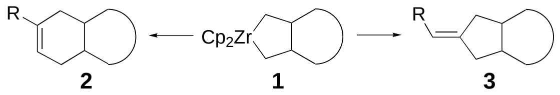
[5] S. Gregoli, M. Olast, A. Bertinochamps, *Radiat. Res.* **1982**, *89*, 238.
[6] E. M. Fielden, S. L. Lillicrap, A. B. Robins, *Radiat. Res.* **1971**, *48*, 421.
[7] D. W. Whillans, *Biochim. Biophys. Acta* **1975**, *414*, 193.
[8] a) K. F. Baverstock, R. B. Cundall, *Radiat. Phys. Chem.* **1988**, *32*, 553; b) M. Cullis, J. D. McClymont, M. C. R. Symons, *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 591.
[9] C. J. Murphy, M. R. Arkin, Y. Jenkins, N. D. Ghatlia, S. H. Bossmann, N. J. Turro, J. K. Barton, *Science* **1993**, *262*, 1025.
[10] M. R. Arkin, E. D. A. Stemp, R. E. Holmlin, J. K. Barton, A. Hörmann, E. J. C. Olson, P. F. Barbara, *Science* **1996**, *273*, 475.
[11] R. E. Holmlin, E. D. A. Stemp, J. K. Barton, *J. Am. Chem. Soc.* **1996**, *118*, 5236.
[12] S. O. Kelley, R. E. Holmlin, E. D. A. Stemp, J. K. Barton, *J. Am. Chem. Soc.* **1997**, *119*, 9861.
[13] S. O. Kelley, J. K. Barton, *Chem. Biol.* **1998**, *5*, 413.
[14] A. M. Brun, A. Harriman, *J. Am. Chem. Soc.* **1992**, *114*, 3656.
[15] A. M. Brun, A. Harriman, *J. Am. Chem. Soc.* **1994**, *116*, 10383.
[16] T. J. Meade, J. F. Kayyem, *Angew. Chem.* **1995**, *107*, 358; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 352.
[17] S. J. Atherton, P. C. Beaumont, *J. Phys. Chem.* **1995**, *99*, 12025.
[18] P. Lincoln, E. Tuite, B. Nordén, *J. Am. Chem. Soc.* **1997**, *119*, 1454.
[19] F. D. Lewis, T. Wa, Y. Zhang, R. L. Letsinger, S. R. Greenfield, M. R. Wasielewski, *Science* **1997**, *277*, 673.
[20] K. Fukui, K. Tanaka, *Angew. Chem.* **1998**, *110*, 162; *Angew. Chem. Int. Ed.* **1998**, *37*, 158.
[21] E. Meggers, D. Kusch, M. Spichty, U. Wille, B. Giese, *Angew. Chem.* **1998**, *110*, 465; *Angew. Chem. Int. Ed.* **1998**, *37*, 460.
[22] a) H.-W. Park, S.-T. Kim, A. Sancar, J. Deisenhofer, *Science* **1995**, *268*, 1866; b) T. Tamada, K. Kitadokoro, Y. Higuchi, K. Inaka, A. Yasui, P. E. de Ruiter, A. P. M. Eker, K. Miki, *Nature Struct. Biol.* **1997**, *11*, 887.
[23] a) S. Priyadarshy, D. N. Beratan, S. M. Risser, *Int. J. Quantum Chem.* **1996**, *60*, 1789; b) S. Priyadarshy, S. M. Risser, D. N. Beratan, *J. Phys. Chem.* **1996**, *100*, 17678; c) D. N. Beratan, S. Priyadarshy, S. M. Risser, *Chem. Biol.* **1997**, *4*, 3.
[24] A. K. Felts, W. T. Pollard, R. A. Freisner, *J. Phys. Chem.* **1995**, *99*, 2929.
[25] S. K. Mukamel, *J. Phys. Chem. A* **1998**, *102*, 1241.
[26] R. A. Marcus, N. Sutin, *Biochim. Biophys. Acta* **1985**, *811*, 265.
[27] A. Harriman, V. Heitz, M. Ebersole, H. van Willigen, *J. Phys. Chem.* **1994**, *98*, 4982.
[28] L. G. Arnaut, S. J. Formosinho, *J. Photochem. Photobiol. A* **1997**, *111*, 111.
[29] P. Fromherz, B. Rieger, *J. Am. Chem. Soc.* **1986**, *108*, 5361.
[30] A. M. Brun, A. Harriman, *J. Am. Chem. Soc.* **1991**, *113*, 8154.
[31] The increased λ value found at shorter separations suggests that the reactants are more exposed to solvent molecules and reside in a less rigid environment.
[32] The literature includes several reports of β values (given in units of Å^{-1}) for electron tunneling in DNA or short synthetic duplexes: $\beta =$ 0.88[14], 0.73[17], 0.64[19], 1.42[20], 1.00[21], <0.2[9], <0.2[10]. A value of $\beta =$ 1.9 Å^{-1} has been given for light-induced electron exchange (that is, simultaneous two-site electron and hole transfer).[15]
[33] S. M. Risser, D. N. Beratan, T. J. Meade, *J. Am. Chem. Soc.* **1993**, *115*, 2508.
[34] a) J. E. Hearst, *Science* **1995**, *268*, 1858; b) A. Sancar, *Biochemistry* **1994**, *33*, 2.

