are resolved for **1**–**3**. The results described here suggest that there is a potentially large and interesting cycloaddition chemistry associated with phosphorus–selenium heterocycles.

Experimental Section

General procedure for **1**–**3**: A toluene solution (10 mL) of [{PhP(Se)(μ-Se)}$_2$] (0.15 mmol) and $R_2N{-}CN$ (1.5 mmol) was heated at reflux for 18 h during which time the solution changed color from red to lime green, with the precipitation of a small quantity of selenium. Upon cooling to room temperature, the solvent was removed in vacuo and the products extracted into dichloromethane (2 mL). Column chromatography using silica (dichloromethane eluant) gave **1**–**3** as yellow solids. Yellow crystals of **1** and **2** were isolated upon layering of a dichloromethane (1 mL) solution of each compound with *n*-hexane at room temperature.

IR: KBr disk; $^{31}P\{^1H\}$ NMR: $CDCl_3$ solvent, 121.5 MHz; MS: FAB$^+$, 3-nitrobenzyl alcohol (3-NOBA) matrix.

1: IR: $\tilde{\nu} = 1528$ s (ν_{CN}), 1109 s (ν_{PC}), 990 s (ν_{PN}), 524 m cm^{-1} (ν_{PSe}); MS: 486 [M^+]; $^{31}P\{^1H\}$ NMR: $\delta = 82.7$ (^1J(P,Se) = 317 Hz).

2: IR: $\tilde{\nu} = 1502$ s (ν_{CN}), 1112 s (ν_{PC}), 997 s (ν_{PN}), 521 s cm^{-1} (ν_{PSe}); MS: 570 [M^+]; $^{31}P\{^1H\}$ NMR: $\delta = 83.9$ (^1J(P,Se) = 324 Hz).

3: IR: $\tilde{\nu} = 1500$ s (ν_{CN}), 1109 m (ν_{PC}), 984 s (ν_{PN}), 512 m cm^{-1} (ν_{PSe}); MS: 566 [M^+]; $^{31}P\{^1H\}$ NMR: $\delta = 81.7$ (^1J(P,Se) = 318 Hz).

Received: December 20, 1999 [Z14425]

---

[1] D. L. An, N. Higeta, K. Toyota, M. Yoshifuji, *Chem. Lett.* **1998**, 17, and references therein.

[2] S. W. Hall, M. J. Pilkington, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *Polyhedron* **1991**, *10*, 261.

[3] J. T. Shore, W. T. Pennington, M. C. Noble, A. W. Cordes, *Phosphorus Sulfur Silicon Relat. Elem.* **1988**, *39*, 153.

[4] J. C. Fitzmaurice, D. J. Williams, P. T. Wood, J. D. Woollins, *J. Chem. Soc. Chem. Commun.* **1988**, 741.

[5] P. T. Wood, J. D. Woollins, *J. Chem. Soc. Chem. Commun.* **1988**, 1190.

[6] K. Eckstein, K. Karaghiosoff, *Phosphorus Sulfur Silicon Relat. Elem.* **1993**, *75*, 257.

[7] K. Eckstein, K. Karaghiosoff, R. Motzer, *Phosphorus Sulfur Silicon Relat. Elem.* **1994**, *93–94*, 185.

[8] I. Baxter, A. F. Hill, J. M. Malget, A. J. P. White, D. J. Williams, *Chem. Commun.* **1997**, 2049.

[9] M. P. Cava, M. I. Levinson, *Tetrahedron* **1985**, *41*, 5061.

[10] I. P. Parkin, M. J. Pilkington, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *Polyhedron* **1990**, *9*, 987.

[11] M. R. St. John Foreman, R. J. Mortimer, A. M. Z. Slawin, J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **1999**, 3419.

