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# Synthesis and structure of $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}PhCH_2CH_2C{=}NPh)]$, a product of an 'intramolecular' hydrogen-transfer reaction

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The reaction of $[Ru_3(CO)_{12}]$ with 3,*N*-diphenylprop-2-enimine yielded the ruthenium cluster compounds $[Ru_2(CO)_6(PhC{=}CHCH_2NPh)]$ **1**, $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}PhCH_2CH_2C{=}NPh)]$ **2**, $[Ru_3(CO)_6(PhC{=}CHCH{=}NPh)_2]$ **3** and $[Ru_4(CO)_{10}(PhC{=}CHCH{=}NPh)_2]$ **4**. A compound of formula $[M_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-imine})]$ like **2** has never been isolated from a reaction of $[Ru_3(CO)_{12}]$ with an azadiene; **2** is the main product of the reaction. X-Ray diffraction analysis showed an imine ligand $\mu_3$-$\eta^2$-co-ordinated to a ruthenium triangle, giving a distorted-square-pyramidal $Ru_3CN$ cluster core. The former C=C double bond of the azadiene ligand has been hydrogenated. This result is confirmed by the IR and NMR spectroscopic properties of **2**.

In recent years there have been a number of attempts to use organometallic cluster compounds as models for metal surfaces in catalytic processes[1] or to use cluster compounds as the catalytic active species itself.[2] Since I am interested in the activation of small molecules especially $CO_2$ by using organometallic catalysts, $[Ru_3(CO)_{12}]$ was treated with α-, β-unsaturated azadienes in order to investigate the catalytic properties of the synthesized compounds.

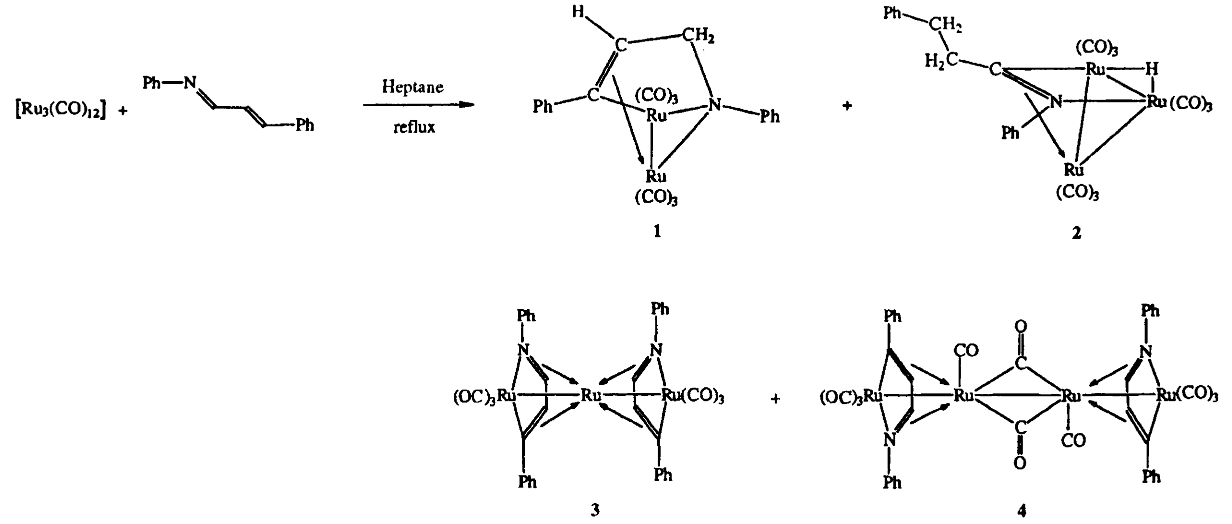
Ruthenium complexes catalyse the reaction of $CO_2$ with alkynes in the presence of amines to yield carbamates.[3] Nickel(0) compounds with 1-azadiene ligands are capable of trapping $CO_2$ and transferring it to other organic molecules, the efficiency of this process being dependent on the nature of the substituents at the N- and C-terminal end of the azadiene ligand. The best results are obtained when using azadienes derived from aromatic amines and cinnamaldehyde derivatives.[4] The reaction sequence of $[Ru_3(CO)_{12}]$ with 1-azadienes of the type $R^1CH{=}CHCH{=}NR^2$ ($R^1$ = Me or Ph; $R^2$ = $Pr^i$, $C_6H_{11}$ or $Bu^t$) is well documented and the mechanism has been investigated in detail.[5] Up to now no results concerning possible catalytic properties of ruthenium–azadiene cluster compounds have been reported.