Inter- or Intramolecular Carbometalation of Nonactivated Alkynes by Zirconacyclopentanes in the Presence of Copper Chloride**

Yuanhong Liu, Baojian Shen, Martin Kotora, and Tamotsu Takahashi*

Addition of metal–carbon bonds to alkynes is an attractive methodology for the construction of complex molecules.[1, 2] This approach has been successfully applied to the formation of stereo-defined alkene derivatives. Alkylzirconocene derivatives have been useful in organic synthesis because they are easily prepared by hydrozirconation of alkenes,[3] by alkylation of $[Cp_2ZrCl_2]$ ($Cp = C_5H_5$), or by olefin coupling on zirconocenes.[4] Carbometalation of nonactivated alkynes with alkylzirconocenes would be a useful synthetic tool. However, to the best of our knowledge, no such reactions have been reported. Here we would like to fill this void and present a novel procedure for the direct conversion of zirconacyclopentanes into six- and five-membered ring carbocycles by means of inter- and intramolecular carbometalation of nonactivated alkynes (Scheme 1).



Scheme 1. Conversion of zirconacycles **1** into five- and six-membered ring carbocycles.

Initially, we investigated the carbometalation[5] of nonactivated terminal alkynes with alkyl- and dialkylzirconocenes in the presence of CuCl because this type of reaction had not been reported previously. The reaction of alkylzirconocenes such as $[Cp_2Zr(n\mathrm{Bu})Cl]$ and $[Cp_2Zr(n\mathrm{Oct})Cl]$, prepared by hydrozirconation of alkenes, with alkynes gave the carbometalated products in low yields (<25%). Further investigation, however, revealed interesting reactivity patterns of dialkylzirconocenes. Thus the reaction of dialkylzirconocenes such as $[Cp_2Zr(n\mathrm{Bu})_2]$ and $[Cp_2Zr(n\mathrm{Oct})_2]$ (**4**) with phenylacetylene in the presence of CuCl afforded, after hydrolysis, a mixture of three products. As shown in Scheme 2, **5**–**7** are obtained when **4** was used as the substrate. Despite the fact that a mixture of products was formed, this result clearly indicated that the carbometalation of nonactivated alkynes by dialkylzirconocene had taken place.

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[**] A part of this work was supported by the Grant-in-Aid for Scientific Research (no. 09440212) from the Ministry of Education, Science, Sports and Culture of Japan.

