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Journal of Organometallic Chemistry 689 (2004) 2720-2725

Journal ofOrgano metallic Chemistry

www.elsevier.com/locate/jorganchem

Aminotroponiminate alkyl and alkoxide complexes of zinc

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> Received 11 March 2004; accepted 27 April 2004 Available online 7 July 2004

Dedicated to Professor Manfred Meisel on the occasion of his 65th birthday

Abstract

Reaction of $\{(iPr)_2ATI\}H$ (($iPr)_2ATI = N$ -isopropyl-2-(isopropylamino)troponiminate) with dimethyl zinc in toluene afforded the methyl complex [$\{(iPr)_2ATI\}Zn-Me$]. Subsequent reaction of [$\{(iPr)_2ATI\}Zn-Me$] with different alcohols gave the alkoxide complexes [$\{(iPr)_2ATI\}Zn-OR$]₂ (R = *i*Pr, *t*Bu, Ph). These compounds, which were investigated by single crystal X-ray diffraction, are dimeric in the solid-state. In the solid-state the metal centers are bridged symmetrically by two μ -oxygen atoms, thus a flat Zn–O–Zn'–O' plane is observed. [$\{(iPr)_2ATI\}Zn-OR$]₂ were used as catalysts for the copolymerization experiments of epoxides and CO₂.

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Keywords: Aminotroponiminate; Coordination chemistry; Copolymerization of epoxides and CO2; N ligands; Zinc

1. Introduction

Recently, there has been a growing interest in zinc alkoxides and carboxylates since it was shown that these compounds exhibit high activity for the copolymerization of epoxides such as cyclohexene oxide and propene oxide and CO₂ under mild conditions [1–4]. Especially Coates et al. [5–8] have demonstrated that zinc alkoxides with bulky β -diiminate ligands in the coordination sphere exhibit unprecedented rates for the (living) copolymerization of cyclohexene oxide and CO₂ to make polycarbonates, the synthesis of poly(lactic acid) by stereoselective ROP of lactide [9,10], and the ring-opening polymerization of β -butyrolactone and γ -valerolactone

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[11]. Recently Rieger et al. [12,13] have shown that the ethylsulfinate ligand is a highly efficient initiating group for the zinc β -diiminate catalyzed copolymerization reaction of CO₂ and epoxides, whereas Chisholm et al. [14] reported hydroxyl end groups in polycarbonates produced by zinc gluterate catalysts. Inoue's [15] discovery of a heterogeneous ZnEt₂/H₂O mixture for copolymerization of CO₂ and propene oxide inspired the development of a number of additional heterogeneous systems. We were interested in the chemistry of zinc complexes with related amindinate ligands. After numerous main group [16,17], d- and f-transition metal complexes [18–20] with aminotroponiminates were prepared, we now report on these compounds as ancillary ligands on zinc alkoxides. Aminotroponiminates $(\{(R)_2 ATI\}^-)$ (A) are bidentate, monoanionic ligands containing a 10 π -electron backbone. Due to the presence of the highly delocalised π -electron system, the nearly planar $\{(R)_2 ATI\}^-$ ligand framework shows little

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reactivity towards most nucleophiles and electrophiles [21].



A preliminary report concerned the coordination chemistry of zinc with the *n*-propyl bridged bis aminotroponiminate $\{(iPr)TP\}^{2-}$. It was shown there that the reactions of $H_2\{(iPr)TP\}$ with dialkyl zinc compounds in toluene lead – in dependence of the stoichiometry – either to bimetallic mono bridged products of the composition $[(RZn)_2\{(iPr)TP\}]$ (R = Me, Et) or to bimetallic double bridged helical products of the composition $[Zn\{(iPr)TP\}]_2$ (Scheme 1) [22].

