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# Synthesis and crystal structures of $[Rh(TTP)(CH_3)]_2(\mu$-CNpy) and $[Rh(TTP)(C_8H_{11})]$ (TTP = 5,10,15,20-tetra(*p*-tolyl)porphyrin dianion; CNpy = 4-cyanopyridine; $C_8H_{11}$ = (5-norbornen-2-yl)methyl)

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**Abstract**

Interaction of $[Rh(TTP)CH_3]$ (TTP = 5,10,15,20-tetra(*p*-tolyl)porphyrin dianion) with bidentate ligands L affords $[Rh(TTP)CH_3]_2(\mu$-L) (L = 4-cyanopyridine (**1**) or 4,4′-bipyridine (**2**)). The structure of **1** has been established by X-ray crystallography. The average Rh–C, average Rh–N(pyrrole), and average Rh–N(CNpy) distances in **1** are 2.032(4), 2.032, and 2.273(4) Å, respectively. The reaction of Na[Rh(TTP)] with (5-norbornen-2-yl)methyl iodide ($C_8H_{11}I$) affords $[Rh(TTP)(C_8H_{11})]$ (**5**), which has been characterized by X-ray diffraction study. The Rh–C and average Rh–N distance in **5** are 2.052(6) and 2.022 Å, respectively.


*Keywords:* Dinuclear; Rhodium porphyrin; Alkyl; Crystal structure

## 1. Introduction

In recent years a variety of oligomeric metal porphyrins and phthalocyanines have been synthesized as components of molecular devices, supramolecular assemblies [1–4], and light-harvesting systems [5]. Of particular interest are a class of metalloporphyrin oligomers based on square-planar [M(por)] (por = porphyrin dianion) cores and bidentate *N*-heterocycles such as pyrazine and 4,4′-bipyridine. Well-defined one-dimensional polymers of the type $[M(por)(L)]_n$ (M = Fe, Ru, Os) have been synthesized and shown to exhibit interesting redox and optical properties [3]. There are, however, relatively few examples of polymeric or oligomeric rhodium porphyrins [6], which may find applications in molecular recognition of amino acids [7] and nucleobases [8]. In this connection, two approaches to polynuclear rhodium porphyrins were attempted: (a) reactions of rhodium porphyrins with bidentate pyridine ligands and (b) metathesis polymerization rhodium porphyrins containing a norbornene functionality. In this paper, we report the synthesis and crystal structure of a 4-cyanopyridine-bridged methylrhodium(III) porphyrin and a σ-bonded (5-norbornen-2-yl)methyl complex of rhodium porphyrin.

## 2. Results and discussion

### 2.1. Dimeric Rh(III) methyl complexes

Ogoshi and coworkers first studied the reactions of amine ligands with methylrhodium(III) porphyrins [9]. It was found that in solution the pyridine adducts $[Rh(OEP)CH_3(L)]$ (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin dianion; L = 4-substituted pyridine) characterized by NMR and UV–vis spectroscopy are in equilibrium with $[Rh(OEP)CH_3]$. In this work, we found that when $[Rh(TTP)CH_3]$ was treated with one equivalent of 4-cyanopyridine (CNpy) a mixture of $[Rh(TTP)CH_3]_2(\mu$-CNpy) (**1**) and

