High-yield syntheses and electrochemistry of *cis*-[RuCl₂(depe)₂] and *cis*-[RuCl(CH₃CN)(depe)₂]⁺PF₆[−]

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Abstract

cis-[RuCl₂(depe)₂] (**1**) (depe = Et₂PC₂H₄PEt₂) is obtained in excellent yield and high isomeric purity by the reaction of [RuCl₂(DMSO)₄] with two equivalents of depe in acetone or ethyl acetate under reflux conditions. One of the chloride ligands is labile and readily displaced by CH₃CN to afford the cationic monosubstitution product *cis*-[RuCl(CH₃CN)(depe)₂]⁺PF₆[−] (**2**), which was isolated as the PF₆[−] salt. The X-ray crystal structure of **1** was determined. The redox properties of **1** and **2** as well as the chloride displacement from **1** by CH₃CN were studied by cyclic and square wave voltammetry

Keywords: Ruthenium; Nitrile complexes; Electrochemistry; X-ray analysis

1. Introduction

The properties of transition-metal complexes depend, inter alia, on the geometric arrangement of the ligands around the metal center. Apart from their different physical characteristics, geometrical isomers may also differ in their chemical reactivities [1]. This point is well illustrated with complexes [RuCl₂(PP)₂], where PP denotes a chelating diphosphine ligand. Chloride substitution has been demonstrated on several occasions to occur much more readily for the *cis* isomers than for the *trans* forms [2–5]. This makes the *cis* isomers of [RuCl₂(PP)₂] valuable starting materials for numerous Ru(II)-phosphine complexes. Unfortunately, reliable, selective and efficient syntheses for such species are limited to the dppm complex (dppm = Ph₂PCH₂PPh₂) [6]. Owing to its ready availability, the ease of chloride substitution and the ability of the [RuCl(dppm)₂]⁺ fragment to isomerize terminal alkynes to vinylidene ligands, *cis*-[RuCl₂(dppm)₂] has been extensively used to prepare a wide variety of ruthenium acetylide, vinylidene [7,8] and allenylidene complexes [9–11], with, in part, possible applications in the area of nonlinear

optics [12,13]. Especially for this latter application the opportunity to tune the electron density of the transition metal fragment, e.g. by inducing more basic diphosphine ligands, is of crucial importance.

We report here efficient high-yield syntheses of *cis*-[RuCl₂(depe)₂] (**1**) (depe = Et₂PC₂H₄PEt₂) and *cis*-[RuCl(CH₃CN)(depe)₂]⁺PF₆[−] (**2**) along with the X-ray crystallographically determined structure of the dichloro complex **1**. We have also investigated the electrochemical behavior of complexes **1** and **2** by cyclic and square wave voltammetry.

2. Results and discussion

2.1. Preparations

Established syntheses for *cis*-[RuCl₂(depe)₂] (**1**) make either uneconomical use of the commercially available, yet still rather expensive depe ligand [14] or inevitably produce mixtures of the *cis* and *trans* isomers with the necessity to remove the often unreactive *trans* form by fractional crystallization [2]. Recently, a selective synthesis of the *trans* isomer of **1** and its use in the preparation of *trans*-bis(alkynyl)-derivatives or the diazido complex *trans*-[Ru(N₃)₂(depe)₂] have been re-

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¹ X-ray structure analysis.

ported [15]. We found now that by simply replacing the source material of the dichlororuthenium(II) fragment from $[\text{RuCl}_2(\text{PPh}_3)_3]$ to $[\text{RuCl}_2(\text{DMSO})_4]$ the *cis*-isomer is produced in high isomeric purity and excellent yield (> 90%). Thus, refluxing a solution of $[\text{RuCl}_2(\text{DMSO})_4]$ and two equivalents of depe in acetone or ethyl acetate overnight produces a pale yellow solution from which almost pure **1** is obtained after drying in vacuo. Small amounts of the *trans* isomer (typically less than 5%) can be removed by washing the crude product with cold petrol ether.

As in the case of the related dppm complex, one chloride is easily replaced from **1** under mild condi-

Fig. 1. Molecular structure and atom numbering scheme of *cis*- $[\text{RuCl}_2(\text{depe})_2]$ (**1**) (only one of the two independent molecules is shown).