In this paper, the synthesis of *N*-isopropyl-2-(isopropylamino)troponiminate zinc methyl $[{(iPr)_2ATI}Zn-Me]$ is reported, along with details of further reactions of this reagent with various alcohols. These reactions lead to dimeric aminotroponiminate zinc alkoxides $[{(iPr)_2ATI}Zn-OR]_2$. In addition the use of the compounds as catalysts in the copolymerization of epoxides and CO₂ is examined.

2. Results and discussion

The zinc alkyl complex [$\{(iPr)_2ATI\}Zn-Me$] (1) was synthesized by reaction of the neutral ligand $\{(iPr)_2$ ATI} H [23] with dimethyl zinc in toluene at low temperature (Scheme 2). Compound 1 was obtained as a yellow crystalline solid with fairly high reactivity towards air and moisture. It was characterized by MS, ¹H and ¹³C NMR spectroscopy. The ¹H and







Fig. 1. Perspective ORTEP view of the molecular structure of **2**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and Angles (°): Zn–O 196.0(2), Zn–O' 198.0(2), Zn–N1 199.8(2), Zn–N2 200.1(2), N1–C1 133.1(3), N2–C2 133.2(3); O–Zn–O' 80.87(7), O–Zn–N1 129.38(8), O'–Zn–N1 121.27(7), O–Zn–N2 125.62(8), O'–Zn–N2 123.93(8), N1–Zn–N2 81.86(8), Zn–O–Zn' 99.13(7).



Fig. 2. Perspective ORTEP view of the molecular structure of 4. Thermal ellipsoids are drawn to encompass 50% probability. Selected bond lengths (pm) and Angles (°): Zn–O 196.7(3), Zn–O' 202.6(2), Zn–N1 197.5(3), Zn–N2 197.4(3), N1–C1 133.8(4), N2–C2 133.7(4); O–Zn–O' 77.93(11), O–Zn–N1 130.26(12), O'–Zn–N1 123.54(12), O–Zn–N2 129.01(12), O'–Zn–N2 119.17(11), N1–Zn–N2 82.65(12), Zn–O–Zn' 102.07(11).

¹³C NMR spectra point to a symmetric coordination of the $\{(iPr)_2ATI\}^-$ ligand in solution. The signal of the isopropyl *CH* of **1** appears as a well-resolved septet. The chemical shift (δ 3.76 ppm) is in the range of the free ligand $\{(iPr)_2ATI\}H$ (δ 3.60) [23]. In the bridged zinc complexes [(RZn)₂{(*i*Pr)TP}] (R=Me, Et) the isopropyl *CH* signal is also slightly downfield shifted compared to the neutral ligand. In comparison to the starting material ZnMe₂ (δ ¹H: 0.51; ¹³C{¹H} –4.2) [24], the signal of the Zn–CH₃ group of **1** is high field

Table 1 Copolymerization results obtained with catalysts 2 and 3^{a}

shifted (δ^{-1} H: 0.00 ppm; ${}^{13}C\{{}^{1}$ H} -9.89 ppm). It is in the same range as that of the bimetallic complex [(MeZn)₂{(*i*Pr)TP}] (δ^{-1} H: -0.07 ppm; ${}^{13}C\{{}^{1}$ H} -10.8 ppm (1)) [22]. Compound 1 was also characterized by EI mass spectroscopy. In the mass spectrum the molecular ion as well as its characteristic fragmentation pattern was observed.

