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Ruthenium Metallodendrimers

Dendritic Stars by Ring-Opening-Metathesis Polymerization from Ruthenium–Carbene Initiators

*Sylvain Gatard, Sylvain Nlate, Eric Cloutet, Georges Bravic, Jean-Claude Blais, and Didier Astruc**

Dendrimers are a rich and appealing field of polymer chemistry.[1] Organic polymerization from dendritic initiators also offers a route to highly branched polymers, and indeed these have been obtained, amongst other methods, by atom transfer radical polymerization (ATRP), anionic polymerization at a focal point of dendrons,[2] and cationic polymerization of styrene using star-shaped initiators.[3] Our goal was to synthesize dendritic stars by polymerization at the branch termini of a core. Therefore, we investigated the synthesis of new stable ruthenium–carbene[4–8] dendrimers[9,10] that would be able to catalyze subsequently the ring-opening-metathesis polymerization (ROMP) of norbornene.[11] Only a few metal–carbene dendrimers are known: these are tetrabranched ruthenium catalysts recently reported by the groups of Hoveyda,[4] van Koten,[5] and Verdonck.[6]

Herein, we report: a) the synthesis of new ruthenium–carbene complexes containing a chelating diphosphane, b) by modeling a dendritic branch, the reversible dimerization of these complexes in concentrated solutions, c) the extension of this synthetic route to three generations of dendritic ruthenium–carbene complexes, d) the ROMP reactions of the latter with norbornene to form metallodendritic stars, and e) the remarkable dendritic effects on the dimerization and polymerization reactions.

We designed a system that should be stable enough to support the dendritic structure and yet be reactive enough for ROMP. Therefore, we selected a chelating diphosphane-ruthenium-carbene framework. The strategy is based on recent breakthroughs. Hoveyda[4] modified the Grubbs catalyst $[RuCl_2(PCy_3)_2](CHPh)]$[7,10] (Cy = cyclohexyl) by introducing an isopropoxy substituent at the *ortho* position of the benzylidene ligand such that the hemilabile chelating ether ligand replaces one phosphane. We chose the PPh_3 version of this system as the PPh_3 group can be substituted by a chelating diphosphane unit containing a dendritic branch. Hofmann

[*] Prof. Dr. D. Astruc, Dr. S. Gatard, Dr. S. Nlate
LCOO, UMR CNRS 5802
Université Bordeaux I
33405 Talence Cedex (France)
Fax: (+33) 5-5684-6646
E-mail: d.astruc@lcoo.u-bordeaux.fr
Dr. E. Cloutet
LCPO, ENSCPB
Université Bordeaux I, 33607 Pessac Cedex (France)
Dr. G. Bravic
ICMCB, 33608 Pessac Cedex (France)
Dr. J.-C. Blais
LCSOB, UMR CNRS 7613
Université Paris VI, 75252 Paris (France)

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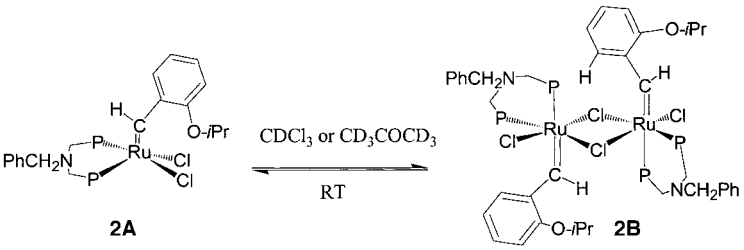
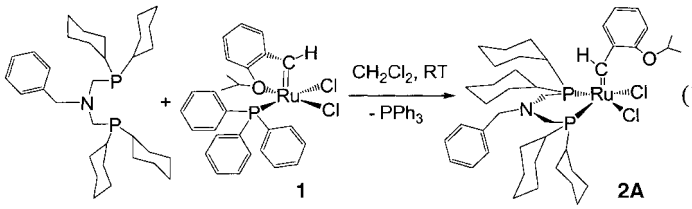
and co-workers showed that the chelating diphosphanes $t\mathrm{Bu_2P(CH_2)}_n\mathrm{P}t\mathrm{Bu_2}$ ($n=1$ or 2) could form ruthenium metathesis catalysts for ring-closing metathesis (RCM) and ROMP after activation with a Lewis acid,[12] and the groups of Fog[13] and Leitner[14] demonstrated that some neutral *cis*-bisphosphane–ruthenium complexes could also be active ROMP catalysts without the addition of a Lewis acid. The dendritic diphosphanes of Reetz et al. have already been used in catalysis[15] and for the attachment of triruthenium carbonyl clusters at the periphery.[16]