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[Rh(TTP)($CH_3$)(CNpy)] (**2**) were formed. Complexes **1** and **2** could be separated by fractional recrystallization and were isolated as crystalline solids (see Section 3). The dimer **1** was isolated in good yield when 0.5 equivalents of CNpy were used. The $\nu_{CN}$ for **1** was located at 1907 $cm^{-1}$, which is lower than for free $\nu_{CN}$ (2200 $cm^{-1}$), due to Rh-to-CN backbonding. On the other hand, the $\nu_{CN}$ for **2** was found at the same frequency as that for free CNpy (ca. 2200 $cm^{-1}$), indicating that the CNpy in **2** binds to Rh via pyridyl nitrogen. The $^1$H-NMR spectrum of complex **1** in $CDCl_3$ shows a doublet at $\delta$ −6.14 with $^2J_{RhH} = 2.7$ Hz, assignable to the axial methyl protons. The observation of only one methyl resonant signal for **1** suggests that in solution there exists a rapid exchange equilibrium among **1**, **2**, and [Rh(TTP)($CH_3$)] on the NMR timescale. It seems likely that the major species at equilibrium are [Rh(TTP)$CH_3$)] and **2**, thus explaining why the ligand chemical shifts for **1** and **2** are more or less identical. Consistent with the rapid exchange process, broad singlets instead of sharp doublets were found for the pyridyl protons in **1** and **2**. It should be noted that pyridine ligand dissociation for [Rh(OEP)$CH_3$(CNpy)] in solution has been previously reported by Ogoshi and coworkers [9]. The solid-state structure of dinuclear **1** has been established by X-ray crystallography. Fig. 1 shows a perspective view of the molecule; selected bond lengths and angles are listed in Table 2. The CNpy ligand in **1** was found to be 50:50 disordered, resulting in pseudo twofold symmetry of the crystal structure. The average Rh–C, average Rh–N(pyrrole), and average Rh–N(CNpy) distances in **1** are 2.032(2), 2.032, and 2.273(4) Å, respectively. The Rh–C distance is similar to that for [Rh(OEP)$CH_3$] (2.031(6) Å) [10]. Similarly, treatment of [Rh(TTP)$CH_3$] with 0.5 equivalents of 4,4′-bpy afforded the 4,4′-bpy-bridged dimer [Rh(TTP)$CH_3$]$_2$(μ-4,4′-bpy) (**3**). The $^1$H-NMR spectrum of **3** shows two signals at $\delta$ 2.86 and 4.99 ppm assignable to the *ortho* and *meta* protons of the 4,4′-bpy ligand, consistent with the symmetric bridging mode of 4,4′-bpy. The cyclic voltammogram for **3** in $CH_2Cl_2$ features two reversible oxidation couples at 0.42 and 0.75 V versus the ferrocenium–ferrocene couple, which are tentatively assigned as the

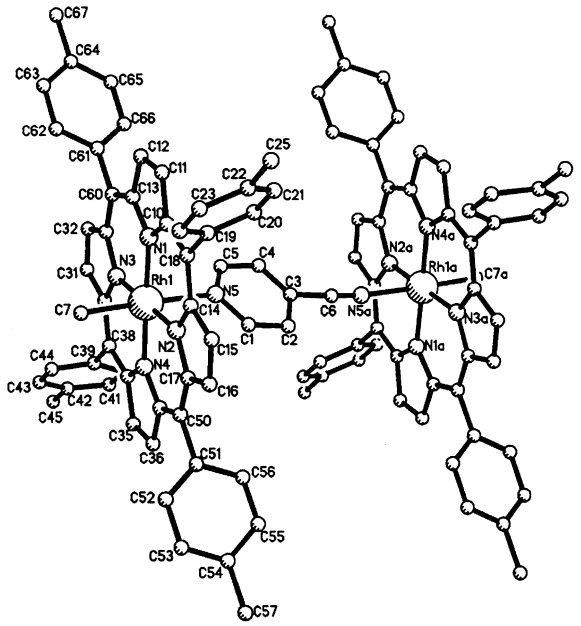



Fig. 1. Crystal structure of [Rh(TTP)($CH_3$)]$_2$(μ-CNpy) (**1**).

Table 1
Crystal data and structure refinement details for [Rh(TTP)$CH_3$]$_2$(μ-CNpy) (**1**) and [Rh(TTP)($C_8H_{11}$)]·$C_6H_{14}$ (**5**·$C_6H_{14}$)

| | **1** | **5**·$C_6H_{14}$ |
|---|---|---|
| Empirical formula | $C_{52}H_{41}N_5Rh$ | $C_{62}H_{61}N_4Rh$ |
| Formula weight | 838.81 | 934.99 |
| Color | Red | Red |
| Habit | Plate | Plate |
| *a* (Å) | 11.238(3) | 13.225(3) |
| *b* (Å) | 12.167(2) | 13.834(2) |
| *c* (Å) | 17.827(4) | 16.729(3) |
| α (°) | 108.11(1) | 72.820(1) |
| β (°) | 99.23(1) | 88.82(2) |
| γ (°) | 100.97(1) | 63.55(2) |
| *V* (Å$^3$) | 2210.6(9) | 2595.9(8) |
| *Z* | 2 | 2 |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ (no. 2) | $P\bar{1}$ (no. 2) |
| $D_{calc}$ (g $cm^{-3}$) | 1.26 | 1.235 |
| *T* (K) | 293 | 293 |
| λ (Å) | 0.71073 | 0.71073 |
| Scan type | ω–2θ | ω–2θ |
| μ ($mm^{-1}$) | 0.426 | 0.369 |
| No. of reflections measured | 7639 | 7922 |
| No. of reflections observed | 5446 ($I>2.0\sigma(I)$) | 5076 ($I>2.0\sigma(I)$) |
| *R* ($F^2$) | 0.0827 | 0.1161 |
| w$R_2$ | 0.01109 | 0.1865 |
| *F*(000) | 866 | 976 |
| Goodness of fit ($F^2$) | 1.040 | 1.059 |