Table 1

Selected bond lengths (Å) and angles (°) for the two independent molecules of **1**

	Molecule 1	Molecule 2
Ru–P(1)	2.345(2)	2.336(2)
Ru–P(2)	2.285(3)	2.284(2)
Ru–P(3)	2.282(2)	2.261(2)
Ru–P(4)	2.358(2)	2.356(2)
Ru–Cl(1)	2.491(2)	2.484(2)
Ru–Cl(2)	2.477(2)	2.487(2)
P(1)–Ru–Cl(1)	91.87(7)	89.81(7)
P(1)–Ru–Cl(2)	86.16(8)	82.99(7)
P(2)–Ru–Cl(1)	174.56(8)	171.95(7)
P(2)–Ru–Cl(2)	89.41(8)	86.15(6)
P(3)–Ru–Cl(1)	83.89(7)	91.79(8)
P(3)–Ru–Cl(2)	169.40(8)	177.34(7)
P(4)–Ru–Cl(1)	87.82(7)	87.39(7)
P(4)–Ru–Cl(2)	92.12(8)	93.28(7)
Cl(1)–Ru–Cl(2)	86.15(8)	86.91(7)
P(1)–Ru–P(2)	84.69(8)	85.29(7)
P(1)–Ru–P(3)	97.78(7)	99.34(8)
P(1)–Ru–P(4)	178.27(7)	175.46(7)
P(2)–Ru–P(3)	100.72(7)	95.30(7)
P(2)–Ru–P(4)	95.50(8)	97.08(7)
P(3)–Ru–P(4)	83.88(7)	84.33(7)

tions. This is demonstrated by adding excess acetonitrile to a CD_2Cl_2 solution of *cis*- $[\text{RuCl}_2(\text{depe})_2]$ (**1**). The solution instantaneously decolorizes to a very pale yellow and the two triplet signals of **1** in ^{31}P NMR are replaced by the XYZ-spin system of the monoacetonitrile substitution product *cis*- $[\text{RuCl}(\text{CH}_3\text{CN})(\text{depe})_2]^+ \text{Cl}^-$. This process may also be followed by electrochemistry as detailed in Section 2.3. The PF_6^- salt *cis*- $[\text{RuCl}(\text{CH}_3\text{CN})(\text{depe})_2]^+ \text{PF}_6^-$ (**2**) is obtained in high yield by stirring a suspension of **1** and excess KPF_6 in a $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ mixture. Apart from its ^{31}P NMR spectrum the low symmetry of this complex is also evident from ^{13}C NMR spectroscopy where all 20 carbon atoms of the depe ligands give rise to separate resonance signals. The carbon atoms of the ethylene bridges are each split into eight line patterns due to coupling to three of the four inequivalent phosphorus nuclei. Resonance signals for the coordinated acetonitrile were located at 124.68 and 3.98 ppm, that is at a slightly lower field than for free acetonitrile as is commonly found for such complexes, e.g. 127.4 and 3.7 ppm for $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\text{CH}_3\text{CN})_2]^+ [\text{16}]$. Despite all our efforts we were not able to detect a band assignable to the $\text{C}\equiv\text{N}$ stretch in the IR. This parallels our observations for the dppm analogue of **2** [17]. Given the substitutional lability of nitrile ligands, **2** may evolve as an excellent precursor to monosubstitution products $[\text{RuClL}(\text{depe})_2]^n$ ($\text{L} = \text{neutral 2-electron donor, } n = 1, \text{L} = \text{anionic donor, } n = 0$) as we have just demonstrated for *cis*- $[\text{RuCl}(\text{NCCH}_3)(\text{dppm})_2]^+ [\text{17}]$.

