Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 691 (2006) 3943–3947

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Note

Strong distortions in hexacarbonyldicobalt complexes by *push–pull* effects

Daniel B. Werz [a,b], Christian Bleiholder [a], Rolf Gleiter [a,*], Frank Rominger [a]

[a] *Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany*

[b] *Laboratory for Organic Chemistry, Swiss Federal Institute of Technology Zürich, ETH Zürich, Wolfgang-Pauli-Strasse 10, CH-8093 Zürich, Switzerland*

Received 17 February 2006; received in revised form 4 May 2006; accepted 11 May 2006

Abstract

Push–pull substituted alkynes with a thioether moiety in the α position and a sulfoxide or a sulfone moiety in the α′ position are reacted with octacarbonyldicobalt to create highly distorted hexacarbonyldicobalt complexes.

Keywords: Cobalt; Carbonyl complexes; Pauson–Khand reaction; *Push–pull*-effects; X-ray structures

1. Introduction

Our knowledge on the geometry of tetrahedral complexes between a CC triple bond and a $[Co_2(CO)_6]$ unit is important for understanding the mechanism of the Pauson–Khand reaction [1,2]. Especially in view of recent discussions concerning electronic effects [3–5] such a detailed knowledge is required. Therefore, we searched for structural informations on possibly electronically perturbed alkyne–$Co_2(CO)_6$ complexes. Among the 331 species listed in the Cambridge Crystallographic Data Base, 186 were not generated from symmetrically substituted alkynes. Among those latter structures, the most prominent were the complexes of **1**–**6** depicted in Chart 1 [5–7]. In **1**–**5** the alkyne unit contains a chalcogen substituent on one side of the triple bond and an alkyl, aryl or ester group on the other. In **6** two highly electronegative substituents are attached to the triple bond. Despite strong donor groups in the case of **1**–**3** and **5**, donor and acceptor groups in **4**, and strong acceptors in **6**, the geometrical changes of the corresponding $[Co_2(CO)_6]$ complexes remain small. In continuation of our efforts to investigate electronically distorted alkynes, we designed a dicobaltatetrahedrane core consisting of an electron-donating group on one side and a very electron-withdrawing group on the other side of the former alkyne unit.

2. Results and discussion

For this purpose we chose a sulfide to act as a donor in the α position and a sulfoxide or sulfone, respectively, to act as an acceptor in the α′ position. These two designed compounds **7** and **8** are easily synthesized starting from the well-known bis(*tert*-butylthio)acetylene (**9**) [8]. Oxidation of **9** with a slight excess (1.15 eq. and 2.35 eq.) of *m*-chloroperbenzoic acid (*m*CPBA) in chloroform at 0 °C to room temperature for 2 days afforded the *push–pull*-substituted alkynes **7** and **8**. It is interesting to note that *m*CPBA is a nucleophilic oxidizing agent which converts the in situ generated sulfoxide to the sulfone, but not to the bis-sulfoxide. Aqueous work-up and subsequent column chromatography furnished the pure compounds in 69% (**7**) and 57% (**8**) yield (Scheme 1).

According to quantum chemical calculations (HF/3-21G//B3LYP-3-21G) [9] these species exhibit highly polarized triple bonds. Expressed in terms of MO theory, the

---

[*] Corresponding author. Tel.: +496221548400.

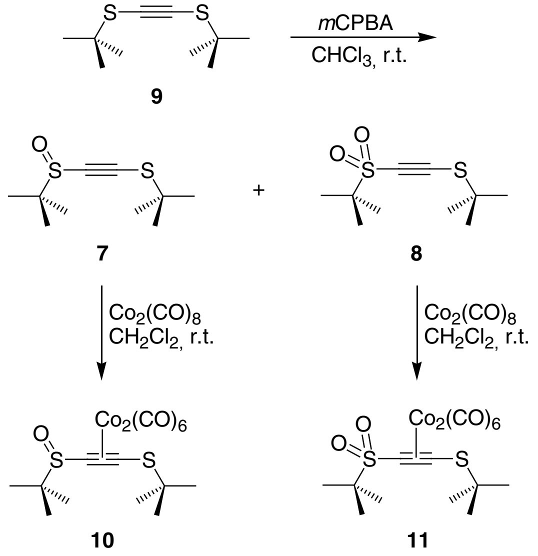
E-mail addresses: werz@org.chem.ethz.ch (D.B. Werz), rolf.gleiter@oci.uni-heidelberg.de (R. Gleiter).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.05.016

