

Electrochemical and Spectroscopic Studies on σ -Phenyl Ruthenium Complexes $Ru(CO)Cl(C_6H_4R-4)(P'Pr_3)_2$

Christina S. Muck,[‡] Michael Linseis, Hannah Welte, Sabrina Weickert, Malte Drescher,¹⁰ and Rainer F. Winter*,[‡]

Fachbereich Chemie der Universität Konstanz, Universitätsstraße 10, D-78457 Konstanz, Germany

Supporting Information

ABSTRACT: A series of mononuclear σ -phenyl ruthenium complexes $Ru(CO)Cl(C_6H_4-R)(P^iPr_3)_2$ (R = OMe, CH₃, H, F, CF₃) were synthesized and analyzed with respect to their electrochemical and spectroscopic properties. To these ends, cyclic voltammetry, IR, and UV/Vis/NIR spectroelectrochemistry as well as EPR spectroscopy on their one-electron oxidized radical cations were employed. Experimental work is complimented by quantum chemical calculations. Our studies reveal that the σ -phenyl ligand strongly contributes to the HOMO and actively participates in the redox processes. Despite comparatively smaller ligand contributions, the redox potentials, the position of the CO stretch as well as the oxidation induced CO band shifts are more sensitive toward the σ -Hammett parameter of the 4substituent than for related styryl complexes with the same Ru(CO)-



 $Cl(P'Pr_3)_2$ metal coligand platform. The comparatively high spin density/positive charge at the 4-position of the phenyl ligand leads to oxidatively induced dehydrodimerization of the radical cation of the parent phenyl complex $Ru(CO)Cl(C_6H_5)(P^iPr_3)_2$ (1) to the biphenylene-bridged dinuclear complex $[\{Ru(CO)Cl(P^iPr_3)_2\}_2(\mu-C_6H_4-C_6H_4-4_4)']^{n+}$ (6ⁿ⁺). The latter was identified in spectroelectrochemical experiments and authenticated by independent preparation of neutral 6 and monitoring of its spectroelectrochemical behavior.

INTRODUCTION

Aryl ruthenium complexes of the type $Ru(CO)Cl(Ph)L_n$ (L = PPh_{3} , $P'Pr_{3}$, PCy_{3} , $P'Bu_{2}Me$; n = 2 or 3) are selective olefin isomerization catalysts¹ and serve as precursors for hydro-silylation and -borylation catalysts.^{2,3} A widely used synthesis of such σ -aryl ruthenium complexes is the reaction of $RuClH(CO)(PR_3)_n$ (*n* = 2 or 3, depending on the phosphane ligand) precursors with organomercury³⁻⁸ or organotin compounds.^{4,9} Substitution of a chlorido ligand from Ru- $(CO)Cl_2(P^tBu_2Me)_2$ with PhLi proved to be another viable route to the corresponding phenyl complex.^{3,10} For L = P^tPr_3 , alternative syntheses via coordinatively unsaturated, highly reactive 14 valence electron (VE) hydride complexes were developed. Werner et al. reported the formation of the ruthenium monohydride dihydrogen species RuClH(H₂)- $(P^{i}Pr_{3})_{2}$ by heating RuCl₂(COD) with $P^{i}Pr_{3}$ in butan-2-ol under a H₂ atmosphere. On treatment with Et₂O, this species converts to the dihydride complex $RuCl_2H_2(P'Pr_3)_2$.^{11,12} Starting from this precursor, Caulton and co-workers generated $\text{RuClH}(P^{i}Pr_{3})_{2}$ by HCl elimination with lithium 2,2,6,6-tetramethylpiperidide.^{13,14} van der Schaaf et al. later elaborated a simplified one-pot synthesis of this 14 VE ruthenium hydride precursor, which avoids the isolation of sensitive and highly reactive intermediates.¹⁵ The latter complex was found to react with benzaldehyde to provide the phenyl carbonyl complex Ru(CO)Cl(Ph)(PⁱPr₃)₂.¹⁶ More

recently, $Ru(CO)Cl(Ph)(P^iPr_3)_2$ was also identified as a decomposition product of Grubbs catalysts of generation I in the presence of benzylic alcohol.¹⁷ Taken together, the above procedures offer a convenient access to σ -aryl ruthenium complexes which avoids the use of toxic organomercury or -tin compounds.

Besides the parent phenyl complex, several representatives of complexes $Ru(CO)Cl(Ph^{R})(PPh_{3})_{2}$ with 2- or 4-substituted σ phenyl ligands PhR have appeared in the literature. These studies addressed the influence of the substituents on the propensity of the aryl ligand to undergo migratory insertion into a ruthenium carbonyl or ruthenium nitrile bond to provide the corresponding acyl or iminoacyl complexes or the impact of the 2-substituent on the structures of these complexes.^{5,7,18,19} Thus, 2-halogeno, 2-formyl, or 2-nitro substituents serve as additional 2 e⁻ donors and thereby increase the VE count at the otherwise electron deficient 16 VE Ru atom to $18.^{3,7,8,19-21}$ As a consequence, the structures of these complexes change from square pyramidal with the phenyl substituent at the apical site to distorted octahedral with the 2-substituted aryl ligand in a chelating binding mode.

A comprehensive account on the impact of these substituents on the physical properties of these complexes is,

Received: April 24, 2018

however, still lacking. This is in stark contrast to the situation in closely related styryl ruthenium complexes, where a profound influence of the 4-substituents at the phenyl ring on the half-wave potentials for the oxidation, $E_{1/2}^{0/+}$, was noted.²²⁻²⁶ This is due to the strongly redox noninnocent character of the styryl ligand in these environments. The relatively small \dot{CO} band shifts of 40–70 cm⁻¹ on oxidation,^{24,27} the observation of EPR spectra in fluid solution at r.t. for their radical cations, often with resolved hyperfine splittings (hfs) to the 99/101Ru and ³¹P nuclei, and only moderate deviations of the g values from the free-electron value g, provide compelling evidence for large contributions of the styryl ligands to the HOMO of these complexes and the SOMO of their associated radical cations. These were also confirmed by quantum chemical calculations.^{22,26,27} The close relationship between σ -styryl and σ -phenyl complexes, which are formally related by the insertion of an alkyne into the Ruphenyl bond,^{3,28} prompted us to extend our previous studies on styryl complexes to their less well-studied phenyl congeners. The results are reported herein.

RESULTS AND DISCUSSION

Synthesis and Characterization. Following the procedures of van der Schaaf and Caulton of Scheme $1,^{15,16}$ we





prepared five mononuclear σ -phenyl ruthenium complexes with different 4-substituents, ranging from the methoxy donor to the CF₃ acceptor, by reaction of the in situ generated 14 VE complex $RuClH(P'Pr_3)_2$ with the corresponding 4-substituted benzaldehyde to provide target complexes 1-5. The established pathway involves coordination of the benzaldehyde to the electron-deficient ruthenium ion as the initial step. Formation of the corresponding acyl dihydrogen complex $RuCl(C=OC_6H_4R-4)(H_2)(P^iPr_3)_2$ can either occur through oxidative addition of the aldehyde O=C-H bond or by a 1,2hydrogen shift to a hydroxycarbene intermediate with subsequent H atom transfer from the hydroxyl substituent to the hydride ligand. CO deinsertion and hydrogen loss then produce the final product.¹⁶ This sequence of events is accompanied by a color change from red brown to purplish brown. The pure carmine-colored σ -phenyl complexes were obtained in moderate yields of 41-55% after a simple purification process.

All complexes were characterized by multinuclear (${}^{1}H$, ${}^{31}P{}^{1}H$, ${}^{13}C{}^{1}H$ and, in the case of complexes 4 and 5,

¹⁹F{¹H}) NMR spectroscopy (see Figures S1–S17). Systematic effects of the 4-substituents on the chemical shifts are particularly evident for the *ipso*, *para*, and *meta* carbon atoms of the substituted phenyl ring. Decreasing electron-donating/ increasing electron-withdrawing properties of the 4-substituent shift the resonance signal of the *ipso* carbon atom to lower field in the order 2 < 4 < 3 < 1 < 5 ($\Delta \delta = 25$ ppm). An identical ordering is obtained for the resonance signals of the protons in *meta* ($\Delta \delta = 0.44$ ppm) and *ortho* positions ($\Delta \delta = 0.24$ ppm; positions are provided with respect to the ruthenium atom) of the phenyl ligand as well as the ³¹P{¹H} resonance ($\Delta \delta = 0.8$ ppm, see the Experimental Section).

As was previously observed for similar five- and sixcoordinated ruthenium aryl complexes including 1, the NMR spectra show clear signs of slow rotation of the aryl ligand around the Ru– C_{ipso} bond.^{6,16,29,30} Thus, their ¹³C NMR spectra feature two separate resonance signals for the ortho carbon atoms neighboring the $Ru-C_{ipso}$ bond. Moreover, the ¹H NMR spectra show a broad singlet resonance for the attached protons with a half-peak width of 60-90 Hz. In the case of complex 3, two separate ¹³C resonances were also observed for the meta phenyl resonances. The observations that replacement of the trans-disposed carbonyl ligand in cis,cis,cis-Ru(CO)₂Cl(Ph)(PMe₂Ph₂)₂ by a nitrile ligand and increasing acceptor substitution at the 4-position of the phenyl ligand in complexes mer-Ru(CO)Cl(C_6H_4R-4){P(OMe₃)}₃ increase the energy barrier for aryl rotation were taken as an indication that the latter is of electronic rather than steric origin.⁶ Indeed, the preferred orientation of the phenyl ligand parallel to the Cl-Ru-CO vector maximizes overlap between the Ru d_{π} orbital, which is not involved in back-donation to the π -accepting carbonyl ligand, and the π^* orbital of the phenyl ligand.

