# Bonding and Electron Delocalization in Ruthenium(III) $\sigma$ -Arylacetylide Radicals [*trans*-Cl( $\eta^2$ -dppe)\_2RuC=C(4-C<sub>6</sub>H<sub>4</sub>X)]<sup>+</sup> (X = NO<sub>2</sub>, C(O)H, C(O)Me, F, H, OMe, NMe<sub>2</sub>): Misleading Aspects of the ESR Anisotropy

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The bonding within the series of  $[trans-Cl(\eta^2-dppe)_2RuC \equiv C(4-C_6H_4X)]^{n+}$  complexes  $(1-X^{n+}; n = 1, 0 \text{ and } X = NO_2, C(O)H, C(O)Me, F, H, OMe, NMe_2)$  has been examined by IR, ESR, and UV-vis-near-IR spectroscopy together with computational modeling. A strong substituent effect is evidenced for radical delocalization from the metal to the functional arylacetylide fragment. This effect is also apparent in the large anisotropy change of their ESR signatures. DFT calculations substantiate these experimental observations and permit discussion of the influence of the X substituent on spin delocalization in compounds containing isolobal metal fragments. Evidence is given that the ESR anisotropy alone cannot reliably be used to compare the metallic character of the unpaired electrons in closely related families of pseudo-octahedral cationic Ru(III) functional arylacetylides with rhombic symmetry when the complexes possess different coordination spheres. ESR anisotropy constitutes nevertheless a useful benchmark for this purpose within the presently investigated  $1-X^+$  family.

## Introduction

Over the past few years, electron-rich electroactive group 8 metal acetylide complexes have attracted particular attention as redox-switchable building blocks for the realization of molecular-based devices, in a similar fashion to the ubiquitous ferrocenyl group.<sup>1,2</sup> For instance, it has been shown on several occasions that electron-rich acetylide fragments of d<sup>6</sup>-transition metals such as "*trans*-Cl( $\eta^2$ -dppe)<sub>2</sub>RuC=C-" or "( $\eta^2$ -dppe)( $\eta^5$ - $C_5Me_5$ )FeC=C-" permit the efficient redox control of linear and nonlinear optical activities, when incorporated in suitable molecular architectures.<sup>3–5</sup> This particular property rests on the fact that these organometallic units behave as strongly electronreleasing groups in their neutral (d<sup>6</sup>) closed-shell state but not in their mono-oxidized (d<sup>5</sup>) cationic state. This has been evidenced in several investigations on functional mononuclear Fe(II) and Ru(II) model compounds such as 1-X, 2-X, and 3-X (Chart 1), in which the X substituent was varied from strongly electron-withdrawing to strongly electron-releasing.<sup>6-8</sup> However, we think that in order to utilize such metal-containing fragments in new functional architectures, a better knowledge of their electronic characteristics is needed.

By deriving the electronic substituent parameters of the organometallic end groups in 1-X, 2-X, and 3-X, we have

previously shown that the electron-releasing capability of "*trans*-Cl( $\eta^2$ -dppe)\_2RuC=C-" is larger than that of "( $\eta^2$ -dppe)( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)FeC=C-" and somewhat lower than that of the ruthenium analogue of the latter, "( $\eta^2$ -dppe)( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)RuC=C-.7 On the basis of its electronic substituent parameter (ESP), this Ru(II) fragment is comparable to an amino substituent.<sup>9</sup> It has also been shown that d<sup>5</sup> paramagnetic cations such as **2-X**<sup>+ 7,10</sup> or **3-X**<sup>+ 11,12</sup> possess one electronic hole (or unpaired electron) that is significantly delocalized over the arylacetylide ligand.

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Chart 1. Selected Mononuclear Acetylide d<sup>6</sup> Complexes



These studies have also evidenced that this hole is somewhat more delocalized in  $2-X^+$  than in  $3-X^{+,7}$  With these results in mind, it is of particular interest to investigate more closely how the "trans-Cl( $\eta^2$ -dppe)<sub>2</sub>RuC=C-" fragment, in a given redox state, influences the electronic properties of selected functional complexes such as 1-X and  $1-X^+$  and to carefully compare these data with those of the corresponding 2-X and  $2-X^+$  relatives, in order to gain a deeper understanding of the similarities and differences between these isolobal and isoelectronic organometallic end groups.

We therefore report in the following (i) the synthesis and characterization of a new 1-X complex featuring the strongly electron-releasing dimethylamino substituent (1-NMe<sub>2</sub>), (ii) an investigation of the electronic substituent effects in a series of Ru(II) complexes composed of this new compound complemented by previously reported analogues functionalized with less electron-releasing substituents ( $X = NO_2$ , C(O)H, C(O)Me, F, H, and OMe), (iii) the characterization of these compounds in their mono-oxidized Ru(III) state along with a study of electronic substituent effects in this state, (iv) an extensive theoretical study using density functional theory (DFT) calculations of selected Ru(II) and Ru(III) model compounds, and (v) a comparative discussion of the bonding within the "Ru-C=C-1,4-C<sub>6</sub>H<sub>4</sub>-" core between 1-X/1-X<sup>+</sup> and 2-X/2-X<sup>+</sup>, with particular emphasis placed on spin delocalization in the Ru(III) radicals in relation to their ESR signatures.

## Results

Synthesis and Characterization of the Ru(II) Complexes. To date, several Ru(II) complexes of type 1-X featuring strongly electron-withdrawing to moderately electron-releasing substituents have been reported.<sup>13,14</sup> The compounds required for the present study ( $X = NO_2$ , C(O)H, C(O)Me, F, H, and OMe) were therefore obtained according to these procedures. However, a complex possessing a strongly electron-releasing group, e.g. the dimethylamino group, was also needed for comparison. The synthesis of this complex was undertaken according to an original procedure inspired from the Ru(II) allenylidene synthesis recently reported by Touchard and coworkers.<sup>15</sup> Instead of starting from the known  $cis-(\eta^2-dppe)_2RuCl_2$  precursor complex,<sup>16</sup> this synthetic approach starts from the triflate Ru(II) precursor<sup>2,17</sup> and allows isolation of the corresponding vinylidene salt under mild conditions from paradimethylaminophenylacetylene (Scheme 1). The latter complex was not characterized, but rather was deprotonated using 'BuOK to yield the desired Ru(II) acetylide complex (1-NMe<sub>2</sub>) in modest yield (37%) after chromatographic separation. This new complex was completely characterized by elemental analysis, mass spectrometry, and routine spectroscopies (Supporting Information).

The cyclic voltammetry (CV) of the previous Ru(II) compounds along with their IR and <sup>13</sup>C NMR spectra in solution were systematically recorded. As expected from previous



investigations on these compounds, 13,14,18 the metal-centered pseudoreversible Ru(II)/Ru(III) oxidation was detected close to the ferrocene redox potential (the use of 3-NO<sub>2</sub> as internal calibrant allowed accurate evaluation of the  $E^{\circ}$  values for these

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(X = NO<sub>2</sub>, C(O)H, C(O)Me, F, H, OMe, NMe<sub>2</sub>)

Table 1. IR Data and Ru(III/II) Oxidation Potentials for  $[trans-Cl(\eta^2-dppe)_2Ru(C=C-C_6H_4X)]^{0/+}$  Complexes in CH<sub>2</sub>Cl<sub>2</sub> Solution (cm<sup>-1</sup>)

cmpd X	$\begin{array}{c} \operatorname{Ru}(\mathrm{II}) \\ \nu_{\mathrm{C}=\mathrm{C}} \end{array}$	$\begin{array}{c} \operatorname{Ru(III)} \\ \nu_{\mathrm{C}\equiv\mathrm{C}} \end{array}$	$\Delta \nu_{C \equiv C}{}^{a}$	$\begin{array}{c} \operatorname{Ru(III/II)} \\ E^{\circ c} \end{array}$				
NO <sub>2</sub>	2051 2023(sh)	1928	-123 <sup>b</sup>	0.63				
C(O)H	2069(sh) 2049	1909	$-140^{b}$	0.55				
C(O)Me	2062 2036(sh)	1906	$-156^{b}$	0.54				
F	2074	1910	-164	0.46				
Н	2068	1908	-160	0.44				
OMe	2076	1922	-154	0.36				
NMe <sub>2</sub>	2076	1890	-186	0.14				

<sup>*a*</sup> Neutral vs oxidized  $\nu_{C=C}$  difference. <sup>*b*</sup>  $\Delta \nu_{C=C}$  value with the most intense peak. <sup>*c*</sup> All *E*° values in V vs SCE. Conditions: CH<sub>2</sub>Cl<sub>2</sub> solvent, 0.1 M (N<sup>n</sup>Bu<sub>4</sub>)(PF<sub>6</sub>) supporting electrolyte, 20 °C, Pt electrode, sweep rate 0.100 V s<sup>-1</sup>. The ferrocene/ferricinium (Fc/Fc<sup>+</sup>) couple was used as an internal reference for potential measurements.

electrochemical processes). Note that another irreversible oxidation above 1.2 V vs SCE can also be detected for all compounds. In addition, in the case of the nitro-substituted complex 1-NO<sub>2</sub>, the nitro reduction is observed at -1.26 V vs SCE, while for the dimethylamino-substituted complex 1-NMe<sub>2</sub> a second pseudoreversible event, corresponding to the amine oxidation, is detected at ca. 0.64 V vs SCE. In the <sup>13</sup>C NMR spectra, the characteristic quintuplet signal corresponding to the  $\alpha$ -acetylide carbon atom was detected in most cases, exhibiting coupling with the four equivalent equatorial phosphorus nuclei of ca. 15 Hz. A high-field 500 MHz NMR spectrometer was required to identify this weak signal for 1-F, 1-OMe, and 1-NMe<sub>2</sub>. IR spectra recorded in dichloromethane solutions reveal intense  $v_{C=C}$  bands in the 2050–2075 cm<sup>-1</sup> spectral range (Table 1). The shoulder apparent on this absorption band when electronwithdrawing substituents are present possibly arises from Fermi coupling.19