## Results and Discussion

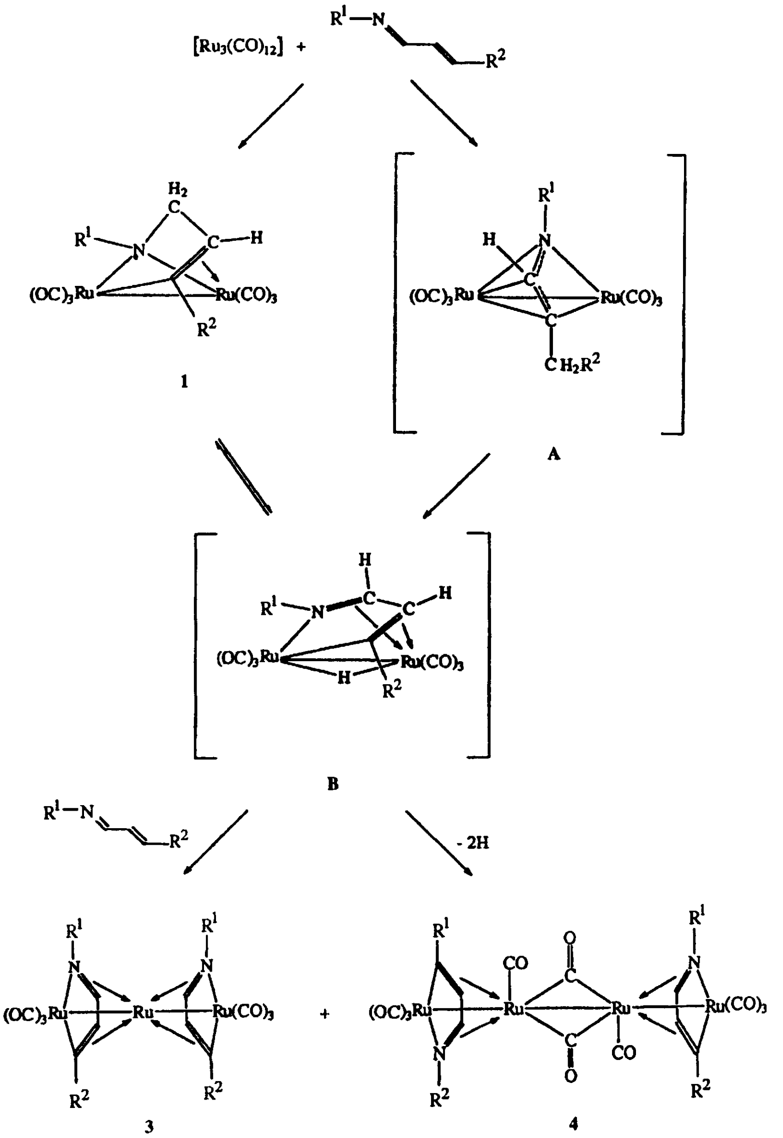
The reaction of $[Ru_3(CO)_{12}]$ with 3,*N*-diphenylprop-2-enimine in refluxing heptane leads to a mixture of four ruthenium–azadiene compounds, which can be separated by column chromatography (Scheme 1). Compounds **1**, **3** and **4** are derivatives of ruthenium–azadiene clusters which were described earlier.[6] The mechanism of the $[Ru_3(CO)_{12}]$–azadiene reaction reported yields two dinuclear ruthenium clusters **1** and **A** as the first isolable products (Scheme 2).[6a] In analogy, here compound **1** was obtained, in which the azadiene is converted into an enylamide ligand by a formal 1,3-hydrogen shift from the C-terminal end of the azadiene to the carbon atom next to the nitrogen atom (Schemes 1 and 2). Compound **A**, which has not been isolated in this study, contains an azaallyl ligand, formed by a formal 1,2-hydrogen shift from one olefinic carbon atom to the C-terminal end of the former azadiene (Scheme 2). Both compounds **1** and **A** have been shown to produce clusters of type **4** *via* a common intermediate **B**,[6a] and by use of an excess of azadiene also clusters of type **3** (Scheme 2).[6b,c] So the formation of the compounds **1**, **3** and **4** can be explained by well known facts. In addition, here the formation of cluster **2** has also been observed, which contains a $\mu_3$-$\eta^2$-co-ordinated imine ligand in which the former C=C double bond has been hydrogenated (Scheme 1). Up to now this reaction has never been seen in $[Ru_3(CO)_{12}]$–azadiene systems. Cluster compounds of the type $[M_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-imine})]$ (M = Fe, Ru or Os) have been synthesized either by conversion of cluster-bound nitriles[7] or isocyanides[8] or by formal dehydrogenation of cyclic secondary amines[9] or $NEt_3$ respectively.[10] Only two such clusters have been obtained from reactions using an imine. The reaction of $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ (dppm = $Ph_2PCH_2PPh_2$) with $PPh_2(C_6H_4CHO\text{-}2)$ is reported to give $[Ru_3(CO)_6(\mu\text{-}H)(\mu_3\text{-}PhC{=}NC_6H_4PPh_2)(\mu\text{-dppm})]$, but not with $[Ru_3(CO)_{12}]$ as the starting material.[11] On the other hand the formation of $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}PhC{=}NPh)]$ from $[Ru_3(CO)_{12}]$ and benzylideneaniline has been described.[12] It was shown that the product is the catalytically active species in a hydrogen-transfer reaction to form *N*-phenylbenzylamine from benzylideneaniline using $Pr^iOH$ as the hydrogen donor and $[Ru_3(CO)_{12}]$ as the catalyst precursor. Quite a lot of hydrogen-transfer reactions are catalysed by tri- and tetra-nuclear ruthenium cluster compounds.[13] So in the reaction of $[Ru_3(CO)_{12}]$ with 3,*N*-diphenylprop-2-enimine it is likely that co-ordination of the azadiene *via* the C=N double bond to a trinuclear ruthenium carbonyl moiety leads to activation of the conjugated C=C double bond, which then is hydrogenated in the sense of an intramolecular hydrogen-transfer reaction. So this reaction is a new pathway for a primary adduct of azadiene to $[Ru_3(CO)_{12}]$ instead of producing **1** and **A** by fragmentation of the $Ru_3$ moiety. It seems to be energetically favoured, if azadienes with aromatic substituents at the N- and C-terminal ends are used, since **2** is the main product of the reaction. The source of hydrogen is obviously the formation of the compounds **1**, **3** and **4**, where *e.g.* that of **4** can only proceed *via* a formal loss of two hydrogen atoms (Scheme 2). The reaction of $[Ru_3(CO)_{12}]$ with other types of azadiene; *e.g.* those in which the C=C double bond is part of a carbocyclic or heterocyclic system or with prochiral azadienes and by using other hydrogen-donor systems may lead to interesting reactions. Investigations in this field are ongoing.