$R'-\!\equiv\!-R$

	R'	R		R'	R
1	Me	SMe	**4**	CO_2Et	SMe
2	*t*-Bu	SMe	**5**	Ph	SePh
3	Ph	SMe	**6**	SF_6	CF_3

Chart 1.



Scheme 1.

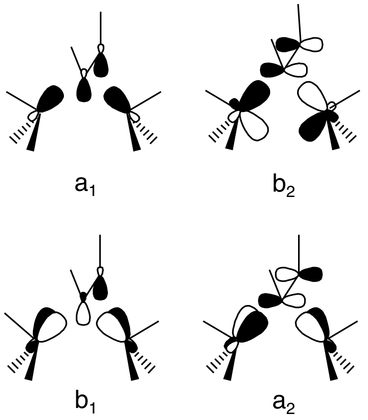


Fig. 1. Important interactions between alkyne and $Co_2(CO)_6$ fragment shown schematically.

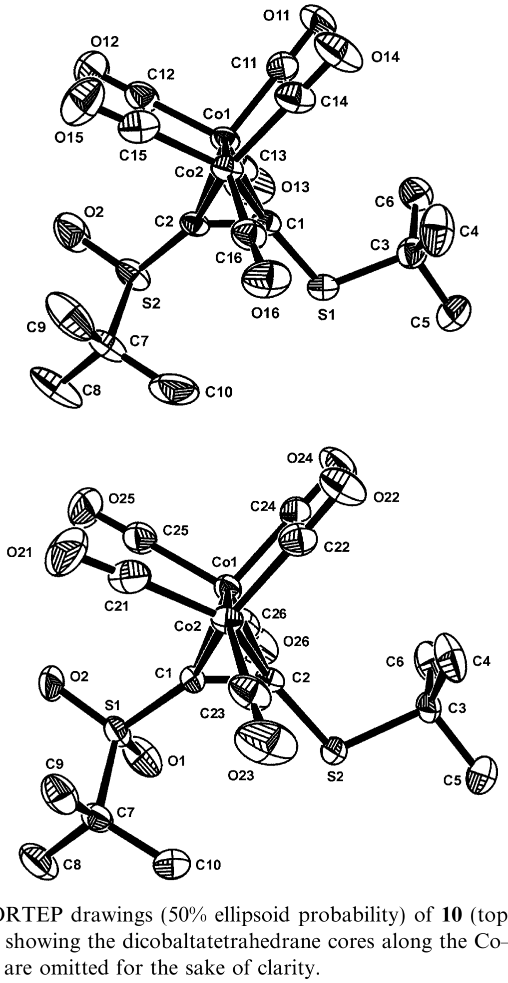


Fig. 2. ORTEP drawings (50% ellipsoid probability) of **10** (top) and **11** (bottom) showing the dicobaltatetrahedrane cores along the Co–Co axis. H atoms are omitted for the sake of clarity.

AO coefficients of the acetylenic carbons show large differences, a necessary prerequisite to obtain highly distorted hexacarbonyldicobalt complexes. In Fig. 1, we show the four orbitals resulting from the interaction of the filled b_2 and a_1 and the empty b_1 and a_2 orbitals of a bent alkyne with corresponding orbitals (empty 1 b_2, 2 a_1 and filled 1 b_1 and 1 a_2 orbitals) of the $Co_2(CO)_6$ fragment [10]. Due to the strong asymmetry of the alkyne MOs the metal–carbon interactions on the acceptor side of the alkyne are stronger than on the donor side.

