Synergetic Effects of Oxidative and Coordinative Promotors to Increase the Yield of a Twofold Pauson−Khand Reaction

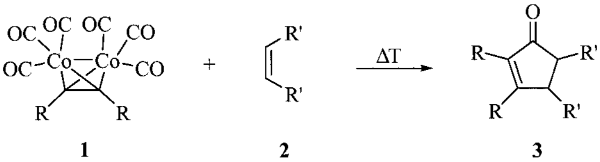
Rolf Gleiter,*[a] J. Hilko Schulte,[a] and Daniel B. Werz[a]

Keywords: Alkynes / Chalcogens / Cobalt / Pauson−Khand reaction

Four medium-sized cyclic diynes (**7**, **15**–**17**), two cyclic dithiadiynes (**18**, **19**) and two cyclic tetrathiadiynes (**20**, **21**) were starting materials for Pauson–Khand reactions with ethylene and (octacarbonyl)dicobalt under four different conditions: **A** with 1 equivalent *n*-butylmethyl sulfide (BMS), **B** with 7.5 equivalents dimethyl sulfoxide (DMSO), **C** with 7.5 equivalents DMSO and 1 equivalent BMS and **D** with 7.5 equivalents DMSO and 7.5 equivalents BMS as additives. In the cases of **7** and **15**–**17**, the yields increased strongly by applying protocol **C**. For **18**–**21**, no increase in the yields was found under conditions **A**–**D**. These differences are discussed and ascribed to intramolecular S–Co interactions in the cases of **18**–**21**.

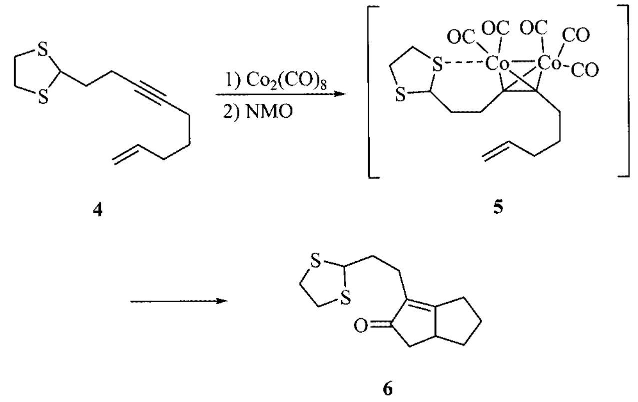
Introduction

A widespread method to prepare cyclopentenone and its derivatives uses alkynes, olefins and carbon monoxide as building blocks.[1−6] The latter unit is usually provided by octacarbonyl dicobalt. This protocol, named as the Pauson−Khand reaction,[7,8] has gained interest due to several improvements that have increased the yields and selectivity of the reaction. Especially helpful was the use of mild oxidation agents as promoters.[9,12] It is generally accepted that reagents such as dimethyl sulfoxide (DMSO)[11] or *N*-methylmorpholine *N*-oxide (NMO)[9,10] remove one of the CO groups of the intermediate alkyne−$Co_2(CO)_6$ complex **1** by oxidizing it to carbon dioxide (Scheme 1).



Scheme 1

Other species which were used to accelerate the reaction were donor ligands such as ethers, amines, or sulfides,[12−14] which are able to stabilize an empty site on the cobalt nucleus in **1** by a reversible complexation. An interesting case is one in which sulfides are tethered to the alkyne unit in the homopropargylic or bis(homopropargylic) position of the triple bond, such as in **4** (Scheme 2).[14] Treatment of **4** with $Co_2(CO)_8$ and 10 equivalents of the monohydrate of NMO in dichloromethane at ambient temperature gave rise to complex **5**. Heating the latter complex at 71 °C yielded the cyclopentenone derivative **6** after 15 minutes.