### Structure determinations

By means of recrystallization of clusters **1**–**4** from mixtures of light petroleum (b.p. 40–60 °C) and $CH_2Cl_2$ it was possible to grow crystals suitable for X-ray analysis.



Scheme 1



Scheme 2

**[$Ru_2(CO)_6(PhC{=}CHCH_2NPh)$] 1.** The molecular structure of compound **1** is shown in Fig. 1, and selected bond lengths and angles are collected in Table 1. The structure shows a $Ru_2(CO)_6$ moiety which adopts a nearly ecliptic conformation. This unit is bridged by a 6e-donating enylamide ligand. In the formation of this ligand a formal 1,3-hydrogen shift from C(9) to C(7) has taken place. The hydrogen atoms at C(8) and C(7) have been determined by Fourier difference calculations. The Ru–N bond lengths are identical. The Ru–C bond lengths are different, the Ru(1)–C(9) bond being considered to be a σ bond, whereas the interaction between Ru(2) and the enylamide ligand represents a π bond. So the bond lengths 208.0 [Ru(1)–C(9)],

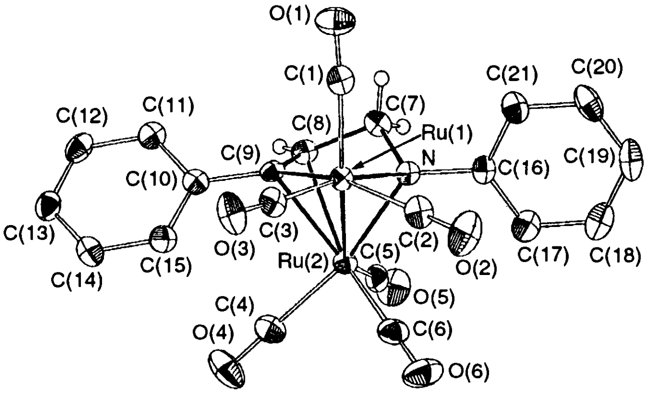


**Fig. 1** Solid-state structure of $[Ru_2(CO)_6(PhC{=}CHCH_2NPh)]$ **1**

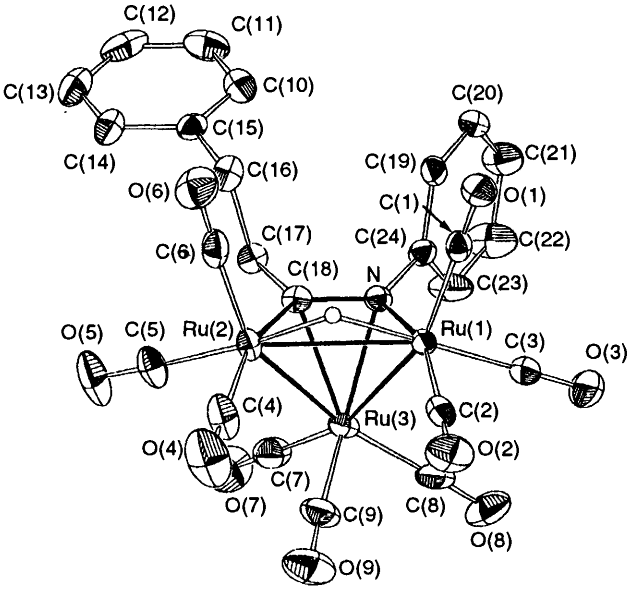


**Fig. 2** Solid-state structure of $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}PhCH_2CH_2C{=}NPh)]$ **2**

**Table 1** Selected bond lengths (pm) and angles (°) of $[Ru_2(CO)_6(PhC{=}CHCH_2NPh)]$ **1**

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 268.5(1) | Ru(1)–N | 210.8(3) |
| Ru(1)–C(9) | 208.0(4) | Ru(2)–N | 210.4(3) |
| Ru(2)–C(8) | 228.0(4) | Ru(2)–C(9) | 227.1(4) |
| N(1)–C(7) | 149.2(5) | C(7)–C(8) | 149.4(5) |
| C(8)–C(9) | 138.0(5) | N–C(16) | 144.9(5) |
| C(9)–C(10) | 148.8(5) | | |
| N–Ru(1)–C(9) | 76.3(1) | Ru(1)–C(9)–C(8) | 113.1(3) |
| C(9)–C(8)–C(7) | 117.8(3) | C(8)–C(7)–N | 100.0(3) |
| C(7)–N–Ru(1) | 110.2(2) | Ru(1)–C(9)–C(10) | 128.3(3) |
| C(8)–C(9)–C(10) | 118.6(3) | Ru(1)–N–C(16) | 122.7(2) |
| C(7)–N–C(16) | 113.8(3) | Ru(1)–Ru(2)–N | 50.47(8) |
| Ru(1)–Ru(2)–C(8) | 71.31(9) | Ru(1)–Ru(2)–C(9) | 48.76(9) |
| N–Ru(2)–C(8) | 62.8(1) | N–Ru(2)–C(9) | 72.36(1) |

Dihedral angles (°): C(1)–Ru(1)–Ru(2)–C(5), 33.3, C(2)–Ru(1)–Ru(2)–C(6) 22.7, C(3)–Ru(1)–Ru(2)–C(4) 10.7; deviations from plane Ru(1)–C(7)–C(8)–H(8)–C(9)–C(10) (pm): Ru(1) −5.3, C(7) 13.6, C(8) −8.8, H(8) −7.3, C(9) −2.3, C(10) 10.1.

