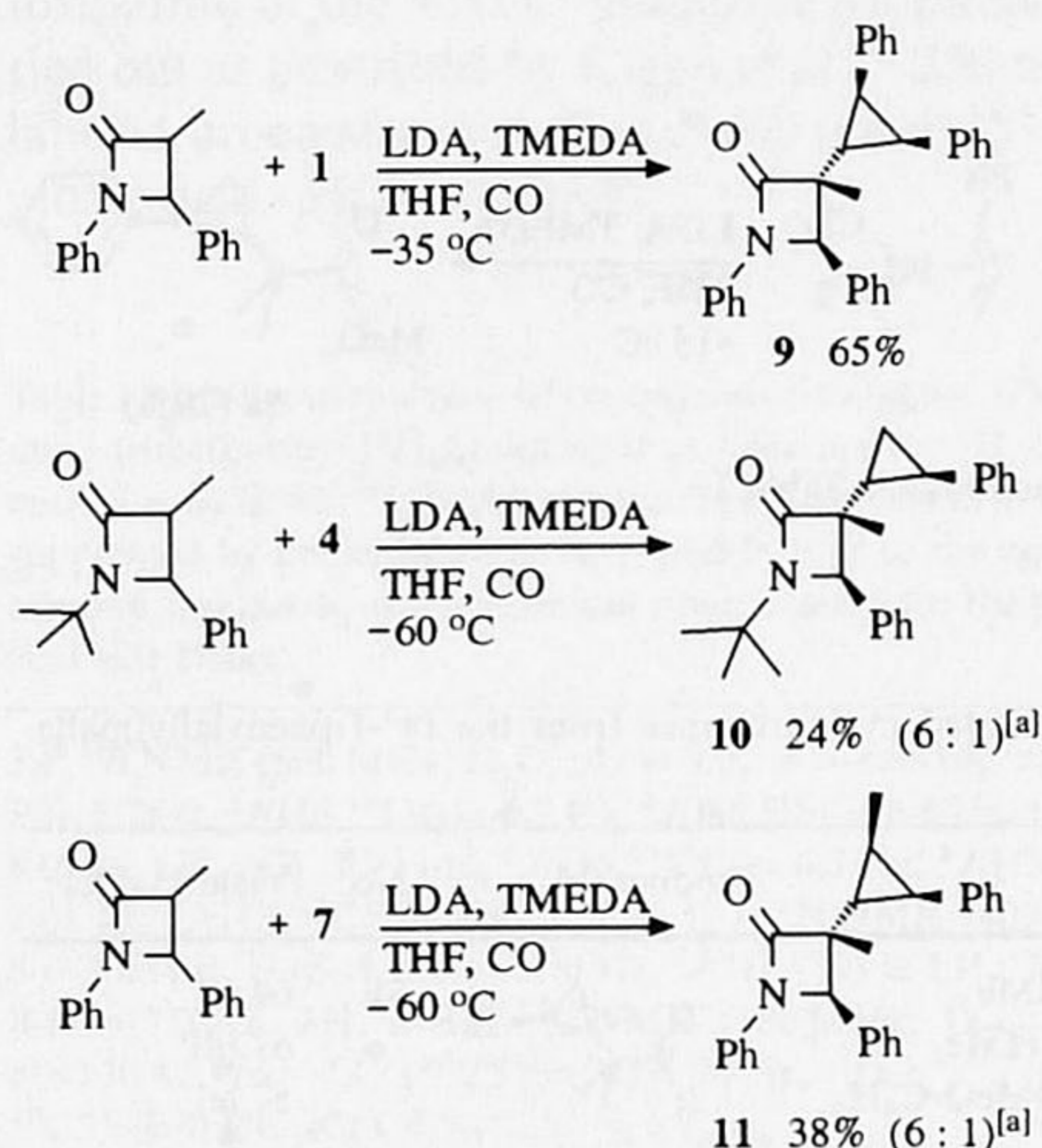


The cyclopropanation was also applied to  $\beta$ -lactams, which are of potential interest in medicinal chemistry. Again, preparation of the mixed 1-methyl-2-phenylcyclopropane derivative with complex **7** was feasible (Scheme 4). Regarding the stereochemis-



Scheme 4. [a] Mixture of diastereomers (not separable by column chromatography).

try, the phenyl groups, which are *W*-configured in the  $\eta^3$ -allyl complex **1**, are *cis* to each other in the products and therefore, potentially repel each other. The incoming nucleophile is *trans* to the two phenyl groups. Similarly, the *W*-configured  $\eta^3$ -allyl complex **7** furnishes cyclopropane derivatives **8** (Scheme 3) and **11** (Scheme 4), in which the methyl and phenyl groups are *cis* to each other. Thus, in all reactions studied the formation of substituted cyclopropane is clearly disrotatory (13 examples).<sup>[4]</sup>

In summary, nucleophilic cyclopropanation of ( $\eta^3$ -allyl)palladium complexes is facilitated by terminal phenyl groups relative to methyl groups in the allyl ligand (aryl effect). The cyclopropanes are built up stereoselectively, and a quarternary carbon center<sup>[5]</sup> exocyclic to the three-membered ring is installed with ease.

#### Experimental Procedure

Tetrahydrofuran was distilled over sodium/benzophenone under nitrogen. ( $\eta^3$ -Allyl)palladium complexes were prepared from allyl alcohols or allyl chlorides by the method of Bosnich et al. [2a].

General procedure for generating carbanions: To a solution of lithium diisopropylamide (LDA) (1.1 mmol) or potassium bis(trimethylsilyl)amide (KHMDs) (1.66 mL, 1.1 mmol, 15% in toluene) in dry THF (5 mL) under nitrogen was added the protonated nucleophile (1.1 mmol) at  $-78^\circ\text{C}$ . After the solution had been stirred for 10 min it was warmed up to  $0^\circ\text{C}$  and 10 min later recooled to  $-78^\circ\text{C}$ . If LDA was used as a base, TMEDA (0.17 mL, 1.1 mmol) was added, and the resulting solution was stirred until required.

Cyclopropanation: The dimeric ( $\eta^3$ -allyl)palladium chloride complex (0.275 mmol) in dry THF (5 mL) was placed in an oven-dried flask under nitrogen. The solution was cooled to  $-78^\circ\text{C}$  and TMEDA (0.17 mL) was added. After warming the mixture to the temperature given in the Tables, the carbanion solution (see above) was added dropwise through a double-tipped needle. Attachment of a CO balloon caused the reaction mixture to turn black and palladium to precipitate. After stirring for 30 min and warming to room temperature, the solvent was evaporated in vacuo and diethyl ether (50 mL) was added. The mixture was filtered and the filtrate washed with water. The aqueous layer was re-extracted with diethyl ether and the combined organic layers were washed with brine (20 mL), dried with  $\text{MgSO}_4$ , and concentrated. The resulting oil was purified by flash chromatography (silica gel, cyclohexane/diethyl ether, 5:1) to give the product as a colorless oil or solid.

Spectroscopic data of **3a**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  = 7.02 (m, 10H,  $\text{H}_{\text{arom}}$ ), 3.72 (s, 3H,  $\text{OCH}_3$ ), 2.45 (d,  $J$  = 6 Hz, 2H,  $\text{PhCH}$ ), 2.09 (t,  $J$  = 6 Hz, 1H, cyclopropyl CH), 1.29 (s, 6H,  $(\text{CH}_3)_2\text{C}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz, APT(Attached Proton Test) technique: primary and tertiary carbons give negative ( $\downarrow$ ) signals,

secondary and quarternary carbons give positive ( $\uparrow$ ) signals:  $\delta$  = 177.78 $\uparrow$ , 137.84 $\uparrow$ , 128.96 $\downarrow$ , 127.73 $\downarrow$ , 125.73 $\downarrow$ , 51.91 $\downarrow$ , 41.71 $\uparrow$ , 33.49 $\downarrow$ , 27.41 $\downarrow$ , 23.48 $\downarrow$ .