Scheme 2

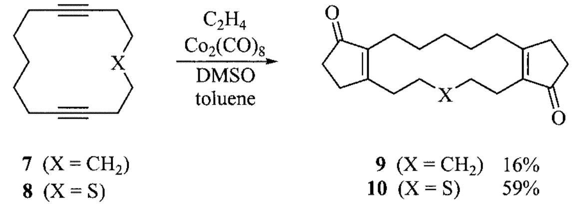
Our attention to the role of intramolecular sulfur interactions in Pauson−Khand reactions arose when we compared the results of a twofold Pauson−Khand reaction of 1,8-tetradecadiyne (**7**) and 1-thiatetradeca-4,11-diyne (**8**) with ethylene.[15] In the first case, we obtained only 16% of the product **9**, while in the latter the yield of **10** was 59% (Scheme 3).

The assumption of an intramolecular sulfur participation gained further strength when we found in complexes **11**−**13** that the chalcogen centers replace one CO group in the $[C_2Co_2(CO)_6]$ cluster in the pseudoaxial position.[16] Similarly, for complex **14**, generated from 1,4,7-trithiacyclotrideca-9,11-diyne and two equivalents of $Co_2(CO)_8$, one CO

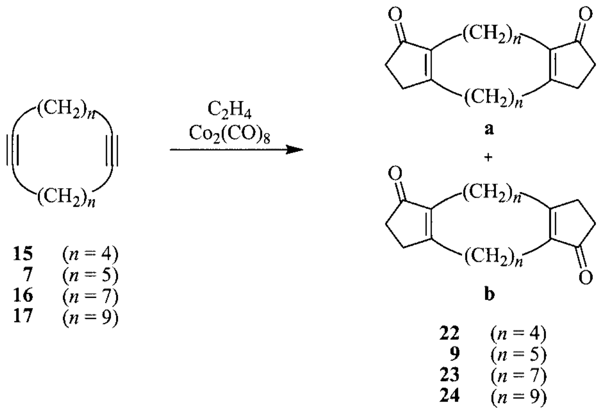
---

[a] Organisch-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax: (internat.) +49-6221-544205
E-mail: rolf.gleiter@urz.uni-heidelberg.de

DOI: 10.1002/ejoc.200400290

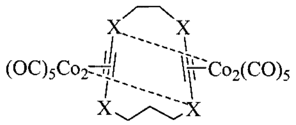


Scheme 3

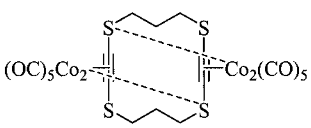


Scheme 4

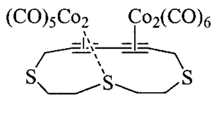
in the pseudoaxial position of one $[C_2Co_2(CO)_6]$ cluster is also replaced by a sulfur center.[17]



11 (X = S)
12 (X = Se)



13

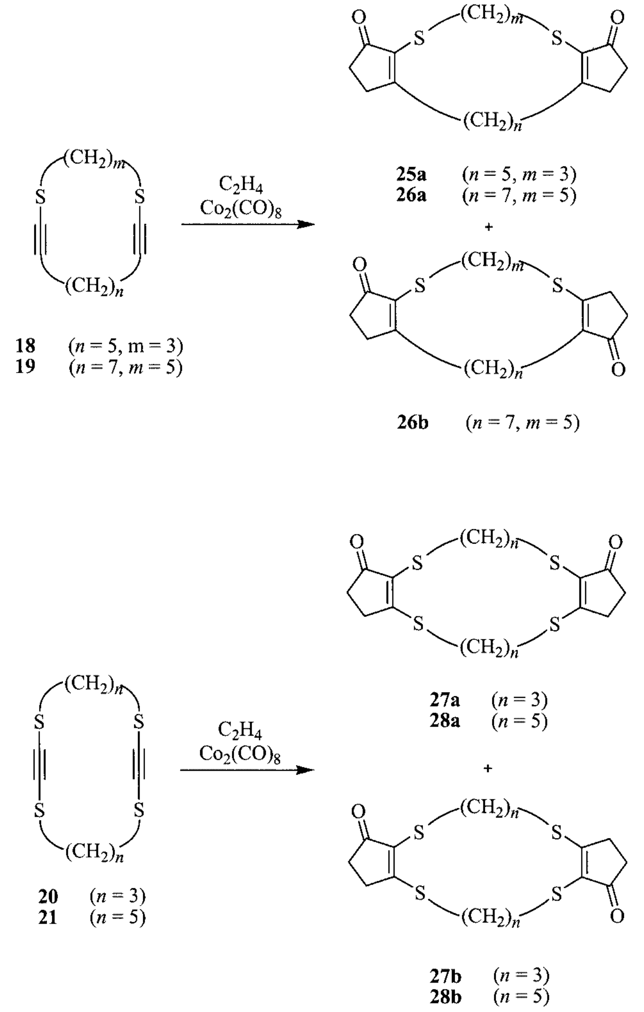


14

Spurred by these results we decided to compare the outcome of Pauson−Khand reactions with cyclic diynes and cyclic thiadiynes with ethylene as the olefinic component under four different reaction protocols.