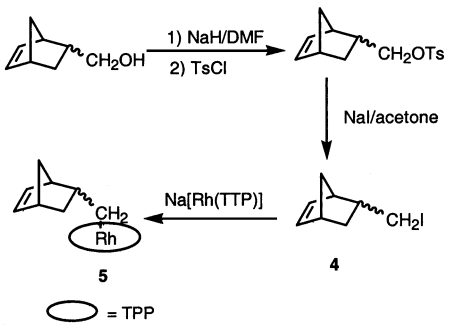
Table 2
Selected bond lengths (Å) and angles (°) for[Rh(TTP)$CH_3$]$_2$(μ-CNpy) (**1**)

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Rh(1)–N(1) | 2.038(3) | Rh(1)–N(2) | 2.028(3) |
| Rh(1)–N(3) | 2.029(4) | Rh(1)–N(4) | 2.032(3) |
| Rh(1)–N(5) | 2.273(4) | Rh(1)–C(7) | 2.032(4) |
| *Bond angles* | | | |
| N(1)–Rh(1)–N(2) | 89.94(14) | N(1)–Rh(1)–N(3) | 89.97(14) |
| N(1)–Rh(1)–N(4) | 179.19(14) | N(1)–Rh(1)–N(5) | 91.89(13) |
| N(1)–Rh(1)–C(7) | 90.4(2) | N(2)–Rh(1)–N(3) | 179.9(2) |
| N(2)–Rh(1)–N(4) | 90.03(14) | N(2)–Rh(1)–N(5) | 90.79(13) |
| N(2)–Rh(1)–C(7) | 89.4(2) | N(3)–Rh(1)–N(4) | 90.06(14) |
| N(3)–Rh(1)–N(5) | 89.15(13) | N(3)–Rh(1)–C(7) | 90.7(2) |
| N(4)–Rh(1)–N(5) | 87.29(13) | N(4)–Rh(1)–C(7) | 90.4(2) |
| N(5)–Rh(1)–C(7) | 177.7(2) | | |

porphyrin ring oxidation and Rh(IV/III) couple, respectively. Similar oxidation potentials were found for [Rh(TTP)$CH_3$] under the same conditions. The observed $\Delta E_p$ values of ca. 100 mV for the oxidation couples for **3** are consistent with single electron transfer processes.

### 2.2. Rh(III) (5-norbornen-2-yl)methyl complex

Norbornene and its derivatives are known to undergo facile ring-opening metathesis polymerization (ROMP) in the presence of ruthenium carbene catalysts, notably [Ru(=CHPh)($PCy_3$)$_2Cl_2$] or the Grubbs' catalyst, to give poly(norbornene)s [11]. To this end an attempt was made to prepare a σ-bonded (5-norbornen-2-yl)methyl complex of rhodium porphyrin, which may be used as a precursor to rhodium-containing poly(norbornene)s. (5-Norbornen-2-yl)methyl iodide ($C_8H_{11}I$) (**4**) was synthesized by tosylation of commercially available 5-norbornene-2-methanol with tosyl chloride in the presence of $Et_3N$, and subsequent reaction with NaI in acetone. Treatment of Na[Rh(TTP)], which was prepared in situ from [Rh(TTP)I] and $NaBH_4$ [10], with **4** afforded the rhodium (5-norbornen-2-yl)methyl complex [Rh(TTP)($C_8H_{11}$)] (**5**), isolated as an air-stable solid (Scheme 1).




Scheme 1.