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### Copper(II)-Mediated Oxidative Coupling of Bis(dimethylaminomethyl)aryl ruthenium Complexes to give [(terpy)Ru<sup>III</sup>(pincer-pincer)-Ru<sup>III</sup>(terpy)](CuCl<sub>2</sub>)<sub>4</sub>\*\*

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In the course of our studies on the catalytic, electro-, and photochemical properties of bis(dimethylaminomethyl)aryl metal complexes in which the aryl ligand is the monoanionic

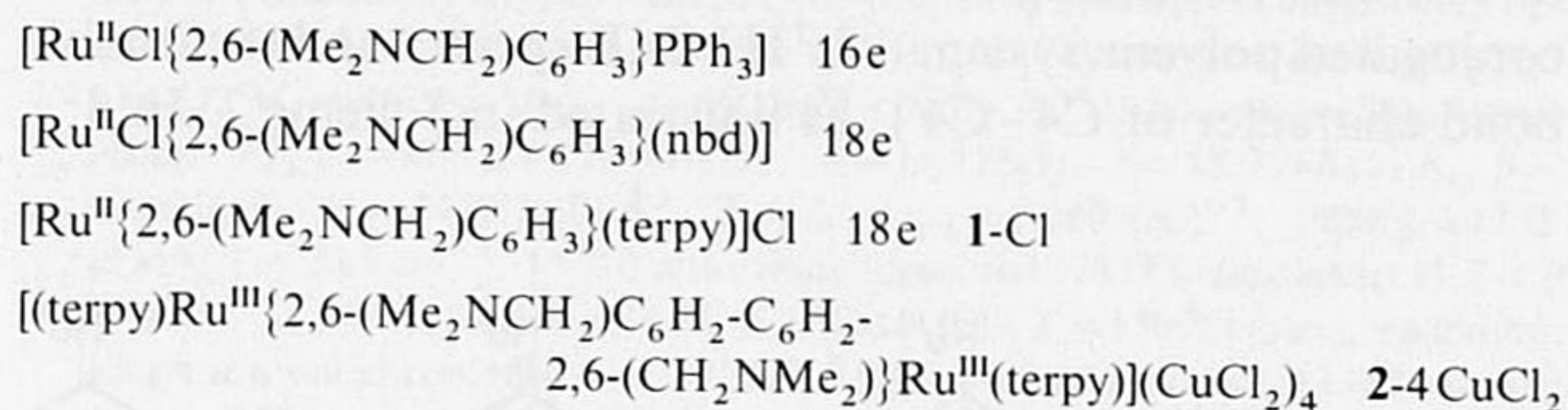
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[\*\*] This work was supported in part (A. L. S. and N. V.) by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO). This collaborative work is part of a COST-D4 approved programme. Ligand abbreviations: pincer = [2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sup>-</sup>, pincer-pincer = [2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>-2,6-(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]<sup>2-</sup>, dpb-dpb = [2,6-(2-pyridyl)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>-2,6-(2-pyridyl)<sub>2</sub>]<sup>2-</sup>, terpy = 4'-(*p*-tolyl)-2,2':6',2''-terpyridine, terpy = 2,2':6',2''-terpyridine.

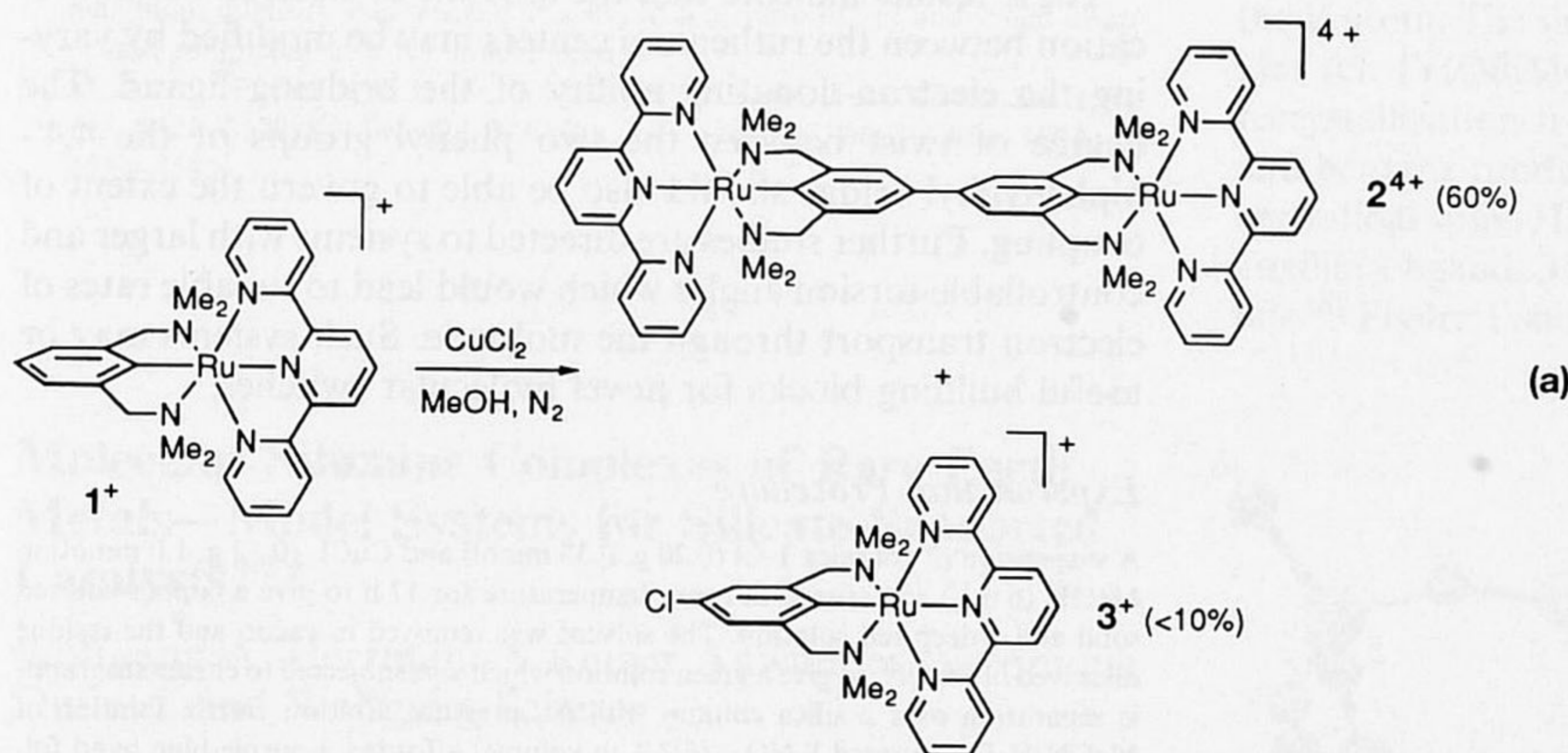
[2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>]<sup>-</sup> (*trans*-pincer),<sup>[1]</sup> we synthesized a series of novel 16e<sup>-</sup> and 18e<sup>-</sup> complexes of Ru<sup>II</sup> (Scheme 1).<sup>[2]</sup> We now report that **1-Cl** undergoes a selective C4–C4' coupling mediated by CuCl<sub>2</sub> leading to the formation of a unique binuclear complex **2-4CuCl<sub>2</sub>**, abbreviated as [(terpy)Ru<sup>III</sup>(pincer-pincer)Ru<sup>III</sup>(terpy)](CuCl<sub>2</sub>)<sub>4</sub>. Surprisingly **2<sup>4+</sup>** is diamagnetic and