(3)

Starting from benzyl amine, we synthesized the new diphosphane model $\mathrm{PhCH_2N(CH_2PCy_2)_2}$, **1**, and the corresponding air-stable green monoruthenium-carbene complex **2** [Eq. (1)], as well as the three first generations of dendritic deep-green alkylidene complexes: **3** (G_1, Ru_4P_8), **4** (G_2, Ru_8P_{16}), and **5** (G_3, $Ru_{16}P_{32}$) in which the Ph group of **1** is replaced by the dendritic branch [Eq. (2)]. The X-ray crystal structure of **2A**[17] (Figure 1; there is a second isomer **2B**, see below) shows the geometry about the Ru center is a distorted tetragonal pyramid. It also shows that the ether group of the hemilabile ligand is not coordinated, unlike in Hoveyda's complex,[4] and confirms the chelation of the diphosphane ligand. The angle of the carbenic carbon atom with the Ru center and the aryl carbon atom is slightly larger (127°) than the classic 120° angle expected for an sp^2-hybridized carbon center. The ^{1}H NMR spectrum of **2A** in dilute $CDCl_3$ shows a triplet ($^3J_{H,P}=15.7$ Hz) at $\delta=15.66$ ppm arising from the carbene hydrogen atom. The spectrum of a concentrated $CDCl_3$ solution of **2A** indicates the presence of an additional carbene hydrogen atom ($\delta=16.96$ ppm; $^3J_{H,P}=13.3$ Hz). Likewise, the ^{31}P NMR spectrum of this concentrated solution contains, in addition to the major singlet, a doublet of doublets suggesting the presence of another ruthenium carbene complex **2B** in which the two phosphorus groups are not equivalent. The equilibrium found between these two carbene complexes **2A** and **2B** in a concentrated solution is independent of the nature of the solvent (CD_3COCD_3, $CDCl_3$) and on the addition of $n\mathrm{Bu_4NCl}$. The equilibrium constant (being the same at different concentrations) fits that of a monomer–dimer equilibrium [Eq. (3), $K=5.5\pm0.5$ mol^{-1}L at 25 °C] and is strongly temperature dependent. This equilibrium is displaced, as expected for entropic reasons, towards the dimer at −40 °C ($K=117\pm10$ mol^{-1}L). The downfield shift of the resonance



(1)

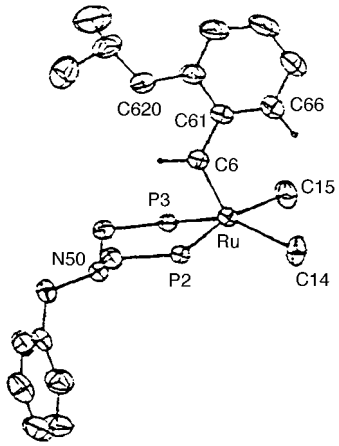
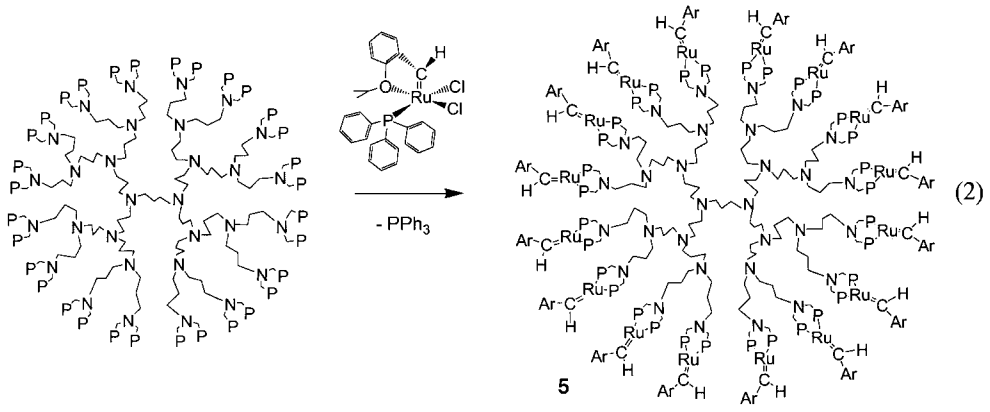