The hexacarbonyldicobalt complexes **10** and **11** were obtained by reacting the alkynes **7** and **8**, respectively, with an equimolar amount of octacarbonyldicobalt in dichloromethane at room temperature. The reactions as well as the purifications by flash column chromatography with mixtures of hexane/ethyl acetate have to be performed in the darkness. Single crystals of the light-sensitive compounds suitable for X-ray diffraction analyses were obtained from *n*-hexane/dichloromethane at room temperature. ORTEP drawings of **10** and **11** are shown in Fig. 2.

As anticipated from our theoretical considerations, the *push–pull* effects are reflected in dramatic distortions of the dicobaltatetrahedrane core. The commonly observed local C_{2v} symmetry is no longer existent, the two Co atoms are skewed to the more sterically demanding side. A more detailed analysis of the geometry revealed a shortening of the distances between the Co atoms and the acetylenic carbons on the side of the acceptor (a_1, a_2), and a lengthening of these bonds adjacent to the donor (a_3, a_4) as shown in Fig. 3. The distances between Co and the CO ligands also show considerable differences: the Co–CO bonds of the pseudoequatorial CO ligands toward the side of the acceptor (b_1, b_2) are longer than to the side of the donor (b_3, b_4).

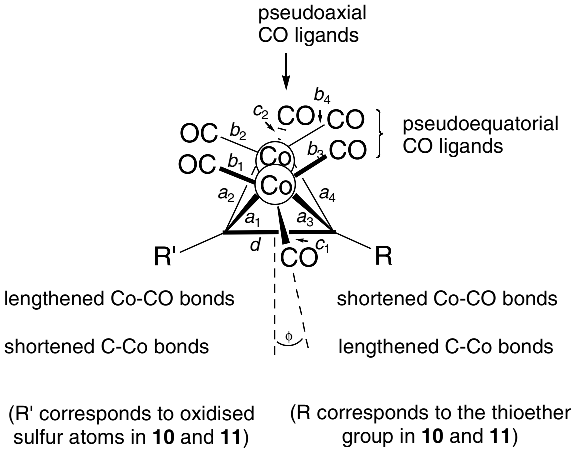


Fig. 3. Distorted dicobaltatetrahedrane core (schematically) and definition of important bond lengths and the torsion angle ϕ.

Another parameter of interest are the torsion angles ϕ of the pseudoaxial CO ligands; they attain values of 13–21° in contrast to symmetrical complexes where this value is equal to 0°. The oxidized sulfur atoms of the complexes **10** and **11** lie no longer in the S–C–C plane perpendicular to the Co–Co axis. The C–S(O)$_n$ bond is bent out of this plane by 14° (SO_2) and 17° (SO), respectively.

To exclude crystal packing effects as cause for these distorted structures, we performed DFT (B3LYP/3-21G) [9] geometry optimizations on **10** and **11**. Table 1 compares X-ray data of the dicobalthexacarbonyl complexes of **1**–**6** and the complexes **10** and **11**; for the compounds **10** and **11** also the DFT results are given.

3. Conclusion

We designed a highly polarized triple bond by means of strong *push–pull* substituents. For this purpose, we chose a sulfide as donating unit and a sulfoxide or sulfone moiety as accepting unit. These alkynes were reacted with octacarbonyldicobalt in order to furnish the hexacarbonyldicobalt complexes. The molecular structures of these species were studied by means of X-ray diffraction. Highly distorted dicobaltatetrahedrane cores were observed. The experimental results were corroborated by DFT calculations. The observations are the result of the highly polarized triple bond. High reactivity is expected and currently under investigation.