Scheme 1. Bis(dimethylaminomethyl)aryl Ru<sup>II</sup> complexes. nb = norbornadiene.

has as striking structural feature a perfectly planar 4,4'-biphenyldiyl bridge connecting the two Ru<sup>III</sup> centers. Moreover, the mixed-valence complex **2<sup>3+</sup>** displays strong electronic communication between the two metal centers.<sup>[3]</sup>

Complex **1-Cl** is an air-stable and water-soluble complex. Its reaction with three equivalents of CuCl<sub>2</sub> in dry and O<sub>2</sub>-free MeOH, led to the green complex **2-4CuCl<sub>2</sub>** in good yield (60%) together with a minor deep red product (<10%), which was identified as **3-PF<sub>6</sub>** [Eq. (a)]. Complex **2-4CuCl<sub>2</sub>** is slightly sol-



uble in CH<sub>2</sub>Cl<sub>2</sub> but has a good solubility in polar solvents like MeCN, MeOH, or H<sub>2</sub>O. Analytical data (<sup>1</sup>H NMR, FAB-MS, and cyclic voltammetry (CV)) suggested that not only oxidation of the Ru<sup>II</sup> center in **1** to Ru<sup>III</sup> had occurred but also that **2<sup>4+</sup>** is a diruthenium species formed by coupling of two units of **1<sup>+</sup>**.

The formation of **2-4CuCl<sub>2</sub>** by oxidation of **1-Cl** is unexpected in view of our early findings that oxidation of the arylnickel(II) complex [Ni<sup>II</sup>{2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}X] (X = Cl, Br) with dihalogens or copper(II) halides results in quantitative formation of the trivalent arylnickel complex [Ni<sup>III</sup>{2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>}X<sub>2</sub>]. Thus, in the latter reaction a clean one-electron oxidation of the nickel center occurs,<sup>[1]</sup> whereas the reaction of **1<sup>+</sup>** with Cu<sup>II</sup> leads to oxidation of both the ruthenium(II) center and the aryl ring. Formally the formation of **2<sup>4+</sup>** can be seen as an oxidation of the C4–H bond. Obviously in the course of this process, besides C–C coupling, also competing ligand-transfer oxidation of the mononuclear ruthenium(III) intermediate with CuCl<sub>2</sub> takes place leading to formation of the 4-Cl derivative **3<sup>+</sup>**.

An X-ray structure determination<sup>[4]</sup> established that **2<sup>4+</sup>** is indeed a binuclear complex containing a perfectly planar 4,4'-biphenyldiyl unit which connects the two octahedrally coordinated ruthenium centers through C1 and C1', respectively. A PLUTON view is presented in Figure 1. Each ruthenium center

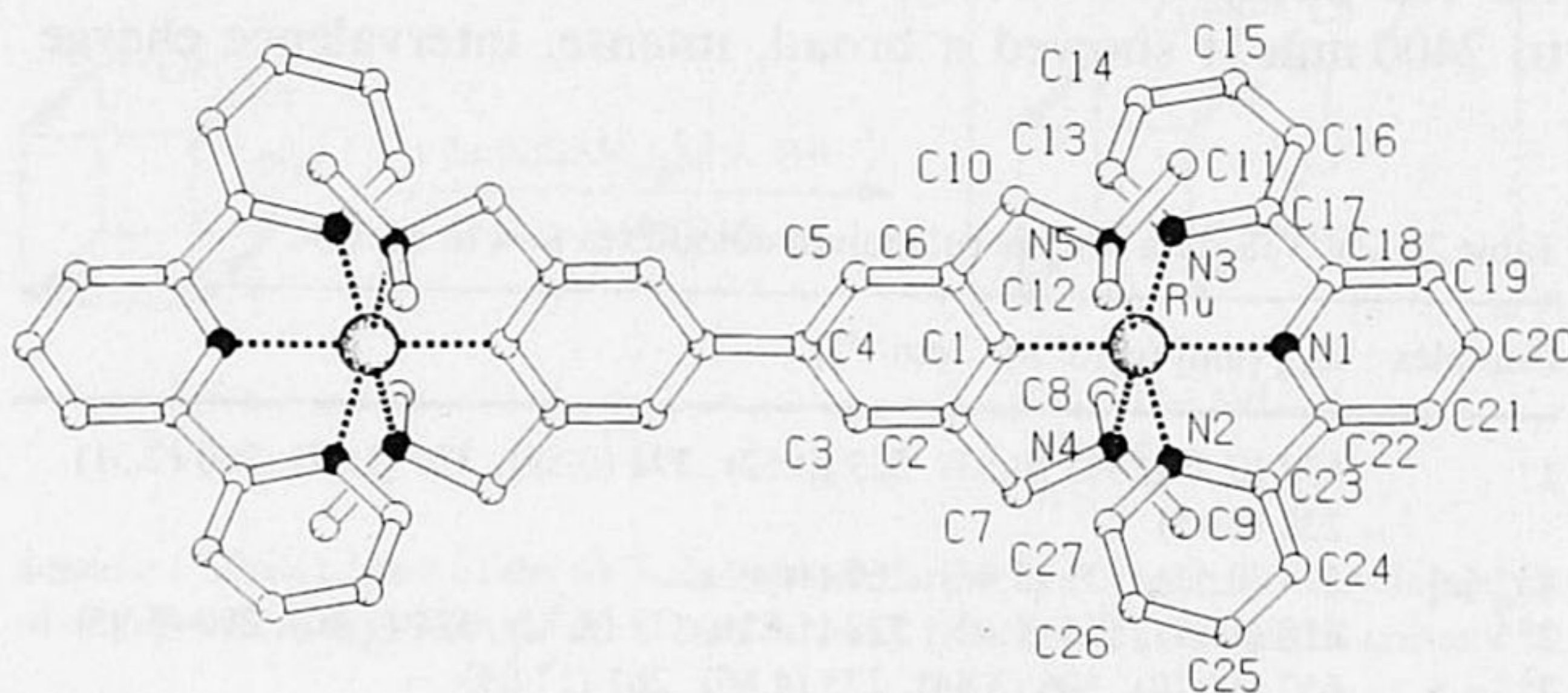


Fig. 1. PLUTON plot of the solid-state structure of **2-4CuCl<sub>2</sub>**. The CuCl<sub>2</sub><sup>-</sup> ions, diethyl ether molecules (solvent of crystallization), and hydrogen atoms are omitted for clarity. Relevant bond lengths [Å], bond angles [°] and dihedral angles [°] are included in the text.