In order to probe substituent effects on the energy barrier for phenyl rotation in the present series of complexes, we performed temperature-dependent ¹H NMR measurements of complexes **2**, **4**, and **5**. We observed decoalescence of the protons *ortho* to the Ru– C_{ipso} atom into two doublets at $\delta \sim$ 8.1 and ~7.4 ppm with a (de)coalescence temperature of 280 K for compounds **2** and **4** and 290 K for **5** (see Figures S18– S20). ΔG^{\ddagger} values derived from line-shape analysis are 56.4 kJ/ mol for complex **4**, 55.7 kJ/mol for complex **2**, and 54.3 kJ/ mol for complex **5** (data for T = 300 K).

Electrochemistry. In their cyclic voltammograms (CVs), complexes 1–4 undergo one chemically and electrochemically reversible one-electron oxidation as shown in Figures 1 and S21–S24. Half-wave potentials range from 210 to 620 mV versus the $Cp_2Fe^{0/+}$ redox standard (Table 1). They increase in the order 2 < 3 < 1 \approx 4 < 5 and largely follow the inductive and mesomeric effects of the 4-substituents.

For complex 5, the oxidation process is chemically still reversible but seems to suffer from sluggish electron transfer kinetics as shown by the rather large peak potential splitting ΔE_p of 185 mV at $\nu = 100$ mV/s between the reverse and forward waves and even larger splittings at higher sweep rates. Considering the large contributions of the aryl ligands to the HOMO/SOMO of these complexes (vide infra), one can speculate that after oxidation the particularly electron-poor 4trifluoromethyl radical ligand constitutes an even stronger π acceptor than the CO ligand. This might trigger structural rearrangement to another isomer, where the aryl radical has displaced the CO ligand from the basal site opposite the π donating chlorido ligand to the apical site. For 2, which is the



Figure 1. Cyclic voltammogram of complex 1 ($\nu = 100 \text{ mV/s}$) in CH₂Cl₂ at T = 293 K with 0.1 M NBu₄PF₆ as the supporting electrolyte.

Table 1. Electrochemical Data for All Complexes^a

complex	$E_{1/2}$	$\Delta E_{ m p}$	$i_{ m pa}/i_{ m pc}$
1	410	59	0.96
2	210/960	59	0.99/0.3
3	320	62	0.97
4	420	66	0.99
5	620	185	0.91
6	120/415	59/61	0.99/0.96
^a All notentials i	n mV (+3 mV) in	CH.Cl./NBu.F	$PE_{c}(0.1 \text{ M}) \text{ at } T =$

All potentials in mV (± 3 mV) in CH₂Cl₂/NBu₄PF₆ (0.1 M) at T = 293 K relative to the Cp₂Fe^{0/+} couple ($E_{1/2} = 0$ mV).

most-electron-rich complex of this series, a second wave corresponding to the further oxidation of the radical cation to the dication was observed at $E_{1/2} = 960$ mV. This process is, however, associated with only poor chemical reversibility. Similar observations have been made for the related 4-methoxystyryl complex.²³

The impact of the 4-substituents at the aryl ligand on the electrochemical properties of these complexes is best probed by plotting their half-wave potentials against the Hammett electronic substituent parameter σ . Figure 2 demonstrates the close adherence to a linear relation and compares the data set of present complexes 1–5 to that of the corresponding or similar styryl complexes with the same Ru(CO)Cl(PⁱPr₃)₂



Figure 2. Dependence of the half-wave potentials of ruthenium σ -phenyl complexes on the σ -Hammett parameters of the 4-substituent at the phenyl ring with those of the corresponding or similar styryl analogs.^{23,24}

(={Ru}) metal coligand entity.^{23,24} Similar results have also been reported for styryl complexes of the *mer*-Ru(CO)Cl-(PMe₃)₃ fragment.²⁵

Remarkable differences between representatives of the two closely related families of complexes are the intrinsically higher half-wave potentials of the σ -aryl complexes and the ca. 55% steeper slope of the linear best-fit compared to their styryl congeners. Both these differences are obviously rooted in the smaller extension of the conjugated metal—organic π -system in the present σ -aryl complex series. As we will discuss in the following, the effect of the smaller π -system even overrides the opposing effect of a smaller σ -aryl ligand and, concomitantly, larger {Ru} contributions to the redox orbital.

IR and EPR Spectroscopy. In metal carbonyl (M–CO) complexes, the ordinary ligand \rightarrow metal σ -donor bond is augmented by back-donation of electron density from occupied d_{π} orbitals of the metal ion to the CO antibonding π^* orbitals of the carbonyl ligand(s). This synergistic nature of a M-CO bond makes the energy of the CO stretching vibration a sensitive indicator of the electronic properties of the metalcoligand entity. The latter has found extensive use to determine the electronic properties of vast series of phosphane or carbene ligands (e.g., through the Tolman electronic parameter TEP; $^{31-34}$ for a recent perspective on the shortcomings of the traditional TEP see ref 35). Comparing the $\nu(CO)$ values of complexes in two adjacent redox states also provides insight into the metal versus ligand character of the redox orbital (i.e., the molecular orbital where the electron is extracted from or added to). A metal-centered oxidation usually causes a shift $\Delta \tilde{\nu}(CO)$ of 120–150 cm⁻¹ as exemplarily shown by the *trans*- $[\operatorname{Ru}(\operatorname{CO})_3(\operatorname{PR}_3)_2]^{0/+}$ (R = Ph, benzyl, 4-tolyl, cyclohexyl) family of complexes.³⁶ Much smaller shifts are, however, to be expected in the case of ligand-centered redox chemistry. The complexes $\{Ru(CO)Cl(EPh_3)_2\}_2(\mu-1,4-1)$ dioxido-9,10-anthraquinone) (E = P, As; $\Delta \tilde{\nu}$ (CO) = 25 cm⁻¹) provide recent examples of such a situation in complexes with a similar Ru-coligand environment.37

The members of the present series of complexes reveal a noticeable dependence of $\tilde{\nu}(CO)$ on the electronic properties of the 4-substituent at the phenyl ligand (Table 2). Thus,

Table 2. Selected IR Data for All Complexes^a

			-	
complex	neutral	cation	$\Delta \tilde{\nu}$	$\tilde{\nu}(C=C)$
1	1905	1979	74	1564 (s)
2	1908	1973	65	1566 (w→vs)
3	1903	1974	71	1554 (w→vs)
4	1911	1985	74	1556 (w→vs)
5	1915	1993	78	1590 (s→w)
6	1905	1969, 1982 ^b	65, 77	

^{*a*}In CH₂Cl₂/0.1 M NBu₄PF₆ at r.t.; energies in cm⁻¹. ^{*b*}For 6^{2+} ; radical cation 6^+ has two Ru(CO) bands at 1921 and 1943 cm⁻¹.

 $\tilde{\nu}(CO)$ increases from 1903 cm⁻¹ in tolyl complex 3 to 1915 cm⁻¹ in the CF₃-substituted congener 5. We resorted to IR spectroelectrochemistry to generate and spectroscopically characterize their corresponding radical cations. Graphical representations of the outcomes of these experiments can be found as Figures 3 and S25–S27 (note that complex 1 constitutes a special case that will be discussed in a separate section of this manuscript). We observed (i) that the differences of $\tilde{\nu}(CO)$ between the individual complexes increases from 12 cm⁻¹ for the neutral complexes to 20



Figure 3. IR spectroscopic changes in the region of the ν (CO) and ν (C=C) vibrations on oxidation of complex 2 to 2⁺.

cm⁻¹ for their radical cations and (ii) that the oxidationinduced CO band shifts of 65 to 78 cm⁻¹ are distinctly smaller than those expected for a strictly metal-centered oxidation. This confirms strong contributions of the σ -aryl ligand to the redox orbital (Table 2). The present complexes thus resemble their styryl complex relatives, for which strongly redox noninnocent ligand behavior³⁸⁻⁴⁰ was previously established.^{22,24,27,41}

As was observed for their electrochemical properties, the slopes of the best-fit lines obtained from plotting $\tilde{\nu}(CO)$ versus the Hammett parameter σ (see Figure 4) are significantly



Figure 4. Comparison of $\tilde{\nu}(CO)$ IR frequencies in the neutral and mono-oxidized states of ruthenium aryl complexes with those of ruthenium alkenyl species.

steeper for the σ -phenyl complexes than those for their styryl relatives, irrespective of the oxidation state. Moreover, oxidation-induced CO bandshifts $\Delta \tilde{\nu}$ (CO) are consistently larger for the phenyl complexes (c.f. 65 cm⁻¹ for 2/2⁺ versus 57 cm⁻¹ for the 4-methoxystyryl complex; 74 cm⁻¹ for 1/1⁺ versus 65 cm⁻¹ for the corresponding styryl complex; 78 cm⁻¹ for 5/5⁺ versus 67 cm⁻¹ for the 4-CF₃-substituted styryl analog).^{22,24} This provides additional evidence for a larger

{Ru}/smaller σ -phenyl contribution to the HOMO of the neutral/SOMO of the oxidized complexes compared to their styryl congeners.