2.2. The structure of *cis*- $[\text{RuCl}_2(\text{depe})_2]$ in the solid state

cis- $[\text{RuCl}_2(\text{depe})_2]$ crystallizes in the monoclinic space group *Pc* with pairs of two independent molecules in the unit cell ($Z = 4$). Fig. 1 depicts one of these molecules along with the atom numbering scheme. Relevant bond distances and angles for both molecules are collected in Table 1. Data pertaining to the X-ray structure determination are provided in Table 2. Only a few of the crystallographically characterized complexes $[\text{RuCl}_2\text{P}_4]$ exhibit a *cis* configuration of the two chloride ligands, most notably *cis*- $[\text{RuCl}_2(\text{dppm})_2]$ [18] and *cis*- $[\text{RuCl}_2\{\text{P}(\text{C}_3\text{H}_6\text{PMe}_2)_3\}]$ [19]. In all these complexes the P-atoms, which are *trans* disposed to another P-donor exhibit significantly longer Ru–P distances than those *trans* to chloride. This is a consequence of the strong *trans* effect exerted by P-donor ligands and enhanced Ru ($d\pi$)–P ($p\pi$) back-bonding to P-atoms *trans* to a chloride donor. Placing the two chloride ligands in the equatorial plane, the Ru– P_{ax} distances of **1** are, on average, 2.349 Å as compared to Ru– P_{eq} of 2.278 Å. Comparable data for *cis*- $[\text{RuCl}_2\{\text{P}(\text{C}_3\text{H}_6\text{PMe}_2)_3\}]$ and *cis*- $[\text{RuCl}_2(\text{dppm})_2]$ (**3**) are 2.376 versus 2.266 Å and 2.336 versus 2.316 Å. In line with the above reasoning,

Table 2
Crystallographic data for *cis*-[RuCl₂(depe)₂] (1)

Molecular formula	C ₂₀ H ₄₃ Cl ₂ P ₄ Ru
Formular weight	579.39
Crystal system	monoclinic
Space group	<i>Pc</i>
Unit cell dimensions	
<i>a</i> (Å)	10.546(2)
<i>b</i> (Å)	20.245(4)
<i>c</i> (Å)	13.542(3)
β (°)	108.12(3)
<i>V</i> (Å ³)	2747.9(10)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.401
Absorption coefficient (mm ⁻¹)	1.003
Crystal dimensions (mm)	0.30 × 0.3 × 0.2
<i>F</i> (000)	1204
Absorption coefficient	1.003
Temperature (K)	173(2)
θ Range for data collection	1.87–29.01
Index ranges	–8 ≤ <i>h</i> ≤ 14, –6 ≤ <i>k</i> ≤ 27, –18 ≤ <i>l</i> ≤ 17
Goodness of fit	1.034
Reflections collected	8904
Unique reflections	8449
Data/restraints/parameters	8449/2/481
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	
<i>R</i> ₁	0.0466
<i>wR</i> ₂	0.1106
<i>R</i> ₁ (all data)	0.0614
<i>wR</i> ₂ (all data)	0.1196
Largest difference peak and hole (e Å ⁻³)	1.267 and –0.502

Table 3
Half-wave potentials for *cis*-[RuCl₂(depe)₂] (1) and *cis*-[RuCl(CH₃CN)(depe)₂]⁺ (2) in different solvents

Solvent	<i>E</i> _{1/2} (Ru(II/III), 1)	<i>E</i> _{1/2} (Ru(II/III), 2)
THF	+0.145	+0.670
CH ₂ Cl ₂	+0.220	+0.770
PC ^a	+0.215	+0.710

^a Propylene carbonate.

the *cis* isomers also display considerably longer Ru–Cl bond distances than the respective *trans* forms ([RuCl₂(depe)₂]: 2.485 Å as compared to 2.427 Å in the *trans* isomer [15a]; [RuCl₂(dppm)₂] (3): 2.446 versus 2.426 Å). Due to the larger flexibility of the diphosphine bridge in 1 and the less bulky substituents on the P-atoms, the coordination environment of 1 is much less distorted from octahedral than observed for the dppm analogue. Thus, the chelate bite angle of 72.0° in *cis*-[RuCl₂(dppm)₂] opens to 84.5° in 1. Similar, but less pronounced, trends are found for the angles P_{ax}–Ru–P_{ax} (176.9° in 1 as compared to 171.2° in 3), P_{eq}–Ru–Cl (*trans*) (173.3° in 1 versus 163.7° in 3) and P_{eq}–Ru–P_{ax} for P-atoms belonging to different chelate ligands (97.4° versus 101.6°).

