DALTON
FULL PAPER

Nucleophilic addition reactions on the electron-deficient cluster dication $[H_4Ru_4(C_6H_6)_4]^{2+}$: synthesis and structural characterisation of the water-soluble cluster cations $[H_3Ru_4(C_6H_6)_4(CO)]^+$ and $[H_3Ru_4(C_6H_6)_4(OH)]^{2+}$†

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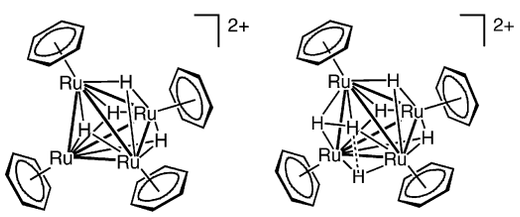
The electron-deficient (58e) cluster cation $[H_4Ru_4(C_6H_6)_4]^{2+}$ **1** was found to react in aqueous solution with simple nucleophiles to give electron-precise (60e) clusters. With carbon monoxide, the cluster cation $[H_3Ru_4(C_6H_6)_4(CO)]^+$ **3** is formed. The reaction with water needs NaN_3 as catalyst and yields the cluster dication $[H_3Ru_4(C_6H_6)_4(OH)]^{2+}$ **4a**; the reaction with alcohols leads to the analogous clusters $[H_3Ru_4(C_6H_6)_4(OR)]^{2+}$ (R = Me: **4b**, R = Et: **4c**, R = $PhCH_2$: **4d**, R = Ph: **4e**, R = 4-EtC_6H_4: **4f**). The single-crystal X-ray structure analyses of the chloride salts of **3** and **4a** reveal a tetrahedral Ru_4 metal core. Each ruthenium atom is coordinated by a η^6-benzene ligand, while the carbonyl or hydroxo ligands are found as μ_3 capping ligands over a triangular face of the Ru_4 tetrahedron.

Introduction

Organometallic clusters have received steadily increasing attention over the last three decades due to their unique structures[1] and properties and, in particular, because of their inherent catalytic potential.[2,3] Owing to the sensitivity of many organometallic compounds towards hydrolysis, organometallic clusters are normally handled in thoroughly dried organic solvents. The rigorous exclusion of water has become a general feature in this field to such an extent that water is rarely considered to be a suitable reaction medium for organometallic clusters.

On the other hand, water is a cheap and environmentally friendly solvent. Therefore, a lot of interest is placed in the development of water-soluble catalysts which allow catalytic reactions under biphasic conditions.[4,5] The organometallic cluster dication $[H_4Ru_4(C_6H_6)_4]^{2+}$ **1** which we reported some years ago[6] was found to be soluble in water and stable towards hydrolysis. It contains a closed tetrahedral Ru_4 metal skeleton with four η^6-benzene ligands at the four ruthenium atoms and four μ_3-hydrido ligands capping the four triangular faces of the Ru_4 tetrahedron. With an electron count of 58, **1** is an electron-deficient cluster, in accordance with Wade's rules (the noble gas configuration would require 60e for a tetrahedral cluster).



1 **2**

Because of this electron-deficiency, **1** is susceptible to react with 2e donors to give 60e clusters. For example, **1** reacts with hydrogen under pressure in aqueous solution to give the 60e cluster **2** which we first reported[6] as the classical hexahydrido cluster $[H_6Ru_4(C_6H_6)_4]^{2+}$ but which turned out to be a tetrahydrido–dihydrogen cluster $[H_4Ru_4(C_6H_6)_4(H_2)]^{2+}$ with an intact H_2 ligand coordinated to the Ru_4 core.[7] In this paper, we report the reactions of the electron-deficient cluster **1** with simple molecules which can function as donor ligands, such as CO, H_2O or ROH.

Results and discussion

The electron-deficient cluster dication $[H_4Ru_4(C_6H_6)_4]^{2+}$ **1** reacts in aqueous solution with carbon monoxide under pressure to give the carbonyl derivative $[H_3Ru_4(C_6H_6)_4(CO)]^+$ **3** which can be isolated as the chloride salt in good yield. The purple crystalline solid $[H_3Ru_4(C_6H_6)_4(CO)]Cl$ is soluble in water and in polar organic solvents.

$$[H_4Ru_4(C_6H_6)_4]^{2+} + CO \xrightarrow[H_2O]{} [H_3Ru_4(C_6H_6)_4(CO)]^+ + H^+$$

1 **3**

Surprisingly, after carbonylation of **1** at 50 °C, the violet aqueous solution contains, in addition to small quantities of **3**, a paramagnetic species which has not been identified so far. However, upon treatment of the crude aqueous solution with molecular hydrogen under pressure, the paramagnetic contamination disappears giving high yields of **3**. It is therefore possible that the paramagnetic species is an intermediate in the formation of **3** from **1**.