In the process of characterizing the Ru(II) complexes we obtained yellow crystals of **1-C(O)Me** by slow evaporation of the solvent from a dichloromethane solution of this complex. Figure 1 discloses the resulting solid-state structure. The complex crystallizes in the triclinic  $P\overline{1}$  space group with one molecule of complex in the asymmetric unit and one-half of a dichloromethane molecule as solvate (see Experimental Section for details). The bond lengths and angles of this complex are not unusual in comparison with available X-ray data for related mononuclear bis-dppe Ru(II) acetylide complexes and warrant no further comments.<sup>14,18</sup>

*In Situ* Generation of the Ru(III) Complexes and IR/ ESR Characterization. The corresponding Ru(III) complexes 1-F[BF<sub>4</sub>], 1-H[BF<sub>4</sub>], 1-OMe[BF<sub>4</sub>], and 1-NMe<sub>2</sub>[BF<sub>4</sub>] were generated *in situ* by oxidizing these compounds with acetylferricinium tetrafluoroborate. An excess of this oxidant was necessary to push the reaction to completion in the case of 1-NO<sub>2</sub>[BF<sub>4</sub>], 1-C(O)H[BF<sub>4</sub>], and 1-C(O)Me[BF<sub>4</sub>]. Monitoring solutions of 1-NO<sub>2</sub>[BF<sub>4</sub>] and 1-OMe[BF<sub>4</sub>] evidenced that the



**Figure 1.** ORTEP diagram of **1-C(O)Me**. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (deg): Ru1–P1 2.3800(12), Ru1–P2 2.3701(11), Ru1–P3 2.3480(11), Ru1–P4 2.3761(12), Ru–Cl1 2.4831(11), Ru1–C1 1.989(4), C1–C2 1.212(6), C2–C3 1.434(6), C3–C4 1.410(6), C4–C5 1.392(7), C5–C6 1.399(7), C6–C7 1.388(7), C7–C8 1.371(6), C8–C3 1.398(6), C6–C9 1.476(7), C9–C10 1.482(8), C9–O1 1.237(6), P1–Ru1–P2 80.80(4), P3–Ru1–P4 82.46(4), P1–Ru1–C1 84.39(4), C11–Ru1–C1 178.60(13), P2–Ru1–C1 84.80(4), Ru1–C1–C2 178.0(4), C1–C2–C3 169.4(5), C2–C3–C4 121.1(4), C4–C5–C6 121.4(5), C6–C7–C8 118.0(4), C7–C6–C9 119.5(5), C6–C9–O1 120.3(5), C10–C9–O1 120.9(4), P1–Ru1/C3–C4 –131.9, P4–Ru1/C3–C4 48.8, C6–C7/C9–O1 5.3.

Ru(III) cations generated this way were stable in dichloromethane over more than 10 min and that their lifetime increased somewhat with electron-releasing substituents. In the case of the complex **1-NMe**<sub>2</sub>, the dimethylamino substituent can also be oxidized if acetylferricinium tetrafluoroborate is present in excess. Thus, when overstoichiometric concentration of oxidant was used for IR monitoring, ferricinium hexafluorophosphate ([ $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe][PF<sub>6</sub>]) was preferred as an oxidant, to ensure that only **1-NMe**<sub>2</sub>[PF<sub>6</sub>] is initially generated.

The reaction is evidenced by a color change to purple-brown, except in the case of the dimethylamino-substituted complex **1-NMe**<sub>2</sub>, for which the reaction medium turns green. For all compounds, new  $\nu_{C=C}$  absorptions are detected in the 1930–1890 cm<sup>-1</sup> spectral range (Table 1) concomitantly with the disappearance of the  $\nu_{C=C}$  band of the reactant. This absorption is rather weak for the complexes with the most electron-withdrawing substituents but becomes more and more intense when the substituent becomes increasingly electron-releasing (Supporting Information).

We followed a similar workup in an ESR probe, but varied the procedure by quenching the reaction medium in liquid nitrogen immediately after admixture of the ferricinium salt. After transferring the tube to the cavity of the ESR spectrometer, a rhombic signal was detected at 80 K (Figure 2 and Table 2). For most compounds, this signal weakens and becomes isotropic after melting of the solvent glass, eventually disappearing when the temperature of the sample returns to ambient. For the Ru(III) complexes with the most electron-releasing substituents such

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**Figure 2.** ESR spectra in  $CH_2Cl_2/1, 2-C_2H_4Cl_2$  (1:1) glasses between 295 and 70 K for **1-NMe**<sub>2</sub><sup>+</sup>.

Table 2. ESR Spectroscopic Data<sup>*a*</sup> for  $[trans-Cl(\eta^2-dppe)_2Ru(C=C-C_6H_4X)][BF_4]$  Complexes

Х	$g_1$	$g_2$	$g_3$	$\langle g \rangle$	$\Delta g$
$NO_2$	1.766	1.955	2.777	2.166	1.011
C(O)H	1.818	1.988	2.683	2.163	0.865
C(O)Me	1.835	1.997	2.650	2.161	0.815
F	1.901	2.046	2.489	2.145	0.588
Н	1.896	2.039	2.519	2.151	0.623
OMe	1.958	2.061	2.309	2.109	0.351
$NMe_2$	1.994	2.040	2.102	2.045	0.108
$NMe_2^b$	1.993	2.037	2.100	2.043	0.107

<sup>*a*</sup> At 77 or 80 K in CH<sub>2</sub>Cl<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (1:1) glass. <sup>*b*</sup> Values for the  $[PF_6^-]$  salt generated *in situ* using  $[(\eta^5-C_5H_5)_2Fe][PF_6]$ .

as  $1-OMe^+$  or  $1-NMe_2^+$ , an isotropic signal can still be observed at room temperature, as shown in Figure 2 in the latter case.<sup>20</sup>

Attempts to characterize these radicals by <sup>1</sup>H NMR analysis were unrewarding, since only the most electron-rich Ru(III) complexes gave rise to sufficiently stable paramagnetic species in solution.<sup>21</sup> Thus, after oxidation of **1-OMe** or **1-NMe**<sub>2</sub> with acetyl ferricinium tetrafluoroborate, the resulting solutions exhibited very broadened signals in the diamagnetic range. These signals, which certainly correspond to the dppe and methyl



**Figure 3.** UV-vis-near-IR spectra of  $CH_2Cl_2$  solutions of (a) **1-NO<sub>2</sub>** and (b) **1-NMe<sub>2</sub>** on application of potentials of ca. 0.9 and 0.2 V, respectively, vs SCE (Fc/Fc<sup>+</sup> = 0.46 V) at 298 K in an OTTLE cell.

protons, were the only ones detected, the more informative and presumably more shifted signals of the functional aryl group remaining undetected.<sup>11</sup>

Spectroelectrochemical Characterization of the Ru(III) Complexes. In order to obtain additional data on these Ru(III) complexes, the electrochemical oxidation of a Ru(II) compound possessing a strongly electron-withdrawing substituent ( $1-NO_2$ ) and of compounds with strongly electron-releasing substituents (1-OMe and  $1-NMe_2$ ) were monitored in an OTTLE cell in the UV-vis-near-IR range (Figures 3a,b). Note that the spectroelectrochemical data for the phenyl complex 1-H have been previously reported by one of us.<sup>4</sup>

Conversion to the corresponding oxidized species  $1-X^+$  was observed, the latter being characterized by a completely different set of absorptions; in the case of compounds with electronreleasing substituents, new intense absorptions appear in the visible and near-IR range, leading to a darker color for the oxidized species. In the OTTLE cell, the oxidations seem to be reversible (in the chemical sense) only for compounds possessing electron-releasing substituents. In contrast, for  $1-NO_2^+$ , clean isosbestic points could not be obtained. The spectrum of the sample obtained after reducing back the *in situ*-generated oxidized species was similar to that of the starting  $1-NO_2$ complex, albeit of smaller intensity in the spectral window scanned. In line with the high reactivity observed for  $1-NO_2^+$ 

<sup>(20)</sup> A noticeable feature in this variable-temperature (VT) study is the occurrence of signals for the three tensors around 160 K narrower than at 70 K. We have currently no firm explanation for that phenomenon. We tentatively relate it to the presence of conformers with quasi-similar ESR signatures. These are possibly different dppe-based conformers but not arylacetylide rotamers, as discussed later. Upon heating beyond the coalescence temperature (presumably around 135 K), the initial inhomogeneously broadened tensors further broaden before eventually sharpening, the latter because of the rapid interconversion taking place between conformers to give the isotropic signal upon melting of the solvent glass. Note also that the increasingly faster relaxation of the electronic spin with temperature should also result in an overall broadening, which explains the overall loss of intensity of the ESR signal upon heating.

<sup>(21)</sup> For instance, a ca. 80% conversion to the carbonyl adduct [*trans*-Cl( $\eta^2$ -dppe)<sub>2</sub>Ru(CO)]<sup>+</sup> was evidenced in the case of **1-NO**<sub>2</sub> when this Ru(II) complex was oxidized using NOPF<sub>6</sub>. This known cationic complex<sup>22</sup> was characterized by mass spectrometry, NMR and IR. MS (ESI): *m/z* 961.1 (M<sup>++</sup>), calc for C<sub>53</sub>H<sub>48</sub>O<sub>1</sub>P<sub>4</sub>Ru<sub>1</sub><sup>+</sup> 961.1 (M<sup>++</sup>). FT-IR ( $\nu$ , KBr, cm<sup>-1</sup>): 1954 (RuC=O). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 42.9 (s, 4P, dppe). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$  in ppm): 7.45–6.70 (m, 80H, *H*<sub>Ar</sub>), 3.19 (m, 8H, *CH*<sub>2</sub>). <sup>31</sup>P NMR reveals that the formation of this compound is apparently accompanied by the formation of a vinylidene-like Ru(II) complex. For a closely related reference see ref 23.

