of the Supporting Information),

Article



Figure 9. Level ordering of  $m \cdot 1_{Me}^{\bullet+}$  and graphical representations of relevant spin orbitals.

	Table 6. Data	Pertaining	to Hus	h Analysis	of the	NIR Bar	nds of m-1•+
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	$\lambda \ [cm^{-1}]$	$\Delta  ilde{ u}_{1/2, ext{theo}}[ ext{cm}^{-1}]$	$\Delta  ilde{ u}_{1/2, ext{exp}}[ ext{cm}^{-1}]$	Г	$H_{ab}  [\mathrm{cm}^{-1}]$	α
band 1	5790	3655	2650	0.28	1003	0.17
band 2	9090	4580	2900	0.35	1485	0.16

but are shifted by 37 and 16 nm (645 and 482  $cm^{-1}$ ), respectively.

The low-energy band hence involves a transition from the  $\beta$ -HOMO to the  $\beta$ -LUMO. The donor orbital is delocalized over the styryl ruthenium part of this molecule, whereas the acceptor orbital is delocalized over the triarylamine subunit with larger contributions of the anisyl rings. This band hence qualifies as an intervalence charge-transfer transition within a molecule that encompasses two different redox systems. The same may also apply to the band at 1070 nm, which our TD-DFT calculations failed to reproduce. The level ordering of Figure 9 strongly suggests that this transition is due to (an) excitation(s) from the  $\beta$ -HOMO-1 and/or the  $\beta$ -HOMO-2 to the  $\beta$ -LUMO. Both these suspect donor orbitals are localized on the ruthenium bis(phosphine) moiety. We therefore assume that this transition is also of IVCT origin. We note here that the observation of multiple IVCT bands is not wholly uncommon and may originate from spin-orbit coupling of the d-levels at a metal-based donor site,<sup>26</sup> low symmetry of the metal-bridge array,<sup>27</sup> or the heavy involvement of the nominal bridge in some but not all of the IVCT bands.<sup>6b,c,10a,28</sup> This latter situation is somewhat similar to that encountered for the  $\beta$ -HOMO to  $\beta$ -LUMO transition if one regards the common phenylene ring as the bridge that is common to both individual redox sites.

The IVCT bands can be analyzed within the theoretical framework of Hush's theory.  $^{29}$  In a mixed-valent system with

nonidentical redox sites, the relation between the reorganization energy  $\lambda$  , the energy at the IVCT band maximum  $\tilde{\nu}_{\rm max}$  and the energy difference  $\Delta G^0$  between the two possible valence tautomers in their vibrational ground states is given by eq  $1.^{30}$ In the case of m-1<sup>•+</sup>, these valence tautomers can be identified as An<sub>2</sub>N<sup>•+</sup>-C<sub>6</sub>H<sub>4</sub>CH=CH-RuCl(CO)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> with an oxidized amine site and  $An_2N-C_6H_4CH=CH-RuCl(CO)(P^iPr_3)_2^{\bullet+}$  with the styryl ruthenium site as the primary oxidation center.  $\Delta G^0$ can be approximated by the half-wave potential difference between the An<sub>3</sub>N<sup>0/+</sup> and the  $(P^{i}Pr_{3})_{2}(CO)ClRu-CH=$  $CHC_6H_4OMe-4^{0/+}$  couples, which both contain the 4-anisyl ring as an integral part of the redox system. It amounts to only  $0.026 \text{ V} (210 \text{ cm}^{-1})$ . The theoretical half-widths of an IVCT band,  $\Delta\tilde{\nu}_{\rm 1/2,theo}$  is given by eq 2. Comparison of these values to the experimental ones derived from spectral deconvolution of the NIR part of the electronic spectrum of **m**-1<sup>•+</sup> (see Table 6) shows that the experimental half-widths are consistently smaller than those calculated for the limiting case of a weakly coupled Class II system. Brunschwig, Creutz, and Sutin have introduced the parameter  $\Gamma^{29c}$  as defined by eq 3, which allows one to discriminate between weakly coupled ( $0 \leq \Gamma \leq 0.1$ ), moderately coupled (0.1  $\leq \Gamma \leq$  0.5), Class II/III borderline ( $\Gamma \approx 0.5$ ), or strongly coupled, delocalized Class III systems ( $\Gamma$ > 0.5) according to the Robin-and-Day classification scheme.<sup>31</sup> The  $\Gamma$  values of 0.28 and 0.35 obtained for the two NIR bands indicate that the electronic coupling between the individual redox sites of **m-1**<sup>•+</sup> is appreciable, but certainly lower than for its *para*-isomer **p-1**<sup>•+</sup>, which is a completely delocalized Class III system.<sup>1</sup>