Figure 1. ORTEP diagram of the solid-state structure of **2A** (thermal ellipsoids set at 50% probability). Selected interatomic distances [Å] and angles [°]: Ru···O620, 4.565(2), Ru-P2 2.3211(6), Ru-P3 2.2798(6), Ru-Cl4 2.3889(8), Ru-Cl5 2.3975(8), C6-C61 1.464(4), Ru-C6 1.860(3); Ru-C6-C61 127. The Cy groups are omitted for clarity.



(2)

Table 1: [1]H NMR chemical shift and relative intensities for the carbene proton of the monomeric and dimeric forms of **2** and dendritic ruthenium complexes **3**–**5**. The relative intensities are given at two concentrations to show the dilution effect.

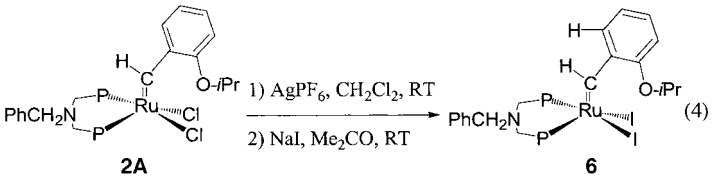
Ru complex	Monomeric form δ[a]	Rel. int.[%][b]	Rel. int.[%][c]	Dimeric form δ[a]	Rel. int.[%][b]	Rel. int.[%][c]
2	15.66	70	56	16.96	30	44
3	15.63	58	87	16.87	42	13
4	15.63	55	81	16.90	45	19
5	15.63	48	77	16.95	52	23

[a] chemical shift δ [ppm] vs $SiMe_4$ in $CDCl_3$ of the carbenic proton. [b] Diluted solution (13 mg Ru complex **2** or 5 mg dendrimer **3**–**5** in 0.3 mL $CDCl_3$). [c] Concentrated solution (34 mg Ru complex **2** or 20 mg dendrimer **3**–**5** in 0.3 mL $CDCl_3$).

signal of the phenyl hydrogen atoms of the carbene ligand found in the [1]H NMR spectra of the Grubbs-type complexes[8,11] is not observed in the [1]H NMR spectrum of Hoveyda's complex,[4] that is, when the oxygen atom of the aryl ether is coordinated to the Ru atom. This shift is observed for both species of the equilibrium of **2A** and **2B**, which discards the possibility of oxygen coordination. Evidence of similar dimeric Ru–carbene species is also found in the [1]H NMR spectrum of **3**, **4**, and **5** ($\delta \approx 16.9$ ppm; Table 1) as a minor signal in addition to the major signal from the monomeric Ru–carbene species ($\delta =$ 15.63 ppm). Remarkably, the intensity of the signal arising from the dimer in the [1]H NMR spectrum of the metallodendrimers **3**, **4**, and **5** increases with dilution contrary to that observed for **2** (**2A** + **2B** Table 1). The difference in behavior between the model complex and the dendridrimers implies the two following phenomena: 1) intradendritic dimerization between two branches is dominant over intermolecular dendritic dimerization (which is reasonable for entropic reasons), 2) the conformation of the dendritic branches depends on the concentration so that the branches expand more easily, and so have more freedom to dimerize in dilute solutions than in concentrated solutions.