[12] X-ray diffraction studies on crystals of **1** and **2**, grown from dichloromethane/*n*-hexane, were performed using a Bruker SMART diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods, the non-hydrogen atoms were refined[17] with anisotropic displacement parameters, hydrogen atoms bound to carbon were idealized and fixed (C–H 0.95 Å). Structural refinements were performed with the full-matrix least-squares method on F^2 using the program SHELXTL-PC.[17] Crystal data for **1**: $C_{12}H_{17}N_4PSe_3$, yellow needles, $0.3 \times 0.2 \times 0.2$ mm^3, $M_r = 485.15$, monoclinic, $a = 9.537(1)$, $b = 12.523(1)$, $c = 14.178(2)$ Å, $\beta = 95.049(2)°$, $F(000) = 936$, $V = 1687.5(3)$ Å^3, $T = 298$ K, space group $P2_1/n$, $Z = 4$, $\mu(Mo_{K\alpha}) = 6.629$ mm^{-1}, $2\theta_{max} = 46°$. Of 7191 measured data 2409 were unique reflections (R_{int} 0.0300) to give $R1$ [$I > 2\sigma(I)$] = 0.0265 and $wR2 = 0.0568$. Crystal data for **2**: $C_{16}H_{21}N_4O_2PSe_3$, yellow needles, $0.2 \times 0.1 \times 0.1$ mm^3, $M_r = 569.22$, monoclinic, $a = 6.807(1)$, $b = 16.023(1)$, $c = 18.983(1)$ Å, $\beta = 94.787(1)°$, $F(000) = 1112$, $V = 2063.28(7)$ Å^3, $T = 293$ K, space group $P2_1/c$, $Z = 4$, $\mu(Mo_{K\alpha}) = 5.444$ mm^{-1}, $2\theta_{max} = 46°$. Of 10306 measured data 2970 were unique reflections (R_{int} 0.2251) to give $R1$ [$I > 2\sigma(I)$] = 0.0618 and $wR2 = 0.1017$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-138177 for **1** and -138178 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[13] R. Richter, J. Sieler, L. K. Hansen, R. Köhler, L. Beyer, E. Hoyer, *Acta. Chem. Scand.* **1991**, *45*, 1.

[14] A. Hordvik, J. A. Porter, *Acta. Chem. Scand.* **1973**, *27*, 485.

[15] A. Hordvik, K. Julshamn, *Acta. Chem. Scand.* **1971**, *25*, 2507.

[16] P. Bhattacharyya, J. Novosad, J. R. Phillips, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **1995**, 1607.

[17] G. M. Sheldrick, SHELXTL, version 5.03, Program for Crystal Structure Solution, University of Göttingen, **1994**.

Highly Regioselective Allylic Alkylation of Dienyl Acetates and Enynyl Acetates Catalyzed by an Iridium Complex**

Ryo Takeuchi* and Keisuke Tanabe

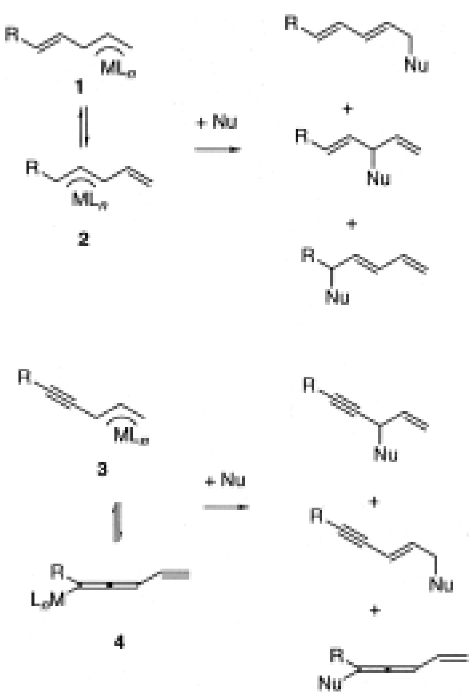
Allylic substitution catalyzed by transition metal complexes that proceed via a π-allylmetal complex is one of the most efficient reactions for selective carbon–carbon and carbon–heteroatom bond formation.[1] The substituent on the π-allyl ligand has a considerable effect on the reactivity and the selectivity. Alkenyl and alkynyl groups are particularly important as substituents on the π-allyl ligand. 1-(1-Alkenyl)-π-allylmetal intermediate **1** isomerizes to 1-alkyl-3-vinyl-π-allylmetal intermediate **2** through a σ-π-σ interconversion.[2] Similarly, 1-(1-alkynyl)-π-allylmetal intermediate **3** isomerizes to the 1-alkyl-3-vinyl-σ-allenylmetal intermediate **4** (Scheme 1).[3] Selective reaction of these intermediates with a nucleophile increases the importance of this type of transformation in organic synthesis. We first reported that an iridium complex was a new and efficient catalyst for allylic alkylation, and showed a different regio- and stereoselectivity compared to those of π-allylpalladium chemistry.[4] We describe here the allylic alkylation of dienyl acetates and enynyl acetates catalyzed by an iridium complex [Eq. (1) and (2)].[5]