is coordinated by the three nitrogen atoms of a terpy and by three atoms of the *N,C,N'* bis-chelating pincer-pincer ligands. Both ruthenium atoms have a formal oxidation state of +3 leading to a cationic charge of +4 for the organometallic part,

which is counterbalanced by the presence of four CuCl<sub>2</sub><sup>-</sup> ions in the unit cell.<sup>[4]</sup> The Ru···Ru intermetallic distance is 10.829(2) Å. A comparison of the various C–C bond lengths in the 4,4'-biphenyldiyl moiety of **2<sup>4+</sup>** shows considerable differences amounting to 0.08 Å, (C2–C3, 1.361(12) vs. C3–C4, 1.441(15) Å), whereas the central C4–C4' bond length has the value of a substantially shortened C–C single bond (1.436(12) Å). These data clearly show that at least in the solid state the π system of the 4,4'-biphenyldiyl bridging moiety in **2<sup>4+</sup>** is completely conjugated between the two Ru<sup>III</sup> metal centers. The extent of this conjugation is reflected in the electrochemical data (CV) of **2<sup>4+</sup>** which

have been compared with those of the mononuclear complexes **1<sup>+</sup>** and **3<sup>+</sup>** (Table 1). Cation **2<sup>4+</sup>** can be reduced to the Ru<sup>II</sup>Ru<sup>III</sup> mixed-valence complex, **2<sup>3+</sup>**, and subsequently to the Ru<sup>II</sup>Ru<sup>II</sup> complex, **2<sup>2+</sup>**. Highly interesting is the large value of *K<sub>c</sub>* (1250) (see Table 1) calculated from the electrochemical data

Table 1. Electrochemical data of complexes **1–4** in MeCN.

Complex [a]	<i>E</i> <sub>1/2</sub> [V] vs. SCE				<i>K<sub>c</sub></i> [b]
	III/II	III,III/III,II	III,II/II,II	II,I [c]	
<b>1<sup>+</sup></b>	0.23	–	–	–1.63	–
<b>2<sup>2+</sup></b>	–	0.24	0.065	–1.66	1250
<b>3<sup>+</sup></b>	0.27	–	–	–	–
<b>4<sup>2+</sup></b> [d]	–	0.505	0.34	–1.55	600

[a] The overall charge corresponds to the complexes with the ruthenium centers in the +2 formal oxidation state. [b] Comproportionation constant. [c] This situation most probably involves the reduced ligand (terpy or terpy) and a divalent Ru center. [d] From ref. [6].

which points to strongly coupled ruthenium centers. The Ru<sup>II</sup>Ru<sup>II</sup> complex **2**<sup>2+</sup> could be independently synthesized from the reaction of **2**<sup>4+</sup> with hydrazine. The UV/VIS spectral values,  $\lambda_{\text{max}}$  and  $\epsilon_{\text{max}}$ , for the mononuclear and binuclear Ru complexes are given in Table 2. The NIR spectrum of the mixed-valence Ru<sup>II</sup>Ru<sup>III</sup> complex, **2**<sup>3+</sup>, obtained by in situ oxidation of the Ru<sup>II</sup>Ru<sup>II</sup> complex with Br<sub>2</sub>,<sup>[5]</sup> was recorded in MeCN from 900 to 2400 nm. It showed a broad, intense, intervalence charge

Table 2. UV/VIS data for the ruthenium complexes 1–4 in MeCN.

Complex	$\lambda_{\text{max}}$ [nm] ( $\epsilon$ [10 <sup>4</sup> M <sup>-1</sup> cm <sup>-1</sup> ])
<b>1</b> <sup>+</sup>	632 (0.55), 593 (0.53), 523 (0.52), 392 (0.59), 324 (3.07), 280 (2.31), 238 (2.15)
<b>1</b> <sup>2+</sup> [a]	574 (0.55), 331 (3.45), 269 (16.05)
<b>2</b> <sup>2+</sup>	618 (1.58), 593 (1.67), 528 (1.81), 377 (3.72), 324 (7.30), 280 (5.95)
<b>2</b> <sup>3+</sup>	657 (11.70), 306 (3.84), 275 (4.66), 201 (17.03)
<b>4</b> <sup>2+</sup>	543 (3.06), 516 (3.06), 287 (11.29), 220 (6.75) [b]

[a] Obtained by in situ oxidation. [b] From ref. [6].

transfer (IVCT) band at 1875 nm ( $\epsilon = 33\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ) with a small overlapping band at 1650 nm (Fig. 2). As expected no NIR band was found for the Ru<sup>II</sup>Ru<sup>II</sup> and Ru<sup>III</sup>Ru<sup>III</sup> species.