<sup>(22)</sup> Szczecpura, L. F.; Giambra, J.; See, R. F.; Lawson, H.; Janik, T. S.; Jircitano, A. J.; Churchill, M. R.; Takeuchi, K. J. *Inorg. Chim. Acta* **1995**, 239, 77–85.

<sup>(23)</sup> Rigaut, S.; Monier, F.; Mousset, F.; Touchard, D.; Dixneuf, P. H. Organometallics **2002**, *21*, 2654–2661.



**Figure 4.** Plot of the Ru(III)/Ru(II) oxidation potentials (V) vs Hammett ESPs ( $\sigma$ ) for **1-X** complexes in CH<sub>2</sub>Cl<sub>2</sub>. The data for the previously reported *meta*-fluoro<sup>9</sup> complex have been added for comparison.

in solution,<sup>20</sup> this suggests that some decomposition occurred for this radical during the measurement.

Linear Free Energy Relationships (LFERs) with Electronic Substituent Parameters (ESPs). To assess the possibility of sizable electronic substituent effects, we have investigated if any correlation could be found between electronic substituent parameters (ESPs) and characteristic redox or spectral signatures of the Ru(II) compounds 1-X. A very good ( $R^2 = 0.98$ ) LFER is obtained between the  $\sigma$  Hammett ESPs<sup>24</sup> and the redox potentials corresponding to the Ru(II)/Ru(III) oxidation of 1-X (eq 1 and Figure 4). In line with related LFERs previously obtained for 2-X and 3-X,<sup>6,7</sup> the positive slope reflects the fact that an electron-releasing substituent renders the ruthenium-centered oxidation more facile, and the almost perfect linear fit suggests an essentially electronic origin for this phenomenon.

$$E_0(\mathbf{V}) = 0.305\sigma + 0.422 \tag{1}$$

Fair to excellent fits were also obtained with the energy (in cm<sup>-1</sup>) of the lowest-lying electronic (MLCT) transition ( $R^2 = 0.99$ ), with the <sup>13</sup>C NMR shifts of the  $\alpha$ - and  $\beta$ -carbon atoms ( $R^2 = 0.98$  and 0.92, respectively) of the acetylide ligand, or with  $\nu_{C=C}$  expressed in cm<sup>-1</sup> ( $R^2 = 0.87$ ) against the  $\sigma^-$  ESPs (Supporting Information).

In the case of the corresponding Ru(III) parents  $1-X^+$ , electron-releasing substituents seem to decrease the Ru(III) acetylide stretching frequency according to the poor correlation obtained. Much more significant LFERs could be evidenced with ESR data (Figures 5a,b). These trends reveal that electron-releasing substituents shift the mean *g*-value  $\langle g \rangle$  closer to the

free electron g-value ( $g_e = 2.0023$ ) and concomitantly reduce the anisotropy  $\Delta g$  of the signal. This means that the organometallic radicals **1-X**<sup>+</sup> resemble organic radicals more and more as the X substituent becomes more and more electron-releasing. The best fits for  $\langle g \rangle$  were obtained with  $\sigma^+$  ESPs, while the best fits for  $\Delta g$  were obtained with the regular Hammett ESPs. The equations of the linear fits for  $\langle g \rangle$  and  $\Delta g$  are given in equations 2a and 2b.

$$\langle g \rangle = 0.047 \sigma_{\rm p}^+ + 2.138$$
 (2a)

$$\Delta g = 0.591\sigma_{\rm p} + 0.577 \tag{2b}$$

**DFT Calculations on Model Compounds.** Theoretical computations were performed on model Ru(II/III) complexes **4-NO<sub>2</sub>/4-NO<sub>2</sub><sup>+</sup>**, **4-H/4-H<sup>+</sup>**, **4-OMe/4-OMe<sup>+</sup>**, **4-NMe<sub>2</sub>/4-NMe<sub>2</sub><sup>+</sup>** and the precursor complex *trans-5*, in which the chelating dppe ligands have been replaced by 1,2-diphosphinoethane (dpe) ligands. Two conformations were considered for **4-X**<sup>0/+</sup> complexes, one where the aryl plane and the ethane bridges of the dpe ligands are roughly parallel ( $4^{l}$ )<sup>0/+</sup> and a second one ( $4^{\perp}$ )<sup>0/+</sup>, where the plane of the functional aryl ring roughly bisects the dpe ligands (Chart 2). For comparison purposes, DFT computations were also performed on **6-NO<sub>2</sub><sup>+</sup>**, **6-H<sup>+</sup>**, **6-OMe<sup>+</sup>**, and **6-NMe<sub>2</sub><sup>+</sup>** in two similar conformations (i.e., with the plane of the functional aryl ring bisecting the dpe and cyclopentadienyl ligands).

The structures of the 4-X model compounds were optimized without symmetry constraints. The largest energetic differences between the two conformations are found with electron-releasing groups, with a maximum of ca. 0.02 eV between the two conformations examined. The most stable configuration is that in which the functional aryl ring is roughly parallel to the dpe ethylene bridge, consistent with the available X-ray data for several 1-X representatives.<sup>14,18,25</sup> As a check for the computational accuracy, we have verified that the bond lengths found for 4<sup>II</sup>-NO<sub>2</sub> after optimization matched quite well those reported for 1-NO<sub>2</sub> by Long et al. (Supporting Information).<sup>18</sup> Energies of the frontier molecular orbitals (MOs) for Ru(II) complexes are shown in Figure 6. The computations reveal that the rotation of the Cl(dpe)<sub>2</sub>Ru fragment around the acetylide axis slightly affects the HOMO-LUMO gap (up to 0.12 eV), as well as the MO ordering. Nevertheless, the global description of the electronic structure remains very similar, whatever orientation of the ruthenium moiety is retained for the neutral systems. The two closely lying highest occupied MOs (HOMO and HO-MO-1) are mainly metal and acetylide in character (ca.



**Figure 5.** (a) Plot of the ESR mean *g*-value and (b) of the *g*-tensor anisotropy vs Hammett ESPs for  $[trans-Cl(\eta^2-dppe)_2RuC \equiv C(4-C_6H_4X)][BF_4]$  complexes **1-X**<sup>+</sup> (X = NO<sub>2</sub>, C(O)H, C(O)Me, F, H, OMe, NMe<sub>2</sub>).



Figure 6. Molecular orbital diagram of the Ru(II) complexes 4<sup>||</sup>-NO<sub>2</sub>, 4<sup>||</sup>-H, 4<sup>||</sup>-OMe, and 4<sup>||</sup>-NMe<sub>2</sub>. Frontier MOs having a sizable metallic character are indicated on the left-hand side.

Chart 2. Mononuclear Model Complexes Used in the DFT Calculations and Numbering Scheme Used



46–13% and 30–39%, respectively). These MOs roughly correspond to the perpendicular  $\pi$ -manifolds on the acetylide ligand. The HOMO corresponds to the  $\pi$ -manifold conjugated with the X substituent except in the complex 4<sup>II</sup>-NO<sub>2</sub>, where the order is inverted. The phenylacetylide character of these two MOs increases slightly concomitantly with the decrease of the Ru character, when going from 4-NO<sub>2</sub> to 4-OMe. For all the compounds, the LUMOs are Ru–P antibonding, except for 4-NO<sub>2</sub>, where the LUMO is an MO essentially localized on the NO<sub>2</sub> fragment. Accordingly, this complex shows a markedly smaller HOMO–LUMO gap than the other 4-X complexes. Without this specific difference, the HOMO–LUMO gap slightly decreases when going from the most electron-withdrawing substituent to the most electron-releasing one (from 2.72 to 2.22 eV).

The computed ionization potentials for 4-X correlate linearly with the first oxidation potentials measured for the corresponding 1-X complexes by cyclic voltammetry (Supporting Information). Upon oxidation, one electron is removed from the HOMO or HOMO-1 depending on the substituent and on the conformation of the functional aryl ring. Regardless of the nature of the substituent, the most stable conformation of  $4-X^+$  radicals is the perpendicular one (Table 3). The energies of the six frontier spin-MOs ( $\alpha$  and  $\beta$ ) possessing a strong metal character (two unoccupied and four occupied) are shown in Figure 7 for these complexes in the perpendicular conformation ( $4^{\perp}$ -**X**)<sup>+</sup>. Calculations reveal that the metal contribution to the higher lying spin-MOs is dominated by one type of d atomic orbital. Actually, the SOMO and the two lower lying MOs correspond to the "t<sub>2g</sub>" set of the Ru(III) ion (pseudo- $O_h$  symmetry). However, both the  $\alpha$ -SOMO and  $\alpha$ -SOMO-1 contain an important acetylide character (Supporting Information). In the case of **4-NO**<sub>2</sub><sup>+</sup>, aryland nitro-based MOs (SOMO-3, SOMO-6, and SOMO-7) are found between these filled d-based spin-orbitals. In **4-X**<sup>+</sup> radicals, the filled frontier  $\pi$ -spin-orbital of dominant  $d_{xz}$ character is more strongly stabilized by electron-withdrawing substituents than is that of  $d_{yz}$  character, resulting in a crossing between these spin-orbitals for **4-NO**<sub>2</sub><sup>+</sup>.<sup>7,12</sup> The rotation of the

<sup>(24) (</sup>a) March, J. Advanced Organic Chemistry Reactions, Mechanisms and Structures, 4th ed.; J. Wiley & Sons: New York, 1992. (b) Hansch, C.; Leo, A.; Taft, R. W. Chem. Rev. **1991**, *91*, 165–195.

<sup>(25)</sup> Note that in the Ru(II) complexes, the stability of the parallel conformation is possibly also enforced by the steric hindrance of the phenyl groups of the dppe ligands and by packing forces in the crystal. In solution at ambient temperature, however, the rotation of the functional aryl group around the acetylide axis is facile for these compounds.