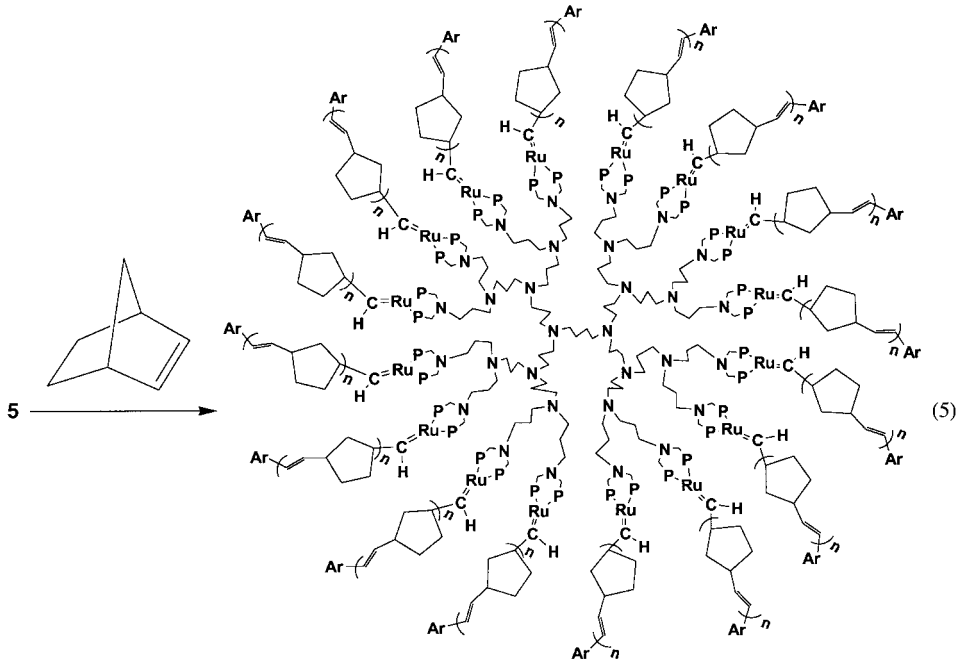
At low temperature (−40 °C), the monomer–dimer equilibrium is not changed, which is not surprising since the entropic factor present for the model is not applicable in the intradendrimer dimerization.

Addition of two equivalents of $AgPF_6$ to a solution of **2** in CH_2Cl_2 at room temperature followed by the addition of NaI in acetone gives the diiodo analogue **6** [Eq. (4)]. Dimerization in concentrated solution also occurs for **6**, and is even more marked (dimerization constant: $K = 20 \pm 2$ mol^{-1} L at 25 °C) than for the dichloro complex **2**. Thus, a new family of ruthenium carbene complexes is accessible using this sequence.



2A 6 (4)

ROMP of norbornene was found to proceed with **2** and the dendritic Ru–carbene complexes **3**–**5** at room temperature [Eq. (5); concentration 1.9×10^{-4} mol L^{-1}], although no coordination site next to the benzylidene ligand is available to generate the active metallacyclobutane intermediate in the ground state of these complexes.[18] Complex **6** is much less reactive than **2** and, for instance, no ROMP activity is observed for **6** at room temperature. These results support the