The IR spectra of the σ -phenyl complexes feature another prominent band near 1550 cm⁻¹, which is attributed to the C=C stretching/C-H bending vibration of the (substituted) phenyl ligand. This band also shows distinct changes on oneelectron oxidation, though only in terms of intensity and not in terms of position (Table 2). For complexes 1-4, this band is rather weak in the neutral state but strongly gains in intensity during oxidation (see Figures 3, S25, and S26). The opposite holds true for acceptor-substituted 5 (Figure S27). This parallels the behavior in the related series of styryl complexes, where a similar dependence of the intensity of this vibrational mode from the polarization of the conjugated metal–organic π -system was observed.²⁴

EPR spectroscopy on the radical cations was executed on the chemically oxidized complexes. The latter were generated using 1,1'-diacetylferrocenium-hexafluoroantimonate (1–4) or tris(4-bromophenyl)ammoniumyl-hexafluoroantimonate (5) as the oxidizing agent in order to obtain information on the spin density distributions. Like their styryl complex congeners, and in agreement with a strong ligand character of the SOMO rather than a genuine Ru(III) formulation, the oxidized forms of the present complexes exhibit isotropic EPR signals in fluid solution with resolved hfs A to the ³¹P and ^{99/101}Ru nuclei but without any resolved hfs to aryl protons. Figure 5 exemplarily



Figure 5. Comparison of experimental (top black curve) and simulated (bottom blue curve) EPR spectra of complex cations 2^+ (left) and 4^+ (right) in CH₂Cl₂ solution at r.t.

shows the spectra of radical cations 2^+ and 4^+ ; those of the other complex cations can be found as Figures S28 and S29. Relevant data from these studies as extracted by digital simulation of the EPR spectra are collected in Table 3. In keeping with larger metal/smaller ligand contributions to the SOMO, the g_{iso} , $A(^{31}P)$ and $A(^{99/101}Ru)$ values of the present phenyl complexes are larger than those of their styryl congeners (c.f. $g_{iso} = 2.0448$, $A(^{31}P) = 21.5$ G for the parent

Table	3. 3	EPR	Parameters	for	the	Chemically	Oxidized
Comp	lexe	es ^a)					

complex	g _{iso}	$A(^{31}P)$	$A(^{99/101}{ m Ru})$
1+	2.0661	42.3	16.8
2 ⁺	2.0446	32.2	16.8
3+	2.0583	38.0	16.8
4 ^{+b}	2.0637	42.8	14.4
5+	2.0743	55.3	21.6
6+	2.0341	13.8	9.1

 $^{a}\rm{CH}_{2}\rm{Cl}_{2}$ r.t., hyperfine splitting constants hfs in Gauss (G). $^{b}\rm{Additional}$ hfs to one $^{19}\rm{F}$ nucleus of 18.7 G.



Figure 6. Calculated compositions of selected MOs for the full models of complexes 2 (top) and 5 (bottom) and their associated radical cations.

styryl complex, and $g_{iso} = 2.038$, $A(^{31}P) = 18.4$ G, $A(^{99/101}Ru) =$ 9.6 G for the radical cation of the 4-S-acyl derivative).^{22,42} Our data also indicate a strong influence of the 4-substituent on the spin density distribution and a monotonous increase of the g_{iso} and $A(^{31}P)$ values with decreasing donor capabilities of the latter. At low temperature (123 K, X-band), the EPR signals of the complex cations 2^+-4^+ become anisotropic with observable splittings into two tensor components (see Figures S30–S32). Additional EPR spectra of 2^+ , 3^+ , and 4^+ recorded at Q-band frequencies and at T = 50 K are considerably broadened compared to the corresponding X-band spectra. This is attributed to a g-tensor anisotropy of the axial or rhombic type as suggested by spectral simulations (see Table S1 and Figure S33).

Quantum Chemical Calculations. Quantum chemical calculations based on density functional theory (DFT) were conducted on complexes 2, 3, and 5 in order to provide additional insight into the composition of their frontier MOs and the impact of the phenyl substituents as well as to explore the feasibility of an oxidation-induced isomerization of radical cation S^+ . Figure 6 displays percent fragment contributions for the crucial frontier MOs of neutral complexes 2 and 5 as the two extreme cases in terms of electron-donating/-withdrawing properties of the 4-substituent and their associated radical cations, while Figures S34–S36 provide more extensive compilations for complexes 2, 3, and 5. Graphical representations of the immediate frontier orbitals of complex 2 are shown in Figures 7 and S37–S39. One immediately notes that the HOMO constitutes a strongly mixed orbital with sizable



Figure 7. Contour plots of LUMO to HOMO-2 of full model complex 2.

contributions of the $\{Ru(P^iPr_3)_2\}$ fragment and the phenyl ligand. In agreement with our experimental results, the contributions of the phenyl ligand to the HOMO increase from 39% in 5 to 49% in 3 and 59% in 2 with a concomitant decrease of Ru/P^iPr_3 contributions from 61% to 51% and 41%. Respective values for their styryl congeners are 62%/74% ligand and 38%/26% combined Ru/P^iPr_3 contributions for the

Article

Organometallics

 CF_{3} -/methoxy-substituted complexes. These trends fully conform to our experimental results, including the higher sensitivity toward the identity of the 4-substituents in the present phenyl complexes.

Our calculations also indicate that the SOMO of the corresponding radical cations strongly resembles the HOMO of the neutral complexes (Figures S37–S39). This pertains to the spin densities as well as the charge distribution as derived from NBO analysis. Figure 8 provides a graphical account of



Figure 8. Calculated spin densities for the radical cations $2^{\bullet+}$, $3^{\bullet+}$, and $5^{\bullet+}$.

the former, while Tables S2–S4 list the numerical values of the spin and charge densities on the individual fragments. In keeping with the previous trends, complex 5⁺ has 79% of its charge on the metal entity and 21% on the aryl ligand, while the computed ratio is 57%/43% for donor-substituted complex 2⁺. Spin densities run closely parallel with a 78%/22% {Ru}/ phenyl ligand distribution for complex 5⁺ and a 53%/47% distribution for complex 2⁺. Taken together, our results clearly justify the notion that the σ -aryl ligands are redox noninnocent in this particular coordination environment.

Computed energies of the ν (CO) bands match the experimental data qualitatively well as indicated in Table S5. Oxidation-induced CO band shifts of complexes 2 and 3 $\Delta \tilde{\nu}$ (CO) are underestimated by 9 and 7 cm⁻¹, respectively. In contrast, a greater discrepancy of 14 cm⁻¹ was obtained for the $5/5^+$ pair of complexes. Consideration of the alternative isomer, where the CO ligand occupies the apical and the 4-CF₃-substituted aryl radical ligand is in the basal plane, opposite the Cl donor ligand, reduces the discrepancy to 6 cm⁻¹. We nevertheless note that the latter isomer was computed to be 25 kJ/mol higher in energy.

UV/Vis/NIR Spectroscopy. The electronic spectra of the neutral aryl ruthenium complexes feature a moderately intense band in the visible (Vis) and a somewhat stronger absorption in the near UV. Time-dependent DFT (TD-DFT) calculations attribute the former to the excitation of an electron from the metal-aryl delocalized HOMO into the {Ru}-based LUMO (for band assignments see Table S6). In agreement with its associated ligand-to-metal charge-transfer (LMCT) character, this band shifts to the red with increasing electron donating capacity of the 4-substituent (i.e., with increasing destabilization of the HOMO and a concomitantly smaller HOMO-LUMO gap; Table 4). The second band corresponds to the HOMO-2 \rightarrow LUMO excitation. The near invariance of its energy toward the 4-substituent at the phenyl ligand agrees with our computational data, which indicate that both MOs are strongly dominated by the {Ru} entity and exhibit only minor contributions of the phenyl ligand.

Oxidation of the aryl ruthenium complexes to the corresponding radical cations induces the growth of a strong absorption band in the visible and of a less intense absorption in the near-infrared (NIR). A representative set of spectra

Table 4. UV/Vis/NIR Data for All Complexes^a

		$\lambda_{\max} [nm] (\varepsilon_{\max} [M^{-1} cm^{-1}])$
	1	499 (2460), 386 (7490), 275 (4330)
	1+	1130 (-), 554 (-), 283 (-), 277 (-)
	2	521 (2750), 387 (8910), 306 (25950)
	2 ⁺	896 (4540), 630 (36400), 339 (55600), 313 (54700)
	3	508 (940), 385 (3300), 282 (11400)
	3 ⁺	1011 (1125), 568 (10200), 328 (18500)
	4	506 (1690), 388 (4780), 296 (15900)
	4+	1044 (1345), 562 (7900), 376 (11800), 299 (23900)
	5	482 (2365), 384 (7400), 284 (68400)
	5 ⁺	1148 (930), 512 (5970)
	6	482 (7520), 385 (21700), 324 (166000)
	6+	1494 (43200), 1240 (24000), 464 (41000)
	6 ²⁺	700 (86000), 390 (44000)
^{<i>i</i>} In	CH ₂ Cl ₂ /0.1	M NBu ₄ PF ₆ at r.t.

recorded during electrolysis of complex 3 in an optically transparent thin-layer electrochemical (OTTLE) cell⁴³ are displayed in Figure 9, while the results for complexes 2, 4, and



Figure 9. Spectroscopic changes of the UV/Vis/NIR spectra during electrochemical oxidation of complex 3 ($CH_2Cl_2/0.1$ M NBu_4PF_{67} r.t.).

5 are displayed as Figures S40-S42. Both transitions exhibit strong positional dependence on the electronic properties of the 4-substituent on the phenyl ligand but in an opposite manner. Thus, with increasing acceptor/decreasing donor capabilities of that substituent the Vis band experiences a blueshift whereas the NIR band is displaced to the red. Obviously both transitions have sizable CT contributions but in opposite directions. According to our TD-DFT calculations, the NIR band is associated with MLCT, reflecting the excitation of an electron from the ruthenium/coligand based β -HOSO, which closely resembles the HOMO-1 of the neutral complex, to the mixed metal-aryl delocalized β -LUSO (the former HOMO). In contrast, the prominent Vis band seems to change its character from a $\pi \rightarrow \pi^*$ type transition within the conjugated metal-organic π -system in the donor-substituted complexes to a more LMCT-type transition in acceptorsubstituted 5⁺ as inferred from Table S5 and Figures S34-S36 and illustrated by the charge density difference plots of Figures S43-S45. Quite interestingly, the intensity of this band decreases with a higher LMCT and less pronounced $\pi \rightarrow \pi^*$ character.