Table 3. Calculated Mulliken Spin Densities (in electrons) for Selected Atoms in  $[trans-Cl(\eta^2-dpe)_2RuC \equiv C(4-C_6H_4X)]^+$  (4-X<sup>+</sup>) and  $[trans-(\eta^2-dpe)_2RuCl_2]^+$  (trans-5<sup>+</sup>) Complexes (see Chart 2 for atom numbering)

$4-X^+$												
Х		Cl	Ru	$\mathbf{P}^{a}$	$C_{\alpha}$	$C_{\beta}$	$C_1$	$C_2^{\ a}$	$C_3^{b}$	$C_4$	Х	$\Delta E^b$
$NO_2$	$  ^{c}$	0.110	0.366	0.004	0.067	0.275	-0.026	0.090	-0.040	0.111	0.018	742
	$\perp^d$	0.105	0.398	-0.003	0.048	0.265	-0.032	0.095	-0.043	0.116	0.020	0
Н		0.082	0.313	0.000	0.112	0.250	-0.006	0.102	-0.044	0.160	0.000	645
	$\perp^d$	0.081	0.300	-0.001	0.087	0.251	-0.010	0.099	-0.043	0.152	0.000	0
OMe		0.060	0.255	0.001	0.146	0.193	0.038	0.072	-0.004	0.116	0.068	532
	$\perp^d$	0.057	0.294	-0.001	0.124	0.201	0.031	0.072	-0.005	0.111	0.069	0
NMe <sub>2</sub>		0.039	0.195	0.001	0.164	0.140	0.074	0.038	0.035	0.067	0.183	387
	$\perp^d$	0.043	0.235	-0.001	0.142	0.148	0.065	0.040	0.032	0.065	0.173	0
trans-5 <sup>+</sup>		$0.190^{a}$	0.654	-0.007								

<sup>a</sup> Mean value. <sup>b</sup> Relative energy between the two conformations (cm<sup>-1</sup>). <sup>c</sup> Parallel conformation. <sup>d</sup> Perpendicular conformation.



Figure 7. Molecular orbital diagram of the Ru(III) complexes  $(4^{\perp}-NO_2)^+$ ,  $(4^{\perp}-H)^+$ ,  $(4^{\perp}-OMe)^+$ , and  $(4^{\perp}-NMe_2)^+$ . Frontier MOs having a sizable metallic character are indicated on the left-hand side.

functional aryl ring also significantly affects the energies of the frontier orbitals, albeit not their ordering (Supporting Information). The energetic gap between the  $\beta$ -SOMO and  $\beta$ -SOMO-1 is maximized in the most stable  $4^{\perp}$ - $X^+$  conformation.

The spin distributions computed for 4-NO<sub>2</sub><sup>+</sup>, 4-H<sup>+</sup>, 4-OMe<sup>+</sup>, and  $4-NMe_2^+$  are given in Table 3 for two different orientations of the aryl ring. While the spin density is spread over the  $\pi$ -conjugated arylacetylide ligand, it is strongly influenced by the X substituent. Indeed, the atomic spin densities on Ru and  $C_{\beta}$  increase from 0.23 and 0.15 to 0.40 and 0.26 electron, respectively, while that on  $C_{\alpha}$  slightly decreases from 0.14 to 0.05 electron, when going from the most electron-releasing to the most electron-withdrawing substituents, in line with a lesser delocalization of the electronic hole on the X substituent. The spin remains mainly located on the metal and to a lesser extent on the chlorine atom or on the  $C_{\alpha}$  or  $C_{\beta}$  carbon atoms. In terms of overall density, these calculations indicate that more spin density is present on the arylacetylide ligand than on the metallic end group (Table 3). In terms of MO location, the unpaired spin density shows up in the  $\pi$ -manifold conjugated with the aryl ring regardless of the nature of the X substituent and seems to be only marginally affected by rotation (Table 3), in contrast to what happens for  $6-X^+$  radicals (Figure 8).

The *g*-tensor components were computed for 4-X<sup>+</sup>, *trans*-5<sup>+</sup> (Table 4), and 6-X<sup>+</sup> (Supporting Information). These computations reveal a rhombic tensor for all these radicals, as experimentally observed for 1-X<sup>+</sup> and 2-X<sup>+</sup>.<sup>7</sup> Then, for 4-X<sup>+</sup> radicals,



**Figure 8.** Comparison of the spatial distribution of spin densities computed for both conformations of  $[trans-Cl(\eta^2-dpe)_2RuC=C(4-C_6H_4X)]^+$  (X = NO<sub>2</sub> and NMe<sub>2</sub>) model complexes (**4-X**<sup>+</sup>) and the corresponding  $[(dpe)(\eta^5-C_5H_5)RuC=C(C_6H_5)]^+$  analogues (**6-X**<sup>+</sup>). The Mulliken spin density on the ruthenium atom (Spin<sub>Ru</sub>) is also indicated.

sizable substituent effects on the mean *g*-value are clearly evidenced. These complexes exhibit a reduced asymmetry with increasing electron-releasing capability of the X substituent. The

Table 4. Computed ESR g-Values for the Model Complexes  $[trans-Cl(\eta^2-dpe)_2RuC\equiv C(4-C_6H_4X)]^+$  (4-X<sup>+</sup>) and  $[trans-(\eta^2-dpe)_2RuCl_2]^+$  (trans-5<sup>+</sup>)

<b>4-X</b> <sup>+</sup>						
Х	conformer	$g_1$	$g_2$	$g_3$	$g_{iso}$	$\Delta g$
$NO_2$	$\perp$	1.833	1.925	2.645	2.134	0.812
	11	0.632	0.725	3.513	1.623	2.881
	mean	1.233	1.325	3.079	1.879	1.846
Н	$\perp$	1.931	2.009	2.404	2.115	0.473
	11	1.257	1.330	3.219	1.935	1.962
	mean	1.594	1.669	2.812	2.025	1.218
OMe	$\perp$	1.975	2.034	2.218	2.075	0.243
	11	1.819	1.872	2.596	2.096	0.777
	mean	1.897	1.953	2.407	2.086	0.510
NMe <sub>2</sub>	$\perp$	1.986	2.032	2.139	2.052	0.153
	11	1.951	1.988	2.282	2.074	0.331
	mean	1.968	2.010	2.211	2.063	0.243
trans-5 <sup>+</sup>		1.499	1.542	1.752	1.597	0.253

calculations reveal a significantly larger effect of the rotation of the functional phenylacetylide ligand on the mean values and on the anisotropy than that induced by a change of the X substituent (Table 4). The values computed for the perpendicular conformation  $(4^{\perp}-X^{+})$ , the most stable for the oxidized compounds  $4-X^{+}$ , correspond much better with the experimental ESR data determined for  $1-X^{+}$ . Both the anisotropy and the mean *g*-value computed for  $4^{\perp}-X^{+}$  are quite close (within 3%) to the experimental values and follow the observed substituentdependent trends (Table 2). The slight discrepancies are attributed to the simplification of some ligands coordinated to the ruthenium in the model compounds and to the neglect of the surrounding medium (solvent and counterions).

Finally, the first excitation energies were computed for the complexes **4-X/4-X**<sup>+</sup> (Table 5) and for **6-H/6-H**<sup>+</sup> using the TD-DFT approach.<sup>26</sup> The match between the computed values gathered for the most stable **4-X**<sup>*n*+</sup> conformer (*n* = 0, 1) under vacuum and the experimental data obtained in dichloromethane solutions for **1-X**<sup>*n*+</sup> compounds (*n* = 0, 1), where the molecules can thermally rotate, can be considered as satisfying.<sup>27</sup> The most intense transitions (*f* > 0.05) computed for the most stable conformations of the **4-X**<sup>*n*+</sup> (*n* = 0, 1) complexes are given in Table 5, along with the available experimental data for **1-X** complexes.

For the neutral Ru(II) parents (4<sup>II</sup>-X), only a few transitions below 30 000 cm<sup>-1</sup> have a significant oscillator strength ( $f \ge$  0.05). These appear to be multiconfigurational MLCT excitations from metal- and chloride-based MOs toward aryl-based  $\pi^*$  MOs, except for the methoxy complex **1-OMe**. For this compound, the most intense transition involves a dominant charge transfer contribution from metal-centered MOs toward  $\pi^*$  MOs located on the phosphorus. Corresponding absorption bands were experimentally detected (within 2000 cm<sup>-1</sup> error margin) for **1-X** complexes. Computations also reproduce rather well the shift to higher energy of these transitions for **4<sup>II</sup>-X** complexes as the substituent becomes more electron-releasing.

For the cationic Ru(III) congeners, calculations also indicate the occurrence of several intense transitions. Their composition needs to be carefully considered due to the possible occurrence of spin contamination.<sup>28</sup> The present TD-DFT data can nevertheless be used as a rough guide to assign the observed transitions for 1-X<sup>+</sup> (Table 5) taking place at the vis/near-IR edge. The intense transitions calculated around 11 000  $\text{cm}^{-1}$  for 4-X<sup>+</sup> radicals have a dominant LMCT character and mostly originate from MOs on the chlorine atom. Consistent with the measurements on  $1-X^+$ radicals, their oscillator strength is computed to increase with the electron-releasing character of the X substituents, while their energies are only marginally affected. The intense transitions found in the 16 000-23 000 cm<sup>-1</sup> spectral region have no true LMCT character, since no marked charge transfer takes place along the acetylide axis; they are more appropriately described as  $\pi \rightarrow d_{Ru}$ transitions distributed over the chlorine-metal-arylacetylide axis. Transitions with a marked MLCT character are computed at higher energies, around  $30\ 000\ cm^{-1}$ .