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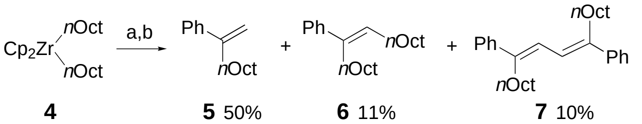
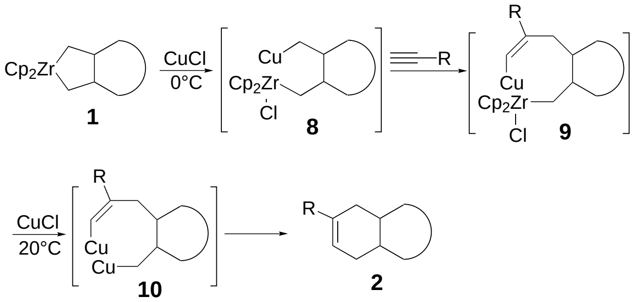


Scheme 2. Reaction of **4** with phenylacetylene. a) PhC≡CH (2 equiv), CuCl (2 equiv), 0 °C →room temperature, 3 h; b) H$^+$.

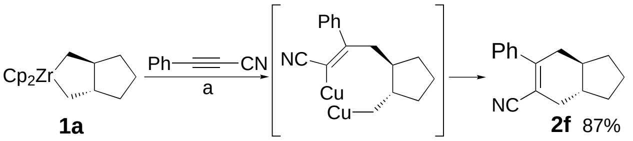
Especially attractive seemed to be the formation of compound **6** which showed the feasibility of carbometalation of an alkyne followed by coupling of alkyl and alkenyl metals.[6, 7]

This result encouraged us to check the reaction of zirconacyclopentanes with nonactivated terminal alkynes in the presence of CuCl, because the second carbon–carbon bond formation after transmetalation is expected to form cyclic products as shown in Scheme 3.[6, 7] In the first step, zirconacyclopentane **1** is transmetalated with CuCl to give the monocopper compound **8** (selective transmetalation of only one Zr–C bond occurs at 0 °C)[8, 9] followed by the *syn* addition[1] of the Cu–C bond to alkyne to yield the intermediate **9**. In **9**, the second Zr–C bond is transmetalated at 20 °C to give the intermediate **10**. This species contains alkenylcopper and alkylcopper moieties and reductively couples to form the six-membered ring compound **2** with concomitant precipitation of copper powder from the reaction mixture.



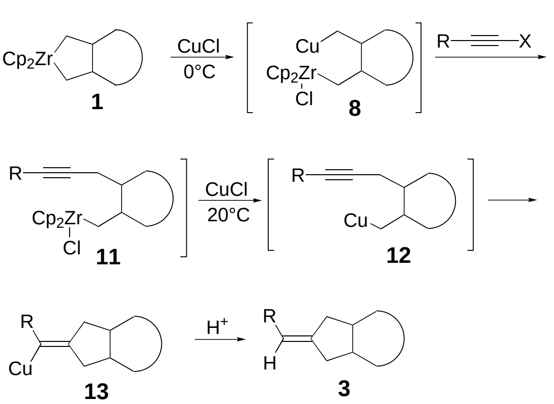
Scheme 3. Formation of six-membered ring compounds by the reaction of zirconacycle **1** with alkynes in the presence of CuCl.

Indeed, the reaction of zirconacyclopentanes of type **1** with alkynes to give compounds of type **2** proceeded as expected, and results are summarized in Table 1. Thus, the reaction of **1a** with phenylacetylene afforded **2a**. The reaction of **1b** with phenylacetylene afforded **2b** as a single product in 70 % yield, and **1b** reacted with ethynylcyclohexene to give **2d** in 85 % yield. Zirconacyclopentane **1c** reacted with phenylacetylene to afford **2e** in 64 % yield. The formation of six-membered ring compounds was also achieved with activated alkynes (Scheme 4). In this case, the first reaction step is Michael addition followed by reductive coupling.



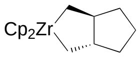
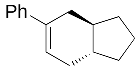
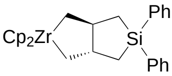
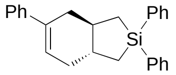
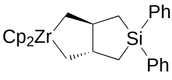
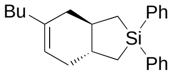
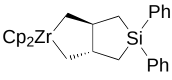
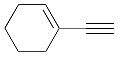
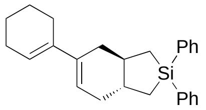
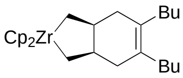
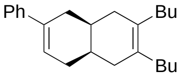
Scheme 4. Reaction of **1a** with 3-phenylpropynonitrile: a) CuCl (2 equiv), 0 °C →room temperature, 6 h.