In situ preparation of 1 and further reaction with *i*-propanol, *t*-butanol, and phenol, respectively, led to the dimeric zinc alkoxides $[{(iPr)_2ATI}Zn-OR]_2$ (R = iPr (2), tBu (3), Ph (4)) (Scheme 2). The new dimeric complexes have been characterized by standard analytical/spectroscopic techniques, and the solid-state structure was established by single crystal X-ray diffraction (Figs. 1 and 2). The room temperature ${}^{1}H$ and ¹³C NMR spectra of 2–4 show a symmetrical pattern for the $\{(iPr)_2ATI\}^-$ ligand. Compared to the starting material 1 (δ 3.76 ppm), the ¹H NMR signals of the isopropyl CH of 2-4, which are well-resolved into a septet, are shifted to lower field (δ 3.92 ppm (2), δ 3.98 ppm (3), δ 3.89 ppm (4)). The solid-state structures of 2-4 were investigated by single crystal X-ray diffraction. A full refinement of the single crystal X-ray structure was possible only for 2 and 4. The structures revealed that 2-4 adopt dimeric structure in the solid-state. This is in agreement with the β -diimine zinc alkoxide complex $[(BDI)Zn-OiPr]_2$ (BDI = N,N'bis(2,6-diisopropylphenyl)-(1,3-dimethyl-1,3-propane divlidene) [9], which also forms a dimer in the solid-

Entry	Catalyst	Cocatalyst ^b	Conditions ^c		Yield of polymer (%)	Yield of polycarbonate by NMR (%)
			PO (ml)	CHO (ml)		
1	2	_		2	<5	_
2	2	_	0.14	1.8	53 ^d	81
3	2	_	0.7	1	_	_
4	2	0.01 eq		2	_	_
5	2	0.01 eq	0.14	1.8	50	54
6	2	0.01 eq	0.7	1	26	53
7	2	0.1 eq		8	29	48
8	2	0.1 eq	0.14	1.8	_	_
9	2	0.1 eq	0.7	1	67 ^d	75
10	3	_		2	44	16
11	3	_	0.14	1.8	5	_
12	3	_	0.7	1	9	_
13	3	0.01 eq	_	2	53	17
14	3	0.01 eq	0.14	1.8	11	_
15	3	0.01 eq	0.7	1	29	67
16	3	0.1 eq		8	64	29
17	3	0.1 eq	0.14	1.8	9	_
18	3	0.1 eq	0.7	1	62	20

^a 100 mg of catalyst in a 5 ml reactor.

^b Tetrahexylammonium benzoate.

^c Reaction temperature: 80 °C, CO₂ pressure 25 bar; reaction time 2 h.

^d Oil.

state. In compounds 2-4 the metal centers are bridged symmetrically by two μ -oxygen atoms. In the center of the Zn-O-Zn'-O' plane, a crystallographic inversion center is observed. The Zn-Zn' distance is 299.83(6) pm in 2 and 310.48(10) pm in 4, and the fourmembered Zn-O-Zn'-O' ring is planar. The fourcoordinated zinc centers in 2 and 4 exhibit a highly distorted tetrahedral geometry. The observed Zn-N bond lengths (Zn-N1 199.8(2) pm, Zn-N2 200.1(2) pm (2), and Zn-N1 197.5(3) pm, Zn-N2 197.4(3) pm (4)) are shorter than in $[(BDI)Zn-OiPr]_2$ (Zn-N: 207.4(4) pm and 205.4(4) pm) [9]. The bond lengths between the zinc and the µ-bridging oxygen atoms are Zn-O 196.0(2) pm and Zn-O' 198.0(2) pm in 2 and Zn-O 196.7(3) pm and Zn-O' 202.6(2) pm in 4. The corresponding O-Zn-O' angles are 80.87(7)° in **2** and 77.93(11)° in **4**.

Copolymerization experiments of epoxides and CO₂ were performed by using 2 and 3 as catalysts. As monomer either propene oxide (PO), cyclohexene oxide (CHO) or a mixture of both was used. Polymerization experiments with 100 mg of catalyst loading were made in neat epoxide at 25 bar of CO₂ pressure at 80 °C reaction temperature. Quenching of the polymerization experiments after 4 h and workup in methanol gave only low yields of the expected polycarbonate. In some cases the polymers do solely consist of polycarbonate. not Using tetrahexylammonium benzoate as cocatalyst did not significantly improve the catalytic activity. The detailed results of the catalytic studies are listed in Table 1.