The results of the allylic alkylation of **5** and **6** are summarized in Table 1. Acetate **5a** reacted with two equivalents of **7a**–**c** in the presence of a catalytic amount of

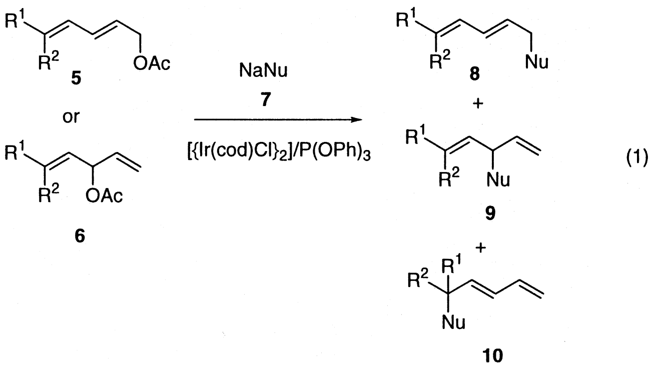
---

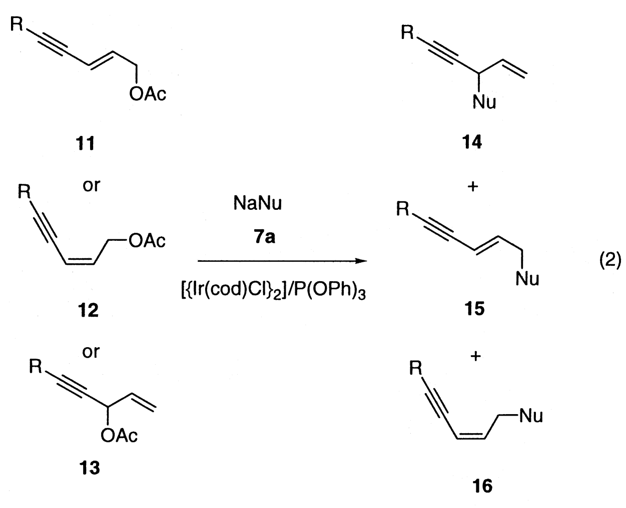
[*] Prof. Dr. R. Takeuchi, K. Tanabe
Department of Environmental Science
Faculty of Science and Graduate School of Integrated Science
Yokohama City University
22-2 Seto, Kanazawa-ku, Yokohama 236-0027 (Japan)
Fax: (+81) 45-787-2218
E-mail: rtakeuch@yokohama-cu.ac.jp

[**] This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 283, "Innovative Synthetic Reactions") from the Ministry of Education, Science, Sports, and Culture, Government of Japan.



Scheme 1. Reaction of intemediates **1** and **3** with a nucleophile. M = metal (Ir, Pd), L = ligands.





11 - 16: R = *n*Bu, Nu = CH(CO$_2$Et)$_2$

[{Ir(cod)Cl}$_2$] (Ir atom 4 mol%; cod = cycloocta-1,5-diene) and P(OPh)$_3$ (P/Ir = 2) at room temperature to give **9aa**, **9ab**, and **9ac**, respectively, in yields of 87–94% (Table 1, entries 1–3). The reaction occurred with perfect regioselectivity at the substituted allylic terminus. No other product was obtained. The reaction of **5a** with **7d**, which is a more bulky nucleophile than **7a**, gave a 6:94 mixture of **8ad** and **9ad** in 84% yield (Table 1, entry 4). Alkylation of **5a** with **7d** was more regioselective at the substituted allylic terminus than that of 2-hexenyl acetate with **7d**. The reaction of 2-hexenyl acetate with **7d** gave a product resulting from alkylation at the unsubstituted allylic terminus in 71% selectivity.[4b]

The [Pd(PPh$_3$)$_4$]-catalyzed reaction of **5a** with **7b** was reported to give a 66:33:1 mixture of **8ab**, **9ab**, and **10ab**, respectively, in 81% yield.[2b] In contrast to the reaction catalyzed by an Ir complex, that catalyzed by a Pd complex gave **8ab** as the major product. This result shows that the iridium catalyst is a useful complement to the palladium catalyst.