4. Experimental

4.1. General remarks

If not otherwise stated all reactions were conducted in oven-dried glassware under an argon atmosphere with magnetic stirring. Chloroform and dichloromethane were dried using CaH_2 and distilled before use. Melting points are uncorrected. Materials used for column chromatography: Silica gel 60 and alumina (Alox III). Alox III was obtained by adding 6% (Vol.) of water to neutral alumina. ^{1}H NMR and ^{13}C NMR were recorded either at 300 and 500 MHz (^{1}H NMR) or 75.5 and 125.8 MHz (^{13}C NMR), respectively, using the solvent as internal standard. The IR spectra were recorded with a FT-IR instrument. The UV light absorption spectra were recorded using a FT-UV spectrometer. Mass spectra were either recorded in the EI+ or in the FD mode. The high-resolution mass spectra (HRMS) were recorded in the EI+ (70 eV) mode. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. The photoelectron (PE) spectra were recorded with a PS18 spectrometer (Perkin–Elmer) equipped with a Helectros lamp at 60–70 °C. The spectra were calibrated with Ar and Xe. A resolution of 20 meV was obtained for the $^2P_{3/2}$ line of Ar.

4.2. Preparation of (*tert*-butylsulfinyl)(*tert*-butylthio)-acetylene (7)

800 mg (3.95 mmol) of bis(*tert*-butylthio)acetylene (**9**) was dissolved in 60 ml of chloroform and 20 ml of petroleum ether. The mixture was cooled to 0 °C and a solution of *m*CPBA (1.08 g, 4.50 mmol) in 30 ml of chloroform was added slowly. The mixture is stirred for 2 d while warming up to room temperature. After 2 d the mixture was cooled to 0 °C and filtered. The filtrate was washed 3 times with 50 ml of $Na_2S_2O_3$ solution, then washed 3 times with 50 ml of $NaHCO_3$ solution. The aqueous phase is reextracted once with chloroform. The combined organic phases are

Table 1
Comparison of relevant bond lengths (pm) and angles (°) (mean values with standard deviations) obtained by X-ray analyses and DFT calculations, respectively, for the hexacarbonyldicobalt complexes of **1**–**6** as well as the complexes **10** and **11**, definitions are given in Fig. 3

	1	**2**	**3**	**4**	**5**	**6**	**10**	**10** (DFT)	**11**	**11** (DFT)
$(a_1 + a_2)/2$	196.2(2)	197.0(2)	196.6(3)	194.3(2)	196.5(5)	192.7(8)	194.3(3)	194.1	192.5(3)	192.5
$(a_3 + a_4)/2$	195.6(2)	196.9(2)	196.9(3)	195.6(2)	195.8(5)	192.9(8)	199.0(2)	200.7	198.4(3)	200.6
$(b_1 + b_2)/2$	182.7(2)	182.4(2)	182.3(4)	183.4(2)	181.8(6)	182.3(8)	184.4(4)	184.4	183.5(3)	184.3
$(b_3 + b_4)/2$	181.5(2)	181.8(2)	183.0(4)	181.8(2)	180.5(6)	182.6(8)	182.2(3)	181.7	181.6(4)	181.7
$(c_1 + c_2)/2$	179.2(2)	179.8(2)	179.2(4)	180.1(2)	178.9(7)	181.5(8)	180.6(4)	178.9	180.7(4)	179.8
d	134.8(2)	134.5(2)	134.3(4)	136.7(2)	133.8(7)	196.2(10)	136.9(4)	136.3	135.5(4)	136.7
Co–Co	246.6(3)	246.1(1)	247.0(1)	247.0(1)	246.4(2)	246.1(2)	246.8(1)	245.7	247.0(1)	246.2
ϕ[a]	7.6(1)	3.2(1)	−3.2(1)	1.6(1)	15.3(2)	9.1(1)	20.1(1)	22.0	21.3(1)	19.4
	6.1(1)	5.4(1)	0.8(1)	5.1(1)	−3.9(4)	−2.3(1)	15.2(1)	−2.9	12.9(1)	−1.9

[a] Torsional angles between the Co–Co axis and the pseudoaxial CO ligands.