3. Conclusions

Reaction of $\{(iPr)_2ATI\}H$ with dimethyl zinc in toluene afforded the methyl complex $[{(iPr)_2ATI}Zn-Me]$. Subsequent reaction of $[{(iPr)_2ATI}Zn-Me]$ with different alcohols gave the alkoxide complexes $[{(iPr)_2ATI}]$ - $Zn-OR]_2$ (R = *i*Pr, *t*Bu, Ph). These compounds are dimeric in the solid-state. The catalytic activity for the copolymerization of CO₂ and epoxides of these compounds is much lower than the those observed for the corresponding β -diimine zinc alkoxide complexes [(BDI)Zn–OR]₂. It was shown earlier that the catalytic activity of the zinc alkoxide complexes strongly depends on the steric and electronic properties of the ligand, which influences the monomer dimer equilibrium of the bimetallic zinc complexes and also influences the approach of the organic monomer to the active site [6]. Apparently, the dimer zinc complexes with the $(iPr)_2ATI$ ligand do not render a favorable combination for epoxide- CO_2 copolymerization activity. This may be either steric $-(iPr)_2ATI$ is less bulky than BDI – or electronic $-(iPr)_2ATI$ is less donating - in origin.

4. Experimental

4.1. General

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware either on a dual manifold Schlenk line or in an argon-filled M. Braun glove box. Hydrocarbon solvents (toluene, n-heptane, and *n*-pentane) were distilled under nitrogen from LiAlH₄. Deuterated solvents were obtained from Aldrich Inc. (all 99 atom % D) and were degassed, dried, and stored in vacuum over Na/K alloy in resealable flasks. NMR spectra were recorded on JEOL JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Mass spectra were recorded at 80 eV on Varian MAT 711. Elemental analyses were carried out with an Elementar vario EL. ZnMe₂ was purchased from Aldrich Inc. in a 2M solution in toluene and $\{(iPr)_2ATI\}H$ [23] was prepared according to the literature procedures.

4.2. $[{(iPr)_2ATI}Zn-Me](1)$

0.64 ml (1.28 mmol, 1.05 eq) of a 2.0 M ZnMe₂ solution in toluene was diluted in 25 ml of toluene. At -78 °C a solution of {(*i*Pr)₂ATI}H (250 mg, 1.22 mmol) in toluene (25 ml) was added. The reaction mixture slowly was warmed up to room temperature and gas evolution was observed. After the gas evolution had stopped (about 3 h) the solution was filtered off, and the solvent was evaporated in vacuum. The resulting yellow solid was washed with *n*-pentane $(3 \times 10 \text{ ml})$ and dried in vacuum. Yield: 287 mg (83%). ¹H NMR (C₆D₆, 400 MHz, 25 °C): $\delta = 0.00$ (s, 3H, $-ZnCH_3$), 1.14 (d, 12H, $-NCH(CH_3)_2$, ${}^{3}J(H,H) =$ 6.11 Hz), 3.76 (sept., 2H, $-NCH(CH_3)_2$, ${}^{3}J(H,H) = 6.18$ Hz), 6.35 (dd, 1H, H₅, ${}^{3}J(H,H) = 9.39$ Hz), 6.57 (d, 2H, $H_{3,7}$, ${}^{3}J(H,H) = 11.23$ Hz), 6.95 (dd, 2H, H_{4,6}, J(H,H) = 9.39 Hz, 10.23 Hz). ${}^{13}C{}^{1}H{}$ NMR (C₆D₆, 100.4 MHz, 25 °C): $\delta = -9.9$ (-Zn*C*H₃), 24.5 (-NCH (CH₃)₂), 48.3 (-NCH(CH₃)₂), 111.6 (C₅), 117.7 (C_{3,7}), 134.5 (C_{4.6}), 160.2 (C_{1.2}). EI-MS m/z (%): -282 (33) $[M]^+$, 267 (51) $[M - CH_3]^+$, 204 (24) $[M - ZnCH_3]^+$.