Acetate **6a**, which is a regioisomer of **5a**, reacted with **7a**–**d** at room temperature to give products in 81–84% yields. Reactions with **7a**, **7b**, and **7c** occurred with perfect regioselectivity at the substituted allylic terminus (Table 1, entries 5–7). The reaction with **7d** gave a 1:99 mixture of **8ad** and **9ad** in 83% yield (Table 1, entry 8). These results strongly suggest the intermediacy of the 1-alkenyl-π-allyliridium intermediate **1** (M = Ir).

Table 1. Allylic alkylation of **5** and **6** catalyzed by the Ir complex.[a]

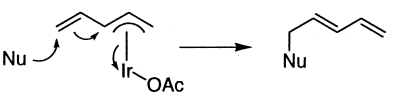
Entry	Substrate	Nu	t[h]	Product	Yield [%][b]	**8**:**9**:**10**[c]
1	R^1 = Me, R^2 = H (**5a**)	CH(CO$_2$Et)$_2$ (**7a**)	3	**8aa**, **9aa**, **10aa**	94	0:100:0
2	R^1 = Me, R^2 = H (**5a**)	CH(CO$_2$Me)$_2$ (**7b**)	3	**8ab**, **9ab**, **10ab**	87	0:100:0
3	R^1 = Me, R^2 = H (**5a**)	CHAcCO$_2$Et (**7c**)	16	**8ac**, **9ac**, **10ac**	93	0:100:0
4	R^1 = Me, R^2 = H (**5a**)	CMe(CO$_2$Et)$_2$ (**7d**)	8	**8ad**, **9ad**, **10ad**	84	6:94:0
5	R^1 = Me R^2 = H (**6a**)	CH(CO$_2$Et)$_2$ (**7a**)	3	**8aa**, **9aa**, **10aa**	84	0:100:0
6	R^1 = Me, R^2 = H (**6a**)	CH(CO$_2$Me)$_2$ (**7b**)	3	**8ab**, **9ab**, **10ab**	81	0:100:0
7	R^1 = Me, R^2 = H (**6a**)	CHAcCO$_2$Et (**7c**)	16	**8ac**, **9ac**, **10ac**	84	0:100:0
8	R^1 = Me, R^2 = H (**6a**)	CMe(CO$_2$Et)$_2$ (**7d**)	3	**8ad**, **9ad**, **10ad**	83	1:99:0
9	R^1 = Ph, R^2 = H (**6b**)	CH(CO$_2$Et)$_2$ (**7a**)	2	**8b**, **9b**, **10b**	92	0:100:0
10	R^1 = *n*Pr, R^2 = H (**6c**)	CH(CO$_2$Et)$_2$ (**7a**)	2	**8c**, **9c**, **10c**	93	0:100:0
11	R^1 = Me, R^2 = Me (**6d**)	CH(CO$_2$Et)$_2$ (**7a**)	3	**8d**, **9d**, **10d**	90	0:100:0
12	R^1 = (*E*)-*n*BuCH = CH, R^2 = H (**6e**)	CH(CO$_2$Et)$_2$ (**7a**)	4	**8e**, **9e**, **10e**	92	0:100:0
13	R^1 = R^2 = H (**6f**)	CH(CO$_2$Et)$_2$ (**7a**)	4	**8f**, **9f**	81	19:81:–

[a] A mixture of **5** or **6** (2 mmol), NaNu (4 mmol), [{Ir(cod)Cl}$_2$] (0.04 mmol), P(OPh)$_3$ (0.16 mmol), and THF (10 mL) was stirred under Ar at room temperature. [b] Yield of isolated product based on **5** or **6**. [c] Determined by gas chromatography and NMR spectroscopy.

Acetates **6b–e** smoothly underwent alkylation with **7a** to give **9b–e** as a single regioisomer in yields of 90–93% (Table 1, entries 9–12). A trienyl system also gave a single product (entry 12). In contrast, allylic alkylation of **6f** with **7a** gave a mixture of regioisomeric products (Table 1, entry 13). This result requires some discussion (see below).

We found that alkylation of a π-allyliridium intermediate monosubstituted at the terminal position occurred with high regioselectivity at the substituted allylic terminus when the substituent is an alkyl or aryl group.[4a–c] Since an alkenyl group is more electron-withdrawing than an alkyl group, an allylic terminus substituted with an alkenyl group is more electron-deficient than an allylic terminus substituted with an alkyl group.[6] Therefore, alkylation occurs at the substituted allylic terminus of intermediate **1** (M = Ir) with perfect regioselectivity. It is clear that oxidative addition of **5** gives intermediate **1** (M = Ir), which then reacts with a nucleophile to give **9** prior to isomerization to **2**. These results show that nucleophilic attack is much faster than isomerization. Oxidative addition of **6** can give either **1** or **2** (Scheme 1). Since a metal complex can approach a terminal alkene more easily than an internal alkene because of steric effect,[7] intermediate **1** (M = Ir) is formed preferentially.