The carbonylated cluster **3** turned out to be a monocation, which means that one hydrido ligand in **1** has been eliminated as a proton during the formation of **3**. In the ^1H NMR spectrum, the three remaining hydrides give rise to only one resonance, whereas the four benzene ligands show up with two singlets in a 1 : 3 ratio. The equivalence of the three hydrides and of three of the four benzene ligands is suggestive of the carbonyl ligand being coordinated in a μ_3 fashion over one of the four triangular faces of the Ru_4 tetrahedron. In accordance

† Dedicated to Professor Gerhard E. Herberich on the occasion of his 65th birthday.

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Table 1 Important bond lengths (in Å) and angles (in °) for **3** and **4a**

$[H_3Ru_4(C_6H_6)_4(CO)]^+$ **3**				$[H_3Ru_4(C_6H_6)_4(OH)]^{2+}$ **4a**			
Ru1–Ru3	2.7323(7)	C21–Ru1–Ru3	94.9(2)	Ru1–Ru3	2.7519(8)	O1–Ru1–Ru2	90.5(2)
Ru1–Ru1′	2.7588(9)	O21–C21–Ru1	129.9(4)	Ru1–Ru1′	2.7494(11)	H1–O1–Ru1	129.9(4)
Ru1–Ru2	2.7720(8)	Ru1–Ru2–Ru1′	60.157(12)	Ru1–Ru2	2.7411(9)	Ru1′–Ru1–Ru3	60.030(12)
Ru1–C21	2.087(7)	Ru3–Ru2–Ru1′	59.678(11)	Ru1–O1	1.963(5)	Ru2–Ru1–Ru3	59.49(2)
Ru2–C21	2.099(9)			Ru3–O1	1.973(8)		
C21–O21	1.226(10)			O1–H1	0.9546		

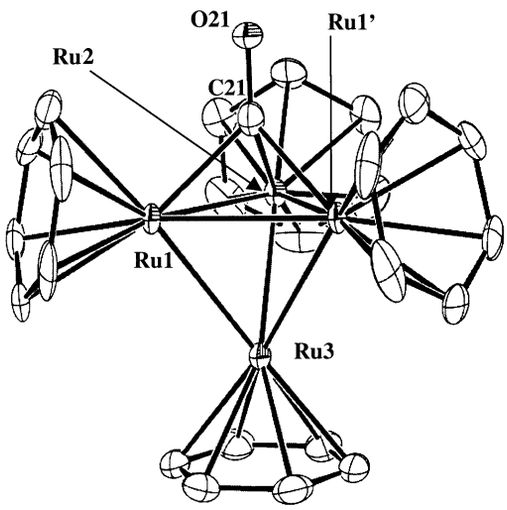
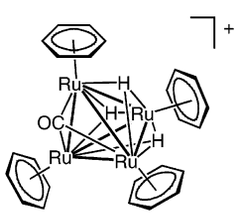


Fig. 1 PLATON diagram for $[H_3Ru_4(C_6H_6)_4(CO)]^+$ **3**.



3

with this assumption, the carbonyl stretching frequency of **3** is found in the infrared spectrum at 1558 cm^{-1}, characteristic for a capping carbonyl ligand.

The single-crystal X-ray structure analysis of [**3**]Cl (chloride salt) reveals a cationic molecule containing a mirror-plane in which lie atoms Ru3 and Ru2. The Ru_4 tetrahedron is closed with 6 Ru–Ru bonds varying between 2.7323(7) and 2.7720(8) Å. The structure of **3** is shown in Fig. 1, important bond distances and angles are given in Table 1. Each ruthenium atom is coordinated in an η^6 fashion to a benzene ligand, the distances between the ruthenium atoms and the six carbon atoms vary between 2.204(6) and 2.245(6) Å, in line with those in $[H_4Ru_4(C_6H_6)_4]^{2+}$ **1**.[6] The carbonyl ligand is found to cap the Ru1–Ru1′–Ru2 triangle, the ruthenium–carbon distances being Ru1–C21: 2.087(7) Å, Ru1′–C21: 2.087(7) Å, Ru2–C21: 2.099(9) Å. The carbon–oxygen distance C21–O21 [1.226(10) Å] is considerably longer than the μ_3-CO bond distance (1.175 Å) in $Ru_3(CO)_9(\mu_3\text{-}NOCH_3)(\mu_3\text{-}CO)$.[8] As expected, the three hydrides in **3** have been localised as μ_3-capping ligands over the three remaining triangular faces of the Ru_4 tetrahedron.