2.3. Electrochemistry

cis-[RuCl₂(depe)₂] (1) and *cis*-[RuCl(CH₃CN)(depe)₂]⁺X[–] (X[–] = Cl[–], PF₆[–]) (2) were studied by cyclic and square wave voltammetry and double-step chronoamperometry. Both complexes exhibit chemically reversible one-electron oxidations to mono- or dicationic Ru(III) forms. All diagnostic criteria such as half-widths of the peak in square wave voltammetry or peak-to-peak separations and half-widths of the forward (anodic) peak in cyclic voltammetry display very similar values as the internal ferrocene standard, which points to fully reversible electron transfer. Half-wave potentials for the Ru(II/III) couples in various solvents as calibrated versus the internal ferrocene standard are provided in Table 3. In contrast to its dppm analogue, 1 is configurationally stable even in the Ru(III) state and does not isomerize to the *trans* isomer upon oxidation, at least not on the conventional time scale of CV and double-step chronoamperometry experiments [20]. According to our observations, the same also holds for *cis*-[RuCl₂(dppe)₂]. Thus, the ready isomerization of *cis*-[RuCl₂(dppm)₂]⁺ may be driven by the strain imposed by the bulky ligands and the short methylene bridge. Substituting the anionic 2e[–] donor chloride with the neutral 2e[–] nitrile donor with the concomitant introduction of an additional positive charge shifts the Ru(II/III) oxidation potential anodically by 0.50–0.55 V, depending on the solvent. Effects of similar magnitude have been observed for *cis*-[RuCl₂(dppm)₂]/*cis*-[RuCl(CH₃CN)(dppm)₂]⁺ [20] (0.56 V) and for the first oxidations of *cis*-[ReCl(NCC₆H₄Me-4)(dppe)₂]/*cis*-[Re(NCC₆H₄Me-4)₂(dppe)₂]⁺ [19] (0.49 V) [21]. Both complexes 1 and 2 undergo further oxidation at peak potentials of +1.060 V for 1 and +1.13 V for 2 at a sweep rate of 0.1 V s^{–1} in propylene carbonate at 295 K. This step is, however, accompanied by fast chemical reactions that cannot be suppressed even at 213 K and at sweep rates up to 5 V s^{–1} such that chemical irreversibility prevails under all conditions. In the case of 2, this second oxidation is a one-electron process. For 1 the number of electrons transferred varies with sweep rate and temperature which points to a chemical decomposition path producing species that are further oxidized at the peak potential of the second oxidation.

The substitutional lability of *cis*-[RuCl₂(depe)₂] (1) is easily demonstrated by electrochemical methods. Incremental addition of CH₃CN to a solution of 1 in CH₂Cl₂ or THF causes the Ru(II/III) wave of 1 (couple A/A' in Fig. 2) to gradually disappear and the concomitant formation of two new features. These are a broad, quasireversible feature (peak B), which is characteristic of the Cl[–] ion in nonaqueous solvents and a reversible one-electron wave, which is assigned to the cationic acetonitrile complex 2 (wave C/C'). These findings complement our NMR results as detailed in Section 2.1.

3. Experimental

3.1. General

The preparation of **1** and **2** were carried out under argon and standard Schlenk conditions. Acetone was freshly distilled from CaSO_4 . Acetone and ethyl acetate (Baker) were degassed by three freeze–pump–thaw cycles before use. 1,2-Bis(diethylphosphino)ethane (depe) (AlfaAesar), KPF_6 (Strem), pentane (Roth) and CH_2Cl_2 (Aldrich) were used as received. $[\text{RuCl}_2(\text{DMSO})_4]$ was prepared according to a literature method [22].

3.2. Instrumentation

NMR: Bruker AC 250. — IR: Elmer Paragon 1000 PC. C,H,N analyses were performed at in-house facilities with an Perkin–Elmer Analyzer 240. All electrochemical experiments were performed in a home-built cylindrical vacuum tight one compartment cell. A spiral shaped Pt wire and a Ag wire as the counter and reference electrodes are sealed directly into opposite sides of the glass wall, while the respective working electrode (Pt or glassy carbon 1.1 mm polished with 0.25 μm diamond paste (Buehler–Wirtz) before each experiment) is introduced via a Teflon screw cap with a suitable fitting. The cell may be attached to a conven-

tional Schlenk line via two sidearms equipped with Teflon screw valves and allows experiments to be performed under an atmosphere of argon with approximately 2.5 ml of analyte solution. The solvents were obtained in the highest available purity from commercial sources (CH_2Cl_2 and propylene carbonate from Fluka (Burdick & Jackson Brand), THF (99.9%) from Roth and freshly distilled under argon from CaH_2 (CH_2Cl_2) or K (THF) before use. Propylene carbonate was saturated with argon prior to the experiment. NBu_4PF_6 (0.25 mM) was used as the supporting electrolyte. Electrochemical data were acquired with a computer controlled EG&G model 273 potentiostat utilizing the EG&G 250 software package.