4.3. $[{(iPr)_2ATI}Zn-OiPr]_2(2)$

3.85 ml (7.71 mmol, 1.05 eq) of a 2.0 M ZnMe₂ solution in toluene was diluted in 25 ml of toluene. At -78 °C a solution of {(*i*Pr)₂ATI}H (1.5 g, 7.34 mmol) in toluene (30 ml) was added. The reaction mixture slowly was warmed up to room temperature and gas evolution was observed. After the gas evolution had stopped (about 3 h) 0.62 ml (8.07 mmol, 1.1 eq) of *i*-propanol was added, immediately followed by gas evolution. Then the solvent was evaporated in vacuum. The

resulting yellow solid was washed with *n*-pentane (3×10 ml) and dried in vacuum. Finally, the product was crystallized from toluene/*n*-heptane (1:2). Yield: 2.03 g (84%). ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ =1.03 (d, 12H, -OCH(CH₃)₂, ³*J*(*H*,*H*)=5.99 Hz), 1.39 (d, 24H, -NCH(CH₃)₂, ³*J*(*H*,*H*)=6.31 Hz), 3.92 (sept., 4H, -NCH(CH₃)₂, ³*J*(*H*,*H*)=6.42 Hz), 4.21 (sept., 2H, -OCH(CH₃)₂, ³*J*(*H*,*H*)=5.97 Hz), 6.27 (dd, 2H, H₅, *J*(*H*,*H*)=9.15 Hz, 8.75 Hz), 6.54 (d, 4H, H_{3,7}, ³*J*(*H*,*H*)=11.31 Hz), 6.96 (dd, 4H, H_{4,6}, *J*(*H*,*H*)=9.27 Hz, 11.95 Hz). ¹³C{¹H} NMR (C₆D₆, 100.4 MHz, 25 °C): δ =24.6 (-NCH(CH₃)₂), 28.5 (-OCH(CH₃)₂), 48.9 (-NCH(CH₃)₂), 66.4 (-OCH(CH₃)₂), 111.4 (C₅), 115.9 (C_{3,7}), 134.9 (C_{4,6}), 159.7 (C_{1,2}). EI-MS *m*/*z* (%): -326 (100) [M/2]⁺, 268 (52) [M/2 - OC₃H₇]⁺, 204 (34) [M/2 - ZnOC₃H₇]⁺. -C₃₂H₅₂N₄O₂Zn₂ (655.55): Calc. C, 58.63, H, 8.00, N, 8.55. Found: C, 58.38, H, 7.76, N, 8.36%.

4.4. $[{(iPr)_2ATI}Zn-O tBu]_2 (3)$

Compound 3 was prepared in an analogous way to 2 by using 3.85 ml (7.71 mmol, 1.05 eq) of a 2.0 M ZnMe₂ solution in toluene, 1.5 g (7.34 mmol) of $\{(iPr)_2ATI\}H$, and 0.77 ml (8.07 mmol, 1.1 eq) of t-butanol. X-ray quality crystals could be grown from *n*-heptane. Yield: 2.04 g (81%). ¹H NMR (C₆D₆, 400 MHz, 25 °C): $\delta = 1.24$ (s, 18H, $-OC(CH_3)_3$), 1.46 (d, 24H, -NCH(CH₃)₂, ${}^{3}J(H,H) = 6.43$ Hz), 3.98 (sept., 4H, – NCH(CH₃)₂, ${}^{3}J(H,H) = 6.44$ Hz), 6.26 (dd, 2H, H₅, J(H,H) = 9.11 Hz, 8.79 Hz), 6.60 (d, 4H, H_{3,7}, ${}^{3}J(H,H) = 11.47$ Hz), 6.94 (dd, 4H, H_{4,6}, J(H,H) = 9.39Hz, 11.07 Hz). ¹³C{¹H}NMR (C₆D₆, 100.4 MHz, 25 °C): $\delta = 24.1$ (-NCH(CH₃)₂), 34.6 (-OC(CH₃)₃), 49.1 (-NCH(CH₃)₂), 71.1 (-OC(CH₃)₃), 112.8 (C₅), 116.0 (C_{3,7}), 134.5 (C_{4,6}), 160.4 (C_{1,2}). EI-MS m/z (%): -340 (25) $[M/2]^+$, 268 (15) $[M/2 - OC_4H_9]^+$, 205 (27) $[M/2 - ZnOC_4H_9]^+$. $-C_{34}H_{56}N_4O_2Zn_2$ (683.60): Calc. C, 59.74, H, 8.26, N, 8.20. Found: C, 59.37, H, 8.03, N, 7.85%.