Although oxidative addition of **6f** gives **17** as the only intermediate, alkylation of **6f** gives a mixture of **8f** and **9f**. Formation of **8f** can be explained by a S_N2'-type nucleophilic attack at a vinyl substituent on the π-allyliridium intermediate **17** [Eq. (3)].[2b] Such a S_N2'-type nucleophilic attack to intermediate **1** (R = Me, M = Ir) can occur, but no corresponding product (**10aa**) is obtained. Steric hindrance from a substituent on a vinylic carbon atom would retard the S_N2'-type nucleophilic attack.



17 **8f** (3)

The isomerization of **9** to **8** by the catalytic effect of the palladium complex under alkylation conditions has been reported.[2a,b] We examined the allylic alkylation of **5a** with **7a** under more severe conditions. The reaction of **5a** with two equivalents of **7a** in the presence of [{Ir(cod)Cl}$_2$]/P(OPh)$_3$ (Ir atom 4 mol%, P(OPh)$_3$ 8 mol%) in refluxing THF for 24 h gave **9aa** in 94% yield as a single product. Product **9** did not isomerize to **8** in the presence of a catalytic amount of the iridium complex.

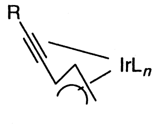
Following the success with the dienyl system we investigated the allylic alkylation of an enynyl system.[8] We examined the allylic alkylation of **11**, **12**, and **13** with **7a**.[9] The structure of the compounds and the ligand used had a considerable effect on the selectivity (Table 2). When P(OPh)$_3$ was used as a ligand the reactions proceeded at room temperature to give products in yields of 83–87% (Table 2, entries 1–3). It is noteworthy that the reaction of **12** with **7a** gave **16**, in which a retention of the *Z* geometry was observed, in 95% selectivity (Table 2, entry 2). Reactions using P(OEt)$_3$ required more forcing conditions to give products. Acetate **13** reacted with **7a** to give products in 91% yield (Table 2, entry 6). Product **14**, resulting from alkylation at the substituted allylic terminus, was obtained with 92% selectivity.

Table 2. Allylic alkylation of **11**, **12**, and **13** with **7a** catalyzed by the Ir complex.[a]

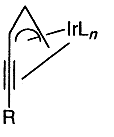
Entry	Substrate	Ligand	Conditions	Yield [%][b]	**14**:**15**:**16**[c]
1	**11**	P(OPh)$_3$	RT, 4 h	87	65:33:2
2	**12**	P(OPh)$_3$	RT, 7 h	86	2:3:95
3	**13**	P(OPh)$_3$	RT, 19 h	83	40:9:51
4	**11**	P(OEt)$_3$	THF, reflux, 21 h	43	21:77:2
5	**12**	P(OEt)$_3$	THF, reflux, 21 h	16	8:8:84
6	**13**	P(OEt)$_3$	THF, reflux, 2 h	91	92:8:0

[a] A mixture of **11**, **12**, or **13** (2 mmol), **7a** (4 mmol), [{Ir(cod)Cl}$_2$] (0.04 mmol), P(OPh)$_3$ or P(OEt)$_3$ (0.16 mmol), and THF (10 mL) was stirred under Ar. [b] Yield of isolated product based on **11**, **12**, or **13**. [c] Determined by gas chromatography and NMR spectroscopy.