dried over Na_2SO_4 and concentrated. After adsorption on celite, the product is purified by column chromatography using silica gel (petroleum ether/EtOAc 5:1). The strongly UV active fractions were combined and the solvent was removed by rotary evaporation. 592 mg (69%) of **7** was obtained as a colourless solid: mp. 35 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.35 (s, 9H, SC(CH_3)$_3$), 1.42 (s, 9H, SOC(CH_3)$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.4 (SOC(CH_3)$_3$), 30.6 (SC(CH_3)$_3$), 50.8 (S*C*(CH_3)$_3$), 59.2 (SO*C*(CH_3)$_3$), 93.2 (*C*C), 98.8 (C*C*); IR (KBr) 2966, 2925, 2899, 2075, 1627, 1471, 1392, 1160 cm^{-1}; UV–Vis (nm, logε, CH_2Cl_2) 236 (4.15), 270 (3.05), 300 (2.10); HRMS (EI+, 70 eV) calcd. $[M+H]^+$, 219.0877, obsd. 219.0892. Elemental analysis ($C_{10}H_{18}OS_2$) calcd.: C, 55.00; H, 8.31; S, 29.37. Found: C, 54.99; H, 8.34; S, 29.45%. Lowest ionization energies derived by PE spectroscopy: $I_{v,j} = 8.5$ eV [π, n(p(S))], 8.9 eV [π, n(sp^n)], 10.1 eV [π, n(p(O))].

4.3. Preparation of (tert-butylsulfonyl)(tert-butylthio)-acetylene (**8**)

800 mg (3.95 mmol) of bis(*tert*-butylthio)acetylene (**9**) was dissolved in 60 ml of chloroform and 20 ml of petroleum ether. The mixture was cooled to 0 °C and a solution of *m*CPBA (2.20 g, 9.18 mmol) in 30 ml of chloroform was added slowly. The mixture is stirred for 2 d while warming up to room temperature. After 2 d the mixture was cooled to 0 °C and filtered. The filtrate was washed 3 times with 50 ml of $Na_2S_2O_3$ solution, then washed 3 times with 50 ml of $NaHCO_3$ solution. The aqueous phase is reextracted once with chloroform. The combined organic phases are dried over Na_2SO_4 and concentrated. After adsorption on celite, the product is purified by column chromatography using silica gel (petroleum ether/EtOAc 5:1). The strongly UV active fractions were combined and the solvent was removed by rotary evaporation. 529 mg (57%) of **8** was obtained as a colourless solid: m.p. 54 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.46 (s, 9H, SC(CH_3)$_3$), 1.50 (s, 9H, SO_2C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.2 (SO_2C(CH_3)$_3$), 30.8 (SC(CH_3)$_3$), 52.2 (S*C*(CH_3)$_3$), 61.0 (SO_2*C*(CH_3)$_3$), 89.0 (*C*C), 92.3 (C*C*); IR (KBr) 2971, 2931, 2869, 2107, 1628, 1462, 1367, 1306, 1161, 1128, 907 cm^{-1}; UV–Vis (nm, logε, CH_2Cl_2) 238 (3.46), 270 (2.31), 300 (2.13); HRMS (EI+, 70 eV) calcd. $[M+H]^+$, 235.0826, obsd. 235.0808. Elemental analysis ($C_{10}H_{18}OS_2$) calcd.: C, 51.25; H, 7.74; S, 27.36. Found: C, 51.52; H, 7.76; S, 27.34%. Lowest ionization energies derived by PE spectroscopy: $I_{v,j} = 8.9$ eV [π, n(p(S))], 10.2 eV [π].

4.4. Preparation of (μ:μ-(tert-butylsulfinyl)(tert-butylthio)-acetylene)hexacarbonyldicobalt (**10**)

100 mg (0.46 mmol) of (*tert*-butylsulfinyl)(*tert*-butylthio)acetylene (**7**) was dissolved in 100 ml of dichloromethane. Octacarbonyldicobalt (157 mg, 0.46 mmol) was added