Fate of Radical Cation 1⁺ and Synthesis and Characterization of Biphenyl-Bridged Diruthenium **Complex 6^{n+}.** The radical cation of parent phenyl complex 1 constitutes a special case and warrants a separate discussion. At initial stages during oxidation of 1 inside the OTTLE cell the spectra clearly indicate that the associated radical cation 1⁺ is formed. Characteristic fingerprints are the Ru(CO) band at 1979 cm⁻¹ and Vis/NIR bands at 1130 and 554 nm. After ca. 40% conversion of the neutral, however, a secondary process commences as indicated by the growth of a new, structured Ru(CO) band with a main peak at 1921 cm⁻¹ and a concomitant, gradual redshift of the original Ru(CO) band to 1974 cm⁻¹. This is accompanied by the appearance of new electronic bands at ca. 1500, 700, and 460 nm. The former can be observed in the IR/NIR as well as UV/Vis/NIR spectra. During the final stages of the electrolysis the Ru(CO) band at 1921 cm⁻¹ as well as the 1500 and 460 nm bands bleach out, while the asymmetric Ru(CO) band at 1974 cm⁻¹ and the broad, structured Vis/NIR band at 700 nm continue to grow. Representative sets of spectra documenting the above sequence of events are shown as Figures S46-S48.

Even more revealing are the spectroscopic changes on reduction of the electrogenerated, oxidized species. IR and UV/Vis/NIR spectroelectrochemistry both indicate that the reduction occurs as two separate, consecutive processes. During the first step, the Ru(CO) band at 1974 cm⁻¹ is gradually replaced by a pair of bands with a weaker absorption at 1943 cm^{-1} and a very intense one at 1921 cm^{-1} . This is paralleled by the bleach of the strong Vis band at 700 nm and the growth of the characteristic NIR features at 1490 and 1242 nm as well as a Vis band at 464 nm. The main features in the IR and Vis/NIR spectra are obviously identical to those observed at intermediate stages during the oxidation of 1. During the second step these bands are completely bleached. Representative spectra are displayed as Figures S49 and S50. The spectra resulting from exhaustive reduction closely resemble those of neutral 1, but with slight shifts of the Vis/ UV bands. Reoxidation reestablishes the new features, thus establishing that a new, stable product, which possesses three interconvertible redox states, has formed.

The two-step redox sequences, the low-energy electronic transitions of the singly and doubly oxidized species and the pattern of two separate Ru(CO) bands for the singly oxidized form are all highly reminiscent of divinyldiarylene-bridged diruthenium complexes such as the divinylbiphenyl, 4,4'divinyl-2,2'-bipyridine, or distyrylethene derivatives. 44,45 This let us suspect that radical cation 1^+ , formed during the initial stages of the electrolysis, couples to ultimately provide biphenyl-bridged diruthenium complex 6 in its respective oxidation state, as governed by the applied electrode potential. Further support for this hypothesis was obtained from EPR spectroscopic experiments after oxidation of 1 with substoichiometric amounts of the 1,1'-diacetylferrocenium oxidant. As shown in Figure 10, these spectra show a fiveline resonance in addition to the three-line pattern of 1⁺. The former signal is characterized by a lower g_{iso} value of 2.0341 and $A(^{31}P)$ and $A(^{99/101}Ru)$ hfs values considerably smaller than those observed for 1^+ (Table 3). Both these observations are readily reconciled with a higher organic parentage of the radical cation and diminished spin density at the {Ru} sites.

In order to prove the above hypothesis we deliberately prepared diruthenium complex 6 from the reaction of in situ generated $RuClH(P^{i}Pr_{3})_{2}$ with 4,4'-diformylbiphenyl, albeit in



Figure 10. Experimental (top black curve) and simulated (bottom blue curve) EPR spectra of complex cations 1^+ and 6^+ obtained after chemical oxidation of 1 with ca. 0.5 equiv of 1,1'-diacetylferrocenium-hexafluoroantimonate in CH₂Cl₂ at r.t.

a rather moderate yield of 21%. Spectroscopic data and the results of the combustion analysis are fully consistent with the formulation of **6** as a biphenyl-bridged diruthenium complex with mutually *trans*-disposed phosphane ligands. Particularly characteristic are the two resonance signals of the aryl protons, which appear as a doublet with a ${}^{3}J_{\rm HH}$ coupling of 8.6 Hz at δ 7.23 ppm for the *meta* and a broad unresolved resonance at δ 7.87 ppm for the *ortho* protons, the latter again as a result of slow rotation of the phenyl ligand, integrating as 4H each, as well as the characteristic triplet resonance at 154.6 ppm (${}^{2}J_{\rm CP}$ = 9.8 Hz) for the Ru-bonded *ipso* carbon atom of the phenyl ligand (see the Experimental Section).

In addition, we were able to grow single crystals of the CH_2Cl_2 disolvate of complex **6** by slow evaporation of a saturated solution of this complex in CH_2Cl_2 . Figure 11 depicts the molecular structure as derived from a single crystal X-ray diffraction experiment. Details to the data collection, structure refinement and unit cell dimensions as well as listings of the derived bond parameters can be found as Tables S7–S9.



Figure 11. X-ray crystallographic structure of the biphenyl-bridged diruthenium complex 6. Hydrogen atoms are omitted for reasons of clarity; ellipsoids are shown at a 50% probability level. Selected bond lengths in Å: Ru–P1 2.413(2), Ru–P2 2.411(2), Ru–C20 2.022(7), Ru–Cl 2.462(2), Ru–C1 1.811(8), C20–C21 1.388(9), C21–C22 1.383(10), C22–C23 1.384(10), C23–C24 1.370(10), C24–C25 1.401(10), C20–C25 1.400(10). Selected bond angles in deg: P1–Ru–P2 169.03(6), Cl–Ru–C1 165.9(2), C20–Ru–C1 89.3(3), C20–Ru–Cl 104.9(2), C20–Ru–P1 94.3(2), C20–Ru–P2 96.6(2).

As in closely related Ru $styryl^{22,23,42,44,46-52}$ and the previously characterized, five-coordinated Ru phenyl complexes,^{3,8,17} the Ru atoms adopt a slightly distorted square pyramidal coordination geometry with the aryl ligand at the apical site and the bulky phosphane and the CO and Cl ligands in mutual trans-positions as the basal sites. This ligand arrangement places the ligand with the strongest σ transinfluence opposite the vacant coordination site while preserving the favorable *trans*-arrangement of the Cl π -donor and the CO π -acceptor ligands. As usual, the Ru atom is displaced out of the basal plane toward the apical ligand (d_{Ru} = 0.288 Å). The Ru…Ru distance of 11.27 Å is even slightly shorter than that of 11.61 Å in 1,4-divinylphenylene-bridged $\{Ru\}-CH=CH-C_6H_2OMe_2-CH=CH-\{Ru\}$.⁴⁸ Also of note is the roughly coplanar arrangement of the Cl-Ru-CO vector and the plane of the biphenyl ligand (note that the average value of the angle between the best planes through the Ru atom, the Cl and the CO ligands, C20, and the biphenyl plane of 5.9° is compromised by the rather large amplitude of ring libration as indicated by the shapes of the thermal ellipsoids).

In the crystal, individual molecules of **6** arrange to onedimensional strands via Ru–Cl···H–CCl₂–H···Cl–Ru hydrogen-bonds to two crystallographically identical CH₂Cl₂ molecules, one positioned above and one below the bridged complex molecules. At 2.622 and 2.634 Å, these H···Cl contacts are by 0.328 and 0.309 Å shorter than the sum of the van der Waals radii. Two additional short contacts of 2.837 Å are formed per "dimer" by hydrogen-bonding of a Cl atom of the CH₂Cl₂ molecules and a methyl proton of the PⁱPr₃ ligand. Figure S51 provides two different views of the resulting packing and association motif. The other solvate molecules occupy voids above or below the biphenyl ligands and are not involved in hydrogen bonding.