The cluster cation **1**, in the form of the chloride salt, is soluble in water, and does not react with water even at elevated temperatures. However, in the presence of an equimolar amount of sodium azide, efficient hydrolysis of **1** is observed to give $[H_3Ru_4(C_6H_6)_4(OH)]^{2+}$(**4a**) which crystallizes as the chloride salt.

The role of the sodium azide in this reaction is not entirely clear. It does not seem to act as a catalyst, since at least equimolar amounts of NaN_3 are required for a quantitative

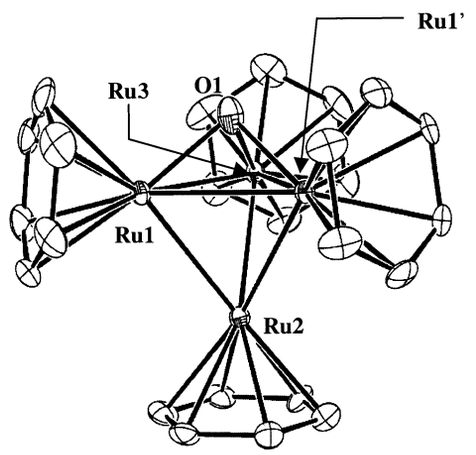
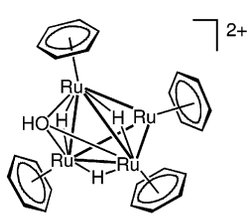


Fig. 2 PLATON diagram of $[H_3Ru_4(C_6H_6)_4(OH)]^{2+}$ **4a**.

$$[H_4Ru_4(C_6H_6)_4]^{2+} + H_2O \xrightarrow[(NaN_3)]{} [H_3Ru_4(C_6H_6)_4(OH)]^{2+} + H_2$$

1 **4a**

reaction. We therefore believe that, first of all, the N_3^- anion adds as a 2e nucleophile to the 58-electron cluster **1** to give a 60e intermediate $[H_4Ru_4(C_6H_6)_4(N_3)]^+$, which then hydrolyses to yield N_2, NH_2^- and **4a**. This assumption is in line with findings in the synthesis of amines from alkyl azides.[9]



4a

The OH bond in **4a** can be identified in the infrared spectrum of the chloride salt by a characteristic ν_{OH} vibration at 3250 cm^{-1}, but the OH group is not seen in the ^1H NMR spectra in CD_3CN or DMSO-d_6, presumably due to an H/D exchange with the deuterated solvent. In addition to this obvious acidity of the OH ligand, the equivalence of the three hydrides and of three of the four benzene ligands in **4a** suggests a μ_3 coordination of the hydroxo ligand. This is confirmed by the single-crystal X-ray structure analysis of the chloride salt of **4a**.

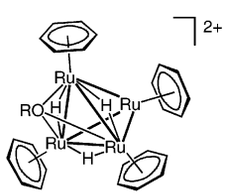
Suitable crystals of [**4a**]Cl_2 were obtained from aqueous solution. The single-crystal X-ray structure analysis shows for the dication a closed tetrahedral metal framework, the six Ru–Ru bond lengths vary from 2.7252(10) to 2.7519(8) Å; the structure of **4a** is shown in Fig. 2, important bond lengths and angles are given in Table 1. The molecule possesses a mirror plane in which lie atoms Ru2, Ru3 and O1. Each ruthenium atom is coordinated in an η^6 fashion to a benzene ligand, the distances between the ruthenium atoms and the six carbon atoms vary between 2.204(6) and 2.245(6) Å, in line with findings in $[H_4Ru_4(C_6H_6)_4]^{2+}$ **1**.[6] The hydroxo ligand is found as a μ_3 cap