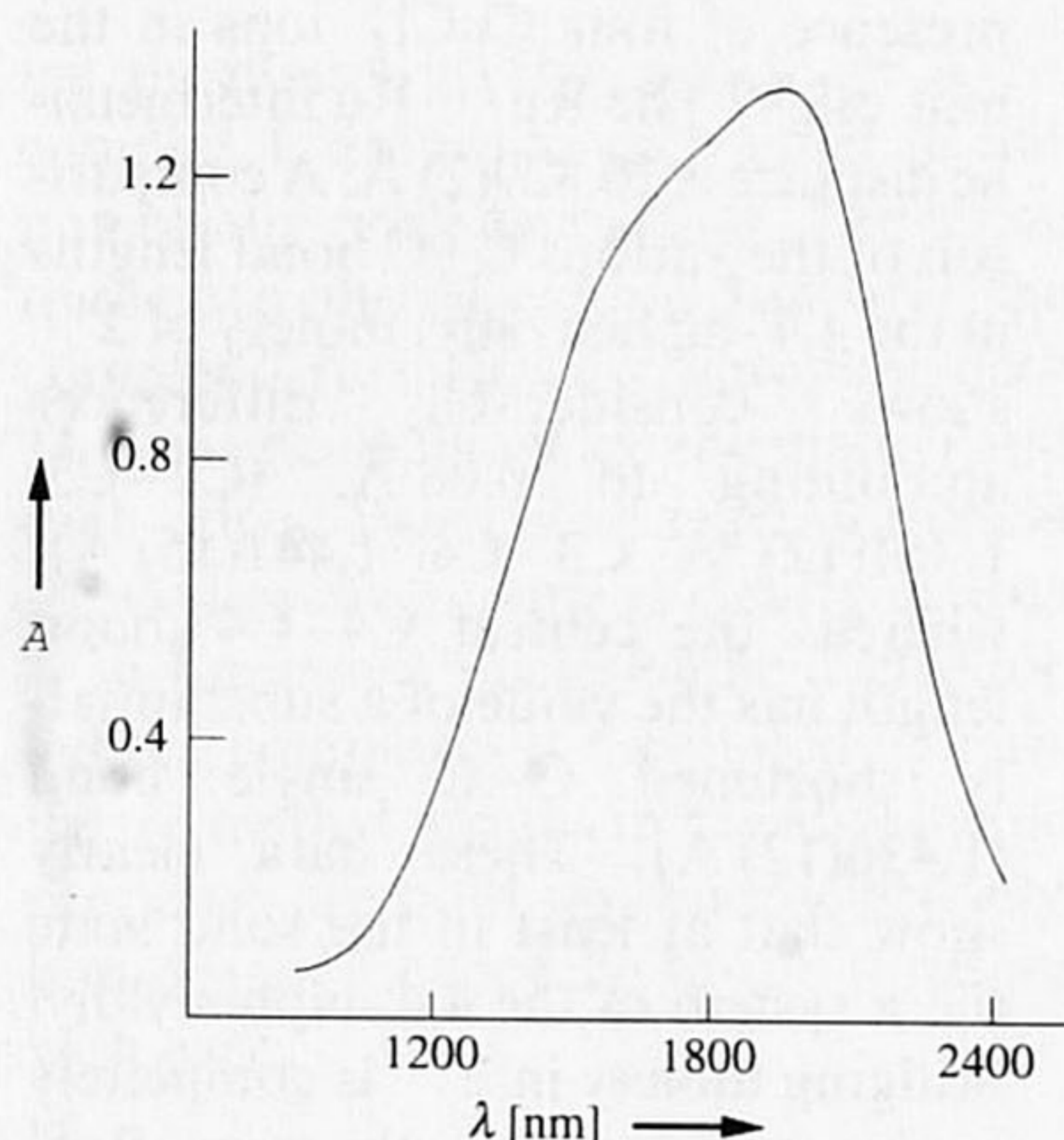
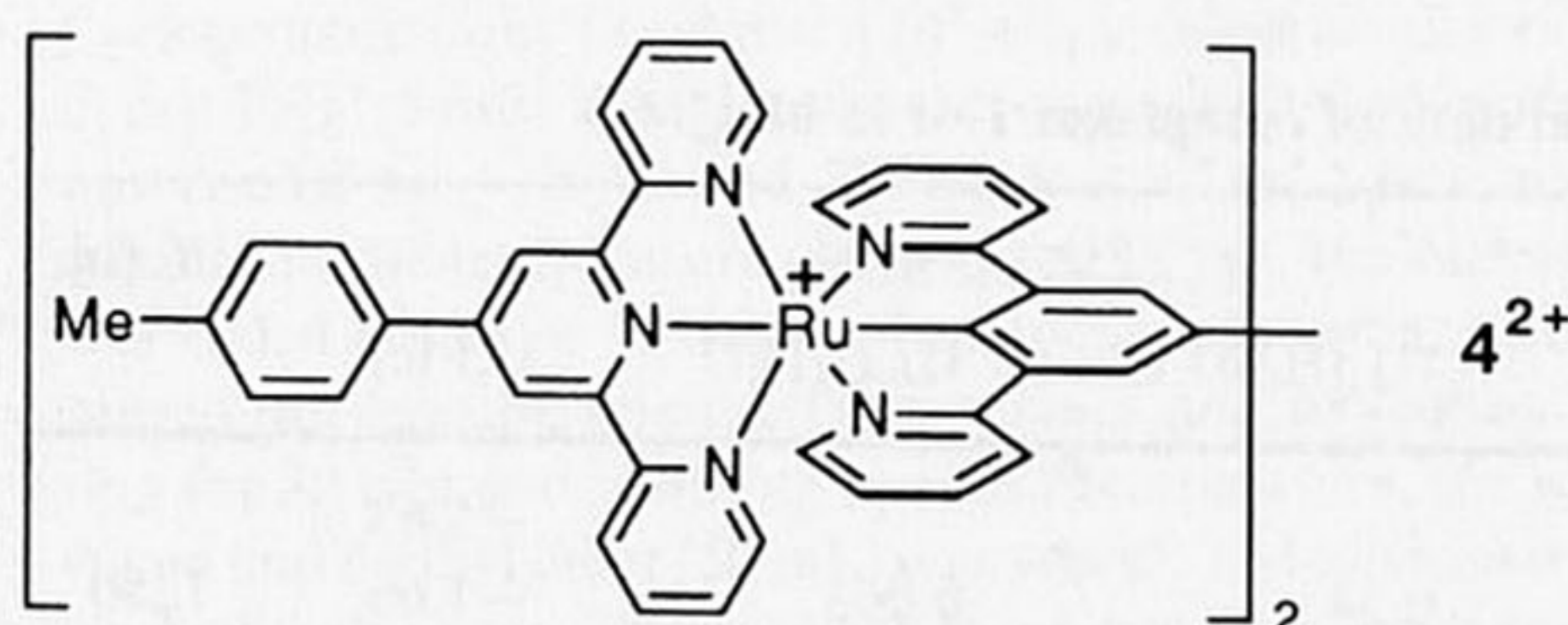


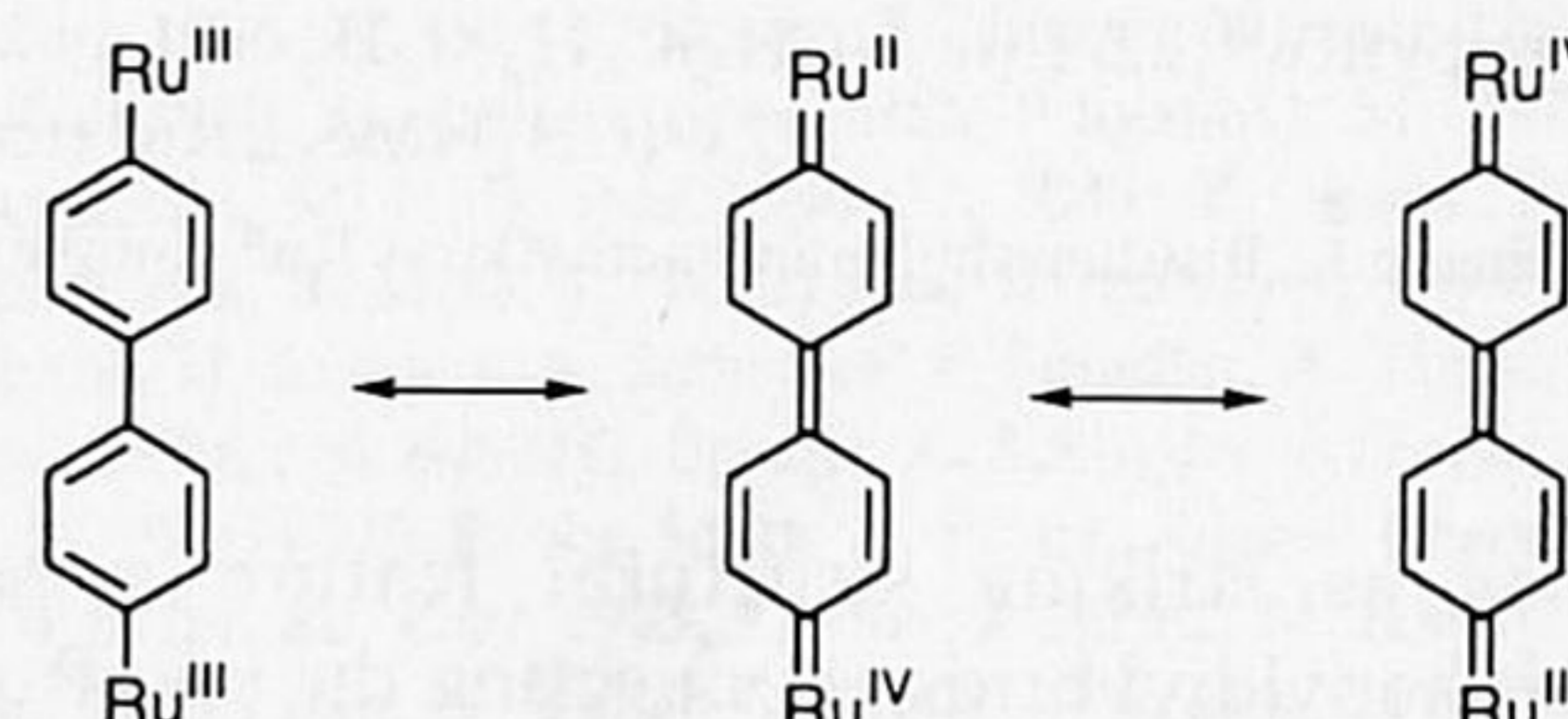
Fig. 2. NIR spectrum of complex **2**<sup>3+</sup> in the intervalence charge transfer region.