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idea that the primary coordination of an olefin is disfavored by the increased *trans* effect of iodo substituent (compared to chloro substituent) as shown by Grubbs for his catalyst.[11,18] Remarkably, ROMP proceeds more rapidly with the metallodendritic Ru–carbene complexes than for the monomeric model **2**. For instance, after 3.5 h at 25 °C in $CDCl_3$, the conversions are: **3** (G_1):94 %, >**4** (G_2):65 %, >**5** (G_3):59 %, >**2** (model):traces. A reason for the dramatically increased rate of polymerization with the dendrimers compared to **2** is that the metal–ligand bonds are more labile in the dendrimers because of interbranch collisions of the metal groups. For instance, phosphane dissociation plays an important role in the Grubbs catalyst.[18] More mechanistic and theoretical studies are needed to get a better insight into this phenomenon. Among the dendrimers, it is also interesting that the rate decreases when the generation number is increased. We believe that this negative dendritic effect arises from the increased bulk around the ruthenium centers when the generation number increases, a classic phenomenon in metallodendrimers. Indeed, the solubility of the metallodendritic carbene complex of this series drops at the fourth generation, which is also a sign of steric congestion. On the other hand, the variation of the monomer:dimer ratio upon dendritic generation increase from G_1 to G_3 is very weak and largely insufficient to explain the decrease in polymerization activity.

Gratifyingly, the molar masses of each branch could be determined after cleavage of the metallodendritic cores (Table 2). From this, we checked the number of "arms" in all cases. The fact that the observed number-average molecular weight ($\bar{M}_{n(obs)}$) are similar to the theoretical values is an excellent indication that all the Ru–carbene species of the dendrimers are efficient initiators, that is, they are converted into propagating species yielding metallodendritic stars.

In conclusion, we have synthesized new ruthenium–carbene complexes that have a chelating diphosphane ligand and characterized them thoroughly including by X-ray crystalographic studies, and we have shown that these complexes reversibly dimerize in concentrated solution. Metallodendritic analogues were synthesized for three generations, and the influence of the concentration on their dimerization was shown to be the opposite of that observed for the (nondendritic) complex **2**. This observation is consistent with an essentially intradendritic dimerization that is favored by expansion of the wedges allowed by dilution. ROMP of norbornene is much faster with the metallodendrimers than with the model, probably because interbranch collisions make the metal–ligand bonds more labile, but the polymerization rates decrease as the generation number increases as a result of the inhibiting steric effects. These dendritic effects are of interest, because they play a key role in understanding the chemistry, the catalytic properties, and the physico-chemistry of branched macromolecules.

Table 2: SEC data for the norbornene polymers obtained by cleavage of the metallodendritic stars using ethyl vinyl ether after polymerization with various norbornene (nb):Ru ratios.

Complex	nb:Ru	$\bar{M}_n$ obs[a]	$\bar{M}_w/\bar{M}_n$	$\overline{DP}_n$[a]	conv.[b]	*trans*[c]
2	100:1	5300	2.7	53.2	63	82
3	400:1	8000	3.4	85.1	100	77
4	800:1	9500	3.2	101.1	98	86
5	1600:1	9541	2.2	101.5	98	80

SEC = size exclusion chromatography, [a] Polymerization in $CDCl_3$ (4 mL); $\bar{M}_{n(obs)}$: observed number-averaged molecular weight; $\bar{M}_n$: weight-average molecular weight. $\overline{DP}_n$: average number of norbornene units in the polymer in THF based on polystyrene standard (detector: refraction indice). [b] Conversion [%] determined by ^{1}H NMR spectroscopy. [c] *trans*/*cis* Proportions: *trans* [%] determined by ^{1}H NMR spectroscopy.

Experimental Section

General procedure for the synthesis of the metal–carbene complexes: the mixture of di or dendritic phosphane DAB-dendrimer-$(N(CH_2PCy_2)_2)_{16}$ (DAB = diaminobutane) and $[RuCl_2(=CH\text{-}o\text{-}O\text{-}iPrC_6H_4)PPh_3]$ was stirred at room temperature under nitrogen for 72 h (24 h for the diphosphane). The reaction mixture was concentrated under reduced pressure to about 2 mL, and pentane (20 mL) was added. A green powder precipitated, and was then dried under high vacuum.