228.0 [Ru(2)–C(8)] and 227.1 pm [Ru(2)–C(9)] respectively have expected values. The enylamide ligand shows a rather long double bond between C(8) and C(9) as well as two single bonds for C(7)–C(8) and C(7)–N. The double-bond character of C(8)–C(9) is not only confirmed by the angles at C(8) and C(9) and the bond length, but also by the planarity of the Ru(1)–C(9)–C(8)–C(7)–C(10)–H(8) unit, clearly indicating the $sp^2$ hybridization of C(8) and C(9).

**Table 2** Selected bond lengths (pm) and angles (°) of $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}PhCH_2CH_2C{=}NPh)]$ **2**

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 293.7(1) | Ru(1)–Ru(3) | 267.5(2) |
| Ru(2)–Ru(3) | 273.6(2) | Ru(1)–N | 210.5(5) |
| Ru(2)–C(18) | 204.7(5) | N–C(18) | 137.1(7) |
| Ru(3)–N | 219.8(5) | Ru(3)–C(18) | 225.4(5) |
| C(17)–C(18) | 151.4(8) | C(16)–C(17) | 152.8(8) |
| C(15)–C(16) | 149.4(7) | N–C(24) | 144.6(5) |
| Ru(1)–H(1) | 182(6) | Ru(2)–H(1) | 179(6) |
| Ru(1)–Ru(2)–C(18) | 68.0(2) | Ru(2)–Ru(1)–N | 67.7(1) |
| Ru(1)–N–C(18) | 110.2(3) | Ru(2)–C(18)–N | 114.1(4) |
| Ru(1)–Ru(3)–Ru(2) | 65.74(4) | Ru(1)–Ru(3)–N | 50.0(1) |
| N–Ru(3)–C(18) | 35.9(2) | C(18)–Ru(3)–Ru(2) | 47.2(1) |
| Ru(1)–Ru(3)–C(18) | 71.0(1) | Ru(2)–Ru(3)–N | 70.8(1) |
| C(15)–C(16)–C(17) | 112.5(5) | C(16)–C(17)–C(18) | 110.6(5) |
| C(17)–C(18)–N | 118.8(5) | C(18)–N–C(24) | 121.3(4) |

Deviation from plane Ru(1)–Ru(2)–Ru(3) (pm): H(1) 19.4.

**Table 3** Selected bond lengths (pm) and angles (°) of $[Ru_3(CO)_6(PhC{=}CHCH{=}NPh)_2]$ **3**

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 271.5(1) | Ru(1)–N(1) | 218.5(4) |
| Ru(1)–C(10) | 215.1(5) | Ru(1)–C(11) | 215.2(5) |
| Ru(1)–C(12) | 217.4(4) | Ru(2)–N(1) | 208.1(4) |
| Ru(2)–C(12) | 209.4(4) | N(1)–C(10) | 138.7(6) |
| C(10)–C(11) | 138.1(8) | C(11)–C(12) | 136.3(8) |
| N(1)–C(9) | 138.6(5) | C(12)–C(18) | 140.7(6) |
| N(1)–C(9X) | 159.1(6) | C(12)–C(18X) | 160.8(6) |
| Ru(2)–Ru(1)–Ru(2A) | 95.0(1) | N(1)–Ru(2)–C(12) | 76.3(2) |
| Ru(2)–N(1)–C(10) | 115.2(3) | N(1)–C(10)–C(11) | 115.7(4) |
| C(10)–C(11)–C(12) | 116.0(4) | C(11)–C(12)–Ru(2) | 115.5(4) |
| Ru(2)–N(1)–C(9) | 135.1(3) | C(10)–N(1)–C(9) | 106.9(4) |
| Ru(2)–C(12)–C(18) | 137.3(4) | C(11)–C(12)–C(18) | 104.6(4) |
| Ru(2)–N(1)–C(9X) | 119.9(3) | C(10)–N(1)–C(9X) | 124.8(4) |
| Ru(2)–C(12)–C(18X) | 115.2(3) | C(11)–C(12)–C(18X) | 129.2(4) |

Angles between planes (°): [N(1)–C(10)–C(11)–C(12)]–[C(4)–C(9)] 40.3, [N(1)–C(10)–C(11)–C(12)]–[C(4X)–C(9X)] 39.1, [N(1)–C(10)–C(11)–C(12)]–[C(13)–C(18)] 40.5 and [N(1)–C(10)–C(11)–C(12)]–[C(13X)–C(18X)] 43.1.

**$[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\eta^2\text{-}PhCH_2CH_2C{=}NPh)]$ 2.** Fig. 2 shows the crystal structure of **2** and bond lengths and angles are given in Table 2. The hydrogen atoms at C(16) and C(17) as well as the μ-hydrogen atom were determined by Fourier difference analyses. Compound **2** is constituted of a ruthenium triangle which is co-ordinated by a $\mu_3\text{-}\eta^2$-imine ligand giving a distorted square-pyramidal $Ru_3CN$ cluster core. Besides the imine ligand, all ruthenium atoms are co-ordinated by three terminal CO groups. As in all structurally characterized $[M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}RC{=}NR')]$ (M = Fe, Ru or Os) derivatives[7–12] the metal–metal bond, which is bridged by the imine and by the hydrogen [in **2** Ru(1)–Ru(2)] is longer than the other two metal–metal bonds. The bridging hydride ligand lies approximately in the plane of the ruthenium triangle. Since the imine is co-ordinated to three metal atoms, the C=N double bond is elongated in comparison to normal C=N double-bond distances.[14] The bonds at C(16) and C(17) are clearly single bonds and the bond angles show the co-ordination to be tetrahedral as expected for $sp^3$-hybridized carbon atoms.

