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Ruthenium(II) Complexes with (2,4,6-Cycloheptatrien-1-ylidene)ethenylidene Ligands: Strongly Polarized Allenylidene Complexes

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The syntheses of cationic ruthenium(II) allenylidene complexes [(**1a**−**e**)PF_6] of the type $[CpRu({=}C{=}C{=}CR_2)(PPh_3)_2]PF_6$ (**1a**, R_2C: =cycloheptatrienylidene; **1b**, R_2C: =2,7-dimethyl-4,5-benzocycloheptatrienylidene; **1c**, R_2C: =2,7-diphenyl-4,5-benzocycloheptatrienylidene; **1d**, R_2C: = dibenzo[*a*,*e*]cycloheptatrienylidene; **1e**, R_2C: = 4,5-dihydrodibenzo[*a*,*e*]cycloheptatrienylidene) are reported. In the series **1a**−**e**, the decreasing ability of R_2C: to stabilize a positive charge results in a tuning of the electronic and optical properties by changing the relative contributions of the two canonical forms $[Ru^+]{=}C{=}C{=}CR_2$ (**A**) and $[Ru]{-}C{\equiv}C{-}CR_2^+$ (**B**), which is studied particularly by NMR and UV/visible spectroscopy. The first molecular hyperpolarizabilitiy β of (**1b**)PF_6 has been determined by hyper Raleigh scattering. The X-ray crystal structures of (**1b**)PF_6, (**1d**)$PF_6{\cdot}CH_2Cl_2$, and the acetylide complex $CpRu(C{\equiv}C{-}C_7H_7\text{-}2,4,6)(PPh_3)_2$ are presented.

Introduction

In recent years, the chemistry of metallacumulenes $M({=}C)_n{=}CR_2$ incorporating ligands, which are higher cumologs of alkylidene ($n = 0$)[1] and vinylidene complexes ($n = 1$),[2] has increased significantly. Since the discovery of the first allenylidene complexes ($n = 2$) in 1976 by Fischer et al.[3] and Berke,[4] their number has grown continuously, and several synthetic routes have now been established.[2,5] Another landmark in the chemistry of highly unsaturated metallacumulenes was the isolation of the first pentatetraenylidene complex in 1994 by Touchard et al.,[6] which was followed by reports from Werner et al.[7] and Roth and Fischer[8] on the first neutral transition-metal complexes of the type $M{=}C{=}C{=}C{=}C{=}CR_2$.

Besides their interesting chemical properties, compounds containing linear unsaturated carbon chains[9] are attractive due to their potential use in material science, e.g. nonlinear optics.[10] To the best of our knowledge, the nonlinear optical properties of allenylidenes and their higher cumologs have not yet been studied, although the determination of the quadratic nonlinearities of related acetylide ruthenium(II) complexes proved to be very promising.[11] Recently, we and others have reported on the syntheses of organometallic mono-[12] and bimetallic[13] sesquifulvalene derivatives exhibiting notably high first molecular hyperpolarizabilities β. In these polarizable, dipolar molecules,

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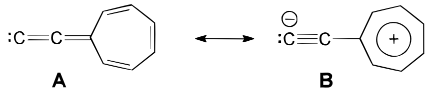


Figure 1. Canonical presentations for (2,4,6-cycloheptatrien-1-ylidene)ethenylidene.

cyclopentadienyl and cycloheptatrienyl metal fragments are in a π-conjugated electron donor/acceptor arrangement, which meets the requirements for the classical design of organic compounds with large second harmonic generation (SHG) efficiencies.[14] Thus, the suitability of the cycloheptatrienyl (tropylium) unit to act as a strong electron acceptor in NLO compounds has stimulated us to incorporate this structural feature into metallacumulenes, and we have initiated a program to synthesize allenylidene complexes of the type **1** with a (2,4,6-cycloheptatrien-1-ylidene)ethenylidene ligand (Figure 1) and derivatives thereof. Complexes of related carbenes such as cycloheptatrienylidene have been studied by Jones and co-workers.[15]

Generally, the structural parameters in allenylidene complexes indicate a substantial contribution from two different mesomeric structures, $M{=}C{=}C{=}CR_2$ (**A**) and $M^-{-}C{\equiv}C{-}CR_2^+$ (**B**).[5] In **1**, the well-known ability of the tropylium system to effectively stabilize a positive charge[16] should lead to compounds with strong dipolar characteristics (canonical form **B**), possibly resulting in interesting physicochemical properties. Furthermore, coordination of the seven-membered cycloheptatrienyl ring to other transition-metal fragments[17] offers the option to synthesize heterobimetallic metallacumulenes and to study electronic and magnetic interaction through these new ligands.

In this contribution, we report on the syntheses and characterization of several cationic complexes [(**1**)PF_6] of the type $[CpRu({=}C{=}C{=}CR_2)(PPh_3)_2]PF_6$ (Figure 2), containing various (cycloheptatrienylidene)ethenylidene ligands, $R_2C{=}C{=}C$:, with R_2C: ranging from cycloheptatrienylidene in **1a** to 4,5-benzocycloheptatrienylidenes in **1b**,**c** and dibenzo[a,e]cycloheptatrienylidene in **1d**. Complex **1e** was synthesized for reasons of comparison and contains a 4,5-dihydrogenated ligand, which can be regarded as a "true" allenylidene.