On the basis of these results, we envisioned that the formation of five-membered ring compounds could be achieved by intramolecular carbometalation of alkylzirconocene to a nonactivated alkynyl moiety in the presence of CuCl. However, in this case, we had first to develop a method for the preparation of alkylzirconocenes which contain an alkynyl moiety. This step was easily solved by the selective coupling of one Zr–C bond of zirconacyclopentane with an alkynyl bromide.[10] The overall reaction mechanism was assumed to be as described in the Scheme 5, although further



Scheme 5. Formation of five-membered ring compounds by the reaction of zirconacycle **1** with alkynyl bromides in the presence of CuCl.

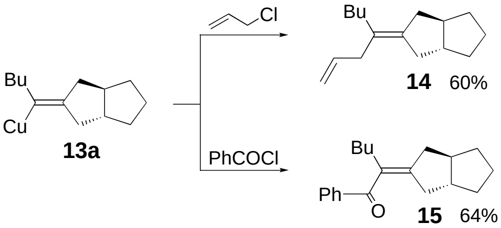
Table 1. Results of the reaction of zirconacyclopentanes with nonactivated alkynes in the presence of CuCl.[a]

Zirconacycle	Alkyne	t [h]	Product	Yield [%][b]
 **1a**	Ph—≡	3	 **2a**	56[c] (50)
 **1b**	Ph—≡	6	 **2b**	70[d] (61)
 **1b**	Bu—≡	12	 **2c**	– (52)
 **1b**		1	 **2d**	85[d] (78)
 **1c**	Ph—≡	12	 **2e**	64[c] (56)

[a] Conditions: 2 equiv of CuCl; solvent THF. [b] Yield of isolated products in parentheses. [c] Yield determined by gas chromatography (GC). [d] Yield determined by ^{1}H NMR spectroscopy.

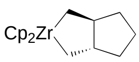
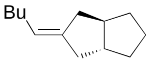
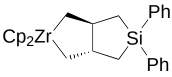
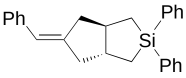
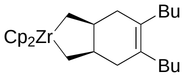
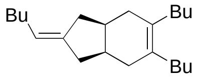
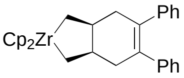
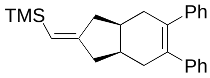
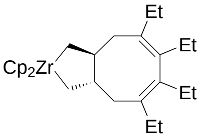
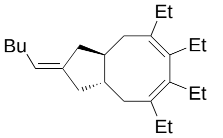
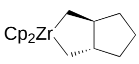
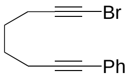
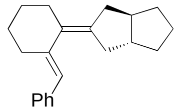
investigation is necessary to elucidate the mechanism. In the first step, zirconacyclopentane **1** is transmetalated with CuCl to monocopper compound **8** followed by cross-coupling with alkynyl bromide to give an intermediate **11**, of which the second Zr–C bond undergoes transmetalation at 0 °C to give **12**. Then, the intermediate **12** undergoes intramolecular carbometalation to give **13**, which after hydrolysis affords the five-membered ring compound **3**.

The vinylcopper intermediate **13a** reacted with electrophiles such as allyl chloride and benzoyl chloride at room temperature to give the corresponding products **14** and **15** in 60 and 64 % yields (Scheme 6). The reaction proceeded as expected, and results are summarized in Table 2. Thus, the reaction of **1a–e** with alkynyl bromides gave the corresponding five-membered ring compounds **3a–e** in good yield by means of intramolecular carbometalation of the nonactivated alkyne moiety. When 1-bromo-8-phenyl-1,7-octadiyne was used as a substrate, reaction with **1a** resulted in the formation of **3f** by tandem double intramolecular carbometalation. As in the previous case, this intramolecular cyclization also proceeds with activated alkynes. Thus, the reaction of **1e** with ethyl-3-bromopropynoate resulted in the formation of **3g** in 61 % yield (Scheme 7). However, in this case the reaction with the triple bond is a Michael reaction.