Alkynes coordinate with metals more strongly than alkenes. To explain the product distributions of the reactions of **11–13**, we must consider the coordination of an alkynyl group to an Ir center. We previously proposed that the electron-withdrawing property of P(OPh)$_3$ promoted the carbonium ion character at the substituted allylic terminus, thus directing a nucleophile to this position.[4a,b] With intermediate **18**, coordination of an alkynyl group would reduce the carbonium ion character at the substituted allylic terminus and so decrease the selectivity in forming **14**.[10] Therefore, nucleophile attack occurs to some extent at the unsubstituted allylic terminus to give **15** and **16**. Oxidative addition of **12** gives *anti*-π-allyl intermediate **19**. We previously disclosed that the nucleophilic attack to an *anti*-π-allyliridium intermediate occurred at the unsubstituted allylic terminus to give a *Z*-configured product in high selectivity.[4b,d] Similarly, nucleophilic attack on **19** occurs at the unsubstituted allylic terminus to give **16** in high selectivity. Alkylation of 1-alkyl- or aryl-2-propenyl acetate suggested that a *syn*-π-allyliridium intermediate was formed preferentially.[4a,b] The reaction of **13** gave **14** and **16**, which suggests the formation of **18** as well as **19**. The increased stability of **19** arising from the coordination of an alkynyl group facilitates its formation. The reaction of **11** and **12** did not go to completion when P(OEt)$_3$ was used as a ligand. In contrast, the reaction of **13** gave products in 91% yield. Acetate **13** is more reactive than **11** and **12** as a result of the presence of a terminal alkene, which is approached by the metal complex more easily than an internal alkene. The reaction of **13** using P(OEt)$_3$ as a ligand gave **14** regioselectively. Although it is not yet clear why P(OEt)$_3$ gives a good result, it might retard the coordination of an alkynyl group to the Ir center.



18



19

Further mechanistic study and the synthetic application of 1-(1-alkenyl)-π-allyliridium and 1-(1-alkynyl)-π-allyliridium intermediates are underway.

Experimental Section

9aa: **5a** (280 mg, 2.0 mmol), triphenylphosphite (49.6 mg, 0.16 mmol), and [{Ir(cod)Cl}$_2$] (26.9 mg, 0.04 mmol) were stirred in THF (5.0 mL) under an Ar atmosphere. In a separate flask, diethyl malonate (641 mg, 4.0 mmol) was added to a slurry of sodium hydride (96 mg, 4.0 mmol) in THF (5.0 mL). The resulting solution was added to the former by syringe and the combined mixture was stirred at room temperature for 3 h. After **5a** was consumed, diethyl ether and H_2O were added to the mixture, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried ($MgSO_4$). The solvent was evaporated in vacuo. Purification of the residue by column chromatography (*n*-hexane/AcOEt = 98/2) gave **9aa** as a colorless oil (452 mg; yield 94%).

Received: January 24, 2000 [Z 14586]

---

[1] a) Pd: J. Tsuji, *Palladium Reagents and Catalysts*, Wiley, Chichester, **1995**, p. 290; b) Mo: F. Glorius, A. Pfaltz, *Org. Lett.* **1999**, *1*, 141; c) Mo: B. M. Trost, I. Hachiya, *J. Am. Chem. Soc.* **1998**, *120*, 1104; d) W: R. Pretot, G. C. Lloyd-Jones, A. Pfaltz, *Pure Appl. Chem.* **1998**, *70*, 1035; e) Rh: R. Takeuchi, N. Kitamura, *New J. Chem.* **1998**, *22*, 659; f) Rh: P. A. Evans, J. D. Nelson, *J. Am. Chem. Soc.* **1998**, *120*, 5581; g) Ir: B. Bartels, G. Helmchen, *Chem. Commun.* **1999**, 741; h) Ru: Y. Morisaki, T. Kondo, T. Mitsudo, *Organometallics* **1999**, *18*, 4742.

[2] a) Pd: Y. I. M. Nilsson, P. G. Andersson, J. E. Backvall, *J. Am. Chem. Soc.* **1993**, *115*, 6609; b) Pd: B. M. Trost, R. C. Bunt, *J. Am. Chem. Soc.* **1998**, *120*, 70; c) Mo: B. M. Trost, S. Hildbrand, K. Dogra, *J. Am. Chem. Soc.* **1999**, *121*, 10416.

[3] For the isomerization of a σ-propargylic complex to a σ-allenyl complex, see a) S. Ogoshi, Y. Fukunishi, K. Tsutsumi, H. Kurosawa, *J. Chem. Soc. Chem. Commun.* **1995**, 2485; b) S. Ogoshi, Y. Fukunishi, K. Tsutsumi, H. Kurosawa, *Inorg. Chim. Acta.* **1997**, *265*, 9.