Results and Discussion

The alkynes used were the cyclic diynes **7** and **15**−**17** (Scheme 4), the cyclic dithiadiynes **18** and **19**, as well as the cyclic tetrathiadiynes **20** and **21** (Scheme 5). The four different reaction protocols that we chose were: 1 equivalent of *n*-butylmethyl sulfide (BMS) (**A**), 7.5 equivalents of DMSO (**B**), 7.5 equivalents of DMSO + 1.0 equivalent of BMS (**C**) and 7.5 equivalents of DMSO + 7.5 equivalents of BMS (**D**).



Scheme 5

As products, we isolated the tricyclic systems **9** and **22**−**28** (Scheme 4). In the cases of the symmetric cyclic diynes **7** and **15**−**17**, the two regioisomeric products **a** and **b** of **9** and **22**−**24**, respectively, were isolated in a 1:1 ratio as determined by NMR spectroscopic experiments. Due to the relatively long alkane tethers of **9** and **22**−**28**, the separation of the regioisomers was tedious.

When the cyclic dithiadiynes **18** and **19** were used, the product isomers with the sulfur substituent in the α-position to the carbonyl group were favored. In the case of **18**, we isolated only **25a**, whereas for the larger cycle **19**, the regioisomers **26a** and **26b** were obtained in a 1:1 ratio (Scheme 5). The products isolated from the cyclic tetrathiadiynes were the **a** and **b** regioisomers of the products **27** and **28** also in a 1:1 ratio as shown in Scheme 5. The structural assignments of all products are based on NMR spectroscopic data and also on X-ray data for **26a** and **28b**. The molecular structure of **28b** is shown in Figure 1. It is worth noting that the SCH_2 moieties in the β-positions are situated in the plane of the cyclopentenone rings, whereas the SCH_2 bonds in the α-positions are perpendicular to it. This conformation indicates conjugation between the *p*-type lone pair of the sulfur atom and the electron-poor α,β-unsaturated π-system.

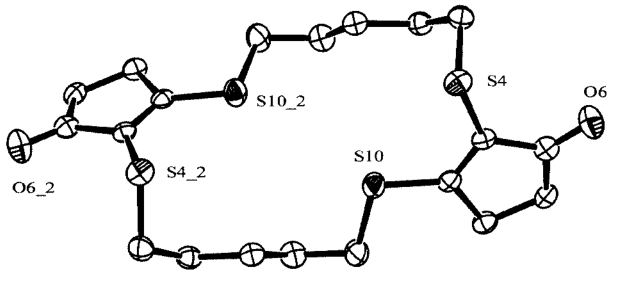


Figure 1. ORTEP plot (50% ellipsoid probability) of the molecular structure of **28b**

The yields obtained with protocols **A−D** are compared in Figure 2. These results reveal a considerable difference in the yields of the products **9** and **22−24** when compared with those of the sulfur containing rings (**25−28**).

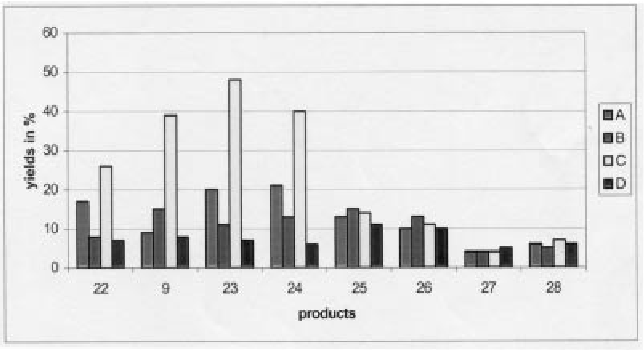


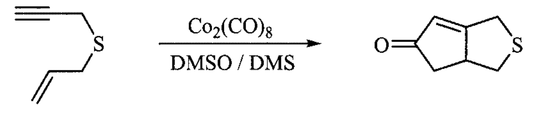
Figure 2. Yields of products **9** and **22−28** according to procedures **A−D** (toluene, 110 °C, 50 bar ethylene)