**$[Ru_3(CO)_6(PhC{=}CHCH{=}NPh)_2]$ 3.** The crystal structure of compound **3** is shown in Fig. 3 and bond lengths and angles are given in Table 3. Derivatives of the trinuclear cluster **3** have been structurally characterized earlier[6b–d] and it has been pointed out that they are isolobally related to ruthenocene. Compound **3** contains two $[Ru(CO)_3(PhC{=}CHCH{=}NPh)]$ moieties both being $\eta^5$-co-ordinated to a central ruthenium atom. Atom Ru(1) is located on the crystallographic mirror

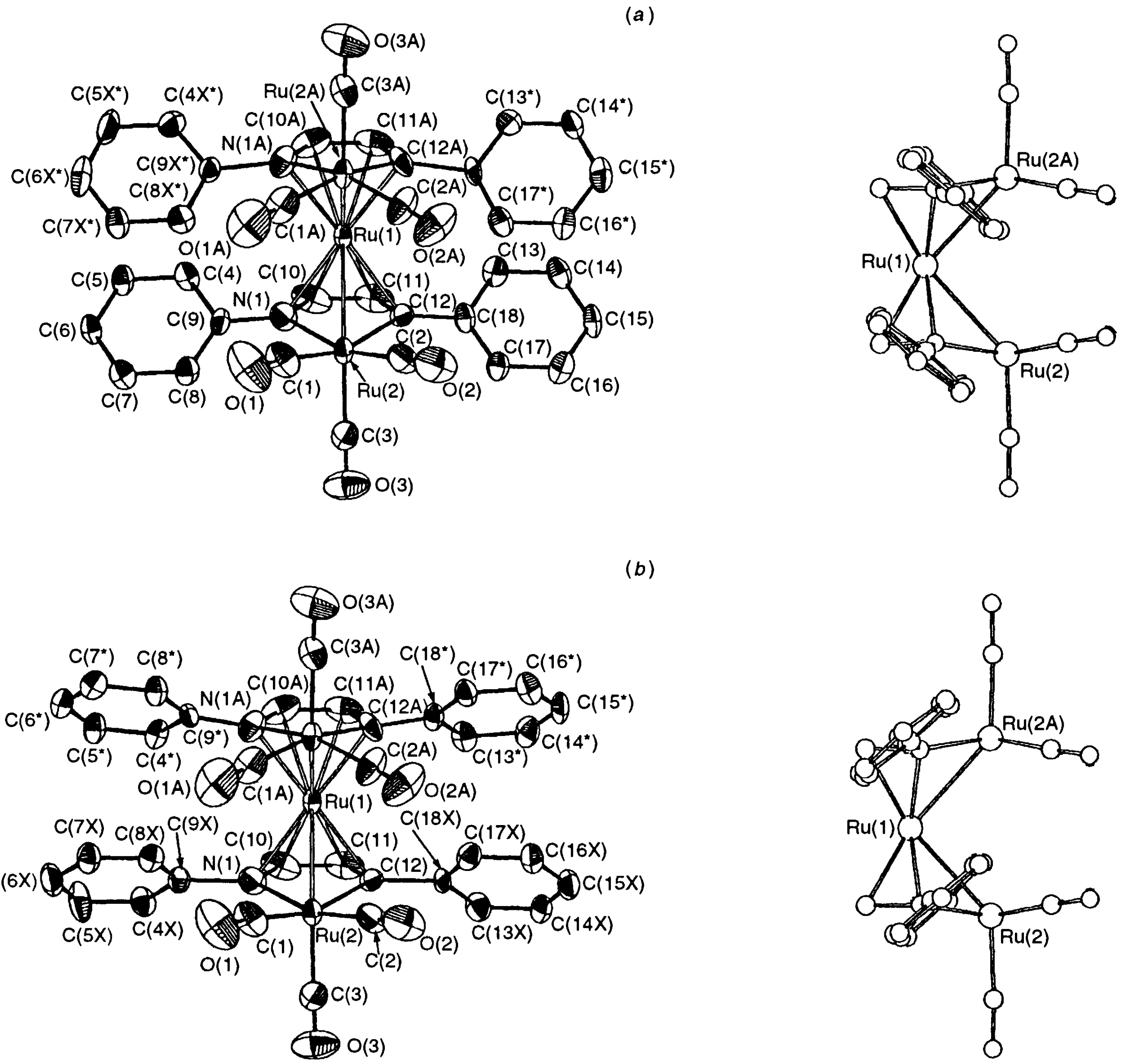


**Fig. 3** Solid-state structure of $[Ru_3(CO)_6(PhC{=}CHCH{=}NPh)_2]$ **3**: isomers with the phenyl substituents rotated clockwise (*a*) and anticlockwise (*b*) out of the azadiene plane when looking down the Ph–N–C–Ph axis of the ligand

plane so that the two azaruthenacyclopentadienyl systems show an eclipsed conformation. The Ru(1)–Ru(2) bond length and the angle Ru(2)–Ru(1)–Ru(2A) are of the same size as those previously reported.[6b–d] Bond lengths between nitrogen and carbon atoms in the azaruthenacyclopentadienyl system are of similar values corresponding to delocalization of $\pi$ electrons in this ligand. The phenyl substituents at N(1) [C(4)–C(9)] and C(12) [C(13)–C(18)] are not coplanar with the azadiene unit of the azaruthenacyclopentadiene system because of steric interaction with the carbonyl ligands co-ordinated to the ring ruthenium atom. They are statistically disordered in a way that one pair of phenyl substituents is rotated clockwise out of the azadiene plane when looking down the PhN(1)–C(12)Ph axis [C(4)–C(9) and C(13)–C(18), Fig. 3(*a*)] and the other pair of phenyl rings is rotated anti-clockwise out of the plane [C(4X)–C(9X) and C(13X)–C(18X), Fig. 3(*b*)]. In both cases the angle of rotation is approximately 40°. As a result of the reflection at the crystallographic mirror plane through Ru(1) one obtains two isomers of **3** statistically occupying the same site in the crystal. One isomer consists of the phenyl substituents C(4)–C(9), C(13)–C(18) and those produced by reflection of C(4X)–C(9X), C(13X)–C(18X) [Fig. 3(*a*)], whereas the second shows C(4X)–C(9X), C(13X)–C(18X) and the symmetry equivalents of C(4)–C(9), C(13)–C(18) [Fig. 3(*b*)].