$$\lambda = \tilde{v}_{\max} - \Delta G^0 \tag{1}$$

$$\Delta \tilde{v}_{1/2,\text{theo}} = [16(\ln 2)RT\lambda]^{1/2} = [2310\lambda]^{1/2} \text{ at rt}$$
(2)

$$\Gamma = 1 - \theta$$
, where  $\theta = \Delta \tilde{\nu}_{1/2, exp} / \Delta \tilde{\nu}_{1/2, theo}$  (3)

$$H_{ab} = 0.0206 (\tilde{v}_{\text{max}} \varepsilon_{\text{max}} \Delta \tilde{v}_{1/2, \text{exp}})^{1/2} / r_{ab}$$
<sup>(4)</sup>

$$\alpha = H_{ab} / \tilde{v}_{\text{max}} \tag{5}$$

Hush's theory also allows one to derive the electronic coupling parameter  $H_{ab}$  from the IVCT band parameters via eq 4, where  $r_{ab}$  denotes the effective charge-transfer distance of the mixed-valent system. This parameter is traditionally approximated by the geometrical distance between the centers of the nominal redox sites. Even in clear-cut cases such as cyanidebridged dimetal complexes or analogues of the Creutz-Taube ion where the redox sites are readily identified as the metal atoms, the effective charge-transfer distance is significantly smaller than the metal---metal distance.<sup>32</sup> A particularly instructive example is the 4,4'-bipyridine-bridged, "elongated" version of the Creutz-Taube ion,  $[(NH_3)_5Ru-(\mu-4,4'-bipy) Ru(NH_3)_5$ <sup>5+</sup>. Although this system is a weakly coupled mixedvalent system of Class II with 95% charge localization on one ruthenium site, the difference dipole moment between the adiabatic charge-transfer states and, consequently, the chargetransfer distance  $r_{ab}$  are less than 50% of the value expected for the transfer of a full charge between the individual ruthenium atoms.<sup>32a</sup> Even larger discrepancies are found in systems where the effective redox system extends onto the nominal bridge or when the ground state of the mixed-valent system is more strongly delocalized.<sup>6d,16a,32c,33</sup>

Given these results, half the ruthenium—nitrogen distance of  $\mathbf{m}-\mathbf{1}^{\bullet+}$  ( $d(\operatorname{Ru}\cdots\operatorname{N} = 7.80$  Å based on the experimental structure of  $\mathbf{m}-\mathbf{1}$  and 7.96 Å based on the optimized structure of  $\mathbf{m}$ - $\mathbf{1}_{Me}^{\bullet+}$ ) may be a realistic estimate of  $r_{ab}$ . This would give  $H_{ab}$  values on the order of 1000 and 1500 cm<sup>-1</sup> for the IVCT bands at the lower and the higher energies, respectively (see Table 6). Finally, the ground-state delocalization parameter  $\alpha$ , which measures the percentage of charge shifted from one redox site to the other, is given by the ratio of  $H_{ab}$  to the energy at the IVCT band maximum (eq 5). In internal consistency with the assignment of both NIR bands as IVCT transitions, their  $\alpha$  parameters are practically identical. In further agreement with the values of their  $\Gamma$  parameters, they place  $\mathbf{m}-\mathbf{1}^{\bullet+}$  in the régime of a moderately coupled mixed-valent system of Class II.