The $^1$H-NMR spectrum of **5** is complex apparently due to the presence of both *exo* and *endo* forms of the 5-norbornene-2-methyl ligand. The resonant signals for the axial norbornene protons for **5** are in general more upfield than those for **4** due to the porphyrin ring current. The multiplets in $\delta$ −4.72 to −5.11 and $\delta$ 4.80 to 6.26 are tentatively assigned to the axial methylene and the olefinic protons, respectively. The FAB mass spectrum shows the signal for a molecular ion at $m/z$ 878 corresponding to [Rh(TTP)($C_8H_{11}$)]$^+$. The UV–vis spectrum of **5** in $CH_2Cl_2$ shows a soret band at 413 nm, which is close to that for [Rh(TTP)$CH_3$]. The identity of **5** was unambiguously confirmed by X-ray crystallography. To our knowledge, this is the first example of the Rh σ-norbornenylmethyl complex. Fig. 2 shows a perspective view of **5**; selected bond lengths and angles are listed in Table 3. The geometry around Rh is distorted square pyramidal. The Rh–C (2.052(6) Å) and average Rh–N (2.022 Å) distances are comparable to those for **1**. A preliminary study showed that the reaction of **5** with [Ru(=CHPh)($PCy_3$)$_2Cl_2$] [11] led to isolation of a purple solid, presumably an oligomer of **5**. However, the molecular weight of this purple material is rather low ($M_w \approx 5600$ according to gel permeation chromatography). High-molecular-weight oligomers were not obtained, possibly due to steric hindrance of the bulky porphyrin ring in monomer **5**. The steric repulsion among the porphyrin monomers may be relieved if a longer spacer between the norbornene functionality and Rh, e.g. a hexylene instead of methylene group, is used. The synthesis of this kind of norbornenylalkyl rhodium porphyrins is underway.

In summary, we have demonstrated that substitutionally inert alkylrhodium porphyrins may serve as building blocks for rhodium porphyrin oligomers. The alkylrhodium porphyrin monomers may be linked together via either coordination bonding with bidentate pyridine ligands or polymerization of the axial alkyl group.

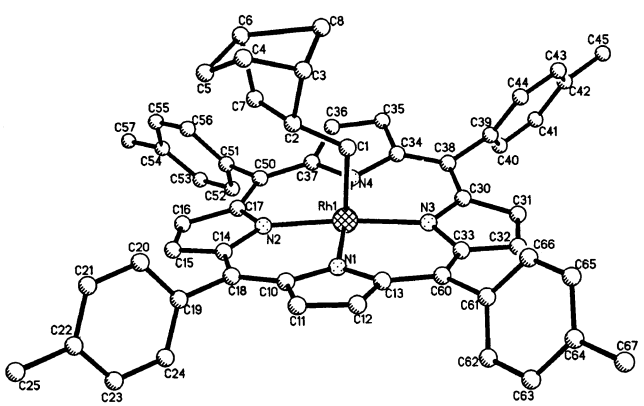
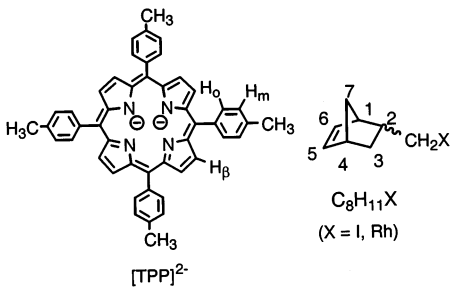



Fig. 2. Crystal structure of [Rh(TTP)($C_8H_{11}$)] (**5**).

Table 3
Selected bond lengths (Å) and angles (°) for [Rh(TTP)($C_8H_{11}$)] (**5**)

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Rh(1)–N(1) | 2.028(4) | Rh(1)–N(2) | 2.023(4) |
| Rh(1)–N(3) | 2.017(4) | Rh(1)–N(4) | 2.020(4) |
| Rh(1)–C(1) | 2.052(6) | | |
| *Bond angles* | | | |
| N(1)–Rh(1)–N(2) | 90.0(2) | N(1)–Rh(1)–N(3) | 90.1(2) |
| N(1)–Rh(1)–N(4) | 179.9(2) | N(1)–Rh(1)–C(1) | 89.2(2) |
| N(2)–Rh(1)–N(3) | 173.9(2) | N(2)–Rh(1)–N(4) | 90.0(2) |
| N(2)–Rh(1)–C(1) | 99.6(2) | N(3)–Rh(1)–N(4) | 90.0(2) |
| N(4)–Rh(1)–C(1) | 90.8(2) | | |




Scheme 2.