The yields of **25−28** vary only slightly. There is relatively no change in these amounts between the various protocols used. In contrast to these results are those obtained from the cyclic hydrocarbons **7** and **15−17**. The yields for the products **9** and **22−24** vary between 9−21%, 8−15% and 7−11% when we only consider protocols **A**, **B** and **D**. These values are similar to those found for **25−28**. However, if we consider the yields recorded for protocol **C**, the values are considerably higher and vary between 26% and 48%. These values are in the range of the yields that have been obtained previously by carrying out the reaction in supercritical ethylene with only DMSO as promoter (at 130 °C and 110 bar).[15b]

To rationalize the large differences between the reactivities of **7** and **15−17** on one side and those of **18−21** on the other, we assume that in the latter case transannular Co−S interactions similar to those found in **11−14** play an important role. The bonds between sulfur and cobalt are assumed to be relatively strong and therefore, the various protocols have no influence on the yields of the products. The slightly higher yields for **25** and **26** than **27** and **28** might be traced back to only one transannular Co−S bond in the dithia complexes relative to the tetrathia complexes in which two strong transannular Co−S bonds are assumed.[16] The very similar behavior of the one-sided donor-substituted diynes **18−19** as compared with **20−21**, which have donor substituents on both sides of the alkyne units, indicates that polar effects, as discussed controversially in the literature,[18,19] are of no importance.

In **7** and **15−17**, the Pauson−Khand reaction is initiated either thermally (protocol **A**) or oxidatively by DMSO (protocol **B**). This approach reveals relatively low yields, in the order of 10−20% as anticipated for twofold Pauson−Khand reactions.[15] In the case of protocol **C**, there seems to be a synergetic effect in so far as the oxidative promoter DMSO generates a free coordination site at one cobalt nucleus. This position is occupied in a *reversible* manner as long as a low concentration of BMS is present. If a surplus of BMS is available (protocol **D**), the position occupied by BMS at the cobalt center is no longer functionally reversible, and as a result the yield decreases to values close to those found for the products of **18−21** (**25−28**).

A similar synergetic effect was reported when **29** was treated under Pauson−Khand conditions with DMSO in the presence of 10 equivalents of dimethyl sulfide (DMS) (Scheme 6).[20] The yield for the intramolecular Pauson−Khand reaction, which affords **30**, was reported to be 65%.



29 **30**

Scheme 6

Conclusion

From our experiments we conclude that a mixture of weak donor molecules in low concentration and a weak oxidation agent will create an intermediate for the Pauson−Khand reaction that increases the yield considerably. This synergetic effect of the two promoters allows yields of the Pauson−Khand products in the same order as those obtained with supercritical ethylene.

Experimental Section

General Methods: The reactions were conducted in oven-dried glassware. Toluene was dried with sodium/benzophenone and distilled before use. Petroleum ether, diethyl ether and dichloromethane were distilled before use. Melting points are uncorrected. Materials for column chromatography: Silica gel 60 (Macherey−Nagel), Alox III was prepared from neutral aluminum oxide (Merck) and 6% deionized water. ^1H and ^{13}C NMR were recorded with either a Bruker Avance 300 or a Bruker Avance 500 using the solvent as internal standard. IR: Bruker Vector 22 FT-IR. HRMS(EI): JEOL JMS-700. Elemental analyses were carried out by Mikroanalytisches Laboratorium der Universität Heidelberg. The starting materials were prepared according to literature methods.[21] If not otherwise noted, the products were diastereomeric mixtures of the tricyclic diones.