Table 2
Crystal data and structure refinement for **8**, **10** and **11**

	8	**10**	**11**
Chemical formula	$C_{10}H_{18}O_2S_2$	$C_{16}H_{18}O_7S_2Co_2$	$C_{16}H_{18}O_8S_2Co_2$
Formula weight (g/mol)	234.38	504.31	520.31
Crystal size (mm)	0.48 × 0.09 × 0.06	0.32 × 0.19 × 0.18	0.26 × 0.15 × 0.01
Crystal shape	Polyhedron	Irregular	Plate
Crystal system	Monoclinic	Trigonal	Monoclinic
Space group	$P2_1/c$	$P3_2$	$P2_1/n$
a (Å)	5.8509(2)	9.2650(1)	10.2912(1)
b (Å)	12.2507(4)	9.2650(1)	15.0376(1)
c (Å)	18.0395(3)	21.7419(3)	14.9375(3)
β (°)	92.883(1)	90	105.837(1)
V (Å^3)	1291.39(6)	1616.29(3)	2223.91(5)
$D_{calc.}$ (g cm^{-3})	1.205	1.554	1.554
Z	4	3	4
F(000)	504	768	1056
$\theta_{min}/\theta_{max}$ (°)	2.01/25.67	0.94/27.44	1.96/26.34
h_{min}/h_{max}	−6/7	−11/12	−12/12
k_{min}/k_{max}	−14/14	−12/12	−18/18
l_{min}/l_{max}	−21/21	−28/28	−18/18
Absorption coefficient, μ (mm^{-1})	0.389	1.765	1.716
Max./min. transmission	1.00/0.87	1.00/0.89	1.00/0.85
Reflections collected	8706	16757	21033
Independent reflections	2444	4908	4536
Observed reflections	1730	4747	2767
Parameters	133	251	259
$R(F)$	0.036	0.023	0.041
$R_w(F^2)$	0.081	0.044	0.063
S (GOF) on F^2	1.01	1.04	0.97
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	0.28, −0.26	0.33, −0.17	0.31, −0.42

in one portion at room temperature. The mixture wrapped by aluminium foil to exclude daylight was stirred for 2 h. After removal of the solvent and adsorption on celite, the product is purified by flush column chromatography using ALOX III (*n*-hexane/diethylether 100:1). The product containing fractions were combined and the solvent was removed by rotary evaporation. 153 mg (66%) of **10** was obtained as a greenish-black solid: m.p. 100 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.44 (b, 18H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.7 ($SOC(CH_3)_3$), 30.1 ($SC(CH_3)_3$), 47.5 ($SC(CH_3)_3$), 59.1 ($SOC(CH_3)_3$), 95.9 (CS), 104.3 (OSC), 197.9 (CO); IR (KBr) 2966, 2926, 2097, 2063, 1628, 1458, 1366, 1160 cm^{-1}; UV–Vis (nm, logε, CH_2Cl_2) 280 (4.10), 326 (3.90), 400 (3.19), 568 (2.68), 590 (2.68); MS (FD) calcd. $[M]^+$ 504.

4.5. Preparation of (μ:μ-(tert-butylsulfonyl)(tert-butylthio)-acetylene)hexacarbonyldicobalt (**11**)

100 mg (0.43 mmol) of (*tert*-butylsulfonyl)(*tert*-butylthio)acetylene (**8**) was dissolved in 100 ml of dichloromethane. Octacarbonyldicobalt (147 mg, 0.43 mmol) was added in one portion at room temperature. The mixture wrapped by aluminium foil to exclude daylight was stirred for 2 h. After removal of the solvent and adsorption on celite, the product is purified by flush column chromatography using ALOX III (*n*-hexane/EtOAc 5:1). The product containing fractions were combined and the solvent was removed by rotary evaporation. 132 mg (59%) of **11** was obtained as a black solid: m.p. 123 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.51 (b, 18H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.8 ($SO_2C(CH_3)_3$), 30.1 ($SC(CH_3)_3$), 47.5 ($SC(CH_3)_3$), 62.4 ($SO_2C(CH_3)_3$), 197.3 (CO), due to the low solubility and their bad relaxation the former alkyne carbons could not be detected; IR (KBr) 2969, 2104, 2070, 2040, 1987, 1680, 1607, 1458, 1365, 1294, 1112 cm^{-1}; UV–Vis (nm, logε, CH_2Cl_2) 262 (4.06), 310 (3.81), 332 (3.72), 400 (2.98), 584 (2.48); MS (FD) calcd. $[M]^+$ 504.