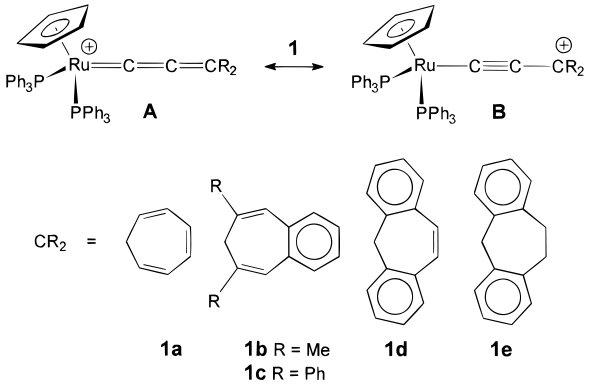
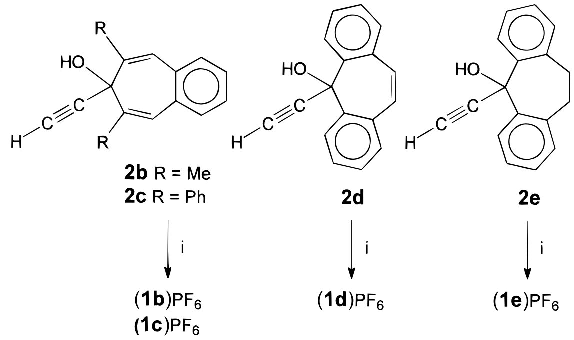


Figure 2. Canonical presentations for cationic ruthenium(II) allenylidene complexes **1a**–**e**.

Scheme 1[a]



[a] Reagents: (i) $CpRu(PPh_3)_2Cl$, NH_4PF_6, MeOH.

Results and Discussion

Syntheses. The most straightforward method of access to allenylidene complexes is the direct activation of propargyl alcohols by electron-rich metal fragments.[5a,b,d–h, j–q,18] Thus, the alkynols **2b**–**e** (Scheme 1) are suitable starting materials for the syntheses of the cationic complexes **1b**–**e**. They were obtained by 1,2-addition of (trimethylsilyl)acetylene to the corresponding ketones[19] and consecutive desilylation in methanolic KOH solution.[20] The alkynols are white crystalline solids and are stable at ambient temperature.[21] The X-ray crystal structures of **2c**,**d** have been reported elsewhere.[22] The reaction of $CpRu(PPh_3)_2Cl$ with the alcohols **2** and NH_4PF_6 in methanol (room temperature, 15 h) led to deeply red to blue colored solutions (Scheme 1). After evaporation of the solvent, extraction with dichloromethane, and precipitation with diethyl ether, complexes (**1b**–**e**)PF_6 were obtained analytically pure in high yield.

The route outlined in Scheme 1 could not be applied to the synthesis of **1a**, as tropone (cycloheptatrienone) is resistant toward 1,2-additions due to aromatic stabilization.[23] Alternatively, 7-ethynyl-1,3,5-cycloheptatriene (**3**) synthesized by addition of HC≡CMgBr to 7-methoxy-1,3,5-cycloheptatriene[24] seemed to be a promising starting material. The acetylide ruthenium(II)

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[21] It has to be noted that especially in the case of **2b**, occasional slow decomposition in solution with re-formation of the ketone and evolution of acetylene was observed. After heating of solutions of **2b** in diethyl ether for several hours, the 2,7-dimethyl-4,5-benzotropone was isolated quantitatively.

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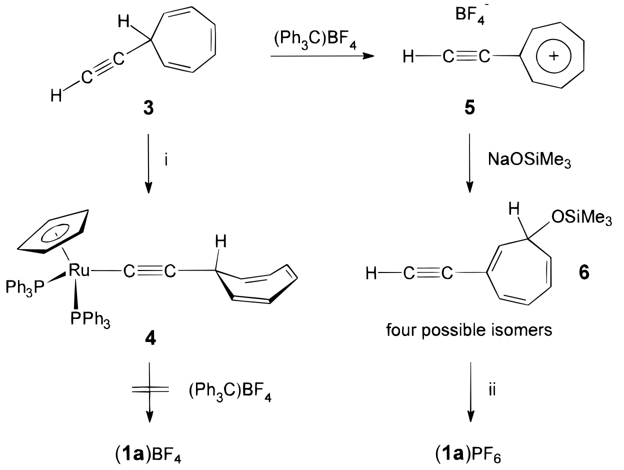
Scheme 2[a]



[a] Reagents: (i) (1) $CpRu(PPh_3)_2Cl$, MeOH, (2) Na; (ii) $CpRu(PPh_3)_2Cl$, NH_4PF_6, MeOH.

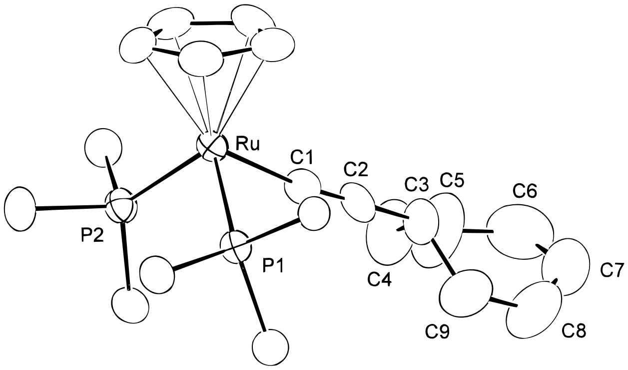


Figure 3. ORTEP drawing of **4**. Only the *ipso*-carbon atoms of the PPh_3 ligands are shown.