In order to assign the shoulder at ca. 12 160 cm<sup>-1</sup> for **1-NMe**<sub>2</sub><sup>+</sup> (Figure 3), we examined more closely the computed excitations possessing a dominant ligand field (LF) character. For each **4-X**<sup>+</sup> complexes, two d-d forbidden transitions corresponding to SOMO-1/SOMO and SOMO-2/SOMO excitations were found. While the former LF excitation always constitutes the lowest energetic transition (2930-5460 cm<sup>-1</sup>,  $f < 2 \times 10^{-4}$ ), the second is computed to occur at higher energy and appears to be slightly more intense (13 200-16 000 cm<sup>-1</sup>,  $f < 3 \times 10^{-3}$ ).<sup>29</sup> However, for **4-NMe**<sub>2</sub><sup>+</sup>, the match with the shoulder experimentally observed at 12 160 cm<sup>-1</sup> for **1-NMe**<sub>2</sub><sup>+</sup> remains poor.<sup>30</sup> More likely, this shoulder corresponds to a vibronic transition involving the acetylide stretch in the LMCT excited state, since an energetic difference of 1940 cm<sup>-1</sup> is found with the absorption attributed to this state (Table 1).

#### Discussion

This work has afforded evidence for the existence of sizable electronic substituent effects for 1-X and  $1-X^+$  complexes. These are immediately apparent in the linear dependence of the redox potentials (Figure 4) corresponding to the first oxidation of these complexes on the Hammett ESPs,<sup>31</sup> but also on other characteristic signatures for the Ru(II) and Ru(III) complexes (Figure 5 and Supporting Information).

Substituent Effects on the Bonding in the Ru(II) Complexes. In a similar manner to these of 2-X, electron-releasing substituents facilitate the oxidation of the neutral 1-X complexes. Comparison with data previously reported for 2-X reveals that for a given substituent the ruthenium-centered oxidation of 1-X takes place at slightly higher potentials (210-230 mV) than for the corresponding 2-X analogues.<sup>7</sup> This was expected on the basis of the slightly lower electronreleasing capability of the "*trans*-Cl( $\eta^2$ -dppe)<sub>2</sub>RuC=C-"

<sup>(26)</sup> Because of the simplified structure considered for these model compounds, any transitions involving the  $\pi$  or  $\pi^*$  MOs of phenyl rings of the dppe ligand in **1-X** and **1-X**<sup>+</sup> are overlooked. Since  $\pi \rightarrow \pi^*$  transitions of this kind are expected above 35 000 cm<sup>-1</sup> (ca. 4.3 eV), excitations were not computed above this value.

<sup>(27)</sup> To a have a perfect fit with the experimental data, a systematic study of all the conformers should have been done (dynamical study). However, results for  $4^{||}$ -X and  $4^{\perp}$ -X or  $4^{||}$ -X<sup>+</sup> and  $4^{\perp}$ -X<sup>+</sup> indicate that rotation of the functional aryl ring induces an energetic shift up to 5000 cm<sup>-1</sup>, which largely overwhelms the solvent effect without actually changing the nature of the transitions. Under such circumstances, calculations including the solvent effect were not systematically undertaken.

<sup>(28)</sup> Casida, M. E.; Ipatov, A.; Cordova, F. In *Time-dependent Density-functional Theory*; Marques, M. A. L., Ullrich, C., Nogueira, F., Rubio, A., Gross, E. K. U., Eds.; Springer: Berlin, 2006.

<sup>(29)</sup> Even when located in the spectral range investigated, the oscillator strengths of these forbidden LF transitions are however seemingly insufficient to permit their detection under the spectro-electrochemical conditions used to generate the  $1-X^+$  radicals.

<sup>(30)</sup> Alternatively these SOMO–1/SOMO LF transitions could correspond (within 3300 cm<sup>-1</sup>) with the lowest intensity transitions detected in the near-IR range which were attributed to " $\pi$ –d" transitions. However, on the basis of calculations, such an assignment is poorly supported by the substituent effect on their energies. Indeed, according to the present computations, all these forbidden LF transitions should be shifted toward higher energies ( $\Delta E \approx 2020 \text{ cm}^{-1}$ ) when the X substituent becomes more electron-releasing.<sup>12</sup>

Table 5. Energy (cm<sup>-1</sup>) and Composition of the First Excitation Energies (oscillator strength  $f \ge 0.05$ , transition percentage  $\ge 7\%$ ) below 35 000 cm<sup>-1</sup>, Computed for [*trans*-Cl( $\eta^2$ -dpe)\_2Ru(C=C-C<sub>6</sub>H<sub>4</sub>X)]<sup>n+</sup> (4<sup>||</sup>-X/4<sup>⊥</sup>-X<sup>+</sup>;  $n = 0, 1; X = NO_2, H, OMe, NMe_2$ ) Model Complexes vs Experimental Values (cm<sup>-1</sup>) for the Corresponding [*trans*-Cl( $\eta^2$ -dpe)\_2Ru(C=C-C<sub>6</sub>H<sub>4</sub>X)]<sup>n+</sup> Complexes (1-X/1-X<sup>+</sup>;  $n = 0, 1; X = NO_2, H, OMe, NMe_2$ )

Х	calculated <sup><i>a</i></sup> $\nu_{\max}$ ( $f^{b}$ )	composition	major assignment	observed <sup><i>a</i></sup> $\nu_{\max}$ ( $\epsilon^c$ )
		<i>n</i> =	= 0	
$NO_2$	18 670 (0.36)	86% 59a→61a 12% 58a→61a	$Ru \rightarrow C_6H_4NO_2$	20 750 (13.1)
	23 915 (0.17)	12 % 58a ~ 61a 80% 58a→61a	$Cl \rightarrow C_6H_4NO_2$	$\mathrm{nd}^d$
	32 125 (0.07)	10% 59a→61a 69% 51a→61a	$ClRuC \equiv C \rightarrow C_6H_4NO_2$	
	22 720 (0 14)	10% 50a→61a 28% 50a→68a	$P_{\rm H} \rightarrow P + C \parallel NO$	30,300-34,000 (sh 5,8-11,0)
	55 750 (0.14)	28% 59a→67a	$\mathrm{Ku} \rightarrow \mathrm{F} + \mathrm{C}_6\mathrm{H}_4\mathrm{NO}_2$	50 500-54 000 (sii, 5.8-11.9)
		16% 59a→69a		
		10% 59a→70a		38 460 (34 7)
Н	27 100 (0.07)	61% 52a→55a	$Ru \rightarrow C_6H_5$	nd <sup>d,e</sup>
	20.825 (0.28)	33% 52a→57a		21 2505 (22 0)5
	30 833 (0.28)	49% 52a→57a 23% 52a→55a 10% 50a→55a 7% 52a→61a	$\mathrm{Ku} \rightarrow \mathrm{C}_6\mathrm{H}_5$	51 550° (23.0)°
OMa	25 830 (0.06)	82% 580	$P_{\rm H} \rightarrow C \parallel OM_{\rm P}$	$38480^e(50.0)^e$
Ome	23 850 (0.00)	82% 58a→64a	$Ku \rightarrow C_6 H_4 O Me$	lid
	31 700 (0.39)	36% 58a→65a	$Ru/Cl \rightarrow P/C_6H_4OMe$	33 560 (sh, 21.0)
		25% 58a→64a 11% 56a→61a		
		10% 58a→61a		
	34 420 (0.08)	65% 56a→61a	$Cl/Ru \rightarrow C_6H_4OMe/P$	$\mathrm{nd}^d$
		1470 J7a 000a		38 760 (sh. 41.4)
NMe <sub>2</sub>	23 695 (0.06)	92% 61a→64a	$Ru \rightarrow P/C_6H_4NMe_2$	24 000 (sh, 4.0-6.0)
	31 250(0.48)	53% 61a→69a 31% 59a→64a		32 470 (26.0)
	32 430 (0.27)	63% 59a→64a	$Ru \rightarrow P/C_6H_4NMe_2$	$\mathrm{nd}^d$
		19% 61a→69a		
		8% 59a→69a		40,000 (46.7)
		n	= 1	
$NO_2$	11 070 (0.11)	92% 58a→60a (β)	$Cl \rightarrow Ru$	11 600 (5.0)
-	17 540 (0.06)	82% 52a→60a (β)	$Cl/P \rightarrow Ru$	16 500 (2.4)
	21 910 (0 28)	$14\% 59a \rightarrow 61a (\alpha)$ 71% 59a $\rightarrow 61a (\alpha)$	$R_{\mu} \rightarrow NO$ .	22,220 (sh 4,6)
	21 910 (0.20)	11% 52a→60a (β)		22 220 (31,4.0)
	27 590 (0.12)	39% 57a→61a ( $\alpha$ )	$Cl \rightarrow NO_2$	25 510 (5.2)
		13% 46a→60a (β)		
	33 800 (0.11)	77% 59a→65a (α)	$Ru \rightarrow C \equiv CC_6H_4NO_2$	30 300 (sh, 10.2)
ц	11,500 (0,00)	$86\% 500 \rightarrow 520 (\beta)$	$C1 \rightarrow P_{11}$	$37\ 000\ (32.1)$ 12 $040^e\ (10\ 0)^e$
11	11 500 (0.05)	$10\% 49a \rightarrow 52a (\beta)$	Ci Ku	12 040 (10.0)
	18 150 (0.12)	90% 46a→52a (β)	$ClRuC \equiv CC_6H_5 \rightarrow Ru$	$16\ 980^e\ (1.0)^e$
	29.030 (0.28)	75% 52a→55a (α)	$R_{11}/C_1 \rightarrow C \equiv CC_c H_{\epsilon}$	$27290^{e}(7.0)^{e}$ 29.830 <sup>e</sup> (13.0) <sup>e</sup>
	29 000 (0.20)	10% 50a→55a (β)		29 030 (13.0)
	35 570 (0.10)	44% 50a→55a ( $\beta$ ) 20% 50a→55a ( $\alpha$ )	$CIRu \rightarrow C \equiv CC_6H_5$	$35\ 710^e\ (52.9)^e$
		29% 50a-55a (u)		$36\ 510^e\ (53.0)^e$
OMe	11 460 (0.14)	91% 56a→58a (β)	$Cl \rightarrow Ru$	11 960 (11.9)
	16 360 (0.10)	77% 54a→58a (β) 14% 52a→58a (β)	$ClRuC \equiv CC_6H_4OMe \rightarrow Ru$	17 120 (2.6)
	27 630 (0.30)	$72\% 58a \rightarrow 61a (\alpha)$	$Ru \rightarrow C \equiv CC_6H_4OMe$	26 180 (13.8)
	20 (10 (0 00)	8% 58a→62a (α)		20 500 (1, 5, 0)
	28 640 (0.08) 34 720 (0.06)	82% 58a→62a (α) 58% 57a→64a (α)	$Ru \rightarrow C_6H_4$ $Ru \rightarrow P$	28 /00 (sh, 7.8) 35 900 (sh 41 0)
		11% 56a→61a (β)		
		10% 58a→66a (α)		27,500 (45,0)
NMe <sub>2</sub>	11 300 (0.20)	90% 59a→61a (β)	Cl → Ru	10 220 (14.7)
· · · 2				12 160 (sh, 4.8)
	15 560 (0.13)	86% 57a→61a (β)	$ClRuC \equiv C \rightarrow Ru$	16 950 (0.8)
	26 920 (0.52) 33 680 (0.12)	86% 61a→64a (α) 48% 60a→67a (α)	$Ku \rightarrow C \equiv C C_6 H_4 NMe_2$ $Ru/Cl \rightarrow P/C \equiv C - C_2 H_4 NMe_2$	24 150 (15.3) 32 680 (15.8)
	55 000 (0.12)	$19\% 59a \rightarrow 64a (\beta)$ $16\% 59a \rightarrow 64a (\alpha)$		52 000 (1510)