**$[Ru_4(CO)_{10}(PhC{=}CHCH{=}NPh)_2]$ 4.** The molecular structure of compound **4** is shown in Fig. 4 and bond lengths and angles are given in Table 4. As for **1** and **3**, derivatives of **4** have been reported earlier, being the thermodynamically most stable products when heating $[Ru_3(CO)_{12}]$ with 1-azadienes.[6e,f]

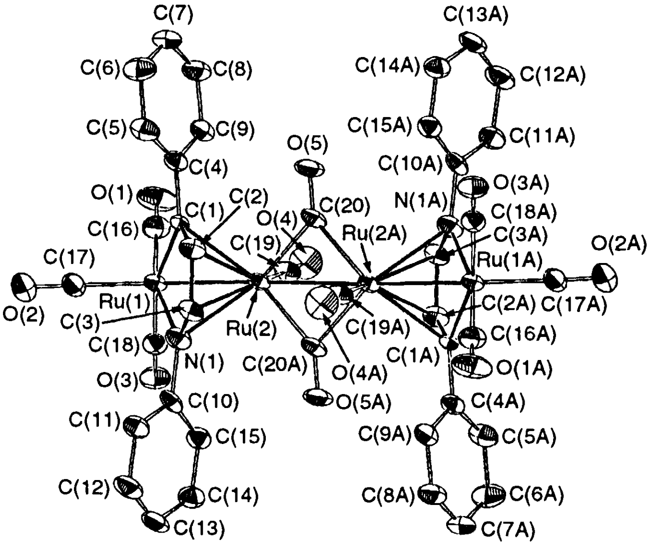
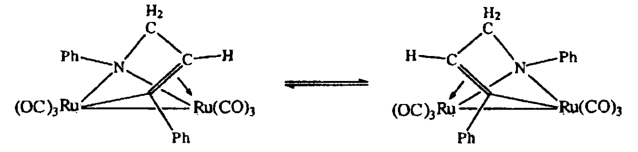


**Fig. 4** Solid-state structure of $[Ru_4(CO)_{10}(PhC{=}CHCH{=}NPh)_2]$ **4**



Scheme 3

Compound **4** consists of two azaruthenacyclopentadienyl ligands which are connected by a central $Ru_2(CO)_4$ unit showing two terminal and two bridging CO ligands. Between Ru(2) and Ru(2A) there is a crystallographic centre of inversion. The four ruthenium atoms therefore comprise a nearly linear chain with the central Ru–Ru bond being about 8 pm longer than Ru(2)–Ru(1). The bond lengths and angles in the azaruthenacyclopentadiene ligand as well as the steric arrangement of CO groups are as expected.[6e] Since the molecule possesses a centre of inversion the azaruthenacyclopentadiene ligands occupy *trans* positions.

### Spectroscopy

The IR and NMR data for compound **1**–**4** are given in Table 5. The spectroscopic properties of **1**, **3** and **4** correspond to those reported earlier for their analogues.[6] The pattern of bands in the IR spectra is identical to those described in the literature. The $^1H$ and $^{13}C$ NMR spectra of **3** and **4** show the expected chemical shifts and coupling patterns. In the $^1H$ NMR spectrum of **4** the resonance for one of the olefinic protons cannot be observed. It is likely that this resonance has been shifted into the region of the aromatic protons. For derivatives of **1** a fluxional behaviour in solution has been reported, which can be interpreted in terms of a 'windshield wiper' motion of the asymmetrically bridging amide ligand (Scheme 3).[6a] By means of temperature-dependent $^1H$ NMR spectroscopy it can be shown that the same dynamic process occurs for **1**. The activation barrier was determined to be 76 ± 5 kJ mol$^{-1}$, about the same as reported[6a] for derivatives of **1** containing alkyl ligands as terminal groups of the amide ligand. At room temperature the signals for the methylene protons are broad so that no coupling constants can be determined. Lowering the temperature to 190 K leads to a sharpening of the signals giving two doublets and resolving the coupling between the two methylene protons to 9.8 Hz. No coupling of the methylene protons with the proton at the imine carbon atom is observed.

The IR spectrum of compound **2** shows a pattern typical for cluster compounds of the type $[M_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-imine})]$[7–12] indicating a square-pyramidal $Ru_3CN$ cluster core. In the $^1H$ NMR spectrum a singlet at δ −18.2 is observed for the μ-hydrogen atom. The aromatic protons give a multiplet at δ 6.5–7.1. The two methylene groups, which are obtained by formal hydrogenation of the former C=C double bond of the azadiene, show an AA′BB′ pattern, which can be simulated using the program DAISY (Fig. 5).[15] The chemical shifts and coupling constants are given in Table 5. The $^{13}C$ NMR spectrum shows two resonances for the methylene carbon atoms, one at δ 38.8, which represents the carbon in α position to the C=N double bond [C(17), Fig. 2], and the other at δ 52.6 for the carbon atom in the β position [C(16), Fig. 2]. The two-dimensional $^{13}C$–$^1H$-correlated NMR spectrum shows the resonance at δ 38.8 in the $^{13}C$ NMR to be correlated with the signals in the AA′BB′ pattern of the $^1H$ NMR spectrum at δ 2.59 and 2.60, whereas the resonance at δ 52.6 in the $^{13}C$ NMR is correlated to the $^1H$ resonances at δ 2.73 and 2.75 respectively. The CO region of the $^{13}C$ NMR spectrum at room temperature shows four resonances instead of the nine expected from the solid-state structure. This indicates that the compound shows a dynamic behaviour in solution at this temperature as is reported for other derivatives of $[M_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-imine})]$ cluster compounds.[9a,b,10b]