General Procedure for the Preparation of the Tricyclic Diones: The cyclic diyne (1.5 mmol), octacarbonyl dicobalt (1.03 g, 3 mmol) and dry toluene (150 mL) were placed in a high pressure vessel and stirred for 20 min at room temperature. After adding the promoter(s) (**A**−**D**), the vessel was pressurized to 50 bar with ethylene. After stirring at 110 °C for 96 h, the gas was suspended, and the crude reaction mixture filtered through silica gel. Column chromatography on silica gel with light petroleum/diethyl ether (2:1) yielded the products.

Preparation of 22: Starting material: **15** (240 mg, 1.5 mmol), *n*-butylmethyl sulfide (156 mg, 1.5 mmol), according to **A**; DMSO (586 mg, 11.25 mmol) , according to **B**; *n*-butylmethyl sulfide (156 mg, 1.5 mmol) and DMSO (586 mg, 11.25 mmol), according to **C**; *n*-butylmethyl sulfide (1.17 g, 11.25 mmol) and DMSO (586 mg, 11.25 mmol), according to **D**. Column chromatography on silica gel, petroleum ether/diethyl ether (2:1). The yields of **22a**/**22b** were, **A**: 69 mg (17%), **B**: 33 mg (8%), **C**: 106 mg (26%), **D**: 29 mg (7%). Properties: colorless solid, m.p. 120 °C. The analytical data have been reported previously.[15b]

Preparation of 9a/9b: Starting material: **7** (282 mg, 1.5 mmol). The amounts of BMS and DMSO according to procedures **A**−**D** were the same as for **22**. Chromatography on silica gel, petroleum ether/diethyl ether (2:1). The yields of **9a**/**9b** were, **A**: 41 mg (9%), **B**: 68 mg (15%), **C**: 176 mg (39%), and **D**: 36 mg (8%). Properties: colorless solid, m.p. 215 °C. The analytical data have been reported previously.[15a]

Preparation of 23a/23b: Starting material: **16** (367 mg, 1.5 mmol). The amounts of BMS and DMSO according to procedures **A**−**D** were the same as for **22**. Column chromatography on silica gel, petroleum ether/diethyl ether (2:1). The yields of **23a**/**23b** were, **A**: 107 mg (20%), **B**: 59 mg (11%), **C**: 257 mg (48%), **D**: 37 mg (7%). Properties: colorless solid, m.p. 120−121 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11−1.41 (m, 18 H), 1.42−1.59 (m, 4 H), 2.02−2.19 (m, 4 H), 2.23−2.52 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.4 (CH_2), 27.1 (CH_2), 27.8 (CH_2), 28.1 (CH_2), 28.5 (CH_2), 28.8 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 30.9 (CH_2), 34.2 (CH_2), 31.0 (CH_2), 140.3 (C=C), 173.5 (C=C), 210.1 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2923, 2850, 1695, 1636, 1439, 1366, 1028 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 280 nm (4.0). HRMS (EI, 70 eV): calcd. ($C_{24}H_{36}O_2$) 356.2716; found 356.2688.

Preparation of 24a/24b: Starting material: **17** (454 mg, 1.5 mmol). The amounts of BMS and DMSO according to procedures **A**−**D** were the same as for **22**. Column chromatography on silica gel, petroleum ether/diethyl ether (2:1). The yields of **24a**/**24b** were, **A**: 129 mg (21%), **B**: 80 mg (13%), **C**: 247 mg (40%), **D**: 37 mg (6%). Properties of **24a**/**24b**: colorless solid, m.p. 111 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21−1.42 (m, 24 H, CH_2), 1.51−1.57 (m, 4 H, CH_2), 2.13−2.18 (m, 4 H, CH_2), 2.33−2.43 (m, 8 H, CH_2), 2.46−2.48 (m, 4 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.9 (CH_2), 27.2 (CH_2), 27.2 (CH_2), 27.9 (CH_2), 28.1 (CH_2), 28.7 (CH_2), 28.9 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 30.7(CH_2), 34.0 (CH_2), 140.3 (C=C), 173.6 (C=C), 209.8 (CO) ppm. HRMS (EI, 70 eV): calcd. ($C_{28}H_{44}O_2$) 412.3341; found 412.3337.