Table 1. Selected Bond Distances (Å) and Angles (deg) for (1b)PF$_6$, (1d)PF$_6$·CH$_2$Cl$_2$, and 4

	1b	**1d**	**4**
Ru−P1	2.326(3)	2.3400(9)	2.283(3)
Ru−P2	2.324(3)	2.3470(9)	2.288(3)
Ru−C1	1.94(1)	1.895(3)	2.03(1)
C1−C2	1.23(2)	1.267(4)	1.19(1)
C2−C3	1.42(2)	1.352(4)	1.50(2)
C3−C4	1.42(2)	1.480(4)	1.48(2)
C3−C9	1.43(2)	1.469(5)	1.48(2)
C4−C5	1.35(2)	1.414(5)	1.30(2)
C5−C6	1.40(2)	1.456(5)	1.42(2)
C6−C7	1.39(2)	1.333(5)	1.32(2)
C7−C8	1.45(2)	1.440(5)	1.40(2)
C8−C9	1.34(2)	1.420(5)	1.33(2)
Ru−C(Cp)	2.22(1)−2.29(1)	2.231(3)−2.280(3)	2.22(1)−2.24(2)
Ru−C1−C2	170(1)	171.3(3)	173(1)
C1−C2−C3	174(1)	172.4(3)	173(1)
C2−C3−C4	119(1)	117.7(3)	114(1)
C2−C3−C9	115(1)	118.1(3)	114(1)
P1−Ru−P2	101.6(1)	96.66(3)	100.5(1)
C1−Ru−P1	91.1(3)	89.15(9)	89.9(3)
C1−Ru−P2	93.0(3)	97.6(1)	90.6(3)

complex **4** was prepared according to the route developed by Bruce et al.[25] via the cycloheptatrienylvinylidene complex (Scheme 2). The yellow crystals thus obtained were subjected to an X-ray diffraction analysis, and the molecular structure is shown in Figure 3. The central ruthenium atom in **4** is pseudooctahedrally coordinated, and the bond lengths and angles fall in the range observed for other complexes, such as CpRu(C≡CPh)(PPh_3)$_2$ (Table 1).[26]

However, the reaction of **4** with triphenylcarbenium tetrafluoroborate, (Ph_3C)BF_4, proved to be more complex than anticipated. Although the reaction mixture was not fully characterized, it is evident, for instance from mass spectroscopy, that to some extent the triphenylcarbenium cation reacts with **4** by adding to the basic C_β carbon atom to form a vinylidene complex rather than abstracting a hydride to give (**1a**)BF_4. Analogously, formation of a cycloheptatrienylvinylidene complex by addition of $C_7H_7^+$ to CpRu(C≡CPh)(PPh_3)$_2$ has been reported earlier.[27]

The successful strategy for the high-yield synthesis of (**1a**)PF_6 is also outlined in Scheme 2. Hence, ethynyltropylium tetrafluoroborate (**5**) was synthesized from **3** by hydride abstraction. **5** is obtained as a white crystalline solid, which has to be kept in the cold under an argon atmosphere, as it appears to be considerably more sensitive than substituted alkynyltropylium salts of the type (RC≡C−C_7H_6)$^+$X$^-$.[28] The ethynyltropylium cation is the conjugate acid of (2,4,6-cycloheptatrien-1-ylidene)ethenylidene (Figure 1), and we are currently studying the possibility to generate the free allenylidene by deprotonation of **5** with appropriate non-nucleophilic bases.

The addition of sodium trimethylsilanolate proceeded smoothly to give a mixture of the isomeric silyl ethers **6**, which could be purified by Kugelrohr destillation. These protected alcohols reacted rapidly with a methanolic suspension of $CpRu(PPh_3)_2Cl$ in the presence of NH_4PF_6 to form (**1a**)PF_6 as deep violet-blue crystals.

Structural Characterization of Allenylidene Complexes (1b)PF$_6$ and (1d)PF$_6$·CH$_2$Cl$_2$. The molecular structures of the cations **1b** (top) and **1d** (bottom) are depicted in Figure 4. The ruthenium atoms are pseudooctahedrally coordinated, with the allenylidene ligands bound in a linear fashion. Unfortunately, due to severe disorder of the hexafluorophosphate anion in (**1b**)PF_6, the structure could only be refined with reduced accuracy, not allowing a reasonable comparison of the structural parameters of both cations. In **1d**, the observed distances in the metallacumulene chain Ru−C1−C2−C3 (Table 1) fall in the range shown by other ruthenium(II) allenylidene complexes,[5b,o,18] indicating contribution of the two canonical forms [Ru$^+$]═C═C═CR$_2$ (**A**) and [Ru]−C≡C−CR$_2^+$ (**B**) (Figure 2). The dibenzo[*a*,*e*]cycloheptatrienylidene unit adopts a boat conformation owing to repulsion between C3 and the *peri* hydrogens.[29] In contrast, the (2,7-dimethyl-4,5-benzocycloheptatrienylidene)ethenylidene ligand in **1b** is planar and forms a dihedral angle of 21.5(8)° with the pseudomirror plane including C1, Ru, and the centroid