**Table 4** Selected bond lengths (pm) and angles (°) of $[Ru_4(CO)_{10}(PhC{=}CHCHC{=}NPh)_2]$

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 269.8(1) | Ru(2)–Ru(2A) | 277.6(1) |
| Ru(1)–N(1) | 207.9(7) | Ru(1)–C(1) | 210.7(7) |
| C(1)–C(2) | 139(1) | C(2)–C(3) | 142(1) |
| C(3)–N(1) | 139(1) | Ru(2)–N(1) | 232.3(7) |
| Ru(2)–C(1) | 231.1(7) | Ru(2)–C(2) | 230.1(9) |
| Ru(2)–C(3) | 231.2(7) | N(1)–C(10) | 146(1) |
| C(1)–C(4) | 143(1) | | |
| Ru(1)–Ru(2)–Ru(2A) | 177.30(4) | N(1)–Ru(1)–C(1) | 78.7(3) |
| Ru(1)–C(1)–C(2) | 113.8(5) | C(1)–C(2)–C(3) | 116.2(7) |
| C(2)–C(3)–N(1) | 116.5(7) | C(3)–N(1)–Ru(1) | 114.5(5) |
| Ru(1)–N(1)–C(10) | 126.1(5) | C(3)–N(1)–C(10) | 118.3(7) |
| Ru(1)–C(1)–C(4) | 126.8(5) | C(2)–C(1)–C(4) | 118.8(7) |
| N(1)–Ru(2)–Ru(2A) | 131.9(2) | C(1)–Ru(2)–Ru(2A) | 133.6(2) |
| C(2)–Ru(2)–Ru(2A) | 110.5(2) | C(3)–Ru(2)–Ru(2A) | 110.0(2) |

## Experimental

### Reagents and solvents

All procedures were carried out under an argon atmosphere and in anhydrous, freshly destilled solvents. Chromatography was done using silica gel 60 and silanized silica gel 60, 70–230 mesh ASTM (Merck), which were dried at $10^{-2}$ bar ($10^3$ Pa) for 2 d before use. The cluster $[Ru_3(CO)_{12}]$ was prepared as described.[16] 3,*N*-Diphenylprop-2-enimine was prepared by condensation of 3-phenylprop-2-enal with aniline.

### Physical measurements

Infrared spectra were recorded on a Perkin-Elmer FT-IR System 2000 using 0.2 mm KBr cuvettes, NMR spectra on a Bruker AC 200 spectrometer, {$^1H$; 200 MHz with $SiMe_4$ as

**Table 5** Spectroscopic data for the compounds **1**–**4**

| Compound | IR[a] | $^1H$ NMR[b] (δ) | $^{13}C$-{$^1H$} NMR[b] (δ) |
|---|---|---|---|
| **1** | 2080s, 2053vs, 2005vs, 2002vs, 1994s | 3.76 (br, 1 H), 4.24 (br, 1 H), 4.81 (s, 1 H), 6.69–7.19 (m, 10 H) | 75.3, 77.5, 122.2, 125.2, 128.1, 129.2, 129.5, 149.0, 158.0, 191.2, 194.6 (br) |
| **2** | 2092s, 2066vs, 2036vs, 2019vs, 2001s, 1997m | −18.2 (s, 1 H), 2.59[c] ($^2J_{HH}$ = 1.5, $^3J_{HH}$ = 7.4, 10.9), 2.60[c] ($^2J_{HH}$ = 1.5, $^3J_{HH}$ = 11.8, 7.3), 2.73[c] ($^2J_{HH}$ = 1.5, $^3J_{HH}$ = 7.4, 11.8), 2.75[c] ($^2J_{HH}$ = 1.5, $^3J_{HH}$ = 7.3, 10.9), 6.5–7.1 (m, 10 H) | 38.8, 52.6, 125.4, 126.6, 126.9, 137.5, 140.1, 152.8, 192.5, 193.9, 197.2, 212.0 |
| **3** | 2066s, 2048vs, 1994s, 1985 (sh), 1970s | 5.59 (d, 2 H, $^3J_{HH}$ = 1.5), 6.54–6.91 (m, 20 H), 6.93 (d, 2 H, $^3J_{HH}$ = 1.5) | 91.7, 102.2, 125.0, 125.7, 126.2, 127.2, 128.1, 128.5, 148.8, 151.7, 161.3, 190.9, 196.8, 205.4 |
| **4** | 2076vs, 2015 (sh), 1999vs, 1947m, 1781m | 5.22 (d, 2 H, $^3J_{HH}$ = 1.8), 6.81–7.40 (m, 22 H) | |

[a] In $CH_2Cl_2$, 293 K, v = very, s = strong, m = medium, sh = shoulder. [b] Compounds **1** and **2** in [$^2H_8$]toluene at 293 K, **3** and **4** in $CDCl_3$ at 293 K; s = singlet, d = doublet, m = multiplet, br = broad; *J* in Hz. [c] Integration of the whole AA′BB′ system indicates the presence of four protons.