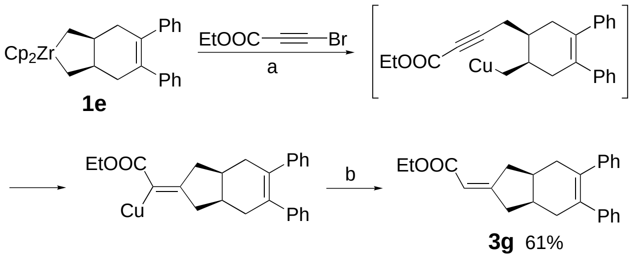


Scheme 6. Reaction of **13a** with electrophiles such as allyl chloride and benzoyl chloride at 20 °C for 2 h.

Table 2. Results of the reaction of zirconacyclopentanes with alkynyl bromides in the presence of CuCl.[a]

Zirconacycle		Alkyne	*t* [h]	Product		Yield [%][b]
	**1a**	Bu—≡—Br	3		**3a**	75 (58)
	**1b**	Ph—≡—Br	1		**3b**	71 (56)
	**1c**	Bu—≡—Br	1		**3c**	72 (55)
	**1e**	TMS—≡—Br	1		**3d**	72 (63)
	**1d**	Bu—≡—Br	3		**3e**	84 (78)
	**1a**		9[c]		**3f**	– (55)

[a] Conditions: 2 equiv of CuCl; solvent THF. [b] Yield determined by GC. Yield of isolated product in parentheses. [c] Reaction carried out at 50 °C.



Scheme 7. Reaction of **1e** with 3-bromopropynoate: a) CuCl (2 equiv), 0 °C → room temperature, 3 h. b) H^+.

Experimental Section

2d: Ethynylcyclohexene (106 mg, 1.0 mmol) and CuCl (198 mg, 2 mmol) were added at 0 °C to a solution of **1b**, prepared from $[Cp_2ZrBu_2]$ (1.0 mmol) and diallyldiphenylsilane (1.0 mmol). The reaction mixture was warmed up to 20 °C, stirred for 1 h, quenched with 3 N HCl, and extracted with hexane. The combined organic extracts were washed with aqueous $NaHCO_3$ and water, then dried ($MgSO_4$) and concentrated in vacuum. Column chromatography on silica gel (hexane) afforded 289 mg (78 %) of **2d** as a colorless oil: ^1H NMR ($CDCl_3$, Me_4Si): $\delta = 0.72-0.84$ (m, 2H), 1.46–1.70 (m, 8H), 1.96–2.30 (m, 6H), 2.52–2.60 (m, 1H), 2.69 (dd, $J = 14.8, 3.8$ Hz, 1H), 5.74 (d, $J = 5.1$ Hz, 1H), 5.81 (brs, 1H), 7.31–7.55 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 20.47$, 20.93, 22.46, 23.13, 25.76, 25.85, 36.92 (2C), 41.29, 42.03, 121.05, 121.69, 127.85 (4C), 129.21 (2C), 134.71 (4C), 136.43, 136.88, 136.90, 137.01; HR-MS calcd for $C_{26}H_{30}Si$: 370.2115, found: 370.2130.

3e: Alkynyl bromide (161 mg, 1.0 mmol) and CuCl (198 mg, 2 mmol) were added at 0 °C to a solution of **1d**, prepared from $[Cp_2ZrBu_2]$ (1.0 mmol) and 4,5,6,7-tetraethyl-1,4,6,9-decatetraene (1.0 mmol). The reaction mixture was warmed up to 20 °C, stirred for 3 h, quenched with 3 N HCl, and extracted with hexane. The combined organic extracts were washed with aqueous $NaHCO_3$ and water, then dried ($MgSO_4$) and concentrated in vacuum. Column chromatography on silica gel (hexane) afforded 256 mg (78 %) of **3e** as a colorless liquid: ^1H NMR ($CDCl_3$, Me_4Si): $\delta = 0.81-1.40$ (m, 21H), 1.66–2.12 (m, 12H), 2.12–2.32 (m, 6H), 5.18 (t, $J = 1.8$ Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 12.55$ (2C), 12.79 (2C), 14.04, 22.49, 22.61 (2C), 25.65 (2C), 28.95, 31.96, 35.60, 35.85, 36.78, 41.02, 45.39, 45.45, 121.16, 133.86, 133.91, 135.98, 135.99, 140.96; HR-MS calcd for $C_{24}H_{40}$: 328.3128, found: 328.3131.