In conclusion, shifting the site of vinyl ruthenium attachment to the bis(4-anisyl)-(phenyl)amine core of vinyl triarylamine conjugates from the *para* position of **p-1** to the *meta* position in **m-1** has the effect of increasing the oxidation potentials by >200 mV for each consecutive redox step and localizing the hole and the unpaired spin of its associated radical cation on mainly the triarylamine entity, although the intrinsic redox potentials of the likewise electroactive triarylamine and vinyl ruthenium sites are very similar. Partial charge localization in the ground state of mixed-valent **m-1**<sup>•+</sup> changes the character of the low-energy transitions in the near-infrared from chargeresonance absorptions in **p-1**<sup>•+</sup> to styryl ruthenium to triarylaminium IVCT transitions in **m-1**<sup>•+</sup> and significantly decreases their absorptivities. Strong electrochromism and good performance of an alkenyl ruthenium triarylamine conjugate as a (multi)electrochromic dye require therefore an intimate electronic coupling between these nonidentical, but similar, redox-active subunits and high degrees of charge delocalization of their oxidized forms. This concept should also carry over to other systems where two potentially interacting and *per se* electrochromic entities are combined into one compound.

### EXPERIMENTAL SECTION

General Methods. All operations were performed under an atmosphere of purified nitrogen using standard Schlenk techniques. Solvents were dried over and distilled from CaH2 (CH2Cl2, 1,2- $C_2H_4Cl_2$ , LiAlH<sub>4</sub> (*n*-hexane), or sodium (THF, toluene) and degassed by saturation with nitrogen or argon prior to use. The yields refer to analytically pure compounds and were not optimized.  $HRuCl(CO)(P^{i}Pr_{3})_{2}^{21a}$  was prepared according to a modified literature procedure with addition of K2CO3 to neutralize the HCl formed in the reaction. Acetvlferrocenium hexafluorophosphate was prepared according to the literature procedure for the BF<sub>4</sub><sup>-</sup> salt by using AgPF<sub>6</sub> instead of AgBF<sub>4</sub>.<sup>4</sup> All other chemicals were commercial products and used as supplied. Instrumentation: <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, and <sup>31</sup>P NMR spectra were recorded on either a Bruker Avance 400 MHz, a Bruker Avance III Kryo-Platform 600 MHz, or a Varian Inova 400 MHz spectrometer in C<sub>6</sub>D<sub>6</sub>, CD<sub>2</sub>Cl<sub>2</sub>, or CDCl<sub>3</sub> at ambient temperature. Chemical shifts are relative to the residual solvent peaks (<sup>1</sup>H, <sup>13</sup>C) or 100%  $H_3PO_4$  (<sup>31</sup>P). Infrared spectra were obtained on a Nicolet iS10 instrument (Thermo Fischer Scientific Inc.). UV/vis spectra were obtained on an Omega 10 spectrometer from Bruins Instruments or a TIDAS fiberoptic diode array spectrometer (combined MCS UV/NIR and PGS NIR instrumentation) from j&m Analytik AG in HELLMA quartz cuvettes with 1 cm optical path lengths. Elemental analysis (C, H, N) were performed with a Heraeus Elementar Vario MICRO Cube. The equipment for voltammetric and spectroelectrochemical studies and the conditions employed were described elsewhere.<sup>34</sup> Electron paramagnetic resonance (EPR) studies were performed on a MiniScope MS 400 table-top X-band spectrometer from Magnettec. Simulation of the experimental spectra was performed with the EasySpin software.<sup>24</sup> X-ray diffraction measurements were performed at 100(2) K on a Stoe IPDS II diffractometer (graphite monochromator, Mo K $\alpha$  radiation,  $\lambda$  = 0.71073 Å) on crystals mounted on a glass fiber. The structures were solved by direct methods using the SHELX-97 and the SIR program The positions of the hydrogen atoms were calculated by packages.3 assuming an ideal geometry, and their coordinates were refined together with those of the attached carbon atoms applying the riding model. All other atoms were refined anisotropically.