over the Ru1–Ru1′–Ru3 triangular face of the tetrahedron, the ruthenium–oxygen bonds [Ru1–O1 1.963(5) Å, Ru1′–O1 1.963(5) Å, Ru3–O1 1.973(8) Å] are very similar. The hydrogen atom of the hydroxo cap could be located from a Fourier difference map (O1–H1 0.9546 Å). However, only two of the three hydrido ligands could be located. Surprisingly, they are found as μ (and not as μ_3) ligands over the ruthenium–ruthenium edges Ru1–Ru3 and Ru1′–Ru3. The third one, postulated on the basis of NMR and electron-count arguments, should be located as a μ bridge over the Ru1–Ru1′ edge. This is in accordance with the very similar bond lengths found for Ru1–Ru1′ [2.7494(11) Å], Ru1–Ru3 and Ru1′–Ru3 [2.7519(8) Å].

The azide-assisted reaction of **1** with water can be extended to alcohols and phenols. If the reaction is carried out in an aliphatic alcohol ROH, alcoholysis takes place to give the corresponding alkoxo clusters $[H_3Ru_4(C_6H_6)_4(OR)]^{2+}$(R = Me: **4b**, R = Et: **4c**, R = $PhCH_2$: **4d**). The solid phenol and 4-ethylphenol react with **1** in anhydrous tetrahydrofuran to give the analogous derivatives $[H_3Ru_4(C_6H_6)_4(OR)]^{2+}$(R = Ph: **4e**, R = 4-$EtC_6H_4$: **4f**). All cations are isolated as the chloride salts. In the case of the liquid aliphatic alcohols, the yields are quantitative, while with phenols the reaction is incomplete giving yields of less than 50%.

$$\underset{\mathbf{1}}{[H_4Ru_4(C_6H_6)_4]^{2+}} + ROH \xrightarrow[(NaN_3)]{} \underset{\mathbf{4b\text{-}f}}{[H_3Ru_4(C_6H_6)_4(OR)]^{2+}} + H_2$$

The alkoxo clusters **4b–f** must have the same structure as the hydroxo derivative **4a**, since the ^{1}H NMR features are essentially the same. In all cases, only one signal is obtained for the three hydrides, whereas the four benzene ligands give rise to two signals in a 1 : 3 ratio. This equivalence of the three hydrides and of three of the four benzene ligands is in accordance with a tetrahedral Ru_4 cluster containing a μ_3-alkoxo ligand.



4b–f

R	Me	Et	$PhCH_2$	Ph	4-EtC_6H_4
	4b	**4c**	**4d**	**4e**	**4f**

The chloride salts of the alkoxo clusters **4b–f** form air-stable, black-brown solids which easily dissolve in water as well as in polar organic solvents such tetrahydrofuran, acetonitrile, or methanol.

Conclusion

Because of the remarkable stability of the benzene–ruthenium unit towards hydrolysis, cationic benzene–ruthenium clusters are able to bridge the gap between organometallic compounds and classical coordination compounds. Thus the chloride salts of the clusters $[H_4Ru_4(C_6H_6)_4]^{2+}$ **1** and $[H_4Ru_4(C_6H_6)_4(H_2)]^{2+}$ **2** are soluble not only in organic solvents but also in water. The chemistry of these organometallic clusters in aqueous solution has now been extended to alkoxo and even carbonyl derivatives. The chloride salts of all cluster cations reported in this paper are also soluble in organic solvents and in water. Addition of $NaBF_4$ or KPF_6 to the aqueous solutions of all cationic clusters described here causes the quantitative precipitation of the tetrafluoroborate or hexafluorophosphate salts of **3** and **4**.

Experimental

General remarks

Organic solvents were dried and distilled under nitrogen prior to use. All reactions were carried out under nitrogen using standard Schlenk techniques. The cluster compound $[H_4Ru_4(C_6H_6)_4]^{2+}$ **1** (chloride salt) was prepared according to our previous work.[6] All other reagents were purchased and used without further purification. ^{1}H NMR spectra were recorded using a Varian Gemini 200 BB instrument with $SiMe_4$ external standard. Infrared spectra were recorded with a Perkin-Elmer 1720X FT-IR spectrometer. Microanalyses were carried out by the Laboratory of Pharmaceutical Chemistry, University of Geneva, Switzerland.