4.5. [{(*iPr*)₂ ATI}Zn-OPh]₂ (4)

Compound **3** was prepared in an analogous way to **2** by using 0.64 ml (1.28 mmol, 1.05 eq) of a 2.0 M ZnMe₂ solution in toluene, 250 mg (1.22 mmol) of $\{(iPr)_2ATI\}H$, and 0.76 ml ((1.28 mmol, 1.05 eq) of phenol. The final product was crystallized from toluene/*n*-heptane (1:2). Yield 355 mg (80%). ¹H NMR (C₆D₆, 400 MHz, 25 °C): $\delta = 1.28$ (d, 24H, -NCH(CH₃)₂, ³*J*(*H*,*H*)=6.47 Hz), 3.89 (sept., 4H, -NCH(CH₃)₂, ³*J*(*H*,*H*)=6.93 Hz), 6.35 (dd, 2H, H₅, *J*(*H*,*H*)=9.27 Hz, 8.43 Hz), 6.61 (m, 2H, *p*-C₆*H*₅), 6.65 (d, 4H, H_{3,7}, ³*J*(*H*,*H*)=10.99 Hz), 6.70 (d, 4H, *o*-C₆*H*₅, ³*J*(*H*,*H*)=8,39 Hz), 6.90 (m, 4H, *m*-C₆*H*₅), 6.98 (dd, 4H, H_{4,6}, *J*(*H*,*H*)=10.95 Hz, 9.27 Hz). ¹³C{¹H} NMR (C₆D₆, 100.4 MHz, 25 °C):

$$\begin{split} &\delta = 24.2 \quad (-\text{NCH}(C\text{H}_3)_2), \quad 48.7 \quad (-\text{NCH}(C\text{H}_3)_2), \quad 112.3 \\ &(\text{C}_5), \quad 117.4 \quad (\text{C}_{3,7}), \quad 118.6 \quad (\text{Ph}), \quad 118.7 \quad (\text{Ph}), \quad 129.9 \quad (\text{Ph}), \\ &135.3 \quad (\text{C}_{4,6}), \quad 159.5 \quad (\text{C}_{1,2}), \quad 160.7 \quad (\text{Ph}). \quad \text{EI-MS} \quad m/z \quad (\%): \\ &-360 \quad (12) \quad [\text{M}/2]^+, \quad 345 \quad (16) \quad [\text{M}/2 - \text{CH}_3]^+, \quad 267 \quad (7) \\ &[\text{M}/2 - \text{OC}_6\text{H}_5]^+, \quad 251 \quad (10) \quad [\text{M}/2 - \text{OC}_6\text{H}_5, -\text{CH}_3]^+, \quad 204 \\ &(14) \quad [\text{M}/2 - \text{Z}\text{nOC}_6\text{H}_5]^+, \quad 94 \quad (100) \quad [\text{C}_6\text{H}_6\text{O}]. \quad -\text{C}_{38}\text{H}_{48}\text{N}_4\text{-} \\ &\text{O}_2\text{Zn}_2 \quad (723.58): \quad \text{Calc. C}, \quad 63.08, \ \text{H}, \quad 6.69, \ \text{N}, \quad 7.74. \quad \text{Found:} \\ &\text{C}, \quad 62.00, \ \text{H}, \quad 6.24, \ \text{N}, \quad 7.53\%. \end{split}$$

5. Copolymerization experiments

Polymerization reactions were carried out in 5 ml autoclaves equipped with a magnetic stirrer, oil bath heating and a check valve. About 100 mg of catalyst were transferred into the autoclave. Subsequently the monomer and the solvent were added. The reactor was pressurized to 25 bar and heated to 80 °C. After stirring for 4 h the reactor was cooled down, slowly depressurized, and opened. The reaction mixture was slowly precipitated in methanol, stirred, isolated, and dried.