## 3. Experimental

### 3.1. General information

Solvents were purified and distilled prior to use. NMR spectra were recorded on a Bruker ALX 300 spectrometer. Chemical shifts ($\delta$, ppm) were reported with reference to $SiMe_4$. Infrared spectra (Nujol) were recorded on a Perkin–Elmer 16 PC FT-IR spectrophotometer. Mass spectra were obtained on a Finnigan TSQ-7000 spectrometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) Model 273A potentiostat. The working and reference electrodes are glassy carbon and $Ag \mid AgNO_3$ (0.1 M in acetonitrile) electrodes, respectively. Potentials were reported with reference to the ferrocenium–ferrocene couple. Elemental analyses were performed by Medac Ltd, Surrey, UK.

[Rh(TPP)I] and [Rh(TTP)$CH_3$] were prepared according to a literature method [12]. 5-Norbornene-1-methanol (as a mixture of *exo* and *endo* isomers) was obtained from Aldrich Ltd and used as received. Hydrogen atom labeling schemes for TTP and (5-norbornen-2-yl)methyl ($C_8H_{11}$) are shown in Scheme 2.

### 3.2. Preparation of [Rh(TTP)$CH_3$]$_2$($\mu$-CNpy) (**1**)

To a solution of [Rh(TTP)$CH_3$] (50 mg, 0.08 mmol) in $CH_2Cl_2$ (10 ml) was added 0.5 equivalents of CNpy. The mixture was stirred at room temperature (r.t.) for 30 min and half of the solvent was removed in vacuo. Addition of hexane (ca. 20 ml) and cooling at $-10$°C led to isolation of a purple solid, which was collected and washed with methanol. Recrystallization from $CH_2Cl_2$–hexane afforded red crystals (Yield: ca. 50% based on CNpy). Anal. Calc. For $C_{104}H_{82}N_{10}Rh_2$: C, 74.5; N, 4.9; N, 8.4. Found: C, 74.0; H, 5.2; N, 8.1%. $^1$H-NMR ($CDCl_3$): $\delta$ $-6.14$ (d, $^2J_{RhH} = 2.4$ Hz, 6H, RhC$H_3$), 2.69 (s, 24H, $p$-$CH_3$), 3.40 (s br, 2H, $H_o$ of CNpy), 5.92 (s br, 2H, $H_m$ of CNpy), 7.52 (d, $J = 8.0$ Hz, 16H, $H_m$), 8.02 (d, $J = 8.0$ Hz, 16H, $H_o$), 8.77 (s, 16H, $H_\beta$). IR ($cm^{-1}$): 2000 $\nu_{CN}$. If excess CNpy was used a mixture of **1** and the monomer [Rh(TTP)($CH_3$)(CNpy)] (**2**) was formed, as indicated by NMR spectroscopy. When the mixture in $CH_2Cl_2$–hexane was left to stand at r.t. overnight, purple crystals identified as **1** were formed and were collected. Addition of hexane and slow evaporation led to formation of a microcrystalline solid characterized as **2**, which was found to be contaminated with a small amount of **1**. Characterization data for **2**: $^1$H-NMR ($CDCl_3$): $\delta$ $-6.42$ (d, $^2J_{RhH} = 2.40$ Hz, 3H, RhC$H_3$), 2.69 (s, 12H, $p$-$CH_3$), 3.40 (s br, 2H, $H_o$ of CNpy), 5.92 (d, 2H, $H_m$ of CNpy), 7.52 (d, 8H, $H_m$), 8.02 (d, 8H, $H_o$), 8.77 (s, 8H, $H_\beta$).

### 3.3. Preparation of [Rh(TTP)$CH_3$]$_2$($\mu$-4,4′-bpy) (**3**)

This was prepared similarly as for **1** using 4,4′-bpy instead of CNpy. Yield: 75% (based on 4,4′-bpy). $^1$H-NMR ($CDCl_3$): $\delta$ $-6.42$ (d, $^2J_{RhH} = 2.4$ Hz, 6H, RhC$H_3$), 2.65 (s, 24H, $p$-Me), 2.86 (s br, 4H, $H_o$ of 4,4′-bpy), 4.99 (s br, 4H, $H_m$ of 4,4′-bpy), 7.45 (d, $J = 7.9$ Hz, 16H, $H_m$), 7.90 (d, $J = 8.0$ Hz, 16H, $H_o$), 8.58 (s, 16H, $H_\beta$).