2: Yield: 86 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.91–2.60 (m, Cy), 1.32 (d, J = 6.5 Hz; $OCH(CH_3)_2$), 2.94 (m; NCH_2P), 3.69 (s; NCH_2Ph), 4.79 (m; $OCH(CH_3)_2$), 6.70–7.63 (m; H arom), 9.33 (d, $^1J_{H,H}$ = 7.2 Hz, 1H; H arom), 9.55 (d, $^1J_{H,H}$ = 7.2 Hz, 2H; H arom.), 15.66 (t, $^3J_{H,P}$ = 15.7 Hz; Ru=CH), 16.96 ppm (t, $^3J_{H,P}$ = 13.3 Hz; Ru=C*H* **2B**). ^{13}C NMR ($CDCl_3$,100 MHz): δ = 22.8 (s; $OCH(CH_3)_2$), 26.3–30.2 (m; Cy), 34.6 (d, $^2J_{C,P}$ = 23.2 Hz; Cy,), 35.4 (t, $^3J_{C,P}$ = 11.6 Hz; NCH_2Ph), 36.6 (d, $^2J_{C,P}$ = 23.2 Hz, Cy), 37.7 (t, $^3J_{C,P}$ = 11.6 Hz; NCH_2Ph), 38.9 (dd, $^1J_{C,P}$ = 52.6 Hz, $^3J_{C,P}$ = 23.2 Hz; Cy), 41.6 (dd, $^1J_{C,P}$ = 154.8 Hz, $^3J_{C,P}$ = 38.7 Hz; Cy), 45.5 (NCH_2P), 69.3 (NCH_2P), 70.0 (s; $OCH(CH_3)_2$), 70.5 (s, $OCH(CH_3)_2$), 112.0, 112.7, 120.7, 122.1, 128.6, 130.5, 131.1, 132.4, 134.0, 134.2, 135.0, 135.4, 135.7, 136.9, 137.2, 140.5, 143.7, 148.1, 150.4 (C arom), 291.5 (t, $^2J_{C,P}$ = 80.1 Hz; Ru=*C*H), 308.8 ppm (t, $^2J_{C,P}$ = 80.1 Hz, Ru=*C*H); ^{31}P{^{1}H,^{13}C} NMR ($CDCl_3$, 81.03 MHz): δ = 40.9 (s; CH_2PCy_2), 36.8, 412 ppm (dd, $^2J_{P,P}$ = 375 Hz, $^4J_{P,P}$ = 45.9 Hz; CH_2PCy_2); concentration of NMR sample: 0.62 mol L^{-1}; mass (*m*/*z*) calcd for $C_{43}H_{67}P_2OCl_2RuN$: 847.92; found: 812.45 (M^+−Cl), elemental analysis calcd (%) for $C_{43}H_{67}P_2OCl_2RuN$: C 60.91, H 7.96; found: C 60.42, H 7.91.

G_1 Ru_4P_8, **3**: Yield: 65 %; ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.52–4.14 (m; $OCH(CH_3)_2$, Cy, $NCH_2CH_2CH_2N$, $NCH_2CH_2CH_2CH_2CH_2N$, NCH_2–P), 4.70 (m; $OCH(CH_3)_2$), 6.45–7.88 (m; H arom), 9.40 (d, $^1J_{H,H}$ = 9,1 Hz, 4H, H arom), 9.67 (m; H arom), 15.63 (t, $^3J_{H,P}$ = 15,6 Hz, 4H; Ru=CH monomer), 16.87 (m; Ru=CH dimer). ^{31}P{^{1}H,^{13}C} NMR ($CDCl_3$, 81.03 MHz): δ = 40.9 (s, CH_2PCy_2), 38.6–42,1 (m, not well resolved, CH_2PCy_2);concentration of NMR sample: 2×10^{-2} mol L^{-1}; elemental analysis calcd (%) for $C_{160}H_{272}Cl_8N_6O_4P_8Ru_4$: C 58.59, H 8.36; found: C 57.64, H 8.35.