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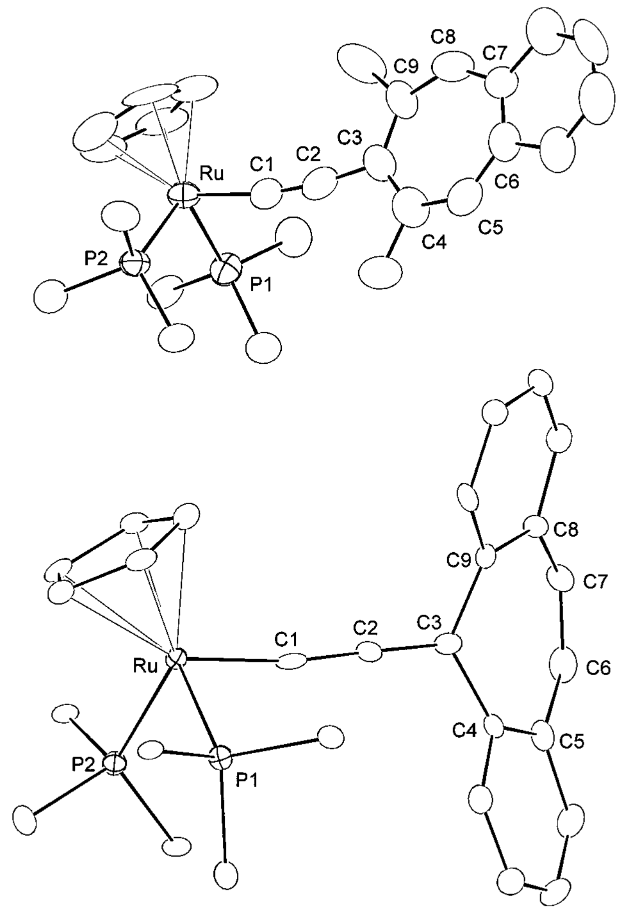

Figure 4. ORTEP drawings of the cations in (**1b**)PF_6 (top) and (**1d**)$PF_6 \cdot CH_2Cl_2$ (different perspective views). Only the *ipso*-carbon atoms of the PPh_3 ligands are shown.

Table 2. Selected ^{13}C and ^1H NMR Resonances for Complexes (1a−e)PF_6

compd	Ru−C_α	C_β	C_γ	C_5H_5	$C_5\mathit{H}_5$
1a	235.4	168.2	153.3	90.4	4.75
1b	257.1	181.2	151.6	91.3	4.83
1c	274.0	204.8	151.7	92.9	4.15
1d	293.1	211.7	158.5	93.0	5.05
1e	296.7	214.7	162.3	93.6	5.09

Table 3. IR and UV/Visible Data for Complexes (1a−e)PF_6

compd	$\tilde{\nu}$(CCC), cm^{-1}	λ_{max}, nm		$\Delta\tilde{\nu}$, cm^{-1} [a]
		$CHCl_3$	CH_3CN	
1a	1971	557	550	−230
1b	1941	596	590	−170
1c	1920	611	601	−270
1d	1928	562	555	−220
1e	1925	502	496	−240

[a] $\Delta\tilde{\nu} = \tilde{\nu}_{max}(CHCl_3) - \tilde{\nu}_{max}(CH_3CN)$.

of the cyclopentadienyl ring, which slightly deviates from the theoretically expected coplanarity.[30]

Spectroscopic Characterization of Allenylidene Complexes (1a−e)PF_6. All complexes (**1a**−**e**)PF_6 are indefinitely stable in air and have been fully characterized by microanalyses and by infrared, UV/visible, mass, and NMR (^1H, ^{13}C) spectroscopy. As mentioned above, the bonding in the cations **1** can be described by the two limiting resonance structures **A** and **B** shown in Figure 2. Variation of the R_2C: moiety in the $R_2C{=}C{=}C$: ligand allows tuning of the electronic and optical properties of the respective allenylidene complexes by changing the relative contributions of these two canonical forms. In **1a**, the positive charge is most strongly stabilized by the cycloheptatrienyl unit, and the ligand can be regarded as an ylidic "tropyliumacetylide" as expressed by **B**. Annelation of one or two benzene rings in **1b**,**c** or **1d**, respectively, decreases the stability of the tropylium system,[16] shifting the electronic structure from **B** to the more metallacumulene-like state **A**.

This trend is easily confirmed by evaluation of the ^{13}C NMR spectra (Table 2). Whereas the C_α and C_β resonances observed for **1e** and **1d** can be compared to those shown by other isoelectronic allenylidene complexes,[5b,o] these resonances are found at consecutively higher field in the spectra of **1c**, **1b**, and **1a**. Accordingly, comparison of the ^1H and ^{13}C cyclopentadienyl resonances (Table 2) indicates that the π-acceptor capabilities of the ligands in **1** decrease in the order **1e** > **1d** > **1b** > **1a**, as a direct relationship between the chemical shift of the cyclopentadienyl group and the degree of electron richness at the metal site has been suggested.[18,31] The high-field shift of the Cp protons in **1c** relative to the other complexes is probably due to shielding by the two phenyl groups. The IR spectra of **1a**−**e** exhibit strong absorptions for the asymmetric ν(CCC) stretching frequency in the range 1920 (**1c**)−1971 (**1a**) cm^{-1}, clearly confirming their metallacumulene nature (Table 3). Although the spectroscopic properties of complexes **1a**−**e** differ significantly within a considerably wide range, the ligands in all compounds are still best described as allenylidene rather than acetylide ligands. This conclusion is supported by comparison with the spectroscopic data found for ruthenium(II) acetylide complexes,[5b,c,25] e.g., **4**, which shows a triplet ($^2J_{PC}$ = 21 Hz) at 93.6 ppm for C_α and a singlet at 111.9 ppm for C_β in the ^{13}C NMR spectrum and an infrared ν(C≡C) absorption at 2086 cm^{-1}.

Complexes **1a**−**e** are intensely colored compounds. Owing to the charge-transfer excitation represented by the resonance structures **A** and **B** (Figure 2), their ultraviolet/visible spectra exhibit a strong and broad band centered at about 500−600 nm (Table 3), with the longest wavelength absorption being observed for **1c**. This trend in λ_{max} indicates that both canonical forms contribute significantly to the ground-state electronic structure of **1a**−**e** and are nearly balanced in **1c**.[32] Destabilization of the tropylium sytem causes a mesomeric shift from **B** to **A**, which is in agreement with the conclusions drawn from the discussion of the NMR data. Furthermore, the complexes only show moderate negative solvatochromism upon changing the solvent from chloroform to acetonitrile ($\Delta\tilde{\nu}$ ranging from −170 to −270 cm^{-1}, Table 3).