**Quantum Chemical Calculations.** The ground-state electronic structures were calculated by density functional theory (DFT) methods using the Gaussian 09<sup>36</sup> program package. In order to reduce computational time to a reasonable limit, P'Pr<sub>3</sub> ligands were replaced by PMe<sub>3</sub>. Open-shell systems were calculated by the unrestricted Kohn–Sham approach. Geometry optimization followed by vibrational analysis was made either under vacuum or in solvent media. The quasirelativistic Wood–Boring small-core pseudopotentials<sup>37</sup> and the corresponding optimized set of basis functions<sup>38</sup> for Ru and 6-31G(d) polarized double- $\zeta$  basis sets<sup>39</sup> for the remaining atoms were employed together with the Perdew, Burke, and Ernzerhof exchange and correlation functional (PBE0).<sup>40</sup> Hyperfine coupling constants of the radical cations m-1<sub>Me</sub><sup>++</sup> and p-1<sub>Me</sub><sup>++</sup> were calculated for the geometry-optimized radical cations with the same basis functions. Solvent effects were described by the polarizable conductor continuum model<sup>41</sup> with standard parameters for 1,2-dichloroethane.<sup>42</sup>

Synthesis and Characterization. N,N-Bis(4-methoxyphenyl)-N-3-bromophenylamine,  $An_2N$ -Br. An 8.60 g (50 mmol) amount of 3bromoaniline, 25.74 g (110 mmol) of 4-iodoanisole, and 1.80 g of 1,10-phenanthroline (5 mmol) were dissolved in 60 mL of toluene, and the solution was heated to 110 °C. KOH (112 mmol) and CuCl (2.8 mmol) were added to the boiling solution, which was stirred under reflux conditions for 72 h. After cooling to room temperature,

#### Organometallics

500 mL of toluene, 500 mL of water, and 10 mL of acetic acid were added. The layers were separated, and the aqueous layer was extracted several times with  $CH_2Cl_2$ . The combined organic layers were dried over MgSO<sub>4</sub>, and the solvent was removed *in vacuo*. Purification by column chromatography (petrol ether/ethyl acetate, 9:1) gave the pure product. Yield = 9.50 g, 24.7 mmol (49%).

<sup>1</sup>H NMR (400 MHz, acetone- $d_6$ ):  $\delta$  7.61 (d,  ${}^3J_{H-H} = 8.8$  Hz, 1H, H2), 7.11 (d,  ${}^3J_{H-H} = 8.9$  Hz, 4H, H6), 7.10 (m, 1H, H3), 6.95 (d,  ${}^3J_{H-H} = 8.8$  Hz, 4H, H5), 6.80 (d,  ${}^3J_{H-H} = 8.8$  Hz, 1H, H4), 6.76 (s, 1H, H1), 3.80 (s, 6H, OMe) ppm.

*N,N-Bis*(4-methoxyphenyl)-*N*-(3-trimethylsilylethynylphenyl)amine, **An**<sub>2</sub>**N-CCTMS**. *N,N*-Bis(4-methoxyphenyl)-*N*-3-bromophenylamine (1.0 g, 2.6 mmol) and trimethylsilylacetylene (5 mmol) were dissolved in a mixture of triethylamine (15 mL) and THF (15 mL). The solution was freeze-pump-thaw degassed (three cycles), and then CuI (10 mol %) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (5 mol %) were added. The reaction mixture was stirred for 48 h at 60 °C in a closed vessel. The completeness of the reaction was controlled by TLC. After full conversion, the mixture was filtered over a Celite pad and eluted with THF. The solvent was removed *in vacuo*. Purification by column chromatography (petrol ether/ethyl acetate, 6:1) gave the product as a yellow oil. Yield = 731 mg, 1.82 mmol (70%).

<sup>1</sup>H NMR (400 MHz, acetone- $d_6$ ):  $\delta$  7.15 (d,  ${}^3J_{H-H} = 8.0$ Hz, 1H, H2), 7.06 (d,  ${}^3J_{H-H} = 8.7$  Hz, 4H, H6), 7.10 (m, 1H, H3), 6.92 (d,  ${}^3J_{H-H} = 8.7$  Hz, 4H, H5), 6.90 (d,  ${}^3J_{H-H} = 8.6$  Hz, 1H, H4), 6.76 (s, 1H H1), 3.80 (s, 6H, OMe) ppm, 0.18 (s, 9H, TMS).