39 060 (41.6)

<sup>*a*</sup> The calculated excited states are <sup>1</sup>A. <sup>*b*</sup> Computed transition moment under vaccum. <sup>*c*</sup> Experimental absorption coefficients ( $\epsilon$ ) in 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>. <sup>*d*</sup> Not detected. <sup>*e*</sup> Taken from ref 4.

fragment relative to the " $(\eta^2$ -dppe) $(\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)RuC=C-" fragment previously evidenced.<sup>32</sup> As indicated by the slopes of the linear fits, this substituent effect on the redox potential is slightly more pronounced than it was for **2-X** complexes (eq 1; 0.305 vs 0.235 for **1-X** vs **2-X**, respectively).

Otherwise, the substituent effect on spectroscopic signatures is quite similar within experimental error for both series (Supporting Information). These data also resemble those reported for the **3-X** iron analogues.<sup>6</sup> Again, the best fits are obtained with  $\sigma^-$  ESPs rather than with regular Hammett

Scheme 3. Valence Bond-Based Representation of the Substituent-Dependent Delocalization of the Unpaired Electron in 1-X and  $1-X^+$  Complexes ([Ru] = trans-(dppe)\_2Ru)



Chart 3. Selected Mononuclear Acetylide d<sup>6</sup> Model Complexes Previously Used in DFT Computations



ESPs in LFER correlations involving spectroscopic data, which tends to indicate the prevalence of mesomeric effects on the bonding.<sup>6,7</sup> A similar valence bond (VB) scheme can thus be proposed to rationalize the observed substituent effects (a in Scheme 3).

In support of such a proposal, DFT calculations performed on the model complexes **4-X** and **6-X** reveal that the electronic structure of **1-X** strongly resembles that of **2-X** or **3-X** in terms of energy ordering of the frontier MOs. This statement is also in line with previous theoretical studies carried out on the related model compounds **7-X** lacking the chelating dpe ligand,<sup>4,5,8,33</sup> but also on previous studies involving piano-stool model complexes such as **8-X** and **9-X**, related to **2-X** and **3-X** (Chart 3).<sup>6,7,10-12</sup> In this connection, a detailed comparison between the frontier MOs of **4-X** and **6-X** in the two redox states is given in Figure 9.

Substituent Effects on the Bonding in the Ru(III) Complexes. The spin delocalization on the arylacetylide fragment also seems to not differ significantly between the two families of Ru(III) cations  $1-X^+$  and  $2-X^+$ , in spite of their different coordination spheres. Calculations on  $4-X^+$  and  $6-X^+$ show that delocalization of the spin density on the arylacetylide ligand is strongly favored by electron-releasing substituents, which efficiently compete with the *trans*-chloride ligand for delocalizing the spin density. Thus, a qualitatively similar VB scheme to that for  $2-X^+$  can also be proposed for  $1-X^+$  to rationalize the observed substituent effect (b in Scheme 3),<sup>6,7</sup> complemented by a new mesomeric form (E) proposed to rationalize the concomitant decrease in spin density observed on the chloro ligand.

A closer examination reveals that while the atomic spin density computed for the most stable conformations of  $4^{\perp}$ - $X^{+}$  and  $6^{\perp}$ - $X^{+}$  are quite similar for most X substituents (Table 6), more significant differences exist for the parallel conformers. While the spatial localization of the spin density is not markedly affected by rotation of the aryl ring in octahedral complexes **4**- $X^{+}$ , significant differences are evidenced in the case of pianostool radical cations **6**- $X^{+}$ , especially when strongly electronattracting X substituents are appended to the aromatic ring (Table 3 and Figure 8).<sup>11,12</sup>

As previously stated for  $2-X/2-X^+$  complexes, a bond weakening of the acetylide linkage takes place upon oxidation of 1-X complexes (Table 1). This effect, which has already been rationalized on the basis of MO considerations,<sup>6,7,12</sup> is slightly larger for the  $1-X/1-X^+$  complexes regardless of the substituent. Considering the rather similar spin distributions for both series of compounds in the oxidized state (b in Scheme 3), the larger bond weakening taking place upon oxidation for 1-X relative to 2-X might be ascribed to a lesser delocalization according to the VB (Scheme 3a) in the neutral state.

Low-Energy Electronic Transitions for 1-X and  $1-X^+$ Complexes. The assignment previously proposed by Stranger and Humphrey for the first intense electronic excitation in 1-H is confirmed here by our TD-DFT computations. As shown by the LFER with the UV data of the 1-X complexes (Supporting Information), the energy of this transition is decreased for electron-withdrawing X substituents, in line with its rutheniumto-aryl MLCT character along the metal—acetylide axis. This substituent effect, reminiscent of that previously reported for 2-X,<sup>7</sup> is also qualitatively reproduced by our computations.

In contrast to the similarity existing between the low lying excited states of the Ru(II) complexes **1-X** and **2-X**, significant differences are evidenced for the corresponding Ru(III) radicals **1-X**<sup>+</sup> and **2-X**<sup>+</sup>. Thus, **1-X**<sup>+</sup> radicals exhibit much more intense electronic absorptions in the near-IR range, as revealed by the available spectral data (Figure 3).<sup>7,10</sup> Still in line with the assignment of the electronic transitions proposed for **1-H**<sup>+</sup> by Stranger and Humphrey and in spite of the different theoretical approach presently used (TD-DFT instead of  $\Delta$ SCF),<sup>4</sup> the most intense near-IR transitions originating from chloride-based MOs. This contrasts with the situation prevailing for **2-X**<sup>+</sup> analogues, for which only very weak transitions with a strong

<sup>(31)</sup> For related works on acetylide complexes evidencing LFERs on redox potentials, see for instance: (a) Ying, J.-W.; Cordova, A.; Ren, T. Y.; Xu, G.-L.; Ren, T. *Chem.-Eur. J.* **2007**, *13*, 6874–6882. (b) Kuo, C.-K.; Chang, J.-C.; Yeh, C.-Y.; Lee, G.-H.; Wang, C.-C.; Peng, S.-M. J. Chem. Soc., Dalton Trans. **2005**, 3696–3701. (c) Hurst, S. K.; Xu, G.-L.; Ren, T. *Organometallics* **2003**, *22*, 4118–4123.

<sup>(32)</sup> Slightly lower  $\sigma_{\rm m}$  and  $\sigma_{\rm p}$  ESPs were found for **1-X** relative to **2-X** (-0.33 vs -0.47 and -0.39 vs -0.52, respectively).<sup>7,9</sup>

<sup>(33) (</sup>a) Delfs, C. D.; Stranger, R.; Humphrey, M. G.; Mac Donagh, A. M. J. Organomet. Chem. 2000, 607, 208–212. (b) Powell, C. E.; Cifuentes, M. P.; McDonagh, A. M.; Hurst, S. K.; Lucas, N. T.; Delfs, C. A.; Stranger, R.; Humphrey, M. G.; Houbrechts, S.; Asselberghs, I.; Persoons, A.; Hockless, D. C. Inorg. Chim. Acta 2003, 352, 9–18.



**Figure 9.** Comparison of the energy (eV) of the frontier MOs of the  $[trans-(\eta^2-dpe)_2ClRuC \equiv C(4-C_6H_5)]^{n+}$  model complexes  $(n = 0,1; 4-H/4-H^+)$  and the corresponding  $[(\eta^2-dpe)(\eta^5-C_5H_5)Ru(C \equiv CC_6H_5)]^{n+}$  analogues  $(n = 0,1; 6-H/6-H^+)$ . The spin-MOs are shown for the cationic species. The most intense (allowed) transitions of these compounds are also drawn.