3.3. Preparation of *cis*- $[\text{RuCl}_2(\text{depe})_2]$ (**1**)

$[\text{RuCl}_2(\text{DMSO})_4]$ (0.78 g, 1.6 mmol) was dissolved in acetone (33 ml) and depe (0.78 ml, 0.69 g, 2.09 eq) was added by syringe. The yellow solution was kept under reflux overnight, then filtered and the solvent evaporated under vacuum. The product was washed with three portions of cold petrol ether (5 ml each) to remove small amounts of the *trans* isomer present in the crude product (in some solvents the singlet signal of the *trans* isomer appears at the very same position as the middle line of the high-field triplet of **1**). The remaining lemon-yellow solid was dried in vacuo to give pure **1** in 90.5% yield (0.839 g). Slightly higher yields of ca. 92% were obtained from ethyl acetate under analogous conditions. The product may contain small amounts of DMSO released during the synthesis. Solid samples of **1** are air stable, but in solution partial oxidation slowly occurs which is accompanied by a colour change to green. *Anal.* Found: C, 41.20; H, 8.46. $\text{C}_{20}\text{H}_{48}\text{Cl}_2\text{P}_4\text{Ru}$. Calc.: C, 41.10; H, 8.28%. ^1H NMR (CDCl_3): δ 2.47 (m, 4H), 2.25 (dqui, $J_{\text{HH}} = 3.76$, $J_{\text{PH}} = 7.44$ Hz, 4H), 2.05 (qui(br.), $J_{\text{PH}} = 7.28$ Hz, 4H), 1.69–1.45 (m, 12H), 1.18 (m, 12H), 0.98 (m, 12H). ^{13}C NMR (CDCl_3): δ 25.2 (dd, $J_{\text{PC}} = 16.1$, 13.0 Hz, $\text{PCH}_2\text{CH}_2\text{P}$), 23.5 (dd, $J_{\text{PC}} = 12.3$, 10.9 Hz, $\text{PCH}_2\text{CH}_2\text{P}$), 21.4 (vt, $J_{\text{PC}} = 10.1$ Hz), 20.4 (vt, $J_{\text{PC}} = 13.2$ Hz), 20.0 (t, $J_{\text{PC}} = 12.3$ Hz), 14.3 (t, $J_{\text{PC}} = 12.9$ Hz) all PCH_2CH_3 , 9.6 (t, $J_{\text{PC}} = 8.0$ Hz), 9.2 (t, $J_{\text{PC}} = 7.6$ Hz), 8.7 (t, $J_{\text{PC}} = 2.1$ Hz), 8.4 (t, $J_{\text{PC}} = 2.1$ Hz), all PCH_2CH_3 . ^{31}P NMR (CDCl_3): δ 60.8, 47.7 (t, $J_{\text{PP}} = 22.5$ Hz).

3.4. Preparation of *cis*- $[\text{RuCl}(\text{CH}_3\text{CN})(\text{depe})_2]^+ \text{PF}_6^-$ (**2**)

1 (220 mg, 0.376 mmol) and KPF_6 (0.275 g, 4 eq.) was dissolved/suspended in CH_2Cl_2 and CH_3CN (10 ml, 7.8 g, 505 eq.) was added by syringe. After 2 h, the pale yellow suspension was filtered and the solvents

Fig. 2. CV traces of *cis*- $[\text{RuCl}_2(\text{depe})_2]$ (**1**) in THF solution at $v = 0.1 \text{ V s}^{-1}$ in the presence of Cp_2Fe as internal standard. (a) No CH_3CN present; (b) after addition of 20 eq. of CH_3CN ; (c) after addition of 80 eq. of CH_3CN .

