Large Second-Order Nonlinear Optical Properties of Novel Organometallic (σ-Aryl−enynyl)ruthenium Complexes

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Summary: Novel homo- and heterobimetallic complexes have been synthesized, and their nonlinear optical properties were evaluated. The effects upon the hyperpolarizability of chain length, configuration of the metal donor group, and kind of metal acceptor group are reported.

The search for suitable nonlinear optical (NLO) active materials has been focused mainly on organic products,[1−4] though in recent years the interest in organometallic complexes has increased drastically.[5−14] It is expected that electron-rich metal moieties such as half-sandwich transition-metal phosphine derivatives may enable the electronic delocalization in appropriate π-conjugated systems attached to the metal. Moreover, the incorporation of the metal into the plane of the conjugated system and the potential introduction of metal−carbon multiple-bond character has been suggested to enhance the NLO response.[12,14]

Here we report novel donor−acceptor complexes which display large quadratic hyperpolarizabilities (β). We have investigated compounds of the following types: (i) alkynyl, enynyl, and polyenynyl indenyl−ruthenium(II) complexes with nitro or cyano substituents at the end of the hydrocarbon chain and (ii) enynyl ruthenium(II)−ruthenium(III) and ruthenium(II)−chromium(0) or tungsten(0) bimetallic complexes in which a donor indenyl−ruthenium(II) moiety and an acceptor metal fragment are bridged by enynyl N-functionalized systems.

Synthesis of the novel complexes is shown in Scheme 1. Treating a THF solution of alkynyl−phosphonio complex **3** with 1 equiv of ^{n}BuLi at −20 °C,[15] subsequently adding unsaturated aldehydes $O{=}C(H)(CH{=}CH)_n$-*p*-C_6H_4A (A = NO_2, CN), and allowing the mixture to reach room temperature resulted in the formation of enynyl complexes **7a**,**b** and **8**. These compounds were obtained as a mixture of the *E* and *Z* stereoisomers in 70−90% yield. In a similar way enynyl complexes **4** and **6** were obtained from the reaction with the corresponding aldehyde or ketone, respectively. The spectroscopic properties of **4**, **6**, **7a**,**b**, and **8** are consistent with the proposed structures, in particular the $\nu_{C\equiv C}$ IR absorption (2027−2041 cm^{-1}) and the typical triplet resonance in the $^{13}C\{^1H\}$ NMR for the Ru−C≡ carbon nucleus at δ 132.47−141.39 ($^2J_{C-P}$ = 22.3−25.1 Hz). The presence of an uncoordinated pyridine ring or a cyano group in complexes **4** and **7b**, respectively, was used for preparing mixed-valence complexes by the reaction with $[M(CO)_5(THF)]$ (M = Cr, W) and $[Ru(NH_3)_5(OSO_2CF_3)]^{2+}$. Workup gave the novel bimetallic enynyl complexes **5a**,**b**, **9a**,**b**, and **10** in 53−82% yield. The IR spectra showed the expected $\nu_{C\equiv C}$ and $\nu_{C=O}$ absorptions, and the $^{13}C\{^1H\}$ NMR spectra exhibited the Ru−C≡ triplet resonances (δ 138.51 ($^2J_{C-P}$ = 24.4 Hz), **5a**; δ 141.67 ($^2J_{C-P}$ = 24.5 Hz), **5b**). Complexes **2**, **12a**,**b**, and **13** with potential NLO properties were also prepared (70−85% yield) through conventional procedures.[16]

All hyperpolarizabilities were determined using hyper-Rayleigh scattering,[17,18] which made it possible to investigate also the ionic species in solution (Table 1).

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(15) Complex **3** can be obtained in a one-pot synthesis as previously described for the analogous complex $[Ru\{C{\equiv}CCH(Ph)(PMe_3)\}(PPh_3)_2(\eta^5\text{-}C_9H_7)][PF_6]$: Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2495. Both alkynyl−phosphonio complexes are excellent substrates for Wittig reactions leading to the formation of new double carbon−carbon bonds.

(16) The alkynyl complex **2** was prepared in 79% yield by the deprotonation of the corresponding vinylidene complex **1**, which is easily formed from the reaction of $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ with (*p*-nitrophenyl)acetylene. Complexes **12a**,**b** and **13** were prepared as described for the analogous bimetallic complexes **9a**,**b** and **10**.