Preparation of 25a: Starting material: **18** (337 mg, 1.5 mmol). The amounts of BMS and DMSO according to procedures **A**−**D** were the same as for **22**. Column chromatography on silica gel, petroleum ether/diethyl ether (2:1). The yields of **25a** were, **A**: 66 mg (13%), **B**: 76 mg (15%), **C**: 71 mg (14%), and **D**: 56 mg (11%). Properties of **25a**: colorless, highly viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80−1.11 (m, 4 H, CH_2), 1.12−1.50 (m, 6 H, CH_2), 1.51−1.82 (m, 6 H, CH_2), 2.11−2.90 (m, 8 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1 (CH_2), 26.4 (CH_2), 27.5 (CH_2), 28.4 (CH_2), 28.9 (CH_2), 29.6 (CH_2), 31.8 (CH_2), 133.0 (C=C), 182.9 (C=C), 206.2 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2930, 2858, 1738, 1697, 1639, 1438, 1053 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 274 nm (3.4). HRMS (EI, 70 eV): calcd. ($C_{18}H_{24}O_2S_2$) 336.1218; found 336.1227.

Preparation of 26a/26b: Starting material: **19** (421 mg, 1.5 mmol). The amounts of BMS and DMSO according to procedures **A**−**D** were the same as for **22**. Chromatography on silica gel, petroleum ether/diethyl ether (2:1). The yields of **26a**/**26b** were, **A**: 59 mg (10%), **B**: 77 mg (13%), **C**: 65 mg (11%), **D**: 59 mg (10%). Properties of **26a**/**26b**: slightly yellow solid, m.p. 150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18−1.61 (m, 32 H, CH_2), 2.29−2.50 (m, 12 H, CH_2), 2.51−2.88 (m, 20 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.1 (CH_2), 27.2 (2 × CH_2), 27.3 (CH_2), 28.7 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 29.0 (2 × CH_2), 29.1 (3 × CH_2), 29.2 (3 × CH_2), 29.3 (3 × CH_2), 29.4 (2 × CH_2), 29.5 (3 × CH_2), 29.6 (2 × CH_2), 29.8 (CH_2), 30.0 (CH_2), 31.1 (CH_2), 31.6 (CH_2), 31.9 (CH_2), 32.0 (CH_2), 34.1 (CH_2), 34.3 (CH_2), 133.3 (C=C), 133.8 (2 × C=C), 137.9 (C=C), 175.3 (C=C), 181.7 (C=C), 182.4 (2 × C=C), 204.9 (CO), 206.5 (3 × CO) ppm. IR (KBr): $\tilde{\nu}$ = 2930, 2858, 1738, 1697, 1639, 1438, 1053 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 282 nm (1.8). HRMS (EI, 70 eV): calcd. ($C_{22}H_{32}O_2S_2$) 392.1844, found 392.1843. $C_{22}H_{32}O_2S_2$·0.2CH_3OH (399.0): calcd. C 66.82, H 8.28; found C 66.67, H 8.14.

Crystal Data of 26a: Triclinic, a = 8.4297(1) Å, b = 10.9520(3) Å, c = 12.4094(3) Å, α = 101.821(1), β = 101.331(1), γ = 107.151(1), V = 1030.29(4) Å^3, space group $P\bar{1}$, Z = 2, $D_{calcd.}$ = 1.266 g·cm^{-3}, F(000) = 424, polyhedron, 0.40 × 0.18 × 0.04 mm, μ = 0.272 mm^{-1}, reflections collected 10740, independent reflections 4697, observed reflections 3462, $R1$ = 0.036, $wR2$ = 0.082, S(Gof) = 1.02, $(\Delta\rho)_{max.}$ = 0.28 e·Å^{-3}; $(\Delta\rho)_{min.}$ = −0.22 e·Å^{-3}.