removed in vacuo. The resulting solid was extracted into CH_2Cl_2 (8 ml) and filtered in order to remove KCl and excess KPF_6 , which will partly dissolve in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ mixtures. After drying in vacuo 244 mg of pure **2** (90.0%) were obtained. *Anal.* Found: C, 35.66; H, 6.94; N, 1.87. $\text{C}_{22}\text{H}_{51}\text{ClF}_6\text{NP}_5\text{Ru}$. Calc.: C, 35.95; H, 6.99; N, 1.90. ^1H NMR (CDCl_3): δ 2.45 (qui, $J_{\text{PH}} = 7.6$ Hz, 1H), 2.26 (m, 2H), 2.23 (qui, $J_{\text{PH}} = 7.7$ Hz, 1H), 2.01 (qui (br), $J_{\text{PH}} = 7.5$ Hz, 5H), 1.91–1.64 (m, 6H), 1.60–1.46 (m, 6H), 1.55 (s, CH_3CN , 3H), 1.33–1.00 (m, 27H). ^{13}C NMR (CD_2Cl_2): δ 124.68 (d, $^3J_{\text{PC}} = 12.7$ Hz, CN), 25.81 (ddd, $J_{\text{PC}} = 31.3, 14.2, 7.1$ Hz, $\text{PCH}_2\text{CH}_2\text{P}$), 23.77 (ddd, $J_{\text{PC}} = 31.0, 14.7, 7.9$ Hz, $\text{PCH}_2\text{CH}_2\text{P}$), 22.99 (d, $J_{\text{PC}} = 25.8$ Hz), 22.71 (d, $J_{\text{PC}} = 25.6$ Hz), 21.61 (d, $J_{\text{PC}} = 25.8$ Hz, all PCH_2CH_3), 20.74–20.14 (m, $2 \times \text{PCH}_2\text{CH}_3$, $1 \times \text{PCH}_2\text{CH}_2\text{P}$), 20.33 (d, $J_{\text{PC}} = 20.2$ Hz, PCH_2CH_3), 19.66 (ddd, $J_{\text{PC}} = 21.6, 9.5, 6.3$ Hz, $\text{PCH}_2\text{CH}_2\text{P}$), 18.35 (d, $J_{\text{PC}} = 27.9$ Hz, PCH_2CH_3), 17.75 (dd, $J_{\text{PC}} = 18.7, 6.6$ Hz, PCH_2CH_3), 14.05 (dd, $J_{\text{PC}} = 18.7, 6.6$ Hz, PCH_2CH_3), 9.40 (d, $J_{\text{PC}} = 7.9$ Hz), 9.33 (d, $J_{\text{PC}} = 6.8$ Hz), 9.14 (d, $J_{\text{PC}} = 7.9$ Hz), 8.82 (d, $J_{\text{PC}} = 6.3$ Hz), 8.14 (d, $J_{\text{PC}} = 7.9$ Hz), 8.09 (d, $J_{\text{PC}} = 7.9$ Hz), 8.06 (d, $J_{\text{PC}} = 7.9$ Hz), 7.99 (d, $J_{\text{PC}} = 6.3$ Hz), all PCH_2CH_3 , 3.98 (s, CH_3CN). ^{31}P NMR (CDCl_3): δ 44.81 (dvt, $J_{\text{PP}} = 273, 9, 21.2$ Hz), 48.65 (ddd, $J_{\text{PP}} = 273.9, 25.9, 16.9$ Hz), 50.94 (ddd, $J_{\text{PP}} = 32.0, 25.9, 21.2$ Hz), 61.09 (ddd, $J_{\text{PP}} = 32.0, 21.2, 16.9$ Hz).

3.5. X-ray analysis of **1**

Rod shaped, yellow single crystals of **1** were grown by slow evaporation of a CH_2Cl_2 /hexane solution. Single crystals were mounted onto glass fibers with high viscosity oil. Data collection was performed at 173(2) K on a Siemens P4 diffractometer with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å, graphite monochromator). The structure solution was solved by direct methods using the SHELXTL 5.1 package. The structure was refined versus F^2 .

4. Supplementary material

Details of the X-ray structure determination of **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 138689. Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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References