In view of the promising results obtained with sesquifulvalene complexes,[12,13] we were encouraged to determine the first molecular hyperpolarizablities β of complexes (**1**)PF_6 using the hyper Raleigh scattering

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technique.[33] Usually, this experiment is performed with a Nd:YAG laser ($\lambda = 1064$ nm), and the frequency-doubled scattered light ($\lambda/2 = 532$ nm) is measured. All complexes (**1**)PF_6 still absorb strongly at 532 nm, and it proved to be difficult to measure the intensity of the scattered light. However, as (**1b**)PF_6 and (**1c**)PF_6 have the smallest absorption at 532 nm and are essentially electronically identical, we determined only the first molecular hyperpolarizability of (**1b**)PF_6 in acetonitrile, giving $\beta = 120 \times 10^{-30}$ esu. Using the two-level model,[34] a static hyperpolarizablity $\beta_o = 19 \times 10^{-30}$ esu can be calculated, but it should be noted that, in our case, this simple model is not a versatile tool, as the frequency-doubled scattered light is still in the region of very strong absorption. Separation of resonance enhancement contributions would require the determination of β at a different basic laser wavelength.

The β value reported here is reasonably high compared to those of organic[35] and organometallic[10,36] compounds of *comparable* chromophor length, but it is smaller than those measured for ruthenium(II) acetylide complexes, e.g., $CpRu(C{\equiv}CC_6H_4NO_2\text{-}4)(PPh_3)_2$ (β(THF) $= 468 \times 10^{-30}$ esu, λ_{max}(THF) = 460 nm).[11] We assume that this enhanced second harmonic generation efficiency is mainly caused by the larger dipole moment difference $\Delta\mu_{eg}$ between the ground state (g) and excited state (e) of the respective CT excitation. According to the two-level model,[34] this results in a higher static hyperpolarizability β_o, outweighing the increasing effect of a lower energy of transition $h\omega_{eg}$ on β_o.[37] To obtain metallacumulenes, which are more suitable for nonlinear optical applications, the following efforts seem to be promising: (a) extension of the metallacumulene chain,[6−8] (b) variation or tuning of the transition metal fragment to achieve the desired optical transparency for frequency-doubling experiments,[12a] and (c) synthesis of heterobimetallic complexes to induce an additional ligand-to-metal charge transfer.

The (2,4,6-cycloheptatrien-1-ylidene)ethenylidene ligand (Figure 1) introduced in this contribution represents the prototype for the design of heterobimetallic allenylidene complexes. The development of a general coordination chemistry based on ligands derived thereof is of interest with regard to electronic and magnetic interactions between different metal sites through this ligand. This coupling might differ significantly from those of other complexes with σ,π-hydrocarbon bridges,[38] such as ferrocenylacetylide,[39] and we will report on these results in due course.

Experimental Section

All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. NMR spectra were recorded on a Bruker AM 250 (250 MHz) instrument. Infrared spectra were taken on a Perkin-Elmer 983 instrument. Elemental analyses (C,H,N) were performed at the Freie Universität Berlin on a Heraeus CHN-Rapid elemental analyzer. Mass spectra were recorded on a Varian MAT 711 instrument and UV/vis spectra on a Perkin-Elmer Lambda 9 UV/visible/near-IR spectrophotometer using 10^{-3} M solutions. $CpRu(PPh_3)_2Cl$,[40] and 7-ethynyl-1,3,5-cycloheptatriene[24] were prepared according to published procedures. The alkynols **2b**−**e** were synthesized as described in ref 22b.

Synthesis of (1a−e)PF_6. General Procedure. A suspension of $CpRu(PPh_3)_2Cl$ (720 mg, 1 mmol) and NH_4PF_6 (200 mg, 1.2 mmol) in 80 mL of methanol was treated with the corresponding alcohol (1.2 mmol); in the case of (**1a**)PF_6, the mixture of silyl ethers **6** was used. Stirring was continued for 15 h, and the solvent was removed in vacuo. The remaining solid was extracted with dichloromethane, and the filtered solution was concentrated to ca. 10 mL. Addition to rapidly stirred diethyl ether (100 mL) precipitated the complexes as intensely colored solids, which were washed with Et_2O and dried in vacuo. Yields ranged from 75 to 90%.

(1a)PF_6. ^1H NMR ($CDCl_3$, 250 MHz): δ 7.33 (m, 6H, C_7 C*H*), 7.17 (m, 30H, C_6H_5), 4.75 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.90 MHz): δ 235.4 (t, $^2J_{PC}$ = 20 Hz, Ru−*C*), 168.2 (Ru−C*C*), 153.3 (Ru−CC*C*), 152.1, 142.5, 140.7 (C_7 *C*H), 136.4 (m, $^1J_{PC}$ = 24 Hz, P−*C*), 133.9 (t, $^2J_{PC}$ = 4 Hz, P−C*C*), 130.2 (P−CCC*C*), 128.4 (t, $^3J_{PC}$ = 4 Hz, P−CC*C*), 90.4 (*C_5*H_5). IR (KBr): ν(CCC) 1971 cm^{-1}. MS (FAB): *m/z* (relative intensity) 805 (3.4) [M$^+$], 691 (3.1) [$(CpRu(PPh_3)_2)^+$], 543 (5.1) [$(M - PPh_3)^+$], 429 (17.4) [$(CpRuPPh_3)^+$]. UV/vis ($CHCl_3$): λ_{max} (ϵ) 557 (19 810) nm (L mol^{-1} cm^{-1}). UV/vis (CH_3CN): λ_{max} (ϵ) 550 (17 940) nm (L mol^{-1} cm^{-1}). Anal. Calcd for $C_{50}H_{41}F_6P_3Ru$ (M_r = 949.86): C, 63.23; H, 4.35. Found: C, 63.07; H, 4.57.