Preparation of 27a/27b: Starting material: **20** (391 mg, 1.5 mmol). The amounts of BMS and DMSO according to procedures **A**−**D** were the same as for **22**. Column chromatography on Alox III in CH_2Cl_2/CH_3OH (200:1). The yields of **27a**/**27b** were, **A**: 22 mg (4%), **B**: 20 mg (4%), **C**: 24 mg (4%), **D**: 26 mg (5%). Properties of **27a**/**27b**: slightly yellow colored viscous oil. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 332 (3.8), 320 (3.9), 294 nm (4.2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.13 (m, 2 H, CH_2), 1.20 (m, 2 H, CH_2), 1.70−1.82 (m, 2 H, CH_2), 2.51−2.54 (m, 4 H, CH_2), 2.70 (m, 2 H, CH_2), 3.01−3.26 (m, 4 H, CH_2), 3.28−3.52 (m, 4 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.0 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 30.2 (CH_2), 30.8 (CH_2), 31.4 (CH_2), 34.5 (CH_2), 129.5 (C=C), 130.1 (C=C), 180.2 (C=C), 181.3 (C=C), 201.8 (CO), 202.3 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2926, 1734, 1683, 1638, 1508, 1436, 1237, 1030 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 332 (3.8), 320 (3.9), 294 nm (4.2). HRMS (EI, 70 eV): calcd. 372.0346; found 372.0352.

Preparation of 28a/28b: Starting material: **21** (475 mg, 1.5 mmol). The amounts of BMS and DMSO according to procedures **A**−**D** were the same as for **22**. Chromatography on Alox III in CH_2Cl_2/CH_3OH (200:1). The yields of **28a**/**28b** were, **A**: 39 mg (6%), **B**: 36 mg (5%), **C**: 46 mg (7%), **D**: 43 mg (6%). Properties of **28a**/**28b**: slightly yellow oil. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 330 (3.5), 298 (3.9), 262 nm (3.6). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13−1.51

(m, 6 H, CH_2), 1.52−1.79 (m, 6 H, CH_2), 2.49−2.68 (m, 6 H, CH_2), 2.67−3.12 (m, 6 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.4 (CH_2), 27.3 (CH_2), 28.6 (CH_2), 28.7 (CH_2), 29.7 (CH_2), 29.8 (CH_2), 30.8 (CH_2), 31.6 (CH_2), 34.6 (CH_2), 39.4 (CH_2), 156.0 (C=C), 181.6 (C=C), 202.0 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2922, 2851, 1675, 1514, 1432, 1235, 1093 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 330 (3.5), 298 (3.9), 262 (3.6). HRMS (EI, 70 eV): calcd. 428.0972; found 428.0952.

Crystal Data of 28b: orthorhombic, a = 9.8233(6) Å, b = 20.7775(12) Å, c = 5.1168(3) Å, V = 1044.36(11) $Å^3$, space group $P2_12_12$, Z = 2, $D_{calcd.}$ = 1.363 $g\cdot cm^{-3}$, $F(000)$ = 456, needle, 0.34 × 0.05 × 0.05 mm, μ = 0.467 mm^{-1}, reflections collected 8209, independent reflections 1658, observed reflections 1358, $R1$ = 0.036, $wR2$ = 0.063, S(Gof) = 1.02, $(\Delta\rho)_{max.}$ = 0.21 $e\cdot Å^{-3}$, $(\Delta\rho)_{min.}$ = −0.20 $e\cdot Å^{-3}$.

X-ray Diffraction Analyses: The reflections were collected with a Bruker Smart CCD diffractometer (graphite-monochromated Mo-K_α radiation). Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using SADABS[22] based on the Laue symmetry of the reciprocal space. The structures were solved by direct methods. The structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique (F^2). The hydrogen atoms were calculated according to stereochemical aspects. Structure solution and refinement were carried out with SHELXTL (5.10) software package.[22] The ORTEP drawing was obtained using the ORTEP-3 for Windows program by L. Farrugia.[23] CCDC-236414 (**26a**) and CCDC-236415 (**28b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: data_request@ccdc.cam.ac.uk].

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft (SFB 623), the Fonds der Chemischen Industrie and BASF Aktiengesellschaft, Ludwigshafen, for financial support. D. B. W. is grateful to the Studienstiftung des deutschen Volkes for a graduate fellowship. We thank Dr. F. Rominger for structure solution and Prof. W. Siebert for fruitful discussions.

---

[1] P. L. Pauson, *Tetrahedron* **1985**, *41*, 5855−5860.

[2] O. Geis, H.-G. Schmalz, *Angew. Chem.* **1998**, *110*, 955−958; *Angew. Chem. Int. Ed.* **1998**, *37*, 911−915.