- [1] (a) J.E. Huheey, E.A. Keiter, R.L. Keiter, *Anorganische Chemie, Prinzipien von Struktur und Reaktivität*, W. de Gruyter, Berlin 1995 (Chapter 13). (b) R.F. Jordan, *Mechanismen anorganischer und metallorganischer Reaktionen*, Teubner, Stuttgart, 1994 (Chapter 3.6).
- [2] M.T. Bautista, E.P. Capellani, S.D. Drouin, R.H. Morris, C.T. Schweitzer, A. Sella, J. Zubkowski, *J. Am. Chem. Soc.* 113 (1991) 4876.
- [3] B. Chin, A.J. Lough, R.H. Morris, C.T. Schweitzer, C. D'Agostina, *Inorg. Chem.* 33 (1994) 6278.
- [4] J.R. Polam, L.C. Porter, *J. Coord. Chem.* 29 (1993) 109.
- [5] A. Mezzetti, A. Del Zotto, P. Rigo, *J. Chem. Soc., Dalton Trans.* (1990) 2515.
- [6] B. Chaudret, G. Commenges, R. Poilblanc, *J. Chem. Soc., Dalton Trans.* (1984) 1635.
- [7] D. Touchard, P. Haquette, N. Pirio, L. Toupet, P.H. Dixneuf, *Organometallics* 12 (1993) 3132.
- [8] R.F. Winter, F.M. Hornung, *Organometallics* 18 (1999) 4005.
- [9] (a) N. Pirio, D. Touchard, P.H. Dixneuf, *J. Organomet. Chem.* 462 (1993) C18. (b) D. Touchard, N. Pirio, P.H. Dixneuf, *Organometallics* 14 (1995) 4920. (c) D. Touchard, N. Pirio, L. Toupet, M. Fettouhi, L. Ouahab, P.H. Dixneuf, *Organometallics* 14 (1995) 5263.
- [10] V. Cadierno, M.P. Gamasa, J. Gimeno, E. Lastra, *J. Organomet. Chem.* 474 (1994) C27.
- [11] (a) R.F. Winter, F.M. Hornung, *Organometallics* 16 (1997) 4248. (b) R.F. Winter, *J. Chem. Soc., Chem. Commun.* (1998) 2209. (c) R.F. Winter, *Eur. J. Inorg. Chem.* (1999) 2121.
- [12] A.J. Hodge, S.L. Ingham, A.K. Kakkar, M.S. Khan, J. Lewis, N.J. Long, D.G. Parker, P.R. Raithby, *J. Organomet. Chem.* 488 (1995) 205.
- [13] (a) A.M. McDonagh, I.R. Whittall, M.G. Humphrey, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 519 (1996) 229. (b) A.M. McDonagh, I.R. Whittall, M.G. Humphrey, D.C.R. Hockless, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 523 (1996) 33. (c) A.M. McDonagh, M.P. Cifuentes, I.R. Whittall, M.G. Humphrey, M. Samoc, B. Luther-Davies, D.C.R. Hockless, *J. Organomet. Chem.* 526 (1996) 99. (d) I.R. Whittall, M.G. Humphrey, S. Houbrechts, J. Maes, A. Persoons, S. Schmid, D.C.R. Hockless, *J. Organomet. Chem.* 544 (1997) 277.
- [14] J. Chatt, R.G. Hayter, *J. Chem. Soc.* (1961) 896.
- [15] (a) I.E. Buys, L.D. Field, A.V. George, T.W. Hambley, G.R. Purches, *Aust. J. Chem.* 48 (1995) 27. (b) L.D. Field, A.V. George, D.C.R. Hockless, G.R. Purches, A.H. White, *J. Chem. Soc., Dalton Trans.* (1996) 2011.
- [16] F.B. McCormick, D.D. Cox, W.B. Gleason, *Organometallics* 12 (1993) 610.
- [17] R.F. Winter, T. Scheiring, *Z. Anorg. Allg. Chem.* 626 (2000) 1196.
- [18] A.R. Chakravarty, F.A. Cotton, W. Schwotzer, *Inorg. Chim. Acta* 84 (1984) 179.

- [19] M. Antberg, L. Dahlenburg, *Inorg. Chim. Acta* 111 (1986) 73.
[20] B.P. Sullivan, T.J. Meyer, *Inorg. Chem.* 21 (1982) 1037.
[21] (a) M.F.C. Guedes da Silva, J.J. Fraústo da Silva, A.J.J. Pombeiro, C. Amatore, J.-N. Verpaux, *Organometallics* 13 (1994) 3943. (b) M.F.C. Guedes da Silva, J.J. Fraústo da Silva, A.J.J. Pombeiro, C. Amatore, J.-N. Verpaux, *Inorg. Chem.* 37 (1998) 2344.
[22] I.P. Evans, A. Spencer, G. Wilkinson, *J. Chem. Soc., Dalton Trans.* (1973) 204.