(1b)PF_6. ^1H NMR ($CDCl_3$, 250 MHz): δ 8.28 (s, 2H, C_7 C*H*), 7.88 (m, 2H, C_6 C*H*), 7.77 (m, 2H, C_6 C*H*), 7.33 (t, 6H, PCCCC*H*), 7.16 (m, 24H, PCC*H* + PCCC*H*), 4.83 (s, 5H, C_5H_5), 2.56 (s, 6H, C*H_3*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.90 MHz): δ 257.1 (t, $^2J_{PC}$ = 19 Hz, Ru−*C*), 181.2 (Ru−C*C*), 151.6 (Ru−CC*C*), 149.0 (*C*CH_3), 142.2 (C_7 *C*H), 137.8 (CH−*C*−CH), 136.5 (m, $^1J_{PC}$ = 23 Hz, P−*C*), 134.1 (C_6 *C*H), 133.5 (t, $^2J_{PC}$ = 5 Hz, P−C*C*), 132.1 (C_6 *C*H), 130.5 (P−CCC*C*), 128.6 (t, $^3J_{PC}$ = 4 Hz, P−CC*C*), 91.3 (*C_5*H_5), 29.3 (*C*H_3). IR (KBr): ν(CCC) 1941 cm^{-1}. MS (FAB): *m/z* (relative intensity) 883 (11.6) [M$^+$], 429 (25.6) [$(CpRuPPh_3)^+$]. UV/vis ($CHCl_3$): λ_{max} (ϵ) 596 (49 160) nm (L mol^{-1} cm^{-1}). UV/vis (CH_3CN): λ_{max} (ϵ) 590 (38 770) nm (L mol^{-1} cm^{-1}). Anal. Calcd for $C_{56}H_{47}F_6P_3Ru$ (M_r = 1027.97): C, 65.43; H, 4.61. Found: C, 64.82; H, 5.34.

(1c)PF_6. ^1H NMR ($CDCl_3$, 250 MHz): δ 7.90 (s, 2H, C_7 C*H*), 7.78 (m, 2H, C_6 C*H*), 7.69 (m, 2H, C_6 C*H*), 7.64 (d, 4H, C_6 C*H*), 7.31 (m, 12H, C_6 C*H* + PCCCC*H*), 7.16 (t, 12H, PCCC*H*), 6.74 (m, 12H, PCC*H*), 4.15 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.90 MHz): δ 274.0 (t, $^2J_{PC}$ = 18 Hz, Ru−*C*), 204.8 (Ru−C*C*), 153.4 (*C*H), 151.7 (Ru−CC*C*), 145.1, 140.0 (*C*H), 137.3 (CH−*C*−CH), 136.1 (m, $^1J_{PC}$ = 25 Hz, P−*C*), 134.1 (*C*H), 133.3 (t, $^2J_{PC}$ = 5 Hz, P−C*C*), 131.6 (*C*H), 130.4 (P−CCC*C*), 129.4, 129.0 (*C*H), 128.6 (t, $^3J_{PC}$ = 5 Hz, P−CC*C*), 92.9 (*C_5*H_5). IR (KBr): ν(CCC) 1920 cm^{-1}. MS (FAB): *m/z* (relative intensity) 1007 (40.9) [M$^+$], 744 (33.5) [$(M - PPh_3)^+$], 429 (100) [$(CpRuPPh_3)^+$]. UV/vis ($CHCl_3$): λ_{max} (ϵ) 611 (32 500) nm (L mol^{-1} cm^{-1}). UV/vis (CH_3CN): λ_{max} (ϵ) 601 (30 240) nm (L mol^{-1} cm^{-1}). Anal. Calcd for $C_{66}H_{51}F_6P_3Ru$ (M_r = 1152.11): C, 68.81; H, 4.46. Found: C, 69.02; H, 5.15.

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Table 4. Crystallographic Data for (1b)PF_6, (1d)$PF_6 \cdot CH_2Cl_2$ and 4

	1b	1d	4
cryst size, mm	0.40 × 0.20 × 0.20	0.35 × 0.25 × 0.10	0.25 × 0.12 × 0.12
formula	$C_{56}H_{47}F_6P_3Ru$	$C_{59}H_{47}Cl_2F_6P_3Ru$	$C_{50}H_{42}P_2Ru$
fw	1027.98	1134.92	805.92
wavelength, Å	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	10.100(3)	10.104(2)	9.729(2)
b, Å	14.083(2)	13.276(2)	25.647(5)
c, Å	35.822(5)	19.598(3)	18.039(3)
α, deg		93.71(1)	
β, deg	92.03(2)	90.74(2)	92.29(1)
γ, deg		108.55(1)	
V, Å^3	5092(3)	2486(2)	4498(3)
Z	4	2	4
ρ_{calcd}, g/cm^3	1.341	1.516	1.190
μ, mm^{-1}	4.495	5.733	4.403
θ range, deg	$1.0 \leq \theta \leq 22.5$	$2.3 \leq \theta \leq 22.5$	$2.0 \leq \theta \leq 22.5$
index ranges	$0 \leq h \leq 10$	$-10 \leq h \leq 8$	$0 \leq h \leq 10$
	$0 \leq k \leq 15$	$0 \leq k \leq 14$	$0 \leq k \leq 27$
	$-38 \leq l \leq 38$	$-20 \leq l \leq 20$	$-19 \leq l \leq 19$
no. of rflns collected	7407	4941	6455
no. of independent rflns	6639	4527	5884
no. of observed rflns [$F_o^2 \geq 3\sigma(F_o^2)$]	5024	3996	3526
no. of params	598	640	478
R, %	8.92	2.33	6.12
R_w, %	12.70	3.30	8.89