Recently, we reported a similar C–C coupling in the metalation reaction of the potentially terdentate N–C–N ligand 1,3-di(2-pyridyl)benzene (dpb-H) with [Ru(tterpy)]<sup>3+</sup> in the presence of oxygen and silver.<sup>[6]</sup> In the course of that reaction likewise not only a carbon–ruthenium but also a carbon–car-



bon bond was formed which led to **4**<sup>2+</sup>·2PF<sub>6</sub>. The electrochemical and relevant spectroscopic data of **4**<sup>n+</sup> have been included in Tables 1 and 2. A comparison of these data and the structural features of **4**<sup>n+</sup> with those of **2**<sup>p+</sup> leads to the following results.

Binuclear **2**<sup>3+</sup> is among the strongest coupled diruthenium species ( $K_c = 1250$ , NIR band at 1875 nm,  $\epsilon = 33\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ) in spite of a large intermetallic distance (Ru<sup>III</sup>...Ru<sup>III</sup> separation of 10.829(2) Å; this distance is 11.009(2) Å in **4**<sup>2+</sup>). The dihedral angle between the phenyl rings in the 4,4'-biphenyldiyl moiety is practically 0° in **2**<sup>4+</sup> (vs. 22.2(7)° in **4**<sup>2+</sup>). The Ru<sup>III</sup>-4,4'-biphenyldiyl-Ru<sup>III</sup> central unit of **2**<sup>4+</sup> (Ru–C is 1.901(8) Å vs. 1.96(2) Å in **4**<sup>2+</sup>) can be envisaged as a diamagnetic formally Ru<sup>II</sup>–Ru<sup>IV</sup> conjugated polyene system (cf. <sup>1</sup>H NMR spectra and the double bond character of C4–C4'), as illustrated in Scheme 2. In **4**<sup>2+</sup>



Scheme 2. Limiting forms for the Ru<sup>III</sup>-4,4'-biphenyldiyl-Ru<sup>III</sup> system of **2**<sup>4+</sup>.

C4–C4' is 1.51(1) Å with normal aromatic C–C distances in each ring. By changing the CH<sub>2</sub>NMe<sub>2</sub> chelating groups of **2**<sup>3+</sup> for 2-pyridyl units as in **4**<sup>3+</sup>, the electronic communication between the metal centers is decreased ( $K_c = 600$ , NIR band at 1620 nm,  $\epsilon = 26\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ).

These results indicate that the amount of electron communication between the ruthenium centers may be modified by varying the electron-donating ability of the bridging ligand. The degree of twist between the two phenyl groups of the 4,4'-biphenyldiyl bridge should also be able to govern the extent of coupling. Further studies are directed to systems with larger and controllable torsion angles which would lead to tunable rates of electron transport through the molecule. Such systems may be useful building blocks for novel molecular switches.

### Experimental Procedure

A suspension of complex **1**-Cl (0.20 g, 0.35 mmol) and CuCl<sub>2</sub> (0.13 g, 1.0 mmol) in MeOH (6 mL) was stirred at room temperature for 17 h to give a copper-colored solid and a deep red solution. The solvent was removed in vacuo and the residue dissolved in MeCN, to give a green solution which was subjected to chromatographic separation over a silica column with N<sub>2</sub> pressure. Elution with a solution of MeCN/H<sub>2</sub>O/saturated KNO<sub>3</sub>, (6/3/1 in volume) afforded a purple-blue band followed by a red one. The column was then eluted with a 5/5/1 mixture of the previous solvents to afford a major green band. The following workup was then applied to all three fractions: the solutions were concentrated to 1/3 in vacuo, an excess of NH<sub>4</sub>PF<sub>6</sub> in solution in H<sub>2</sub>O was added and the precipitate that formed was filtered off and washed with H<sub>2</sub>O and Et<sub>2</sub>O. The red fraction gave a deep red solid identified as complex **3**-PF<sub>6</sub> (0.04 g) and the green band gave a bronze-colored solid. The latter was dissolved in MeCN (2–3 mL), and the solution was added to CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and toluene (5–8 mL) to give the micro-crystalline red complex **2**<sup>4+</sup> (170 mg, 60%) with PF<sub>6</sub><sup>-</sup> as counteranion.

Elemental analysis for **2**-4PF<sub>6</sub> + CH<sub>2</sub>Cl<sub>2</sub> C 38.54, H 3.53, N 8.17 %; found C 38.88, H 3.76, N 7.98 %. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN and some N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, 25 °C TMS):  $\delta$ (**2**<sup>2+</sup>) = 8.64 (d, <sup>3</sup>J(H,H) = 8.0, 4H), 8.49 (d, <sup>3</sup>J(H,H) = 7.8, 4H), 8.30 (d, <sup>3</sup>J(H,H) = 4.9, 4H), 7.98 (m, 6H), 7.68 (s, 4H), 7.50 (m, 4H), 3.75 (s, 8H; CH<sub>2</sub>), 1.25 (s, 12H; NMe<sub>2</sub>);  $\delta$ (**3**-PF<sub>6</sub>) = 8.60 (d, <sup>3</sup>J(H,H) = 8.0, 2H), 8.45, 8.19 (2m, 4H), 7.98 (t, <sup>3</sup>J(H,H) = 8.0, 1H), 7.91, 7.43 (2m, 4H), 7.24 (s, 2H), 3.60 (s, 4H; CH<sub>2</sub>), 1.18 (s, 12H; NMe<sub>2</sub>); FAB-MS (nitrobenzyl alcohol matrix):  $m/z$  (**2**<sup>2+</sup>): 1195.0, (1195 for (**2**-PF<sub>6</sub>)<sup>+</sup>);  $m/z$  (**3**<sup>2+</sup>): 705.0, (705.0 for (**3**-PF<sub>6</sub>)<sup>+</sup>).