Table 6. Comparison of the Calculated Mulliken Spin Densities for  $[trans-Cl(\eta^2-dpe)_2RuC\equiv C(4-C_6H_4X)]^+$  Complexes  $(4^{\perp}-X^+)$  and  $[(\eta^2-dpe)(\eta^5-C_5H_5)RuC\equiv C(4-C_6H_4X)]^+$   $(6^{\perp}-X^+)$  Complexes  $(X = NO_2, H, OMe, NMe_2)$ 

-/ / -/								
		4⊥.	X <sup>+</sup>			6 <sup>⊥</sup> -2	<b>X</b> <sup>+</sup>	
Х	$NO_2$	Н	OMe	NMe <sub>2</sub>	$NO_2$	Н	OMe	NMe <sub>2</sub>
Cl	0.105	0.081	0.057	0.043				
Ru	0.398	0.360	0.294	0.235	0.377	0.343	0.291	0.231
Cα	0.048	0.087	0.124	0.142	0.026	0.066	0.101	0.124
$C_{\beta}$	0.265	0.251	0.201	0.148	0.282	0.265	0.211	0.155
C <sub>1-4</sub>	0.188	0.253	0.274	0.274	0.191	0.252	0.269	0.271
Х	0.020	0.000	0.069	0.173	0.022	-0.011	0.057	0.154

d-d LF character have been found in the near-IR range, while the more intense LMCT transitions show up below 1000 nm.7,10,12,34 TD-DFT calculations indicate that similar (forbidden) LF transitions take also place in the near-IR range for 1-X<sup>+</sup> radicals. However, given the relatively low oscillator strengths, they are presumably not detected under the spectroelectrochemical conditions employed. The shoulder at 12 160 cm<sup>-1</sup> for  $1-NMe_2^+$  is therefore tentatively assigned as resulting from a  $\nu_{C=C}$  vibronic progression (1940 cm<sup>-1</sup>),<sup>4</sup> similar progressions having often been observed for related organic or organometallic radicals.<sup>35–37</sup> Thus, the notable change in optical properties between  $1-X^+$  and  $2-X^+$  can be ascribed to the presence of chloride-based p-type AOs, which strongly mix with the metalbased d AOs in the frontier MOs of 1-X<sup>+</sup> radicals, and also to the higher symmetry of the coordination sphere of  $1-X^+$ . As previously emphasized,<sup>4</sup> this makes the former type of complexes uniquely suited to exploit third-order NLO redox switching based on multiphotonic absorption properties.

ESR Anisotropy and Spin Delocalization in Ru(III) Radicals. Another noticeable difference between  $1-X^+$  and  $2-X^+$ radicals is manifested in their ESR signature. Indeed, while the substituent effect on the mean *g*-value is rather similar in amplitude for both series, the effect on the anisotropy of the signal is markedly larger for  $1-X^+$  (Figure 10). Thus, solely on the basis of the  $\Delta g$  values, a much larger change in the spin delocalization seems to take place for  $1-X^+$  relative to  $2-X^+$ along the series.

However, the computed spin densities for  $4-X^+$  and  $6-X^+$ clearly indicate that this is not the case (Table 6). In spite of the similar spin distribution, much larger changes in the ESR anisotropies are found for  $4-X^+$  (Table 4) relative to the corresponding  $6-X^+$  cations (Supporting Information). Actually, the anisotropies computed for  $4-X^+$  and  $6-X^+$  are in good accordance with those experimentally derived for  $1-X^+$  and  $2-X^+$ . This evidences that the change in anisotropy from one family of compounds to the other cannot be reliably used to compare the relative magnitudes of spin present at the metal center. However, within a given family, a fair correspondence is apparent between the spin density on the metal center and the computed anisotropies (Figure 10b), especially for  $6-X^+$ , where a good linear correlation can be evidenced ( $R^2 = 0.99$ ). Thus, in spite of the inherent difficulties in studying such Ru(III) radicals by NMR, the changes in spin delocalization in Ru(III) radicals and closely related arylacetylide analogues can be conveniently characterized experimentally by means of ESR. This proves especially true for  $1-X^+$  radicals, considering the large changes in anisotropy presently evidenced along the substituent series.

DFT computations shed light on the origin of the rhombic anisotropy observed for the ESR signals of **1-X**<sup>+</sup> complexes. *A priori*, the latter might have originated from the nonequivalence of the two  $\pi$ -manifolds of the alkynyl ligand induced by the presence of the aryl ring, but also from the presence of two chelating diphosphines, which lower the  $C_{4v}$  symmetry around the ruthenium center. The rhombic signal computed for *trans*- $[(\eta^2-dpe)_2RuCl_2]^+$  suggests that the diphosphine ligands constitute a determining factor in this respect, since the ESR

<sup>(34)</sup> These were alternatively termed  $\beta$ -HOSO $\rightarrow\beta$ -LUSO-1 and  $\beta$ -HOSO $-1 \rightarrow\beta$ -LUSO-1 in a less "localized" description.<sup>10</sup>

<sup>(35)</sup> Maurer, J.; Linseis, M.; Sarkar, B.; Schwederski, B.; Niemeyer, M.; Kaim, W.; Zalis, S.; Anson, C.; Zabel, M.; Winter, R. F. *J. Am. Chem. Soc.* **2008**, *130*, 259–268.

<sup>(36) (</sup>a) Klein, A.; Lavastre, O.; Fiedler, J. Organometallics **2006**, 25, 635–643. (b) Adams, C. J.; Pope, S. J. A. Inorg. Chem. **2004**, 43, 3492–3499.

<sup>(37)</sup> Choi, M.-Y.; Chan, M. C.-W.; Zhang, S.; Cheug, K.-K.; Che, C.-M.; Wong, K.-Y. *Organometallics* **1999**, 2074–2080.



**Figure 10.** (a) Comparative plot of the *g*-tensor anisotropy vs Hammett ESPs for  $[trans-Cl(\eta^2-dppe)_2RuC \equiv C(4-C_6H_4X)][BF_4]$  complexes **1-X**<sup>+</sup> ( $\bullet$ : X = NO<sub>2</sub>, C(O)H, F, H, OMe, NMe<sub>2</sub>) and  $[(\eta^2-dppe)(\eta^5-C_5Me_5)RuC \equiv C(4-C_6H_4X)][OTf]$  complexes **2-X**<sup>+</sup> ( $\blacksquare$ : X = NO<sub>2</sub>, CN, F, H, OMe, NH<sub>2</sub>). (b) Computed ESR anisotropy values against computed spin densities on the metal center for **4-X**<sup>+</sup> ( $\bullet$ ) and **6-X**<sup>+</sup> ( $\blacktriangle$ ) model compounds.

signature computed for *trans*-5<sup>+</sup> should be axial if a pseudo- $C_{4v}$  symmetry is preserved around the ruthenium. *A posteriori*, this emphasizes the need to use **4-X**<sup>+</sup> model compounds instead of **7-X**<sup>+</sup> models to accurately derive ESR parameters by DFT. Then, the good match obtained between ESR tensors calculated for the most stable conformer **4**<sup> $\perp$ </sup>-**X**<sup>+</sup> (Table 4) and the ESR data available for **1-X**<sup>+</sup> radicals (Table 2) strongly suggests that it is largely this particular conformer that is trapped in the solvent-glass at low temperatures.

$$[g_{ij} = g_{e}\delta_{ij} + 2\zeta \sum_{m \neq 0} (\langle 0|\hat{I}_{i}|m\rangle\langle m|\hat{I}_{j}|0\rangle)/(E_{0}-E_{m})] \quad (3)$$

$$g_{xx} = g_{\rm e} + 2\xi (c_0 c_2)^2 / (\Delta_2)$$
 (4a)

$$g_{yy} = g_{e} - 2\zeta (c_0 c_3)^2 / (\Delta_3) - 6\zeta (c_0 c_4)^2 / (\Delta_4)$$
 (4b)

$$g_{zz} = g_{\rm e} - 2\zeta (c_0 c_1)^2 / (\Delta_1)$$
 (4c)

In order to understand further the origin of the observed anisotropy differences between both series of compounds, we decided to use the ligand field approach to derive the value of the anisotropy by following the classic second-order perturbational treatment based on the ruthenium d-orbital contribution, as we did previously with the organoiron radicals  $3-X^+$  (eq 3).<sup>12</sup> Taking the z axis along the acetylide ligand, the expressions of the  $g_{ii}$  values are quite simple given the pseudo- $O_h$  symmetry of these compounds (eqs 4a-c), since the g-tensor is diagonal in this reference system (Figure 11).<sup>38</sup> These equations have been given for a SOMO with  $d_{xz}$  character (i.e., perpendicular conformation), but rigorously similar expressions result for a SOMO of  $d_{yz}$  character (i.e., parallel conformation) with the  $g_{xx}$  expression exchanged for  $g_{yy}$ . Because  $g_{zz}$  dominates the anisotropy of the ESR signal, the main component of the g-tensor anisotropy  $(g_3)$  is along the z direction, similar to the situation prevailing in the case of  $2-X^+$  radicals and for which similar  $g_{zz}$  expressions have been proposed.<sup>7</sup> Thus, the changes in  $\Delta g$  for these compounds have essentially two origins; either they reflect the substituent-induced changes in c<sub>0</sub> and c<sub>1</sub> (eq 4c), which are themselves mostly determined by the changes



**Figure 11.** Schematic spin-restricted representation of the frontier MOs and dominant metal character for  $d^5$  rhombic radicals such as  $[trans-Cl(\eta^2-dppe)_2RuC=C(4-C_6H_4X)]^+$  (1-X<sup>+</sup>).

in the metal-centered spin density, or they reflect the substituentinduced changes in the SOMO/SOMO-1 gaps ( $\Delta_1$ ). Given that similar spin distributions were computed for  $4^{\perp}$ - $\mathbf{X}^+$  and  $6^{\perp}$ - $\mathbf{X}^+$ for a specific substituent, the increased *g*-anisotropy stated for  $4^{\perp}$ - $\mathbf{X}^+$  (Figure 8) must originate from larger relative changes in  $\Delta_1$  along the series, in line with the lower SOMO/SOMO-1 gaps computed for  $4^{\perp}$ - $\mathbf{X}^+$  relative to  $6^{\perp}$ - $\mathbf{X}^+$ .