Consistent with our observations after electrochemically induced conversion of 1⁺, pristine **6** is oxidized in two consecutive, reversible one-electron steps at half-wave potentials of 120 and 415 mV (for a representative voltammogram see Figure S52). We note that the half-wave potential splitting of 295 mV is even slightly larger than that in the divinylphenylene-bridged diruthenium complex {Ru}-CH=CH-C₆H₄-CH=CH-{Ru}-1,4 ($\Delta E_{1/2} = 250 \text{ mV}$)⁵³ or that in the 4,4'-divnylbiphenylene-bridged congener {Ru}-CH=CH-C₆H₄-C₆H₄-CH=CH-{Ru} ($\Delta E_{1/2} = 99 \text{ mV}$).⁴⁴

Moreover, the results of spectroelectrochemical measurements on 6 fully agree with the spectra obtained after oxidatively induced conversion of radical cation 1⁺ as shown in Figures S53-S55. Finally, the EPR spectrum of radical cation 6^+ is superimposable to the five-line EPR signal observed in addition to that of 1⁺ after treatment of 1 with a substoichiometric amount of oxidant (compare Figures 10 and \$56). The nearly identical half-wave potential of the second oxidation of complex 6 to that of the first oxidation of 1 $(E_{1/2} = 410 \text{ mV})$ also explains the complex behavior seen in the IR and UV/Vis/NIR spectroelectrochemical experiments. Thus, 1, 1^+ , 6^+ , and 6^{2+} coexist in solution until 1 is fully consumed. The coupling of unsubstituted 1^+ to ultimately provide 6^{n+} is in stark contrast to the styryl congener {Ru}- $CH = CH - C_6H_5$, where no such reactivity on oxidation was noted.²² This difference is probably rooted in a higher spin density/higher positive charge at the most reactive paraposition of the phenyl complex as compared to its more

delocalized styryl congener. Oxidatively induced dehydrodimerizations of complexes with carbon-rich ligands have been described on several occasions.^{54,55} Examples are the couplings of vinylidene complexes $Cp(CO)_2Mn(=C=CHPh)$ to the ethenyl-bridged bis(carbyne) complex Cp(CO)₂Mn=C-C- $(Ph) = C(Ph) - C \equiv Mn(CO)_2 Cp^{56}$ or of the related Cp*Mn- $(CO)_2$ (=C=CHPh), $Cp(CO)(PPh_3)Mn$ (=C=CHPh), and Cp(dppe)Fe(=C=CHMe) complexes to bis(vinylidene) complexes $\{Mn\}=C=C(Ph)-C(Ph)=C=\{Mn\}$ or $[{Fe}] = C = CMe - CMe = C = {Fe}]^{2+}$, respectively (Cp = η^{5-} C_5H_5 ; $Cp^* = \eta^5 - C_5Me_5$; dppe = 1,2-bis(diphenylphosphanyl)-ethane).^{37,58} Related dehydrodimerizations of complexes $\{M\}-C\equiv CH$ to butadiynediyl-bridged dimetal complexes $\{M\}-C\equiv C-C\equiv C-\{M\}$ on the dual action of an oxidant and a base have also been reported $({M} = Cp(dppe)Fe^{59}$ or $trans-Mn(dmpe)_2(C \equiv CSiMe_3), dmpe = 1,2-bis-$ (dimethylphosphanyl)ethane).⁶⁰ Even closer analogies, however, exist to triarylamines with at least one unsubstituted phenyl ring, which couple oxidatively to tetraarylbenzidines with concomitant proton or H atom loss.⁶¹⁻⁶⁴ This adds another facet to the previously noted resemblance of {Ru} and NAr₂ entities.^{22,65,6}

CONCLUSION

We have prepared and studied mononuclear σ -aryl ruthenium complexes with different *para*-substituents in their neutral and mono-oxidized states and compared them to their styryl ruthenium congeners. Our studies point out that simple aryl ligands are also redox noninnocent when coordinated to the Ru(CO)Cl(PⁱPr₃)₂ entity, albeit to a lesser extent than their styryl analogues. Aryl contribution to the HOMO is even more sensitive to the *para*-substituent than in the styryl case and increases with better electron-donating capabilities of the latter. The larger influence of the *para*-substituent is a direct consequence of the less extended π -system.

All complexes show a reversible one-electron oxidation at a 140–220 mV higher potential with respect to their styryl congeners. The larger oxidation-induced blueshifts of the Ru(CO) band as well as the higher g-values and ³¹P hyperfine coupling constants $A(^{31}P)$ are clear tokens of the larger metal/ lower ligand contribution to the HOMO of the neutral complexes and the SOMO of their one-electron oxidized forms when compared to their styryl congeners. Nevertheless, electrochemical half-wave potentials and $\tilde{\nu}(CO)$ values of the present complexes are more sensitive toward the 4-substituents than for the styryl series, again as a consequence of the smaller extension of the ligand π -system.

The comparatively higher charge/spin density at the 4position of the phenyl ligand also results in a slow dehydrodimerization of initially formed, unsubstituted 1^+ to biphenylene-bridged 6^{n+} during spectroelectrochemical experiments. The identity of the coupling product was confirmed by its independent preparation from 4,4'-diformylbiphenyl and the complete agreement of the spectra of its oxidized forms 6^+ and 6^{2+} with the spectroscopic features observed in our initial in situ experiments. The mechanistic intricacies of the oxidatively induced dehydrodimerization of parent phenyl complex 1 and the exploration of its scope and limitations are the subject of ongoing work in our laboratories. We also defer a detailed analysis of the electronic coupling in mixed-valent 6⁺ to a later occasion and just mention that 6^+ is fully delocalized on the EPR time scale as is evident from identical hfs to the ³¹P nuclei of four P'Pr3 ligands and two 99/101Ru nuclei.

EXPERIMENTAL SECTION

Experimental Methods and Materials. All syntheses were performed under argon atmosphere with dry, distilled, and argonsaturated solvents. Reagents were purchased from commercial sources and used without further purification. ¹H (400 MHz) and ³¹P{¹H} (162 MHz) NMR spectra were recorded with a Bruker Avance III 400 spectrometer; ¹H (600 MHz), ¹³C (151 MHz), and ³¹P (243 MHz) NMR spectra were recorded with a Bruker Avance III 600 spectrometer. Combustion analyses (C, H) were performed at inhouse facilities with an Elementar Analyzer Vario MICRO Cube from Heraeus. RuClH(PⁱPr₃)₂ was prepared according to a modified literature procedure.¹⁵

Cyclic voltammetry was performed in a home-built cylindrical vacuum-tight one-compartment cell. A spiral-shaped Pt wire and an Ag wire as counter and reference electrodes are sealed into glass capillaries, which are introduced through Quickfit screws at opposite sides of the cell. A Pt electrode (diameter 1.6 mm, from BASi) was polished with 1.0 and 0.25 μ m diamond paste (Buehler-Wirtz) and introduced as the working electrode through the top central port and a Teflon screw cap with a suitable fitting. CH_2Cl_2/Bu_4NPF_6 (0.1 M) was used as the supporting electrolyte. Referencing was done with the addition of equimolar decamethylferrocene (Cp*2Fe) as internal standard to the analyte solution after all data of interest had been acquired. Final referencing was done against the ferrocene/ ferrocenium (Cp₂Fe^{0/+}) redox couple with $E_{1/2}$ (Cp*₂Fe^{0/+}) = -550 mV vs Cp₂Fe^{0/+}. Electrochemical data were acquired with a computer-controlled BASi potentiostat. IR as well as UV/Vis/NIR spectroelectrochemical experiments were performed in an optically transparent thin-layer electrochemical (OTTLE) cell, which was custom-built and comprised a Pt mesh working and counter electrodes, as well as a thin silver wire as pseudoreference electrode sandwiched between the CaF2 windows of a conventional liquid IR cell. The working electrode was positioned in the center of the spectrometer beam. The IR spectra were recorded with a Bruker TENSOR-II instrument. The UV/Vis/NIR spectra were obtained with a TIDAS fiber optic diode array spectrometer (combined MCS UV/Vis and PGS NIR instrumentation) from J&M. UV/Vis/NIR spectroscopy was performed with the same setup in HELLMA quartz cuvettes with 0.2 cm optical path length.

Electron paramagnetic resonance (EPR) studies were performed with a tabletop X-band spectrometer MiniScope MS 400 from Magnettech. Q-band EPR spectra were recorded using an ELEXSYS E580 spectrometer equipped with an EN5107D2 Q-band EPR probe head (both Bruker Biospin). A CF935 helium gas flow system (Oxford Instruments) was used for temperature control. Experiments were performed at T = 50 K in quartz glass tubes with 1 mm inner diameter. Measurement parameters were adjusted such that the spectral line shape was not distorted by overmodulation or saturation effects. Data were baseline-corrected by subtraction of a first-order polynomial. A background signal originating from the solvent was used to align the spectra of different samples on the magnetic field axis. For further data analysis, anisotropic EPR spectra recorded in Qband were analyzed by spectral simulations using the function "pepper" from the EasySpin toolbox.⁶⁷ EPR parameters of the isotropic X-band spectra were used to simulate the anisotropic Qband spectra. Only the g-tensor was changed to be anisotropic (axial or rhombic) during the simulations and the line width was adjusted.

X-ray diffraction analysis of a single crystal of **6** was performed at 100 K on a STOE IPDS-II diffractometer equipped with a graphitemonochromated radiation source ($\lambda = 0.71073$ Å) and an image plate detection system. A crystal mounted on a fine glass fiber with silicon grease was employed. The selection, integration, and averaging procedure of the measured reflection intensities, the determination of the unit cell dimensions and a least-squares fit of the 2θ values as well as data reduction, LP-correction, and space group determination were performed using the X-Area software package delivered with the diffractometer. A semiempirical absorption correction was performed.⁶⁸ All structures were solved by the heavy-atom methods. Structure solution was completed with difference Fourier syntheses and full-matrix last-squares refinements using SHELX-2017⁶⁹ and OLEX2,⁷⁰ minimizing $\omega(F_o^2 - F_c^2)^2$. The weighted *R* factor (*wR*²) and the goodness of the fit GOOF are based on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters, while hydrogen atoms were introduced in a riding model. The CIF file has been deposited at the Cambridge Structure Data Base as CCDC 1836397 and can be obtained free of charge via www.ccdc.cam.ac.uk/ conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (+44)1223–336–033, or at deposit@ccdc.cam.ac.uk.