(1d)PF_6. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.82 (d, 2H, C_6 C*H*), 7.71 (t, 2H, C_6 C*H*), 7.54 (d, 2H, C_6 C*H*), 7.39 (t, 2H, C_6 C*H*), 7.30 (t, 6H, PCCCC*H*), 7.25 (s, C_7 C*H*), 7.06 (m, 24H, PCC*H* + PCCC*H*), 5.05 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.90 MHz): δ 293.1 (t, $^2J_{PC} = 19$ Hz, Ru−*C*), 211.7 (Ru−C*C*), 158.5 (Ru−CC*C*), 144.9 (Ru−CCC*C*), 135.6 (m, $^1J_{PC} = 25$ Hz, P−*C*), 135.5 (CH═CH−*C*), 133.3 (t, $^2J_{PC} = 5$ Hz, P−C*C*), 133.1, 132.1, 131.9, 131.5 (*C*H), 130.8 (P−CCC*C*), 129.9 (*C*H), 128.6 (t, $^3J_{PC} = 4$ Hz, P−CC*C*), 93.0 (*C*$_5$H$_5$). IR (KBr): ν(CCC) 1928 cm^{-1}. MS (FAB): *m/z* (relative intensity) 905 (5.6) [M$^+$], 643 (6.1) [(M − PPh_3)$^+$], 429 (6.9) [($CpRuPPh_3$)$^+$]. UV/vis ($CHCl_3$): λ_{max} (ϵ) 562 (21 390) nm (L mol^{-1} cm^{-1}). UV/vis (CH_3CN): λ_{max} (ϵ) 555 (21 170) nm (L mol^{-1} cm^{-1}). Anal. Calcd for $C_{58}H_{45}F_6P_3Ru \cdot CH_2Cl_2$ ($M_r = 1134.91$): C, 62.44; H, 4.17. Found: C, 62.71; H, 4.53.

(1e)PF_6. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.54 (t, 4H, C*H*), 7.32 (t, 6H PCCCC*H*), 7.23 (d, 2H, C*H*), 7.19 (d, 2H, C*H*), 7.08 (m, 24H, PCC*H* + PCCC*H*), 5.09 (s, 5H, C$_5$*H*$_5$), 3.14 (s, 4H, C*H*$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.90 MHz): δ 296.7 (t, $^2J_{PC} = 18$ Hz, Ru−*C*), 214.7 (Ru−C*C*), 162.3 (Ru−CC*C*), 144.1 (Ru−CCC*C*), 141.8 (CH_2CH_2*C*), 135.3 (m, $^1J_{PC} = 24$ Hz, P−*C*), 133.3 (t, $^2J_{PC} = 4$ Hz, P−C*C*), 132.0 (*C*H), 130.8 (P−CCC*C*), 130.7 (*C*H), 128.7 (t, $^3J_{PC} = 4$ Hz, P−CC*C*), 127.3 (*C*H), 93.6 (*C*$_5$H$_5$), 35.1 (*C*H$_2$). IR (KBr): ν(CCC) 1925 cm^{-1}. MS (FAB): *m/z* (relative intensity) 907 (100) [M$^+$], 645 (76.6) [(M − PPh_3)$^+$], 429 (98.2) [($CpRuPPh_3$)$^+$]. UV/vis ($CHCl_3$): λ_{max} (ϵ) 502 (21 880) nm (L mol^{-1} cm^{-1}). UV/vis (CH_3CN): λ_{max} (ϵ) 496 (20 360) nm (L mol^{-1} cm^{-1}). Anal. Calcd for $C_{58}H_{47}F_6P_3Ru$ ($M_r = 1051.99$): C, 66.22; H, 4.50. Found: C, 66.38; H, 4.81.

Synthesis of 4. A mixture of $CpRu(PPh_3)_2Cl$ (726 mg, 1 mmol) and **3** (170 mg, 1.5 mmol) was heated in refluxing methanol (80 mL) for 30 min. The deep red solution was cooled, and ca. 40 mg of sodium was added. **4** precipitated as a yellow solid, which was isolated by filtration, washed with MeOH, and dried *in vacuo*. Yield: 600 mg (75%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.50 (m, 12H, PCCC*H*), 7.20 (t, 6H PCCCC*H*), 7.09 (t, 12H, PCC*H*), 6.61 (m, 2H, C*H*), 6.04 (m, 2H, C*H*), 5.25 (m, 2H, C*H*), 4.24 (s, 5H, C$_5$*H*$_5$), 2.59 (m, 1H, C*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.90 MHz): δ 139.1 (m, $^1J_{PC} = 21$ Hz, P−*C*), 133.8 (t, $^2J_{PC} = 5$ Hz, P−C*C*), 130.4, 128.5 (*C*H), 128.2 (P−CCC*C*), 127.0 (t, $^3J_{PC} = 4$ Hz, P−CC*C*), 122.5 (*C*H), 111.9 (Ru−C*C*), 93.6 (t, $^2J_{PC} = 23$ Hz, Ru−*C*), 84.8 (*C*$_5$H$_5$), 35.7 (C_7 *C*-1). IR (KBr): ν(C≡C) 2086 cm^{-1}. MS (EI, 70 eV): *m/z* (relative intensity) 806 (1.2) [M$^+$], 544 (1.0) [(M − PPh_3)$^+$], 262 (100) [(PPh_3)$^+$]. Anal. Calcd for $C_{50}H_{42}P_2Ru$ ($M_r = 805.90$): C, 74.52; H, 5.25. Found: C, 73.74; H, 5.48.