Received: July 3, 1998 [Z12092IE]
German version: *Angew. Chem.* **1999**, *111*, 966–968

Keywords: alkynes · copper · cyclizations · metalations · zirconium

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[1] For reviews on carbometalation of alkynes, see a) J. F. Normant, A. Alexakis, *Synthesis* **1981**, 841–870; b) B. H. Lipshutz, S. Sengupta, *Org. React.* **1992**, *41*, 135–631; c) I. Marek, J. F. Normant in *Metal-catalyzed Cross-coupling Reactions* (Eds.: F. Diederich, P. J. Stang), WILEY-VCH, Weinheim, **1998**, pp. 271–337.

[2] For conjugate additions, see P. Perlmutter, *Conjugate Addition Reactions*, Pergamon Press, Oxford, **1992**, pp. 339–358.

[3] J. A. Labinger in *Comprehensive Organic Synthesis, Vol. 8* (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, pp. 667–702.
[4] a) K. I. Gell, J. Schwartz, *J. Chem. Soc. Chem. Commun.* **1979**, 244–245; b) C. J. Rousset, D. R. Swanson, F. Lamaty, E. Negishi, *Tetrahedron Lett.* **1990**, *30*, 5105–5108, and references therein.
[5] For carbometalation of terminal alkynes, see references [1a, b].
[6] For intermolecular reductive homodimerization of organocopper compounds, see a) G. M. Whitesides, C. P. Casey, *J. Am. Chem. Soc.* **1966**, *88*, 4541–4543; b) M. Yoshifuji, M. J. Loots, J. Schwartz, *Tetrahedron Lett.* **1977**, 1303–1306.
[7] For intermolecular reductive heterodimerization of organocopper compounds, see J. F. Normant, G. Cahiez, M. Bourgain, C. Chuit, J. Villieras, *Bull. Soc. Chim. Fr.* **1974**, 1656–1666.
[8] a) T. Takahashi, M. Kotora, Z. Xi, *J. Chem. Soc. Chem. Commun.* **1995**, 1503–1504; b) T. Takahashi, Y. Nishihara, R. Hara, S. Huo, M. Kotora, *Chem. Commun.* **1997**, 1599–1600.
[9] For transmetalation of alkylzirconocene to copper, see a) P. Wipf, J. H. Smitrovich, *J. Org. Chem.* **1991**, *56*, 6494–6496; b) L. M. Venanzi, R. Lehmann, R. Keil, B. H. Lipshutz, *Tetrahedron Lett.* **1992**, *33*, 5857–5860; c) P. Wipf, J. H. Smitrovich, C.-W. Moon, *J. Org. Chem.* **1992**, *57*, 3178–3186; d) P. Wipf, W. J. Xu, J. H. Smitrovich, R. Lehmann, L. M. Venanzi, *Tetrahedron* **1994**, *50*, 1935–1954; e) K. Kasai, M. Kotora, N. Suzuki, T. Takahashi, *J. Chem. Soc. Chem. Commun.* **1995**, 109–110.
[10] For a related reaction, see R. Hara, Y. Liu, W.-H. Sun, T. Takahashi, *Tetrahedron Lett.* **1997**, *38*, 4103–4107.

Sodium Salts of the Bipyridine Dianion: Polymer $[(bpy)^{2-}\{Na^+(dme)\}_2]_\infty$, Cluster $[(Na_8O)^{6+}Na_6^+(bpy)_6^{2-}(tmeda)_6]$, and Monomer $[(bpy)^{2-}\{Na^+(pmdta)\}_2]$**