G_2 Ru_8P_{16}, **4**: Yield: 63 %. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.52–4.15 (m; $OCH(CH_3)_2$, Cy, $NCH_2CH_2CH_2N$, $NCH_2CH_2CH_2CH_2CH_2N$, NCH_2-P), 4.71 (m; $OCH(CH_3)_2$), 6.45–8.07 (m; H arom), 9.40 (d, 8H; H arom), 9.63 (m, 16H; H arom), 15.63 (br., 8H, Ru=CH monomer), 16.90 ppm (br.; Ru=CH dimer). ^{31}P{^{1}H,^{13}C} NMR ($CDCl_3$, 81.03 MHz): δ = 40.89 (s; CH_2PCy_2), 38.6–42,1 (m, not well resolved; CH_2PCy_2);concentration of NMR sample: 1.23×10^{-2} mol L^{-1}; elemental analysis calcd (%) for $C_{328}H_{560}Cl_{16}Ru_8O_8P_{16}N_{14}$: C 58.80, H 8.42; found: C 58.64, H 8.25.

G_3 $Ru_{16}P_{32}$, **5**: Yield: 60 %. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.24–4.25 (m; $OCH(CH_3)_2$, Cy, $NCH_2CH_2CH_2N$, $NCH_2CH_2CH_2CH_2CH_2N$, NCH_2-P), 4.71 (m; $OCH(CH_3)_2$), 6.45–8.07 (m; H arom.), 9.40 (m, 16H; H arom.), 9.63 (m, 32H; H arom.), 15.63 (br., 16H; Ru=CH monomer), 16.95 ppm (br.; Ru=CH dimer). ^{31}P{^{1}H,^{13}C} NMR ($CDCl_3$, 81.0 MHz): δ = 40.9 (s; CH_2PCy_2), 38.6–42,1 (m, not well resolved; CH_2PCy_2); concentration of NMR sample: 5.0×10^{-3} mol L^{-1}; ele-

mental analysis calcd (%) for $C_{664}H_{1136}Cl_{32}Ru_{16}O_{16}P_{32}N_{30}$: C 58.90, H 8.46; found: C 58.73, H 8.61.

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Concentration Affects NLO Behavior

Large, Concentration-Dependent Enhancement of the Quadratic Hyperpolarizability of $[Zn(CH_3CO_2)_2(L)_2]$ in $CHCl_3$ on Substitution of Acetate by Triflate**

Francesca Tessore, Dominique Roberto, Renato Ugo, Patrizia Mussini, Silvio Quici, Isabelle Ledoux-Rak, and Joseph Zyss*

Organometallic and coordination compounds can offer a great diversity of tunable electronic properties that act on their second-order nonlinear optical (NLO) response.[1] The quadratic hyperpolarizability, measured by the electric field

[*] Prof. D. Roberto, Dr. F. Tessore, Prof. R. Ugo
Dipartimento di Chimica Inorganica Metallorganica e Analitica
dell'Università di Milano
INSTM UdR di Milano and
Istituto di Scienze e Tecnologie Molecolari del CNR (ISTM)
Via G. Venezian, 21, 20133 Milano (Italy)
Fax: (+39) 02-5031-4405
E-mail: dominique.roberto@unimi.it
Prof. P. Mussini
Dipartimento di Chimica Fisica ed Elettrochimica
dell'Università di Milano
Via G. Venezian, 21, 20133 Milano (Italy)
Dr. S. Quici
Istituto di Scienze e Tecnologie Molecolari del CNR (ISTM)
Via C. Golgi 19, 20133 Milano (Italy)
Prof. I. Ledoux-Rak, Prof. J. Zyss
LPQM, Ecole Normale Supérieure de Cachan
61 avenue du Président Wilson, 94230 Cachan (France)

[**] L = 4,4′-*trans*-$NC_5H_4(CH{=}CH)C_6H_4NMe_2$ or *trans*,*trans*-$NC_5H_4(CH{=}CH)_2C_6H_4NMe_2$. This work was supported by the MIUR and by the CNR (Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate II, year 2000, Research Title: *Sintesi e sviluppo di composti molecolari organometallici e di coordinazione con proprietà di ottica non lineare (NLO) e con proprietà elettriche anisotropiche e isotropiche*).

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