### 3.4. Preparation of (5-norbornen-2-yl)methyl iodide (**4**)

A mixture of 5-norbornene-2-methanol (0.5 g, 4.03 mmol), 4-toluenesulfonyl chloride (1 g, 5.25 mmol), $Et_3N$ (5 ml) in $CH_2Cl_2$ (25 ml) was stirred under nitrogen at r.t. for 5 h. Then NaI (1 g, 6.67 mmol) in *N*,*N*-dimethylformamide (10 ml) was added and the mixture was stirred for 3 h. The resulting mixture was diluted with ethyl acetate (150 ml), and washed five times with water (10 ml). The organic fraction was dried with anhydrous $MgSO_4$ and subjected to column chromatography (silica) using hexane as eluent. The product was isolated as a colorless oil. Yield 50%. $^1$H-NMR ($CDCl_3$): $\delta$ 0.56–0.62 (m, 2H), 1.50–1.54 (m, 1H), 1.93–2.01 (m, 1H), 2.49–2.60 (m, 1H), 2.85–3.02 (m, 4H), 5.99–6.25 (m, 2H). MS (CI): $m/z$ 233 $[M-1]^+$.

### 3.5. Preparation of [Rh(TTP)($C_8H_{11}$)] [$C_8H_{11}$ = (5-norbornen-2-yl)methyl] (**5**)

To a solution of [Rh(TTP)I] (0.06 g, 0.067 mmol) in EtOH (10 ml) was added $NaBH_4$ (4 mg) in 0.5 M NaOH(aq) (2 ml) and the mixture was stirred under nitrogen at r.t. The red mixture turned to orange in ca. 30 min, indicating the formation of Na[Rh(TTP)], and was stirred for a further 30 min. Then one equivalent of **4** was added under nitrogen and the mixture was stirred for 1 h. The solvent was pumped off and the residue was extracted with $CH_2Cl_2$, washed with water ($2 \times 15$ ml), and dried with anhydrous $MgSO_4$. The filtrate was concentrated and chromatographed on alumina. The product was eluted as a red band by $CH_2Cl_2$. Recrystallization from $CH_2Cl_2$–hexane afforded red crystals,

which were suitable for X-ray diffraction study. Yield: 30 mg (50%, based on [Rh(TTP)I]). Anal. Calc. For $C_{56}H_{47}N_4Rh$: C, 76.53; N, 5.4; N, 6.4. Found: C, 76.4; H, 5.3; N, 5.3%. $^1$H-NMR ($CDCl_3$): $\delta$ −4.72 to −5.11 (m, 2H, RhC$H_2$), −3.15 to −3.39 (m, 1H, H$^3$), −0.20 to −1.18 (m, 2H, H$^1$ and H$^4$), 1.57–1.32 (m, 4H, H$^2$ and H$^7$), 2.73 (s, 12H, *p*-Me), 4.80–6.26 (m, 2H, H$^5$ and H$^6$), 7.57 (d, $J = 9.0$ Hz, 8H, $H_m$), 8.07 (m, 8H, $H_o$), 8.78 (m, 8H, pyrrolic H). FABMS: $m/z$ 878 [M$^+$].

## 4. X-ray crystallography

A summary of crystallographic data and experimental details for **1** and **5**·$C_6H_{14}$ are given in Table 1. All data were collected on a Siemens P4 diffractometer. Both structures were solved by direct methods and refined on $F^2$ by full-matrix least-squares analyses. Absorption corrections for both complexes are semi-empirical based on psi-scan data. For **1**, the bridging cyanopyridine ligand was found to be 50:50 disordered. A model based on occupancy of 0.5 each for the two possible sites was used for the refinement. For **5**·$C_6H_{14}$, a model with occupancies of 0.4 and 0.6 of the disordered (5-norbornen-2-yl)methyl group was used. All calculations were performed using the SHELXL [13] crystallographic software package.

## 5. Supplementary material

Crystallographic data for compounds **1** and **5**·$C_6H_{14}$ have been deposited with the Cambridge Crystallographic Data Centre (deposition nos. 140056 and 140057, respectively). 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 www: http://www.ccdc.cam.ac.uk).

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