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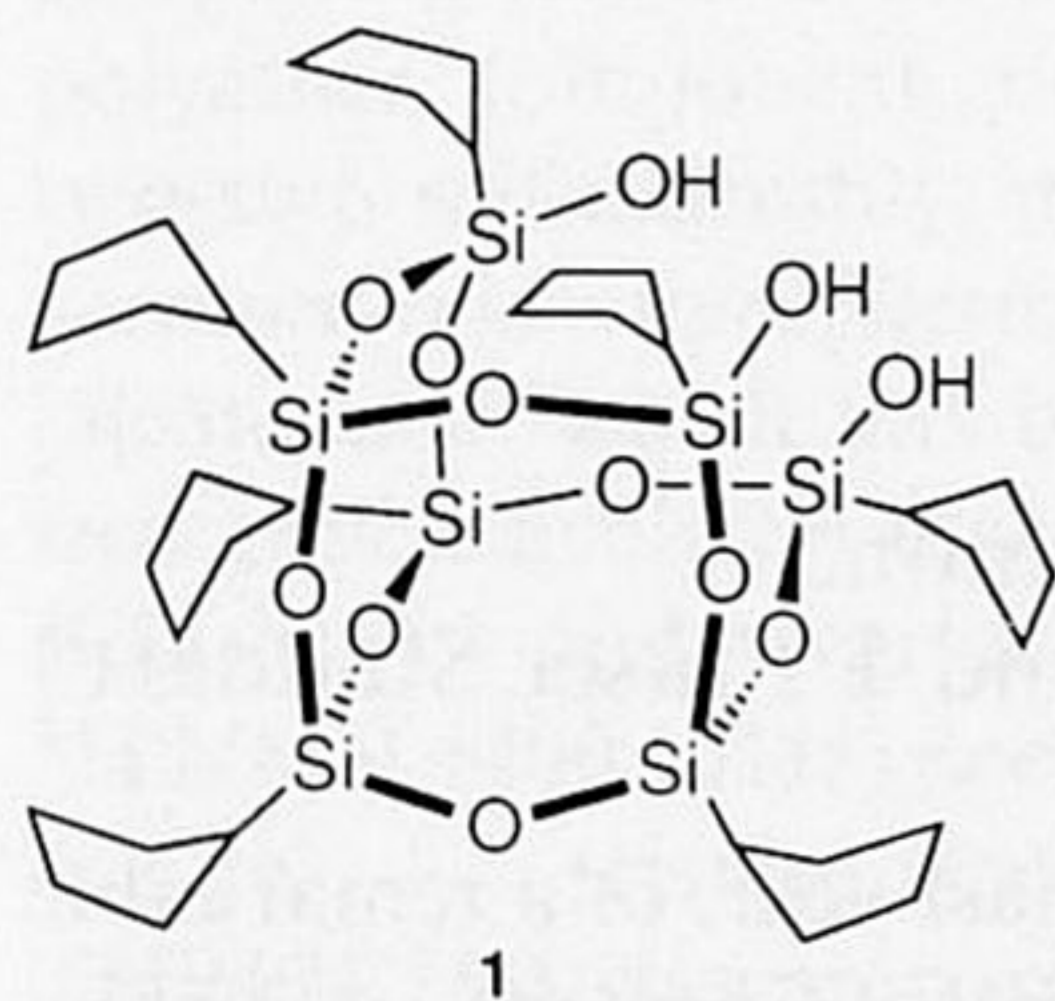
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- [4] 2-4CuCl<sub>2</sub> was crystallized without chromatographic purification, (see Experimental Procedure). Crystals suitable for the X-ray structure analysis were obtained from MeOH/CH<sub>2</sub>Cl<sub>2</sub> layered with Et<sub>2</sub>O. Crystal data for 2-4CuCl<sub>2</sub> · 2Et<sub>2</sub>O, *M<sub>r</sub>* = 867.65, dark crystal (0.20 × 0.20 × 0.25 mm), monoclinic, space group *P*2<sub>1</sub>/*c* with *a* = 12.1907(19), *b* = 18.115(3), *c* = 18.9597(17) Å, β = 125.01(1)°, *V* = 3429.3(10) Å<sup>3</sup>, *Z* = 2, ρ<sub>calcd</sub> = 1.680 g cm<sup>-3</sup>, *F*(000) = 1752, μ(MoKα) = 20.1 cm<sup>-1</sup>, 17010 reflections measured, 7877 independent (1.7 < θ < 27.5°, ω/2θ scan, Δω = (1.28 + 0.35tan θ°), *T* = 150 K, MoKα radiation, graphite monochromator, λ = 0.71073 Å) on an Enraf-Nonius CAD4T rotating anode diffractometer. Data were corrected for Lorentz and polarization effects and for a linear decay of 3%. An empirical absorption correction was applied (DIFABS, correction range 0.819–1.277). The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92). Refinement on *F* was carried out by full-matrix least squares techniques (SHELX76); final *R* value 0.0588, *wR* = 0.0559, *w* = 1/[*s*<sup>2</sup>(*F*) + 0.000114*F*<sup>2</sup>], *S* = 1.537 for 399 parameters and 4379 reflections with *I* > 2.5σ(*I*). Hydrogen atoms were included in the refinement on calculated positions (C–H = 0.98 Å) riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were refined with two common isotropic thermal parameters. Weights were introduced in the final refinement cycles. A final difference Fourier showed no residual density outside –0.83 and 0.85 eÅ<sup>-3</sup> (near Ru). Further details of the structure determination, including atomic coordinates, bond lengths and angles, thermal parameters, and a thermal motion ellipsoid plot are available on request from the Director of the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ (UK) on quoting the full journal citation.
- [5] Br<sub>2</sub> was gradually added to the solution while monitoring the NIR band. Its maximum intensity was reached at a Br<sub>2</sub> to Ru<sub>2</sub> ratio of 1:2 and it had disappeared completely at a 1:1 stoichiometry.
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## Molecular Siloxane Complexes of Rare Earth Metals—Model Systems for Silicate-Supported Catalysts?\*

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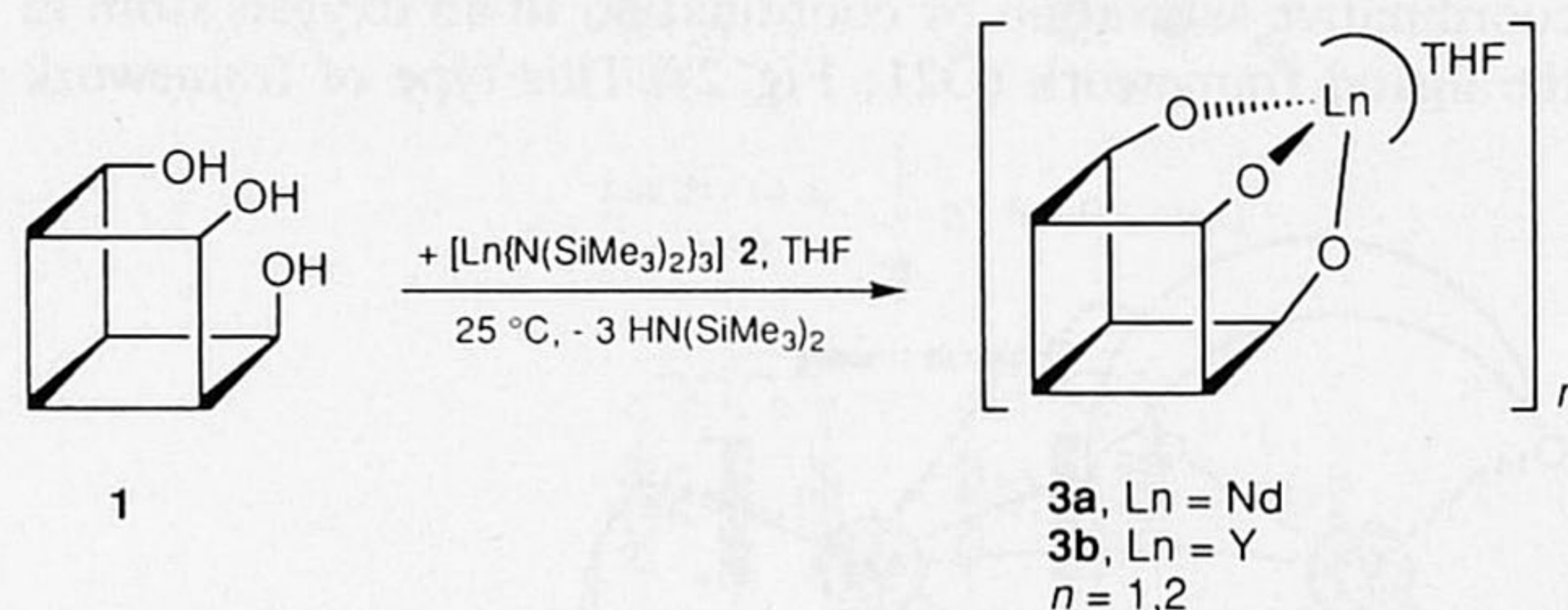
The preparation of realistic models of heterogeneous, SiO<sub>2</sub>-supported transition metal catalysts eluded chemists for many years.<sup>[1]</sup> However, partially condensed oligosiloxanes have lately proved to be reasonable model systems.<sup>[2]</sup> Since lanthanoid-doped zeolite catalysts are of considerable technical importance,<sup>[3]</sup> we have introduced oligosiloxanes such as [(*c*-C<sub>5</sub>H<sub>9</sub>)Si]<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub> **1** as molecular models in the chemistry of the rare earth metals.<sup>[4]</sup>



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[\*\*] Lanthanoid Complexes, Part 7. This work was supported by Osram GmbH and the Alexander-von-Humboldt-Stiftung. We thank Dipl.-Chem. F.-R. Klingan for recording the NMR spectra. – Part 6: W. A. Herrmann, R. Anwander, W. Scherer, F. C. Munck, *J. Organomet. Chem.* **1993**, *462*, 163.