Synthesis of $[H_3Ru_4(C_6H_6)_4(CO)]^+$ 3

A solution of $[H_4Ru_4(C_6H_6)_4]Cl_2$ (cation **1**) (200 mg, 0.25 mmol) in H_2O (20 mL) was heated to 50 °C in a stainless-steel autoclave under CO pressure (50 bar). After 14 h, the autoclave was cooled and the pressure was released. The mixture was filtered, and the resulting purple solution was heated again to 50 °C in a stainless-steel autoclave under a pressure of H_2 (50 bar) for 8 h. After cooling and venting of the autoclave, the solvent was removed under reduced pressure to give pure $[H_3Ru_4(C_6H_6)_4(CO)]Cl$ (cation **3**). Yield 67%. MS: 750 *m*/*z*. Calc. for $C_{25}H_{27}ORu_4Cl$: C, 36.68; H, 3.32. Found: C, 36.17; H, 3.75%. IR (KBr): ν(CO) 1558 cm^{-1}. ^{1}H NMR (CD_3CN, R.T.): δ 5.89 (6H, s), 5.63 (18H, s), −17.14 (3H, s).

Synthesis of $[H_3Ru_4(C_6H_6)_4(OR)]^{2+}$ 4

A solution of $[H_4Ru_4(C_6H_6)_4]Cl_2$ (cation **1**) (200 mg, 0.25 mmol) in 20 mL of water (methanol, ethanol, or benzyl alcohol) was heated to 50 °C (in the case of the solid phenol or 4-ethylphenol, 2.5 mmol were dissolved together with **1** in 20 mL of anhydrous tetrahydrofuran). Then an equimolecular amount of NaN_3 (0.25 mmol) was added, and the mixture was stirred for one hour at 50 °C. After cooling to room temperature, the mixture was filtered, and the solvent was removed under reduced pressure, giving the chloride salt of **4** in analytically pure form.

$[H_3Ru_4(C_6H_6)_4(OH)]Cl_2$ (cation 4a). Quantitative yield. MS: *m*/*z* 734. Calc. for $C_{24}H_{28}ORu_4Cl_2$: C, 35.69; H, 3.49. Found: C, 36.02; H, 3.29%. IR (KBr): ν(OH) 3250 cm^{-1}. ^{1}H NMR (CD_3CN, R.T.): δ 6.13 (6H, s), 5.72 (18H, s), −17.84 (3H, s).

$[H_3Ru_4(C_6H_6)_4(OCH_3)]Cl_2$ (cation 4b). Quantitative yield. Calc. for $C_{25}H_{30}ORu_4Cl_2$: C, 36.54; H, 3.68. Found: C, 36.68; H, 3.86%. ^{1}H NMR (DMSO-d_6, R.T.): δ 6.21 (6H, s), 5.80 (18H, s), 3.18 (3H, s), −17.83 (3H, s).

$[H_3Ru_4(C_6H_6)_4(OCH_2CH_3)]Cl_2$ (cation 4c). Quantitative yield. Calc. for $C_{26}H_{32}ORu_4Cl_2$: C, 37.37; H, 3.86. Found: C, 37.59; H, 3.78%. ^{1}H NMR (DMSO-d_6, R.T.): δ 6.22 (6H, s), 5.80 (18H, s), 4.53 (2H, q), 1.40 (3H, t), −17.83 (3H, s).

$[H_3Ru_4(C_6H_6)_4(OCH_2PH)]Cl_2$ (cation 4d). Yield 85%. Calc. for $C_{31}H_{34}ORu_4Cl_2$: C, 41.47; H, 3.82. Found: C, 41.82; H, 3.95%. ^{1}H NMR (DMSO-d_6, R.T.): δ 7.85–7.40 (5H, m), 6.15 (6H, s), 5.75 (18H, s), 4.62 (2H, s), −17.82 (3H, s).

$[H_3Ru_4(C_6H_6)_4(OPh)]Cl_2$ (cation 4e). Yield 25%. Calc. for $C_{30}H_{32}ORu_4Cl_2$: C, 40.77; H, 3.65. Found: C, 40.36; H, 3.84%. ^{1}H NMR (DMSO-d_6, R.T.): δ 8.05 (2H, dd), 7.55–7.40 (3H, m), 6.15 (6H, s), 5.75 (18H, s), −14.72 (3H, s).