Computational Section. The ground state electronic structures of the full models of complexes 2, 3, and 5 were calculated by density functional theory (DFT) methods using the Gaussian 09 program packages.⁷¹ Geometry optimizations were performed without any symmetry constraints. Open shell systems were calculated by the unrestricted Kohn-Sham approach (UKS). Geometry optimization followed by vibrational analysis was performed in solvent media. Solvent effects were described by the polarizable continuum model (PCM) with standard parameters for 1,2-dichloroethane.⁷² The quasirelativistic Wood-Boring small-core pseudopotentials (MWB)^{73,74} and the corresponding optimized set of basis functions for Ru^{75} and 6-31G(d) polarized double- ξ basis sets⁷⁶ for the remaining atoms were employed together with the Perdew, Burke, and Ernzerhof exchange and correlation functional (PBE0).^{77,78} The GaussSum program package was used to analyze the results,⁷⁹ while the visualization of the results was performed with the Avogadro program package.^{80,81} Graphical representations of molecular orbitals were generated with the help of GNU Parallel⁸² and plotted using the vmd program package⁸³ in combination with POV-Ray.⁸⁴ Electronic transitions were calculated by time-dependent DFT (TD-DFT) method.

General Synthetic Procedure for Complexes 1–5. Under an atmosphere of argon RuCl₂(COD) (200 mg, 0.714 mmol, 1 equiv) was suspended in 'PrOH (15 mL), P'Pr₃ (0.28 mL, 1.46 mmol, 2.05 equiv), and Et₃N (0.20 mL, 1.43 mmol, 2 equiv) were added dropwise. The dark brown suspension was heated under reflux conditions for 4 h. The resulting ochre solution was cooled to r.t., and a solution of the corresponding aldehyde (0.571 mmol, 0.8 equiv) in benzene (10 mL) was slowly added. The reaction mixture was stirred at r.t. for 4 days. The solvent was evaporated and the residue was washed with cold 'PrOH (3 × 15 mL, -20 °C) and *n*-hexane (20 mL). The obtained solid was extracted into CH₂Cl₂ (20 mL). The solvent was removed under reduced pressure to obtain the red to carmine-colored complexes 1–5.

RuCl(CO)(C₆H₅)(PⁱPr₃)₂ (1). Yield: 55% ¹H NMR (400 MHz, C₆D₆): δ 1.10 (dvt, ³J_{HH} = 6.8 Hz, ³J_{HP} = 12.9 Hz, 18H, P(CH(CH₃)₂)₃), 1.14 (dvt, ³J_{HH} = 6.8 Hz, ³J_{HP} = 12.9 Hz, 18H, P(CH(CH₃)₂)₃), 2.60 (m, 6H, P(CH(CH₃)₂)₃), 6.74 (t, ³J_{HH} = 6.9 Hz, 1H, p-C₆H₅), 6.83 (vt, ³J_{HH} = 7.0 Hz, 2H, m-C₆H₅), 7.96 (s br, 2H, o-C₆H₅). ¹³C{¹H} NMR (151 MHz, toluene-d₆, 230 K): δ 19.9 (s, P(CH(CH₃)₂)₃), 20.0 (s, P(CH(CH₃)₂)₃), 24.6 (vt, ¹J_{CP}+³J_{CP} = 9.6 Hz, P(CH(CH₃)₂)₃), 121.7 (s, p-C₆H₅), 126.4 (s, m-C₆H₅), 138.4 (s, o-C₆H₅), 140.9 (s, o-C₆H₅) 156.2 (t, ²J_{CP} = 9.7 Hz, C_{ipso}), 206.4 (t, ²J_{CP} = 13.6 Hz, CO). ³¹P{¹H} NMR (162 MHz, C₆D₆): δ (ppm) = 35.28 (s). Anal. Calcd for C₂₅H₄₇ClOP₂Ru: C, 53.42; H, 8.3. Found: C, 53.71; H, 8.53.

RuCl(*CO*)(*C*₆*H*₄-4-*OMe*)(*P*^{*P*}*P*₃)₂ (2). Yield: 43% ¹H NMR (400 MHz, C₆D₆): δ 1.11 (dvt, ³*J*_{HH} = 5.9 Hz, ³*J*_{HP} = 13.1 Hz, 18H, P(CH(CH₃)₂)₃), 1.15 (dvt, ³*J*_{HH} = 5.9 Hz, ³*J*_{HP} = 13.1 Hz, 18H, P(CH(CH₃)₂)₃), 2.61 (m, 6H, P(CH(CH₃)₂)₃), 3.33 (s, 3H, OCH₃), 6.60 (vdt, ³*J*_{HH} = 9.1 Hz, ⁵*J*_{HH} = 1.6 Hz, 2H, *m*-C₆H₅), 7.77 (s br, 2H, *o*-C₆H₅). ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, 260 K): δ 19.6 (s, P(CH(CH₃)₂)₃), 54.9 (s, OCH₃), 111.8 (s, *m*-C₆H₅), 135.1 (s, *o*-C₆H₅), 139.0 (s, *o*-C₆H₅), 140.5 (t, ²*J*_{CP} = 10.1 Hz, C_{*ipso*}), 155.1 (s, *p*-C₆H₅), 206.2 (t, ²*J*_{CP} = 13.6 Hz, CO). ³¹P{¹H</sup> NMR (162 MHz, C₆D₆): δ 34.81 (s). Anal. Calcd for C₂₆H₄₉ClO₂P₂Ru: C: 52.74; H: 8.34. Found: C: 52.84, H: 8.38.

RuCl(CO)(C₆H₄-4-CH₃)(PⁱPr₃)₂ (3). Yield: 45% ¹H NMR (400 MHz, C₆D₆): δ 1.12 (dvt, ³J_{HH} = 6.8 Hz, ³J_{HP} = 13.6 Hz, 18H,

P(CH(CH₃)₂)₃), 1.16 (dvt, ³J_{HH} = 6.8 Hz, ³J_{HP} = 13.6 Hz, 18H, P(CH(CH₃)₂)₃), 2.13 (s, 3H, CH₃), 2.62 (m, 6H, P(CH(CH₃)₂)₃), 6.72 (d, ³J_{HH} = 8.0 Hz, 2H, *m*-C₆H₅), 7.84 (s br, 2H, *o*-C₆H₅). ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, 230 K): δ 19.3 (s, P(CH-(CH₃)₂)₃), 19.5 (s, P(CH(CH₃)₂)₃), 20.2 (s, CH₃) 23.9 (vt, ¹J_{CP}+³J_{CP} = 9.5 Hz, P(CH(CH₃)₂)₃), 126.2, 127.4, (each s, *m*-C₆H₅), 129.4 (s, *p*-C₆H₅), 135.9 (s, *o*-C₆H₅), 140.8 (s, *o*-C₆H₅), 149.8 (t, ²J_{CP} = 9.7 Hz, C_{*i*pso}), 205.4 (t, ²J_{CP} = 13.7 Hz, CO). ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 35.22 (s).). Anal. Calcd for C₂₆H₄₉ClOP₂Ru: C: 54.20; H: 8.57. Found: C: 53.85, H: 8.65.

 $\begin{array}{l} RuCl(CO)(C_6H_4-4-F)(P^iPr_3)_2 \ (4). \ {\rm Yield:} \ 41\% \ ^1{\rm H} \ {\rm NMR} \ (400 \ {\rm MHz}, \\ C_6D_6): \ \delta \ 1.11 \ (dvt, \ ^3J_{\rm HH} = \ 6.1 \ {\rm Hz}, \ ^3J_{\rm HP} = \ 13.2 \ {\rm Hz}, \ 18{\rm H}, \\ {\rm P}({\rm CH}({\rm CH}_3)_2)_3), \ 1.15 \ (dvt, \ ^3J_{\rm HH} = \ 6.1 \ {\rm Hz}, \ ^3J_{\rm HP} = \ 13.2 \ {\rm Hz}, \ 18{\rm H}, \\ {\rm P}({\rm CH}({\rm CH}_3)_2)_3), \ 2.55 \ ({\rm m}, \ 6{\rm H}, \ {\rm P}({\rm CH}({\rm CH}_3)_2)_3), \ 6.63 \ (vdt, \ ^3J_{\rm HH} = \ 9.2 \ {\rm Hz}, \ ^4J_{\rm HH} = \ 1.7 \ {\rm Hz}, \ 2{\rm H}, \ m-{\rm C}_6{\rm H}_5), \ 7.74 \ ({\rm s} \ {\rm br}, \ 2{\rm H}, \ o-{\rm C}_6{\rm H}_5), \ ^{13}{\rm C}\{^1{\rm H}\} \\ {\rm NMR} \ (151 \ {\rm MHz}, \ {\rm CD}_2{\rm Cl}_2, \ 230 \ {\rm K}): \ \delta \ 19.2 \ ({\rm s}, \ {\rm P}({\rm CH}({\rm CH}_3)_2)_3), \ 10.5 \ ({\rm s}, \ {\rm P}({\rm CH}({\rm CH}_3)_2)_3), \ 19.5 \ ({\rm s}, \ {\rm P}({\rm CH}({\rm CH}_3)_2)_3), \ 13.8 \ ({\rm vt}, \ ^{1}J_{\rm CP} = \ 9.5 \ {\rm Hz}, \ {\rm P}({\rm CH}({\rm CH}_3)_2)_3), \ 112.9 \ ({\rm d}, \ ^{3}J_{\rm CF} = \ 19.2 \ {\rm Hz}, \ m-{\rm C}_6{\rm H}_5), \ 136.7 \ ({\rm s}, \ o-{\rm C}_6{\rm H}_5), \ 140.7 \ ({\rm s}, \ o-{\rm H}_6{\rm H}_5), \ 140.7 \ ({\rm s}$