[4] a) R. Takeuchi, M. Kashio, *Angew. Chem.* **1997**, *109*, 268; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 263; b) R. Takeuchi, M. Kashio, *J. Am. Chem. Soc.* **1998**, *120*, 8647; c) R. Takeuchi, *Polyhedron* **2000**, *19*, 557; d) for allylic amination, see R. Takeuchi, N. Shiga, *Org. Lett.* **1999**, *1*, 265.

[5] R. Takeuchi, K. Tanabe, *Abstr. Pap. 76th Annu. Meet. Chem. Soc. Jpn.* (Yokohama, Japan) **1999**, p. 2B7 34.

[6] The electronegativity of an alkenyl group is bigger than that of an alkyl group, see N. Inamoto, S. Masuda, *Chem. Lett.* **1982**, 1003.

[7] For the stability of an alkenemetal complex, see J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Chemistry*, University Science Books, Mill Valley, **1987**, p. 149.

[8] The alkylation of enynyl acetates catalyzed by a Pd complex has been reported, see E. Keinan, E. Bosch, *J. Org. Chem.* **1986**, *51*, 4006.

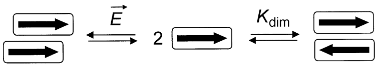
[9] A stereodivergent synthesis of (*E*)- and (*Z*)-2-alken-4-yn-1-ols from 2-propynoic acid has been reported, see R. Takeuchi, K. Tanabe, S. Tanaka, *J. Org. Chem.* **2000**, *65*, 1558.

[10] When the central metal of an alkyne complex is in a high oxidation state, donation of electrons from an alkyne to the metal should be predominant over back donation from the metal to an alkyne. Oxidative additon of an allylic ester to an iridium(I) species gives an iridium(III) species. The Ir centers in intermediates **18** and **19** would be electron-rich because of the donation of electrons from a coordinated alkyne group.

Dipolar Dye Aggregates: A Problem for Nonlinear Optics, but a Chance for Supramolecular Chemistry**

Frank Würthner* and Sheng Yao

The development of nonlinear optical materials requires the optimization of dyes with respect to their molecular electrooptical properties, for example, polarizabilities α, β, and γ,[1] as well as their supramolecular organization.[2] The most investigated $\chi^{(2)}$ nonlinear optical[3] and photorefractive[4] polymeric materials require macroscopic noncentrosymmetry, which is achieved through orientation ("poling") of the dipolar dyes by strong external electric fields. Although large dipole moments are considered to be favorable for a high poling efficiency, a large fraction of the materials based on well-designed chromophores with large dipole moments and excellent (hyper)polarizabilities failed to provide the expected electrooptic response.[5] A possible explanation might be the formation of dye aggregates. According to this concept dipolar dyes are considered to aggregate in an antiparallel fashion as a result of internal electrostatic forces (Scheme 1, right) that counteract the external forces imparted by the electric field during the poling process (Scheme 1, left).[6, 7]



Scheme 1. Model for the competition between internal organization of dipolar dyes by dipole–dipole interactions (right) and external organization by electric-field-induced dipole orientation leading to a noncentrosymmetric metastable dye arrangement as desired for nonlinear optical applications (left).

Herein we will give proof of this mechanism for merocyanine dyes **1** and **2**, which were recently introduced as the most suitable candidates for photorefractive applications on the basis of their molecular properties.[8] However, their incorporation into polymers was critical and led us to use less-dipolar dyes based on aminothiophene and indoline electron-donor groups, for example, dyes **3** and **4**.[9]

The first evidence for strong homoaggregation of dyes **1** and **2**, respectively, came from concentration-dependent UV/Vis spectra, which showed distinct hypsochromically shifted aggregate bands ("H-aggregates") already in dilute solution for solvents with low polarity (Figure 1). The well-defined isosbestic points over the whole accessible concentration range suggest the formation of dimer aggregates, which could be further confirmed by vapor-pressure osmometry (VPO).[10] From the large hypsochromic shifts of about 70 nm and 117 nm (**2**) in the absorption bands we deduce the (**1a**–**h**)

---

[*] Dr. F. Würthner, Dr. S. Yao
Abteilung Organische Chemie II
Universität Ulm
Albert-Einstein-Allee 11, 89081 Ulm (Germany)
Fax: (+49) 731-50-22840
E-mail: frank.wuerthner@chemie.uni-ulm.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft (Wu 317/1), the Fonds der Chemischen Industrie and BASF AG (travel grant for S.Y.). We thank Dr. Udo Werz for 2D NMR experiments and Prof. Peter Bäuerle for his support.