Synthesis of 5. To a solution of **3** (5.0 g, 43 mmol) in 40 mL of dichloromethane was slowly added a solution of triphenylcarbenium tetrafluoroborate (14.0 g, 42 mmol) at −78 °C. Stirring was continued at low temperature for 2 h. The ethynyltropylium salt **5** was isolated by filtration under argon and washed with CH_2Cl_2 and diethyl ether. **5** was obtained as a white crystalline solid, which had to be kept under argon in a refrigerator to avoid decomposition. Yield: 3.0 g (35%). ^{1}H NMR (CD_3CN, 250 MHz): δ 9.13 (m, 6H, C_7 C*H*), 4.80 (s, 1H, C≡C*H*). $^{13}C\{^1H\}$ NMR (CD_3CN, 62.90 MHz): δ 158.1, 156.5, 154.7 (C_7 *C*H), 150.8 (*C*C≡CH), 97.4, 84.4 (*C*≡*C*). IR (KBr): ν(C≡C) 2102 cm^{-1}. MS (FAB): *m/z* (relative intensity) 115 (3.5) [M$^+$]. Anal. Calcd for $C_9H_7BF_4$ ($M_r = 201.96$): C, 53.53; H, 3.49. Found: C, 52.06; H, 4.44.

Synthesis of 6. To a suspension of **5** (3.79 g, 19 mmol) in 80 mL of dichloromethane was added $NaOSiMe_3$ (19 mL of a 1 M solution in CH_2Cl_2). After the mixture was stirred overnight, the solvent was removed *in vacuo*, and the residue was extracted with hexane and filtered. After evaporation of the solvent, the remaining oil was purified by Kugelrohr destillation at 100 °C. The mixture of silyl ethers **6** was obtained as a yellowish oil. Yield: 1.6 g (42%). No attempt was made to fully interpret the NMR spectra. MS (EI, 70 eV): *m/z* (relative intensity) 204 (4.5) [M$^+$], 203 (6.0) [(M − H)$^+$], 189 (100) [(M − CH_3)$^+$], 115 (90.5) [(M − $OSiMe_3$)$^+$], 73 (52.7) [($OSiMe_3$)$^+$].

X-ray Structural Determination of (1b)PF_6, (1d)$PF_6 \cdot CH_2Cl_2$, and 4. Crystals of (**1d**)$PF_6 \cdot CH_2Cl_2$ are air sensitive (loss of solvent), while (**1b**)PF_6 and **4** are airstable. A suitable specimen of (**1d**)$PF_6 \cdot CH_2Cl_2$ was selected at −120 °C using a device similar to that described by Veith and Bärnighausen[41] and mounted in the cold stream [−120(2) °C] of an Enraf-Nonius CAD-4 diffractometer. Crystals of (**1b**)PF_6 and **4** were selected in air and mounted at room temperature on an Enraf-Nonius CAD-4 diffractometer. Important crystal and data collection details are listed in Table 4. Data for all compounds were collected using $\omega-2\theta$ scans. Raw data were reduced to structure factors[42] (and their esd's) by correcting for scan speed, Lorentz, and polarization effects. No crystal

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[41] Veith, M.; Bärnighausen, H. *Acta Crystallogr., Sect. B* **1974**, *30*, 1806.

decay was detected, and empirical absorption corrections (DIFABS)[43] were applied to the raw data. The space groups were found to be $P2_1/n$, $P\bar{1}$, and $P2_1/n$ for (**1b**)PF_6, (**1d**)$PF_6 \cdot CH_2Cl_2$ and **4**, respectively. All structures were solved by Patterson methods. The positional parameters for all non-hydrogen atoms were refined by using first isotropic and later anisotropic thermal parameters. Difference Fourier maps calculated at this stage showed almost all hydrogen positions. However, all hydrogen atoms were added to the structure models at calculated positions [d(C−H) = 0.95 Å][44] and are unrefined. The isotropic temperature factors for hydrogens were fixed to be 1.3 times the B_{eq} of the parent atom. The PF_6^- anion in (**1b**)PF_6 is disordered, and two positions were identified for this anion. All calculations were carried out with the MolEN package.[45] ORTEP[46] was used for all molecular drawings.

Hyper Raleigh scattering. The experiments were performed at a wavelength of 1064 nm with a mode-locked Q-switch Nd:YAG laser (Quantronix 5216). Solutions of *p*-nitroaniline in acetonitrile were used as external reference ($\beta(CH_3CN) = 29.2 \times 10^{-30}$ esu).[47] The general experimental setup is described in ref 33b.

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Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles and figures giving additional views of the structures of (**1b**)PF_6, (**1d**)$PF_6 \cdot CH_2Cl_2$, and **4** (30 pages). Ordering information is given on any current masthead page.

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(42) Neutral scattering factors were used: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B. Terms of anomalous dispersion from: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(43) Walker, N.; Stewart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

(44) Churchill, M. R. *Inorg. Chem.* **1972**, *12*, 1213.

(45) *MolEN: Molecular Structure Solution Procedures. Program Descriptions*; Enraf-Nonius: Delft, 1990. Definition of residuals: $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$, $w = 1/[\sigma(F)]^2$.

(46) Johnson, C. K. *ORTEP II*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

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