*RuCl(CO)(C₆H₄-4-CF₃)(<i>P*ⁱPr₃)₂ (5). Yield: 50% ¹H NMR (400 MHz, C₆D₆): δ 1.01 (dvt, ³J_{HH} = 6.3 Hz, ³J_{HP} = 13.3 Hz, 18H, P(CH(CH₃)₂)₃), 1.06 (dvt, ³J_{HH} = 6.3 Hz, ³J_{HP} = 13.3 Hz, 18H, P(CH(CH₃)₂)₃), 2.52 (m, 6H, P(CH(CH₃)₂)₃), 7.04 (d, J_{HH} = 8.4 Hz, 2H, *m*-C₆H₅), 7.98 (s br, 2H, *o*-C₆H₅). ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, 230 K): δ 19.2 (s, P(CH(CH₃)₂)₃), 19.5 (s, P(CH(CH₃)₂)₃), 23.9 (vt, ¹J_{CP}+³J_{CP} = 9.8 Hz, P(CH(CH₃)₂)₃), 120.4 (s, *m*-C₆H₅), 122.1 (s, *p*-C₆H₅), 126.1 (m, CF₃), 137.0 (s, *o*-C₆H₅), 140.9 (s, *o*-C₆H₅), 165.3 (t, ²J_{CP} = 9.8 Hz, C_{ipso}), 204.7 (t, ²J_{CP} = 13.2 Hz, CO). ³¹P{¹H</sup> NMR (162 MHz, C₆D₆): δ 35.62 (s). ¹⁹F NMR (376 MHz, C₆D₆): δ -61.19 (s). Anal. Calcd for C₂₆H₄₆ClF₃OP₂Ru: C: 49.56; H: 7.36. Found: C: 49.54, H: 6.98.

Synthetic Procedure for Complex 6. Under an argon atmosphere, RuCl₂(COD) (200 mg, 0.714 mmol, 1 equiv) was suspended in PrOH (15 mL). PPr3 (0.28 mL, 1.46 mmol, 2.05 equiv) and Et₃N (0.20 mL, 1.43 mmol, 2 equiv) were added dropwise. The dark brown suspension was heated under reflux conditions for 4 h. The resulting ochre solution was cooled to r.t. and a solution of 4,4'-diformylbiphenyl (0.214 mmol, 0.3 equiv) in benzene (5 mL) was slowly added. The reaction mixture was stirred at r.t. for 4 days. The solvent was evaporated and the residue was washed with cold ⁱPrOH (3 × 15 mL, -20 °C). The residual solid was treated with *n*hexane (20 mL) in a supersonic bath for 1.5 h to remove small amounts of the monoruthenium complex byproduct. The obtained solid was extracted into CH_2Cl_2 (20 mL). The solvent was removed under reduced pressure to obtain the purple complex 6. Single crystals of 6 were obtained as purple plates by slow evaporation of CH₂Cl₂ from the supersaturated mother liquor at room temperature. Yield: 21% ¹H NMR (400 MHz, C₆D₆): δ 1.05 (m, 72H, P(CH(CH₃)₂)₃), 2.53 (m, 12H, P(CH(CH₃)₂)₃), 7.23 (d, ${}^{3}J_{HH} = 8.6$ Hz, 4H, $m - C_{6}H_{5}$), 7.87 (s br, 4H, o-C₆H₅). ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, 230 K): δ 19.90 (s, P(CH(CH₃)₂)₃), 19.92 (s, P(CH(CH₃)₂)₃), 24.4 (vt, ${}^{1}J_{CP} + {}^{3}J_{CP} = 9.6 \text{ Hz}, P(CH(CH_3)_2)_3), 123.6 (s, m-C_6H_5), 134.2 (s, p-C_6H_5), 134.2 (s,$ C_6H_5), 154.6 (t, ${}^2J_{CP}$ = 9.8 Hz, C_{ipso}), 206.3 (t, ${}^2J_{CP}$ = 13.6 Hz, CO). ³¹P{¹H} NMR (162 MHz, $C_6 D_6$): δ 35.30 (s). Anal. Calcd for C₅₀H₉₂Cl₂O₂P₄Ru₂: C: 53.47; H: 8.29. Found: C: 53.51, H: 8.26.

Chemical Oxidation of Complexes 1–4. To generate radical cations 1^+-4^+ , a solution of the corresponding complex (2.1 μ mol, 1 equiv) in 2 mL of CH₂Cl₂ was added to a suspension of 1,1'-diacetylferrocenium-hexafluoroantimonate (4.2 μ mol, 2 equiv) in 2 mL of CH₂Cl₂.

Chemical Oxidation of 5. To generate cation 5^+ , a solution of 5 (2 mg, 3.1 μ mol, 1 equiv) in 2 mL of CH₂Cl₂ was added to a solution of tris(*p*-bromophenyl)ammoniumyl-hexafluoroantimonate (4.45 mg, 6.2 μ mol, 2 equiv) in 2 mL of CH₂Cl₂.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00255.

¹H, ¹³C{¹H}, ³¹P, and, if applicable, ¹⁹F NMR spectra of all complexes, temperature-dependent ¹H NMR spectra of complexes 2, 4, and 5, cyclic voltammograms of complexes 2-6, graphical accounts of UV/Vis/NIR and IR spectroelectrochemical measurements, X- and Qband EPR spectra of the radical cations, graphical and tabulated accounts with compositions of the MOs from HOMO-10 to LUMO+10 for the neutral complexes and the singly occupied MOs of the α and the β manifold of the radical cations, contour plots of selected MOs and charge density difference plots for electronic transitions, details to the structure solution and refinement data for complex 6, and figures showing the hydrogen-bonding interactions with the CH_2Cl_2 solvate molecules (PDF) Cartesian coordinates for compounds 2, 2^+ , 3, 3^+ , 5, and 5^+ (XYZ)

Accession Codes

CCDC 1836397 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: rainer.winter@uni-konstanz.de.

ORCID 💿

Malte Drescher: 0000-0002-3571-3452

Rainer F. Winter: 0000-0001-8381-0647

Author Contributions

[‡]C.S.M. and R.F.W. contributed equally to this work. H.W. and M.L. prepared complex **1** and studied the oxidative dehydrodimerization of its radical cation. All other experimental work and the quantum chemical calculations were performed by C.M.; M.L. aided in the computations. S.W. and M.D. performed the 50 K X-band and Q-band EPR spectroscopy on the radical cations.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Deutsche Forschungsgemeinschaft DFG for providing us with access to the computing facilities of cluster JUSTUS in Ulm, Germany. Bernhard Weibert is thanked for the performance of the X-ray diffraction experiment and the structure solution. We also thank Mario Rapp for his contributions as part of his laboratory course.

REFERENCES

Dinger, M. B.; Mol, J. C. Organometallics 2003, 22, 1089–1095.
 Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. Organometallics 1996, 15, 1793–1803.

(3) Huang, D.; Streib, W. E.; Bollinger, J. C.; Caulton, K. G.; Winter, R. F.; Scheiring, T. J. Am. Chem. Soc. **1999**, 121, 8087–8097.

Organometallics

(4) Barnard, C. F. J.; Deniels, J. A.; Mawby, R. J. J. Chem. Soc., Dalton Trans. 1976, 961–966.

- (5) Roper, W. R.; Wright, L. J. J. Organomet. Chem. 1977, 142, C1–C6.
- (6) Probitts, E. J.; Saunders, D. R.; Stone, M. H.; Mawby, R. J. J. Chem. Soc., Dalton Trans. **1986**, 1167–1173.
- (7) Scott Bohle, D.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. J. Organomet. Chem. **1988**, 358, 411-447.
- (8) Rickard, C. E. F.; Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. J. Organomet. Chem. **1990**, 389, 375-388.
- (9) Clark, G. R.; Flower, K. R.; Roper, W. R.; Wright, L. J. Organometallics 1993, 12, 259-260.
- (10) Saunders, D. R.; Stephenson, M.; Mawby, R. J. J. Chem. Soc., Dalton Trans. 1983, 2473–2477.
- (11) Grünwald, C.; Gevert, O.; Wolf, J.; González-Herrero, P.; Werner, H. Organometallics **1996**, *15*, 1960–1962.
- (12) Wolf, J.; Stüer, W.; Grünwald, C.; Gevert, O.; Laubender, M.; Werner, H. *Eur. J. Inorg. Chem.* **1998**, 1998, 1827–1834.
- (13) Coalter, J. N.; Spivak, G. J.; Gérard, H.; Clot, E.; Davidson, E. R.; Eisenstein, O.; Caulton, K. G. J. Am. Chem. Soc. **1998**, 120, 9388–9389.
- (14) Coalter, J. N., III; Bollinger, J. C.; Huffman, J. C.; Werner-Zwanziger, U.; Caulton, K. G.; Davidson, E. R.; Gerard, H.; Clot, E.;

Eisenstein, O. New J. Chem. 2000, 24, 9–26.

- (15) van der Schaaf, P. A.; Kolly, R.; Hafner, A. Chem. Commun. 2000, 1045–1046.
- (16) Coalter, J. N.; Huffman, J. C.; Caulton, K. G. Organometallics 2000, 19, 3569–3578.
- (17) Dinger, M. B.; Mol, J. C. Eur. J. Inorg. Chem. 2003, 2003, 2827-2833.

(18) Saunders, D. R.; Stephenson, M.; Mawby, R. J. J. Chem. Soc., Dalton Trans. 1984, 539–543.