6. X-ray crystallographic studies of 2, 3 and 4

Crystals of **2** and **4** were grown from a hot toluene/*n*-heptane (1:2) solution. Crystals of compound **3** were obtained from hot *n*-heptane. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the -100 °C cold stream of a Bruker CCD SMART 1000 diffractometer. Subsequent computations were carried out on an Intel Pentium III Personal Computer.

2: Bruker CCD SMART 1000 diffractometer (Mo K α radiation); T=173(2) K; data collection and refinement: SHELXS-97 [25], SHELXL-97 [26]; monoclinic, space group $P2_1/c$ (No. 14); lattice constants a=908.4(2), b=1041.2(12), c=1731.2(3) pm, $\beta=96.628(4)^\circ$, V=1626.4(5) 10⁶ pm³, Z=2; μ (Mo K α)=1.508 mm⁻¹; θ_{max} .= 30.00; 4732 ($R_{int}=0.0308$) independent reflections measured, of which 3451 were considered observed with $I>2\sigma(I)$; max. residual electron density 2.353 and -1.724 e/A^{-3} ; 187 parameters (all non hydrogen atoms were calculated anisotropically; the positions of the H atoms were calculated for idealized positions) $R_1=0.0380$; $wR_2=0.1014$.

3: Bruker CCD SMART 1000 diffractometer (Mo K α radiation); T=173(2) K; data collection and refinement: SHELXS-97 [25], SHELXL-97 [26]; triclinic, space group $P\overline{1}$ (No. 2); lattice constants a=937.8(3), b=955.9(3), c=1964.0(6) pm, $\alpha=92.881(5)^{\circ}$, $\beta=103.203(5)^{\circ}$, $\gamma=90.621(6)^{\circ}$, V=1711.6(9) 10⁶ pm³, Z=2; $\theta_{max}=30.00$; 9361 ($R_{int}=0.0456$) independent reflections measured, of which 6311 were considered observed with $I > 2\sigma(I)$. The structure could not be completely refined. **4**: Bruker CCD SMART 1000 diffractometer (Mo K α radiation); T=173(2) K; data collection and refinement: SHELXS-97 [25], SHELXL-97 [26]; triclinic, space group $P\bar{1}$ (No. 2); lattice constants a=948.2(3), b=975.5(3), c=1077.4(3) pm, $\alpha=113.277(5)^{\circ}$, $\beta=108.043(5)^{\circ}$, $\gamma=90.178(6)^{\circ}$, V=861.4(4) 10⁶ pm³, Z=1; μ (Mo K $_{\alpha}$) = 1.431 mm⁻¹; $\theta_{max.}=30.00$; 4950 ($R_{int}=0.0530$) independent reflections measured, of which 3701 were considered observed with $I>2\sigma(I)$; max. residual electron density 2.403 and -1.875 e/A⁻³; 212 parameters (all non hydrogen atoms were calculated anisotropically; the positions of the H atoms were calculated for idealized positions) $R_1=0.0664$; $wR_2=0.1776$.

7. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a Supplementary Publication Nos. CCDC-233551 and 233552. 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; email: deposit@ccdc.cam.ac.uk).

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (Graduiertenkolleg: Synthetische, mechanistische und reaktionstechnische Aspekte von Metallkatalysatoren), the Fonds der Chemischen Industrie and BASF Aktiengesellschaft.

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