$[H_3Ru_4(C_6H_6)_4(OC_6H_4Et\text{-}4)]Cl_2$ (cation 4f). Yield 45%. Calc. for $C_{32}H_{36}ORu_4Cl_2$: C, 42.15; H, 3.98. Found: C, 41.85; H,

Table 2 Crystal and experimental data for $[H_3Ru_4(C_6H_6)_4(CO)]^+$ **3** and $[H_3Ru_4(C_6H_6)_4(OH)]^{2+}$ **4a**

Formula	$C_{25}H_{31}O_3Ru_4Cl$	$C_{24}H_{46}O_{10}Ru_4Cl_2$
Formula weight	819.23	969.79
Crystal system	Orthorhombic	Monoclinic
Space group	*Cmca*	*Cm*
a/Å	16.5828(12)	9.4441(10)
b/Å	9.5349(9)	16.2936(13)
c/Å	31.467(3)	11.2913(12)
α/°	90	90
β/°	90	106.534(12)
λ/°	90	90
V/Å^3	4975.4(8)	1665.6(3)
Z	8	2
T/K	153 (2)	153 (2)
Wavelength, *λ*(Mo-Kα)/Å	0.71073	0.71073
μ/cm^{-1}	0.2515	0.1978
Reflections collected	12246	6545
Independent reflections	1647	3255
R_{int}	0.1208	0.0507
Reflections with $I > 2\sigma(I)$	1477	2810
*R*1	0.0397	0.0345
*WR*2	0.0951	0.0734

4.12%. ^{1}H NMR (DMSO-d$_6$, R.T.): δ 8.05 (2H, d), 7.35 (2H, d), 6.15 (6H, s), 5.75 (18H, s), 2.35 (2H, q), 1.21 (3H, t), −14.72 (3H, s).

X-Ray structure analyses

Suitable crystals of the chloride salts of the clusters **3** and **4a** were mounted on a Stoe Imaging Plate Diffractometer System (STOE & Cie, 1995) equipped with a one-circle φ goniometer and a graphite-monochromator. Data collections were performed at −120 °C using Mo-Kα ($\lambda = 0.71073$ Å). Exposures were obtained at an image plate distance of 70 mm for **4a** or 90 mm for **3** with $0 < \varphi < 200$ and with the crystal oscillating through 1.5° in φ. The resolution for **3** and **4a** was D_{min}− D_{max} 16.00–0.93 Å and 12.45–0.81 Å, respectively. The structures were solved by direct methods using the program SHELXS-97.[10] The refinement and all further calculations were carried out using SHELXL-97.[11] The hydrogen atoms attached to the benzene rings were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters while the other hydrogen atoms were located from difference Fourier maps and held fixed in their positions. Compound **4a** crystallizes in the noncentrosymmetric space group *Cm* with 4.5 molecules of water per asymmetric unit (Flack parameter $x = -0.03(6)$). An absorption correction was applied for **3** using DIFABS in PLATON99 ($T_{min} = 0.237$, $T_{max} = 0.698$).[12] Significant bond lengths and bond angles are listed in Table 1, crystallographic details are given in Table 2. The figures were drawn with PLATON.[12]

CCDC reference numbers 161653 and 161654.

See http://www.rsc.org/suppdata/dt/b1/b102108g/ for crystallographic data in CIF or other electronic format.

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References

1 *Metal Clusters in Chemistry*, ed. P. Braunstein, L. A. Oro and P. R. Raithby, Wiley-VCH, New York, 1999, vol. 1.
2 P. Braunstein and J. Rosé, in *Comprehensive Organometallic Chemistry 2*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Elsevier, Oxford, 1995, vol. 10, p. 351.
3 *Catalysis by Di- and Polynuclear Metal Cluster Complexes*, ed. R. D. Adams and F. A. Cotton, Wiley-VCH, New York, 1998.
4 *Aqueous-Phase Organometallic Catalysis*, ed. W. A. Herrmann and B. Cornils, Wiley-VCH, New York, 1998.
5 B. Cornils, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1575.
6 G. Meister, G. Rheinwald, H. Stoeckli-Evans and G. Süss-Fink, *J. Chem. Soc., Dalton Trans.*, 1994, 3215.
7 G. Süss-Fink, L. Plasseraud, A. Maisse-François, H. Stoeckli-Evans, H. Berke, T. Fox, R. Gauthier and J. Y. Saillard, *J. Organomet. Chem.*, 2000, **609**, 196.
8 R. E. Stevens, R. D. Guettler and W. L. Gladfelter, *Inorg. Chem.*, 1990, **29**, 451.
9 F. Rolla, *J. Org. Chem.*, 1982, **47**, 4327.
10 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
11 G. M. Sheldrick, SHELXL-97, Universität Göttingen, Göttingen, Germany, 1999.
12 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.