We chose yttrium and neodymium as representatives of the lanthanoids. The metal complexes **3a**, **b** were obtained in quantitative yields according to the silylamide route given in Scheme 1. The course of the reaction was monitored by the



Scheme 1. Each corner of the formula representation corresponds to a cyclopentyl-silicon group; oxygen atoms are found midway between the connected corners.

liberation of the silylamine (GC/MS analysis). **3a**, **b** are readily soluble in all organic solvents, even *n*-pentane, and were characterized by elemental analysis and IR spectroscopy (no ν(SiO–H) bands at ca. 3230 cm<sup>-1</sup> typical of the starting material). Investigations by mass spectrometry (no signals < 300 °C) suggest dimeric structures in the solid state (*n* = 2) as found in the Al<sup>III</sup> and Ti<sup>III</sup> complexes.<sup>[2a, b]</sup> Whilst the <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra could not be conclusively interpreted, the <sup>89</sup>Y NMR spectrum contains a single signal which indicates the presence of a well-defined compound and only one chemical environment of the Y atom. The shift of δ = 196.9 is typical of lanthanoid siloxides (cf. [Y(OSiMe<sub>2</sub>*t*Bu)<sub>3</sub>(THF)<sub>3</sub>], δ = 266.6<sup>[5]</sup>). Attempts at recrystallization from common solvents such as THF, hexane, and benzene produced crystals that were amorphous by X-ray crystallography. However, with triphenylphosphane oxide as an auxiliary ligand, **3b** reacted to give the adduct **4** as single crystals.<sup>[6]</sup> Figure 1 shows the structure of the binuclear complex **4**.

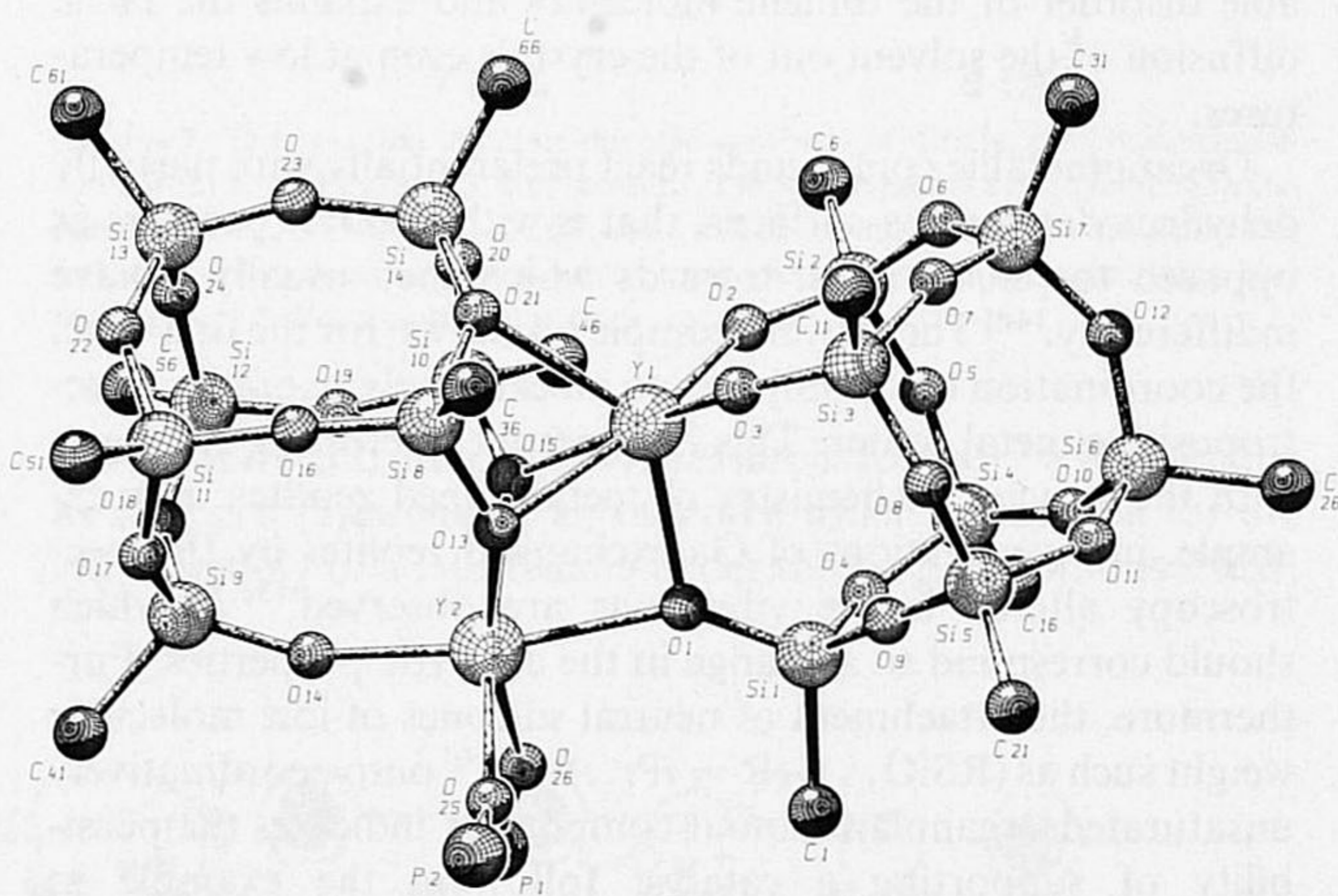


Fig. 1. Model of the molecular structure of **4** in the solid state (SHAKAL representation). To simplify the drawing, the cyclopentyl groups and the four solvent molecules are not completely represented. Selected bond lengths [Å] and angles [°]: Y1-O1 2.239(9), Y1-O2 2.119(7), Y1-O3 2.123(9), Y1-O13 2.422(7), Y1-O15 2.391(8), Y1-O21 2.509(9), Y2-O1 2.384(7), Y2-O13 2.25(1), Y2-O14 2.117(8), Y2-O15 2.255(8), Y2-O25 2.296(8), Y2-O26 2.26(1); Y1-O1–Y2 91.3(3); Y1-O13–Y2 90.0(4), Y1-O15–Y2 90.7(3), Y1-O21–Si8 92.9(4), Y1-O21–Si14 115.4(4), Si14–O21–Si8 141.1(5), Y2-O26–P1 157.0(6), Y2-O25–P2 153.3(6).

Both yttrium atoms have six-fold coordination. In contrast, the addition of the same phosphane oxide auxiliary ligand to the corresponding aluminum complex causes a *cleavage* of the dimer originally present.<sup>[2a]</sup>