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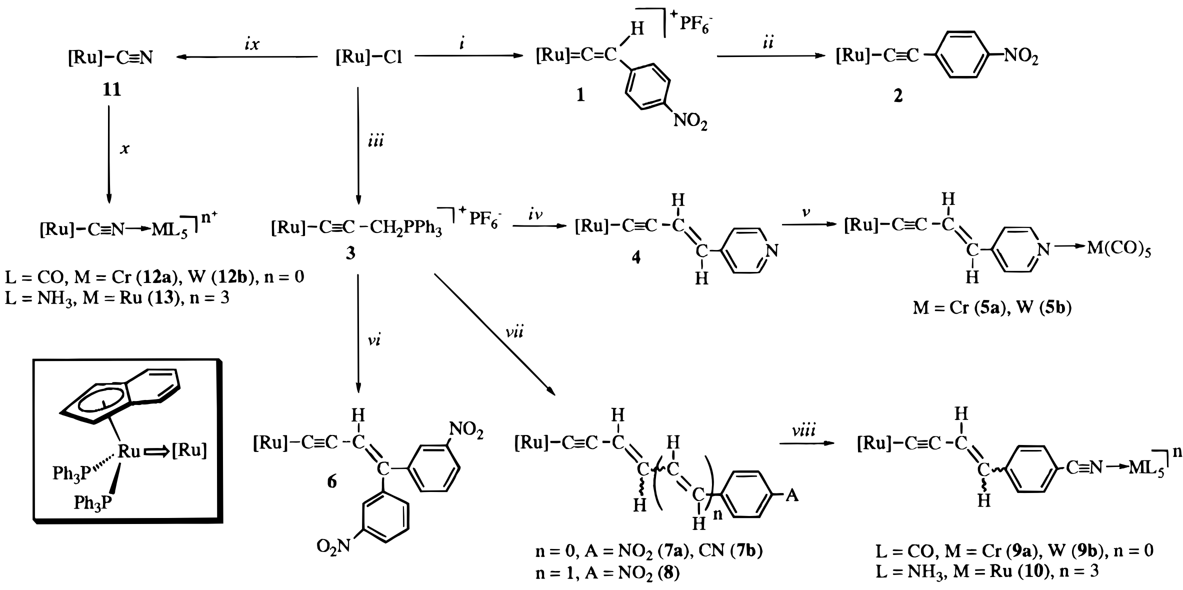
Scheme 1[a]



[a] Reagents and conditions: (i) $NaPF_6$, HC≡C-*p*-$C_6H_4NO_2$, MeOH, reflux; (ii) Al_2O_3, CH_2Cl_2, room temperature; (iii) $NaPF_6$, HC≡CCH_2OH, PPh_3, MeOH, room temperature; (iv) Li^nBu, O=C(H)-*p*-C_5H_4N, THF, −20 °C; (v) $[M(CO)_5(THF)]$, THF, room temperature; (vi) Li^nBu, O=C(*m*-$C_6H_4NO_2)_2$, THF, −20 °C; (vii) Li^nBu, O=C(H)(CH=CH)$_n$-*p*-C_6H_4A, THF, −20 °C; (viii) $n = 0$, A = CN, $[M(CO)_5(THF)]$, THF, room temperature or $n = 0$, A = CN, $[Ru(NH_3)_5(OSO_2CF_3)][CF_3SO_3]_2$, acetone, room temperature; (ix) KCN, MeOH, reflux; (x) $[M(CO)_5(THF)]$, THF, room temperature or $[Ru(NH_3)_5(OSO_2CF_3)][CF_3SO_3]_2$, acetone, room temperature.

Table 1. Wavelength of Maximum Absorptions[a] and First Hyperpolarizabilities[b] for Complexes 1−13

	λ_{max}	β	β_0		λ_{max}	β	β_0
1	379	116	50	**8**	523	1320	34
2	476	746	119	**9a**	442	465	119
4	399	100	37	**9b**	456	700	150
5a	451	260	60	**10**[c]	442	315	80
5b	462	535	71	**11**	396	13	5
6	398	177	67	**12a**	392	25	10
7a	507	1257	89	**12b**	392	40	15
7b	427	238	71	**13**[c]	621	108	26

[a] In nm. [b] Hyper-Rayleigh scattering measurements; the hyperpolarizabilities β (10% error) and the calculated β_0 values are given in 10^{-30} esu. The hyperpolarizabilities are reported in cgs units (esu). They can be converted into SI units (C^3 m^3 J^{-2}) by dividing by a factor of 2.693×10^{20}. *p*-Nitroaniline was used as an external reference.[27] All measurements have been performed in dichloromethane. [c] Acetone solutions.