[3] A. J. Fletcher, S. D. R. Christie, *J. Chem. Soc., Perkin Trans. 1* **2000**, 1657−1668.

[4] K. M. Brummond, J. L. Kent, *Tetrahedron* **2000**, *56*, 3263−3283.

[5] T. Sugihara, M. Yamaguchi, M. Nishizawa, *Chem. Eur. J.* **2001**, *8*, 1589−1595.

[6] [6a] P. L. Pauson, in *Organometallics in Organic Synthesis* (Eds.: A. de Meijere, H. tom Dieck), Springer, Berlin, **1988**, pp. 233−246. [6b] N. E. Schore, in *Comprehensive Organic Synthesis* (Ed.: B. M. Trost), Pergamon, Oxford **1991**, vol. 5, pp. 1037−1062. [6c]N. E. Schore, *Org. React.* **1991**, *40*, 1−90. [6d] N. E. Schore, in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, vol. 12. pp. 703−739.

[7] I. U. Khand, G. R. Knox, P. L. Pauson, W. E. Watts, *J. Chem. Soc., Chem. Commun.* **1971**, 36.

[8] I. U. Khand, G. R. Knox, P. L. Pauson, W. E. Watts, *J. Chem. Soc., Perkin Trans. 1* **1973**, 975−977.

[9] S. Shambayati, W. E. Crowe, S. L. Schreiber, *Tetrahedron Lett.* **1990**, *31*, 5289−5292.

[10] N. Jeong, Y. K. Chung, B. Y. Lee, S. L. Lee, S. E. Yoo, *Synlett* **1991**, 204−206.

[11] Y. K. Chung, B. Y. Lee, N. Jeong, M. Hudecek, P. L. Pauson, *Organometallics* **1993**, *12*, 220−223.

[12] T. Sugihara, M. Yamada, H. Ban, M. Yamaguchi, C. Kaneko, *Angew. Chem.* **1997**, *109*, 2884−2886; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2801−2804.

[13] T. Sugihara, M. Yamada, M. Yamaguchi, M. Nishizawa, *Synlett* **1999**, 771−773.

[14] M. E. Krafft, I. L. Scott, R. H. Romero, S. Feibelmann, C. E. Van Pelt, *J. Am. Chem. Soc.* **1993**, *115*, 7199−7207.

[15] [15a] B. J. Rausch, R. Gleiter, *Tetrahedron Lett.* **2001**, *42*, 1651−1653. [15b] B. J. Rausch, H. Becker, R. Gleiter, F. Rominger, *Synlett* **2002**, 723−726.

[16] D. B. Werz, J. H. Schulte, B. J. Rausch, R. Gleiter, F. Rominger, *Eur. J. Inorg. Chem.* **2004**, 2585−2593.

[17] J. E. Davies, L. J. Hope-Weeks, M. J. Mays, P. R. Raithby, *Chem. Commun.* **2000**, 1411−1412.

[18] F. Robert, A. Milet, Y. Gimbert, D. Konya, A. E. Green, *J. Am. Chem. Soc.* **2001**, *123*, 5396−5400.

[19] J. H. Schulte, R. Gleiter, F. Rominger, *Org. Lett.* **2002**, *4*, 3301−3304.

[20] A. Stumpf, N. Jeong, H. Sunghee, *Synlett* **1997**, 205−207.

[21] [21a] R. Gleiter, R. Merger, B. Treptow, W. Wittwer, G. Pflaesterer, *Synthesis* **1993**, 558−560. [21b] B. Hellbach, R. Gleiter, F. Rominger, *Synthesis* **2002**, 2535−2541. [21c]J. H. Schulte, D. B. Werz, F. Rominger, R. Gleiter, *Org. Biomol. Chem.* **2003**, *1*, 2788−2794. [21d] C. Benisch, S. Bethke, R. Gleiter, T. Oeser, H. Pritzkow, F. Rominger, *Eur. J. Org. Chem.* **2000**, 2479−2488.

[22] G. M. Sheldrick, Bruker Analytical X-ray-Division, Madison, WI, **1997**.

[23] ORTEP-3 for Windows: A Version of Ortep-III with a Graphical User Interface (GUI): L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

Received April 28, 2004