While the ligand field approach constitutes a wonderful tool to qualitatively interpret the origin of the changes in ESR anisotropy, a word of caution is needed here, given that this approach was originally derived for metal-centered radicals. It therefore becomes increasingly more approximate for delocalized radicals such as  $4^{\bot}\!\!\cdot\! X^{+}$  and  $6^{\bot}\!\!\cdot\! X^{+}$  because of the decreasing metal character of the frontier MOs. Thus, while the trends deduced from eqs 4a-c are certainly qualitatively correct when comparing  $4^{\perp}$ -X<sup>+</sup> and  $6^{\perp}$ -X<sup>+</sup>, a quantitative agreement with  $\Delta g$ cannot be expected. Accordingly, when SOMO/SOMO-1 gaps and d AO coefficients extracted from the present DFT calculations are used in eq 4c, much smaller anisotropies are found than those actually computed for these radicals using the ESR routine implemented in the ADF program. Also, according to eqs 4a-c, two of the principal g-tensors values should be above  $g_e$  and one below ( $g_1 < g_e \le g_2 < g_3$ ). This condition is however neither fulfilled by the principal g-tensor components computed by DFT for  $4^{\perp}$ - $X^+$  radicals featuring electron-withdrawing substituents nor by these experimentally measured for 1-X<sup>+</sup> radicals. This is certainly because the SOMO is close in energy

<sup>(38)</sup> In these equations,  $g_e$  stands for the free electron g-value,  $\zeta$  for the spin-orbit coupling constant,  $c_n$  for coefficients of the d AOs in the frontier MOs, according to Figure 11, and  $\Delta_n$  for the absolute values of the corresponding transition energies.



Table 7. Crystal Data, Data Collection, and Refinement Parameters for 1-C(O)Me · 1/2CH<sub>2</sub>Cl<sub>2</sub>

formula	$C_{62}H_{55}Cl_1O_1P_4Ru_1, 1/2CH_2Cl_2$
fw	1118.92
cryst syst	triclinic
space group	$P\overline{1}$
a (Å)	12.9876(5)
$h(\dot{A})$	13.3094(7)
c (Å)	17 4046(7)
$\alpha$ (deg)	74.848(4)
$\beta$ (deg)	75 788(3)
$\gamma$ (deg)	64.045(4)
$V(\Lambda^3)$	2581 1(2)
7 (A )	2581.1(2)
D (a sm <sup>-3</sup> )	2
$D_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.440
cryst size (mm)	$0.32 \times 0.32 \times 0.20$
F(000)	1154
abs coeff $(mm^{-1})$	0.575
number total/unique refns	18 621/10 745
no. of variables	634
final R	0.0523
R	0.1424
goodness of fit/ $F^2$ (S)	1.055
$g_{00}$ $g$	1.033

to the SOMO-1 in these particular cases, rendering the perturbative treatment at second order used to derive these equations no longer valid. In accord with that statement, the proportionality between the metal-centered spin density and  $\Delta g$ computed for  $6^{\perp}$ -X<sup>+</sup> radicals is lost for  $4^{\perp}$ -X<sup>+</sup> radicals with strongly electron-withdrawing substituents (Figure 10b).

Rhombic ESR spectra have recently been reported for closely related octahedral Ru(III) acetylide cations.<sup>36,39</sup> For instance, Maurer and co-workers have reported ESR data for the complexes 10-R, 11-R, and 12-R (Chart 4).35 Similar to our most electron-rich compounds  $1-NMe_2^+$ , the observation of a pseudoisotropic signal at ambient temperatures, along with very weak anisotropy at low temperature ( $\Delta g < 0.03$  for several representatives), was taken as diagnostic of dominantly organicbased radicals.<sup>35</sup> The lower anisotropy of their ESR spectra compared to that of the  $1-X^+$  radicals would suggest a larger electronic delocalization of the unpaired electron on the organic framework for these organometallic radicals. However, subsequent to this investigation, which points out the decisive influence of geometrical and electronic features on the ESR anisotropy for a constant spin distribution, the relative electronic delocalization between 1-X<sup>+</sup>, 10-R, 11-R, and 12-R radicals cannot be reliably inferred from their  $\Delta g$ -values alone, especially when considering the changes taking place in the coordination sphere of these radicals.

#### Conclusion

We have shown here that the family of [trans-Cl( $\eta^2$ dppe)<sub>2</sub>RuC $\equiv$ C(4-C<sub>6</sub>H<sub>4</sub>X)]<sup>*n*+</sup> complexes (1-X<sup>*n*+</sup>; *n* = 0, 1; X = NO<sub>2</sub>, C(O)H, C(O)Me, F, H, OMe, NMe<sub>2</sub>) exhibits sizable electronic substituent effects on their various spectral and redox signatures along the series. These effects on the bonding of these compounds are comparable to those previously reported for the related family of ruthenium analogues  $[(\eta^2 \text{-dppe})(\eta^5 \text{-}$  $C_5Me_5$ RuC= $C(4-C_6H_4X)$ ]<sup>*n*+</sup> (**2-X**<sup>*n*+</sup>). They can be similarly rationalized by resonance with different cumulene-like VB mesomers, depending on the redox state of the complex (Scheme 3). ESR measurements on  $1-X^+$  radicals and DFT calculations on corresponding Ru(III) model complexes reveal an important influence of the substituent on the electronic spin delocalization along the functional arylacetylide ligand. In spite of a much more pronounced change in anisotropy of the ESR spectra along the  $1-X^+$  series compared to  $2-X^+$ , a comparable electronic delocalization is computed to take place. This finding can be rationalized on the basis of simple ligand field considerations. It evidences that ESR anisotropy does not constitute a reliable (and absolute) reporter permitting comparison of the metalcentered spin densities of different families of functional arylacetylide Ru(III) radicals, even when isolobal metalcontaining fragments are considered. However, the large substituent sensitivity of the ESR anisotropy presently evidenced for  $1-X^+$  radicals suggests that this technique constitutes a very accurate method to experimentally gauge the metal-centered spin density for analogous Ru(III) arylacetylides in which the coordination sphere has been preserved. More generally, we believe that the set of data presently gathered on 1-X and 1-X<sup>+</sup> will prove very useful for future studies concerned with monoor polynuclear architectures containing  $[trans-Cl(dppe)_2Ru]^{n+}$ fragments (n = 0, 1).

### **Experimental Section**

Computational Details. DFT calculations were carried out using the Amsterdam Density Functional (ADF) program.40 The model compounds  $[trans-Cl(\eta^2-dpe)_2RuC \equiv C(4-C_6H_4X)]^{n+}$  and  $[(\eta^2-dpe)(\eta^5 C_5H_5$ )Ru-C=C(4-C<sub>6</sub>H<sub>4</sub>X)]<sup>n+</sup> (X = NO<sub>2</sub>, H, OMe, NMe<sub>2</sub>; n = 0, 1) were used in order to reduce computational effort. Electron correlation was treated within the local density approximation (LDA) in the Vosko-Wilk-Nusair parametrization.41 The nonlocal corrections of Becke<sup>42</sup> and of Perdew<sup>43</sup> were added to the exchange and correlation energies, respectively. The numerical integration procedure applied for the calculations was developed by te Velde et al.<sup>44</sup> The standard ADF TZP basis set was used, i.e., a triple- $\zeta$ Slater-type orbital (STO) basis for Ru 4d and 5s, and a single- $\zeta$ function for 5p of Ru. A triple- $\zeta$  STO basis set was employed for H 1s and for 2s and 2p of C, N, and O, extended with a single- $\zeta$ polarization function (2p for H; 3d for C, N and O). Orbitals up to 1s, 2p, and 4p were kept frozen for C, O and N, P, and Ru, respectively. Full geometry optimizations (assuming  $C_1$  symmetry) were carried out on each complex, using the analytical gradient method implemented by Versluis and Ziegler.45 Geometry optimization convergence criteria were more drastic than default ones (energy change < 0.0005 hartree, atomic position displacement < 0.005 Å). Harmonic vibrational frequency calculations were performed to check that the geometries are stationary points. Spinunrestricted calculations were performed for all the open-shell

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systems considered. The Cartesian coordinates of the optimized geometries are given as Supporting Information.

Time-dependent density functional theory (TD-DFT) calculations were performed on the optimized structures. The excitation energies and oscillator strengths were calculated following the procedure described by van Gisbergen and co-workers.<sup>46</sup> In this case, the functional PBE was used.<sup>47</sup> The EPR g-tensor calculations were calculated as implemented in ADF.<sup>48</sup> In this case, relativistic corrections were taken into account using the ZORA (zeroth order regular approximation) spin—orbit Hamiltonian with the appropriate basis set.<sup>49</sup>

**Crystallography.** Data collection of crystals of **1-C(O)Me** · 1/2CH<sub>2</sub>Cl<sub>2</sub> was performed on an APEXII Bruker-AXS diffractometer (Table 7) at 110 K. The structure was solved by direct methods using the SIR97 program,<sup>50</sup> and then refined with full-matrix least-squares methods based on  $F^2$  (SHELX-97)<sup>51</sup> with the aid of the WINGX program.<sup>52</sup> All non-hydrogen atoms were refined

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with anisotropic thermal parameters. H atoms were included in their calculated positions. A final refinement on  $F^2$  with 12775 unique intensities and 658 parameters converged at  $wR(F^2) = 0.1883$  (R(F) = 0.0846) for 8075 observed reflections with  $I > 2\sigma(I)$ . Selected bond lengths and angles are given in Figure 1.

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**Supporting Information Available:** Experimental part for the synthesis and characterization of **1-X** complexes. Solution IR and UV-vis-near-IR spectra for selected  $1 \cdot X^{n+}$  (n = 0,1) complexes. LFERs obtained for **1-X**. Fitting data (slopes and  $R^2$  indices). Composition of the frontier MOs computed for **4-X/4-X**<sup>+</sup>, comparison of bonding parameters, correlations between computed IPs and measured  $E^0$  values, dipole moments, low-lying excitations computed for **4-X/4-X**<sup>+</sup> and low-lying excitations computed for **6-H/6-H**<sup>+</sup>. Spin densities and ESR parameters computed for **6-X**<sup>+</sup>. CIF files for **1-C(O)Me**•1/2CH<sub>2</sub>Cl<sub>2</sub>. Final atomic positional coordinates, with estimated standard deviations, bond lengths and angles and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 668173. This material is available free of charge via the Internet at http://pubs.acs.org.

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