- (19) Flower, K. R.; Garrould, M. W.; Leal, L. G.; Mangold, C.; O'Malley, P. J.; Pritchard, R. G. *J. Organomet. Chem.* **2008**, 693, 408–416.
- (20) Clark, G. R.; Headford, C. E. L.; Roper, W. R.; Wright, L. J.; Yap, V. P. D. Inorg. Chim. Acta **1994**, 220, 261–272.
- (21) Rickard, C. E. F.; Roper, W. R.; Woodgate, S. D.; Wright, L. J. J. Organomet. Chem. 2000, 607, 27-40.
- (22) Maurer, J.; Linseis, M.; Sarkar, B.; Schwederski, B.; Niemeyer, M.; Kaim, W.; Záliš, S.; Anson, C.; Zabel, M.; Winter, R. F. J. Am. Chem. Soc. 2008, 130, 259–268.
- (23) Ott, I.; Kowalski, K.; Gust, R.; Maurer, J.; Mücke, P.; Winter, R. F. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 866–869.
- (24) Abdel-Rahman, O. S.; Maurer, J.; Záliš, S.; Winter, R. F. Organometallics 2015, 34, 3611-3628.
- (25) Wu, X.; Weng, T.; Jin, S.; Liang, J.; Guo, R.; Yu, G.-a.; Liu, S. H. J. Organomet. Chem. **2009**, 694, 1877–1883.
- (26) Man, W. Y.; Xia, J.-L.; Brown, N. J.; Farmer, J. D.; Yufit, D. S.; Howard, J. A. K.; Liu, S. H.; Low, P. J. Organometallics **2011**, 30, 1852–1858.
- (27) Záliš, S.; Winter, R. F.; Kaim, W. Coord. Chem. Rev. 2010, 254, 1383–1396.
- (28) Crook, J. R.; Chamberlain, B.; Mawby, R. J. J. Chem. Soc., Dalton Trans. 1989, 465–470.
- (29) Ulrich Notheis, J.; Heyn, R. H.; Caulton, K. G. Inorg. Chim. Acta 1995, 229, 187-193.

(30) Buil, M. L.; Esteruelas, M. A.; Goni, E.; Oliván, M.; Oñate, E. Organometallics 2006, 25, 3076–3083.

- (31) Strohmeier, W.; Müller, F. J. Chem. Ber. 1967, 100, 2812-2821.
- (32) Tolman, C. A. Chem. Rev. 1977, 77, 313-348.
- (33) Kühl, O. Coord. Chem. Rev. 2005, 249, 693-704.
- (34) Nelson, D. J.; Nolan, S. P. Chem. Soc. Rev. 2013, 42, 6723-6753.
- (35) Cremer, D.; Kraka, E. Dalton Trans. 2017, 46, 8323-8338.
- (36) Sherlock, S. J.; Boyd, D. C.; Moasser, B.; Gladfelter, W. L. Inorg.
- Chem. 1991, 30, 3626-3632.
- (37) Kamatchi, T. S.; Mondal, S.; Scherer, T.; Bubrin, M.; Natarajan, K.; Kaim, W. *Chem. Eur. J.* **2017**, *23*, 17810–17816.

- (38) Jørgensen, C. K. Coord. Chem. Rev. 1966, 1, 164-178.
- (39) Kaim, W. Inorg. Chem. 2011, 50, 9752-9765.
- (40) Kaim, W. Proc. Natl. Acad. Sci., India, Sect. A **2016**, 86, 445–457.
- (41) Mücke, P.; Linseis, M.; Záliš, S.; Winter, R. F. Inorg. Chim. Acta 2011, 374, 36–50.
- (42) Wuttke, E.; Hervault, Y.-M.; Polit, W.; Linseis, M.; Erler, P.; Rigaut, S.; Winter, R. F. Organometallics **2014**, 33, 4672–4686.
- (43) Krejcik, M.; Danek, M.; Hartl, F. J. Electroanal. Chem. Interfacial Electrochem. 1991, 317, 179–187.
- (44) Scheerer, S.; Rotthowe, N.; Abdel-Rahman, O. S.; He, X.; Rigaut, S.; Kvapilová, H.; Záliš, S.; Winter, R. F. *Inorg. Chem.* **2015**, *54*, 3387–3402.
- (45) Linseis, M.; Záliš, S.; Zabel, M.; Winter, R. F. J. Am. Chem. Soc. 2012, 134, 16671–16692.
- (46) Kowalski, K.; Linseis, M.; Winter, R. F.; Zabel, M.; Záliš, S.; Kelm, H.; Krüger, H.-J.; Sarkar, B.; Kaim, W. Organometallics **2009**, 28, 4196–4209.
- (47) Pichlmaier, M.; Winter, R. F.; Zabel, M.; Záliş, S. J. Am. Chem. Soc. 2009, 131, 4892–4903.
- (48) Wuttke, E.; Pevny, F.; Hervault, Y.-M.; Norel, L.; Drescher, M.; Winter, R. F.; Rigaut, S. *Inorg. Chem.* **2012**, *51*, 1902–1915.
- (49) Polit, W.; Mücke, P.; Wuttke, E.; Exner, T.; Winter, R. F. Organometallics **2013**, 32, 5461–5472.
- (50) Pfaff, U.; Hildebrandt, A.; Korb, M.; Oßwald, S.; Linseis, M.; Schreiter, K.; Spange, S.; Winter, R. F.; Lang, H. *Chem. Eur. J.* **2016**, 22, 783–801.
- (51) Scheerer, S.; Linseis, M.; Wuttke, E.; Weickert, S.; Drescher, M.; Tröppner, O.; Ivanović-Burmazović, I.; Irmler, A.; Pauly, F.; Winter, R. F. *Chem. Eur. J.* **2016**, *22*, 9574–9590.
- (52) Hassenrück, C.; Mücke, P.; Scheck, J.; Demeshko, S.; Winter, R. F. *Eur. J. Inorg. Chem.* **2017**, 2017, 401–411.
- (53) Maurer, J.; Sarkar, B.; Schwederski, B.; Kaim, W.; Winter, R. F.; Záliš, S. Organometallics **2006**, *25*, 3701–3712.
- (54) Valyaev, D. A.; Semeikin, O. A.; Ustynyuk, N. A. Coord. Chem. Rev. 2004, 248, 1679–1692.
- (55) Ustynyuk, N. A.; Gusev, O. V.; Novikova, L. N.; Peterleitner, M. G.; Denisovich, L. I.; Peganova, T. y. A.; Semeikin, O. V.; Valyaev, D. A. J. Solid State Electrochem. 2007, 11, 1621–1634.
- (56) Novikova, L. N.; Peterleitner, M. G.; Sevumyan, K. A.; Semeikin, O. V.; Valyaev, D. A.; Ustynyuk, N. A.; Khrustalev, V. N.; Kuleshova, L. N.; Antipin, M. Y. J. Organomet. Chem. 2001, 631, 47– 53.
- (57) Novikova, L. N.; Peterleitner, M. G.; Sevumyan, K. A.; Semeikin, O. V.; Valyaev, D. A.; Ustynyuk, N. A. Appl. Organomet. Chem. 2002, 16, 530-536.
- (58) Iyer, R. S.; Selegue, J. P. J. Am. Chem. Soc. 1987, 109, 910-911.
 (59) Le Narvor, N.; Lapinte, C. J. Chem. Soc., Chem. Commun. 1993, 0, 357-359.
- (60) Fernández, F. J.; Venkatesan, K.; Blacque, O.; Alfonso, M.; Schmalle, H. W.; Berke, H. *Chem. - Eur. J.* **2003**, *9*, 6192–6206.
- (61) Nelson, R. R.; Adams, R. N. J. Am. Chem. Soc. 1968, 90, 3925–3930.
- (62) Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. J. Am. Chem. Soc. **1966**, 88, 3498–3503.
- (63) Donbavand, M.; Möckel, H. Z. Naturforsch., B: J. Chem. Sci. 1974, 29, 403-407.
- (64) Maddala, S.; Mallick, S.; Venkatakrishnan, P. J. Org. Chem. 2017, 82, 8958-8972.
- (65) Polit, W.; Exner, T.; Wuttke, E.; Winter, R. F. BioInorg. React. Mech. 2012, 8, 85-105.
- (66) Hassenrück, C.; Winter, R. F. Inorg. Chem. 2017, 56, 13517–13529.
- (67) Stoll, S.; Schweiger, A. J. Magn. Reson. 2006, 178, 42-55.
- (68) Herrendorf, W.; Bärnighausen, W. HABITUS. program for the optimization of the crystal shape for numerical absorption correction in X-SHAPE, version 1.06; Fa. Stoe, Darmstadt: Karlsruhe, 1999.
- (69) Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. Adv. 2015, 71, 3–8.

Organometallics

K.; Puschmann, H. J. Appl. Crystallogr. 2009, 42, 339-341. (71) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

(72) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. J. Comput. Chem. 2003, 24, 669–681.

(73) Dolg, M.; Stoll, H.; Preuss, H. J. Chem. Phys. 1989, 90, 1730–1734.

(74) Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. J. Chem. Phys. 1994, 100, 7535-7532.

(75) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123–141.

(76) Hariharan, P. H.; Pople, J. A. Theor. Chim. Acta 1973, 28, 213–222.

(77) Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865–3868.

(78) Adamo, C.; Barone, V. J. Chem. Phys. 1999, 110, 6158-6170.
(79) O'Boyle, N. M.; Tenderholt, A. L.; Langner, K. M. J. Comput. Chem. 2008, 29, 839-845.

(80) Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R. J. Cheminf. 2012, 4, 17.

(81) Avogadro: an open-source molecular builder and visualization tool, version 1.2.0. http://avogadro.cc/.

(82) Tange, O. USENIX Mag. 2011, 36, 42-47.

(83) Humphrey, W.; Dalke, A.; Schulten, K. J. Mol. Graphics 1996, 14, 33-38.

(84) *Persistence of Vision Raytracer*, version 3.7; Persistence of Vision Pty. Ltd.: Williamstown, Victoria, Australia, 2004. http://www.povray.org/download/.