*N,N-Bis*(4-methoxyphenyl)-*N*-(3-ethynylphenyl)amine,  $N_2An$ -*CCH*. *N,N-Bis*(4-methoxyphenyl)-*N*-(3-trimethylsilylethynylphenyl)amine (140 mg, 0.35 mmol) was dissolved in methanol, and a small amount of KOH was added. The mixture was stirred for 3 h until the completeness of the deprotection was shown by TLC and then quenched with water. The aqueous layer was neutralized with 1 N hydrochloric acid and extracted several times with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over MgSO<sub>4</sub>, and the solvent was removed *in vacuo* to provide the product as a yellow-brown solid. Yield = 112 mg, 0.34 mmol (97%).

<sup>1</sup>H NMR (400 MHz, acetone- $d_6$ ):  $\delta$  7.15 (d,  ${}^3J_{H-H} = 8.0$  Hz, 1H, H4), 7.06 (d,  ${}^3J_{H-H} = 8.7$  Hz, 4H, H6), 7.10 (m, 1H, H3), 6.92 (d,  ${}^3J_{H-H} = 8.7$  Hz, 4H, H5), 6.90 (d,  ${}^3J_{H-H} = 8.6$  Hz, 1H, H2), 6.76 (s, 1H, H1), 3.80 (s, 6H, OMe) ppm, 3.11 (s, 1H, C=CH).

 $(4-OMeC_6H_4)_2N(C_6H_4-3-CH=CH-RuCl(CO)(P'Pr_3)_2, m-1. N_N-Bis-(4-methoxyphenyl)-N-(3-ethynylphenyl)amine (34 mg, 0.1 mmol) was dissolved in CH_2Cl_2, and a solution of HRuCl(CO)(P'Pr_3)_2 (48 mg, 0.099 mmol) in CH_2Cl_2 was added dropwise. The color rapidly changed from orange-red to deep red. The solution was stirred for 30 min, and the solvent was removed$ *in vacuo*. The crude product was washed with hexane and then dried*in vacuo*to give the product as a red solid. Yield: 80 mg, 0.097 mmol (97%).

# Chart 2. Numbering Scheme for Signal Assignment for Complex m-1



<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, Chart 2): δ 8.35 (td,  ${}^{3}J_{H-H}$  = 12.8 Hz,  ${}^{3}J_{P-H}$  = 1.1 Hz, 1H, H1), 6.98 (d,  ${}^{3}J_{H-H}$  = 8.4 Hz, 4H, H11), 6.96 (m, 1H, H5), 6.79 (d,  ${}^{3}J_{H-H}$  = 8.4 Hz, 4H, H10), 6.59 (s, 1H, H8), 6.55 (d,  ${}^{3}J_{H-H}$  = 7.9 Hz, 1H, H6), 6.50 (d, 1H,  ${}^{3}J_{H-H}$  = 6.7 Hz H4), 5.86 (td,  ${}^{3}J_{H-H}$  = 12.8 Hz,  ${}^{4}J_{P-H}$  = 2.25 Hz, 1H, H2), 3.80 (s, 6H, OMe), 2.64 (m, 6H, CH(<sup>†</sup>Pr)), 1.19 (m, 36H, PCHCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, benzene-d<sub>6</sub>): δ 203.5 (CO), 156.0 (C12), 150.7 (d,  ${}^{2}J_{PC}$  = 10.5 Hz, C1), 149.3 (C7), 141.6 (C9), 134.3 (C5), 140.3 (C3), 134.7 (d,  ${}^{3}J_{PC}$  = 3.3 Hz, C2), 129.1 (CS), 126.8 (C10) 117.4 (C4, C6, C8), 114.9 (C11), 55.3 (OCH<sub>3</sub>), 24.3 (t,  ${}^{1}J_{P-C} = 9.6$  Hz,  $CH({}^{i}Pr)$ ), 19.5 and 19.4 (each s,  $CH_{3}({}^{i}Pr)$ ) ppm.  ${}^{31}P$  NMR (161.9 MHz,  $CD_{2}Cl_{2}$ ):  $\delta$  38.2 ppm. Anal. Calcd for  $C_{41}H_{62}CINO_{3}P_{2}Ru \times 0.5CH_{2}Cl_{2}$  (1295.42 g/mol): C, 60.39; H, 7.66; N, 1.72. Found: C, 60.21; H, 7.46; N, 1.75.