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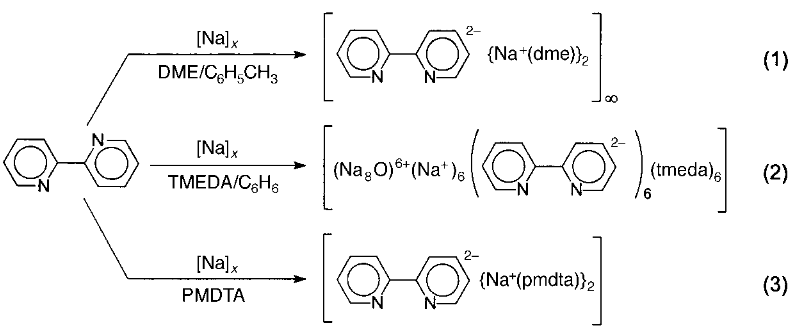
Dedicated to Professor Gottfried Huttner

Polypyridines H_4NC_5-$(C_5NH_3)_n$-C_5NH_4 are excellent chelate ligands for metal cations, and the resulting complexes are suitable model compounds for studying supramolecular self-recognition and ion-pair aggregation to chains, ladders, or networks.[1,2] Despite the numerous known metal cation bipyridyl complexes, a search in the Cambridge Structural Database (version 5.10) produced no hit with regard to structures of alkali metal salts with bipyridine ligands. The preparation and crystallization of contact-ion pairs containing the most advantageous Na^+ ion[3] can be accomplished by the reduction in aprotic solution at a sodium metal mirror; a method employed on numerous occasions for organic compounds.[3,4] In the reactions (1)–(3) contact-ion multiples are formed whose structures are decisively dependent on the cation solvation by the solvent.[5] From dimethoxyethane (DME) and toluene a polymer crystallizes [reaction (1)], from *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) and benzene a novel $Na_{14}^+O^{2-}$ cluster [reaction (2)], and from pentamethyldiethylenetriamine (PMDTA) a monomeric sodium salt of the bipyidine dianion [reaction (3)].



The polymeric contact-ion triple crystallizes as deep red platelets, which according to their structure determination[6] contain two additional toluene molecules in the unit cell. The sodium cations in the chains stretching in *y* direction (Figure 1 A and B) are alternatingly bridged by a bipyridine dianion and two dme ligands; the $Na^+\cdots Na^+\cdots Na^+$ angles are 165°.

The structure determination confirms that the bipyridine dianions are planar (torsion angle $\omega(NC-CN) = 0°$) and that their nitrogen centers adopt a cisoid arrangement. The sodium metal reduction of bipyridine[7,8] shortens the C–C connection between the pyridine rings by 11 pm and stretches the C–N bonds to the bridge carbon centers by 9 pm and the C–C ring bonds by 5 pm. The internal angles of the ring at the carbon bridge centers are compressed by 6°. The sodium cations coordinate to both nitrogen centers and to the bridge carbon centers of the bypridine dianion with $Na^+\cdots N$ distances of 237 and an 240 pm and a $Na^+\cdots C$ distance of 287 pm. Additional $Na^+\cdots O$ contacts exist to both oxygen centers of one dme ligand and two further ones to an inversion symmetric second solvent ligand (Figure 1 C). The mirror-symmetric sodium cations $Na^+\cdots Na^+$ coordinated to the same bipyridine dianion are 332 pm apart, and the $Na^+\cdots O$ contact distances to the second ligand are 374 pm.

As a continuation of our studies into ion aggregation,[8] from a TMEDA/benzene solution under optimized conditions a novel sodium cluster $[((Na_8^+)O^{2-})(Na^+)_6]^{12+}$ has been crystallized as deep red blocks[9] (Figure 2). The cluster is lipophilically wrapped by six bipyridine dianions and six tmeda ligands. The inversion-symmetric Na_{14} cluster, wrapped by six bipyridine dianions and six tmeda ligands, contains a hexagonal bipyramid of Na^+ ions with a disordered O^{2-} dianion in its center (Figure 2 B), which balances the charge of 14 sodium cations and only six bipyridine dianions.

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[**] Interactions in Molecular Crystals, Part 141. The project was generously supported by the Hoechst AG, the Deutsche Forschungsgemeinschaft, the State of Hesse, and the Fonds der Chemischen Industrie. Part 140: H. Bock, Z. Havlas, D. Heß, C. Näther, *Angew. Chem.* **1998**, *109*, 518; *Angew. Chem. Int. Ed.* **1998**, *37*, 502.