4.6. X-ray crystallography and structure solution

The crystallographic data were recorded with a Bruker Smart CCD diffractometer at 200(2) K at a wavelength λ of 0.71073 Å. Relevant crystal and data collection parameters are given in Table 2. Structure solution and refinement was carried out using SHELXTL [11]. An empirical absorption correction was carried out using SADABS [11] based on the Laue symmetry of the reciprocal space. Hydrogen atoms were included at calculated positions. ORTEP drawings were obtained by using the ORTEP-3 for Windows program by Farrugia [12].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 275148 (**8**), 275150 (**10**), and 275149 (**11**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, Fax. (int code) +44(1223)336 033 or e-mail: data_request@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft (SFB 623) and the Fonds der Chemischen Industrie for financial support. D.B. Werz thanks the Studienstiftung des deutschen Volkes for a graduate fellowship.

References

[1] (a) I.U. Khand, G.R. Knox, P.L. Pauson, W.E. Watts, J. Chem. Soc., Chem. Commun. (1971) 36;
(b) I.U. Khand, G.R. Knox, P.L. Pauson, W.E. Watts, J. Chem. Soc., Perkin Trans. 1 (1973) 975–977.
[2] (a) N.E. Schore, in: L.A. Paquette (Ed.), Organic Reactions, vol. 40, Wiley, New York, 1991, pp. 1–90;
(b) O. Geis, H.-G. Schmalz, Angew. Chem. 110 (1998) 955–958; Angew. Chem. Int. Ed. 37 (1998) 911–914;
(c) S.E. Gibson, A. Stevenazzi, Angew. Chem. 115 (2003) 1844–1854; Angew. Chem. Int. Ed. 42 (2003) 1800–1810;
(d) Y.K. Chung, Coord. Chem. Rev. 188 (1999) 297–341;
(e) N. Jeong, Trans. Met. Org. Synth. 1 (1998) 560–577;
(f) K.M. Brummond, J.L. Kent, Tetrahedron 56 (2000) 3263–3283;
(g) T. Sugihara, M. Yamaguchi, M. Nishizawa, Chem. Eur. J. 7 (2001) 1589–1595;
(h) A.J. Fletcher, S.D.R. Christie, J. Chem. Soc., Perkin Trans. (2000) 1657–1668.
[3] (a) M.E. Krafft, R.H. Romero, I.L. Scott, Synlett (1995) 577–578;
(b) M.E. Krafft, R.H. Romero, I.L. Scott, J. Org. Chem. 57 (1992) 5277–5278.
[4] F. Robert, A. Milet, Y. Gimbert, D. Konya, A.E. Greene, J. Am. Chem. Soc. 123 (2001) 5396–5400.
[5] J.H. Schulte, R. Gleiter, F. Rominger, Org. Lett. 4 (2002) 3301–3304.
[6] H. Lang, H. Keller, W. Imhof, S. Martin, Chem. Ber. 123 (1990) 417–422.
[7] T. Henkel, A. Klauck, K. Seppelt, J. Organomet. Chem. 501 (1995) 1–6.
[8] A. Riera, F. Cabré, A. Moyano, M.A. Pericàs, J. Santamaria, Tetrahedron Lett. 31 (1990) 2169–2172.
[9] R.G. Parr, W. Yang, Density-Functional Theory of Atoms and Molecules, Oxford University Press, Oxford, 1989.
[10] D.M. Hoffman, R. Hoffmann, C.R. Fisel, J. Am. Chem. Soc. 104 (1982) 3858–3875.
[11] G.M. Sheldrick, SHELXTL/SADABS, Bruker Analytical X-ray Divison, Madison, WI, 1997..
[12] L. Farrugia, J. Appl. Crystallogr. 72 (1997) 565.