4-OMe- $C_6H_4$ -CH=CH-RuCl(CO)( $P^iPr_3$ )<sub>2</sub>, **2**. To a solution of HRuCl(CO)( $P^iPr_3$ )<sub>2</sub> (120 mg, 0.240 mmol) in 6 mL of CH<sub>2</sub>Cl<sub>2</sub> was added a solution of 32 mg (0.24 mmol) of 4-ethynylanisole, which resulted in an immediate color change from red-orange to purple. The solution was stirred under gentle warming to 45 °C for 30 min, and the solvent removed under vacuum. The resulting solid was dissolved in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub> and precipitated by addition to 30 mL of rapidly stirred methanol, and the solvent was removed by filtration. After repeating this procedure two more times, the resulting purple solid was dried under vacuum to yield 145 mg (0.235 mmol, 98%) of spectroscopically pure complex **2**.

<sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.25 (d, 1H,  ${}^{3}J_{H-H} = 13.44$  Hz, Ru-CH), 6.95 (d, 2H,  ${}^{3}J_{H-H} = 8.78$  Hz, H4), 6.73 (d, 2H,  ${}^{3}J_{H-H} = 8.78$ Hz, H5), 5.90 (dt, 1H,  ${}^{3}J_{H-H} = 13.44$  Hz,  ${}^{4}J_{H-P} = 2.19$  Hz, Ru-CH= CH), 3.73 (s, 3H, OMe), 2.81–2.67 (m, 6H, PCHCH<sub>3</sub>), 1.35–1.21 (m, 36H, PCHCH<sub>3</sub>).  ${}^{13}$ C NMR<sup>43</sup> (150.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 209.4 (t,  ${}^{2}J_{C-P} = 13.14$  Hz, Ru(CO)), 157.0 (s, C6), 146.5 (t,  ${}^{2}J_{C-P} = 10.9$  Hz, Ru-CH), 133.8 (s, RuCH-CH), 132.8 (s, C3), 125.1 (s, C4), 114.0 (s, C5), 55.5 (s, OCH<sub>3</sub>), 24.8 (t,  ${}^{1}J_{P-C} = 9.9$  Hz, CH(<sup>i</sup>Pr)), 20.0 and 19.9 (each s, CH<sub>3</sub>(<sup>i</sup>Pr)).  ${}^{31}$ P{<sup>1</sup>H} NMR (121.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 38.3 (s). Anal. Calcd for C<sub>28</sub>H<sub>51</sub>ClO<sub>2</sub>P<sub>2</sub>Ru (618.15 g/mol): C, 54.40; H, 8.32. Found: C, 54.80; H, 8.41.

# ASSOCIATED CONTENT

#### **S** Supporting Information

X-ray crystallographic data for An<sub>2</sub>N-Br and complexes m-1 and 2, representative voltammetric scans of An<sub>2</sub>N-CCTMS and of complex 2, and IR spectroelectrochemistry of complex m-1 (second oxidation) and UV/vis/NIR spectroelectrochemistry of complex 2, EPR spectra of complex 2, plots of the crucial frontier molecular orbitals of complex m-1, as well as results of TD-DFT calculations on m-1 and its associated radical cation. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have been deposited with the Cambridge Structural Data Base as CCDC 928205 (An<sub>2</sub>N-CCTMS), CCDC 928206 (complex m-1), and CCDC 950385 (complex 2). They can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ; fax (+44) 1223-336-033 or at deposit@ccdc. cam.ac.uk.

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#### Notes

The authors declare no competing financial interest.

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