The external reference method was used, and all molecules were checked for fluorescence that can interfere with the second-harmonic signal.[18,19] In contrast to recent theoretical studies,[13,20] the measured hyperpolarizabilities were among the highest values reported for organometallic materials.[5,6,9]

The corrections for resonance enhancement were made using the two-level model[21] with the absorption band closest to the harmonic frequency. Since the molecules exhibit weaker absorption bands at lower wavelengths, the calculated value will only be an estimate of the static hyperpolarizability (β_0). However, the good correlation[1] found between β_0 and the wavelength of maximal absorption (λ_{max}) seems to justify this procedure. In other words, the optical transition corresponding to the given λ_{max} seems to be the main contributor to β. Only for these compounds for which λ_{max} approaches the harmonic frequency does this simple model lead to an underestimation of β_0, probably due to neglect of damping (*e.g.* as for **7a** and **8**).

Although a triple carbon−carbon bond is known to be less effective as a π-conjugated bridge for NLO materials,[2] the determined hyperpolarizability of **2** is far greater than that of its 4-nitro-β-(dimethylamino)-styrene analogue ($\beta_{1900\ nm} = 35 \times 10^{-30}$ esu), in which the donor is separated from the benzene system through a double bond. This also holds for **7a**, **8**, and their *N*,*N*-dimethylnitrostilbene analogues.[2] The high effectiveness of the half-sandwich [Ru]−C≡C donor moiety, especially compared to metallocene derivatives,[22] is probably due to the in-plane metal-to-ligand charge-transfer (MLCT) transition, opposite to the out-of-plane MLCT transition for metallocenes. The results (compare **2**, **7a**, and **8**) show a large increase in hyperpolarizability on going from the benzene (**2**) to the stilbene form (**7a**). However, the addition of an extra double bond (**8**) has little influence. The decreased hyperpolarizability of **1** compared to **2** emanates most likely from the net positive charge on the ruthenium center, which leads to a decrease of the electron donor ability of the $[Ru]^+$=C=C metal fragment as compared to [Ru]−C≡C. Furthermore, the rather low β value for **6** compared to that for **2** indicates that the increased π-system is insufficient to account for the loss in hyperpolarizability as the *para* acceptor is replaced with the *meta* one. Substitution of the nitro group by a cyano acceptor (**7a** for **7b**) changes β, as generally expected from the difference in acceptor strengths.[1]

Three series of bimetallic complexes have been investigated (**5a**,**b**, **9**−**10**, and **12**−**13**) and the hyperpolarizabilities compared with the monometallic precursor complexes (**4**, **7b**, and **11**, respectively). In general, an increase of β and λ_{max} is observed upon addition of

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the metal group. Previous ZINDO-SOS calculations on (pyridine)metal pentacarbonyl compounds (analogous to **5a**,**b**) suggested that the pyridine ring remains the effective molecular acceptor; the role of the metal group is that of an inductive acceptor of the pyridine lone pair that induces a positive charge on the pyridine ring, which lowers the energy of the pyridine-centered LUMO.[20,23] By assumption that this mechanism also holds for the analogous cyano complexes (**9**−**13**), the differences in the determined hyperpolarizabilities can be explained by the different σ-acceptor effectiveness of the metal atoms attached to the cyano (pyridine for **5a**,**b**) group. Comparison of the chromium and tungsten complexes (**5a**,**b**, **9a**,**b**, and **12a**,**b**) shows that the compounds containing W, which is more capable than Cr of reducing its electron density by π back-donation to CO,[24] indeed display larger hyperpolarizabilities. Similar results have been reported for group 6 metal Fischer type carbene complexes.[25] The differences in hyperpolarizability between the Ru^{II}−Ru^{III} complexes (**10** and **13**) and the corresponding chromium and tungsten derivatives (**9a**,**b** and **12a**,**b**, respectively) show an inverse order in both series (**9**−**10** and **12**−**13**). It is apparent that an explanation for his behavior may require theoretical calculations that should reveal which effect, either the higher intrinsic electronegativity of the Ru(III) center with respect to W(0) and Cr(0) or the presence of the donor NH_3 ligands as compared to the π-acceptor CO ligands, will finally have the largest influence on the LUMO.

It is noteworthy to mention that the bimetallic complexes described in the present work show hyperpolarizabilities surpassing the largest values reported to date for bimetallic compounds.[19,26] That the larger values are determined for the metal−cyanobenzene compounds (**9a**,**b** and **10**) is not unexpected, since the precursor cyanobenzene complex **7b** is a stronger acceptor than the pyridine complex **4**.

In conclusion, a series of novel ruthenium σ-acceptor aryl−enynyl complexes, including homo- and heterobimetallic complexes, have been synthesized. The determined values of the quadratic hyperpolarizabilities, which are significantly larger than those of the more commonly studied metallocene and related derivatives, can be explained by the molecular design. Further work in this direction is in progress.

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Supporting Information Available: Text giving IR and $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ nuclear magnetic resonance spectroscopic data and elemental analytical data for **1**−**13** (9 pages). Ordering information is given on any current masthead page.

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