**Table 6** Crystal and intensity data for compounds **1**–**4***

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Formula | $C_{21}H_{13}NO_6Ru_2$ | $C_{24}H_{15}NO_9Ru_3$ | $C_{36}H_{24}N_2O_6Ru_3$ | $C_{40}H_{24}N_2O_{10}Ru_4$ |
| $M$ | 577.46 | 764.58 | 883.78 | 1096.90 |
| Crystal colour | Yellow | Orange | Red | Red |
| Crystal size/mm | 0.6 × 0.4 × 0.1 | 0.5 × 0.4 × 0.1 | 0.3 × 0.2 × 0.2 | 0.3 × 0.2 × 0.06 |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P2_1/m$ | $P\bar{1}$ |
| $a$/Å | 10.305(3) | 9.819(6) | 9.414(2) | 8.149(4) |
| $b$/Å | 12.359(3) | 10.255(4) | 14.737(6) | 10.051(5) |
| $c$/Å | 16.855(3) | 13.144(3) | 11.805(2) | 12.606(6) |
| $\alpha$/° | 90 | 92.39(3) | 90 | 73.37(4) |
| $\beta$/° | 107.74(2) | 91.68(3) | 97.86(2) | 85.04(4) |
| $\gamma$/° | 90 | 93.90(4) | 90 | 71.59(4) |
| $U$/Å$^3$ | 2044.6(8) | 1319(1) | 1622.4(8) | 962.4(8) |
| $Z$ | 4 | 2 | 2 | 1 |
| $F$(000) | 1128 | 740 | 868 | 534 |
| $D_c$/g cm$^{-3}$ | 1.876 | 1.926 | 1.809 | 1.893 |
| $\mu$/mm$^{-1}$ | 1.515 | 1.747 | 1.482 | 1.600 |
| Absorption correction | ψ scan | ψ scan | — | XABS2[19] |
| Minimum, maximum transmission | 0.82–0.99 | 0.85–0.99 | — | 0.87–1.18 |
| θ range/° | 1–24 | 1–23 | 1–26 | 1–26 |
| Reflections measured | 3322 | 3725 | 3468 | 3932 |
| Independent reflections | 3199 ($R$ = 0.0973) | 3533 ($R$ = 0.0315) | 3308 ($R$ = 0.0275) | 3753 ($R$ = 0.0403) |
| Observed reflections [$F_o^2 > 2\sigma(F_o^2)$] | 2947 | 3507 | 2884 | 2934 |
| No. parameters | 314 | 325 | 287 | 263 |
| Goodness of fit | 1.146 | 1.059 | 1.041 | 1.092 |
| $R1$ | 0.0328 | 0.0362 | 0.0342 | 0.0660 |
| $wR2$ | 0.0843 | 0.1079 | 0.0891 | 0.1697 |
| Final difference map electron density/e Å$^{-3}$ | 0.622 | 0.555 | 0.636 | 2.036 |

* Details in common: Mo-K$\alpha$ radiation ($\lambda$ = 0.710 69 Å): graphite monochromator; 173 K; $\omega$–2$\theta$ scan; scan speed 1–10° min$^{-1}$.

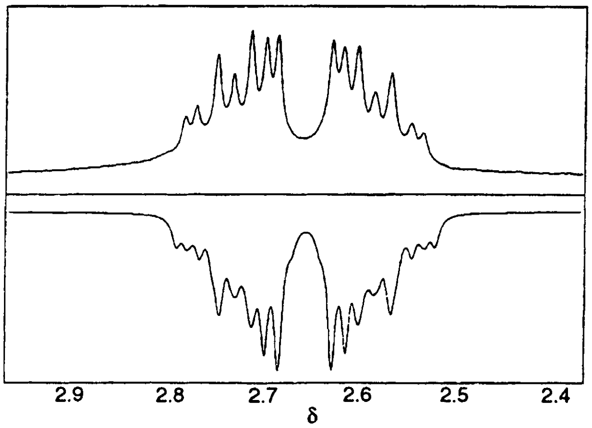


**Fig. 5** Experimental (above) and simulated (below) $^1$H NMR spectra of the methylene proton region of $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}PhCH_2CH_2C{=}NPh)]$ **2**

internal standard, $^{13}$C; 50.32 MHz with $CDCl_3$ (**3**,**4**) or [$^2H_8$]toluene (**1**,**2**) as internal standard}, mass spectra on a Finnigan MAT SSQ710 instrument. Elemental analyses were carried out at the laboratory of the Institute of Organic and Macromolecular Chemistry of the Friedrich-Schiller-Universität Jena. Crystal structure determinations were carried out on an Enraf-Nonius CAD4 diffractometer; the structures were solved by Patterson methods followed by least-squares refinement on $F_o^2$ using the programs SHELXS 86 and SHELXL 93.[17] Hydrogen atoms were included at idealized positions unless otherwise stated. Computation of the structures was done with the program XPMA and the molecular illustrations were drawn using the program ZORTEP.[18] The crystal and intensity data are summarized in Table 6, final atom coordinates are given in Tables 7–10.

Additional material on the structure analyses is available from the Fachinformationszentrum Chemie, Physik, Mathematik GmbH, 76344 Eggenstein-Leopoldshafen 2, Germany by mentioning the deposition numbers CSD-404158 (**1**), -404159 (**2**), -404160 (**3**) and -404161 (**4**), the author and the journal citation. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

## Preparation of the compounds

The cluster $[Ru_3(CO)_{12}]$ (380 mg, 0.59 mmol) and 3,*N*-diphenyl-prop-2-enimine (240 mg, 1.2 mmol) were suspended in heptane (30 cm$^3$) and the solution was refluxed for 8 h. During this period the solution turned from pale yellow to red. After 8 h the solvent was removed under vacuum. The brown oily residue was dissolved in $CH_2Cl_2$ (10 cm$^3$) and silanized silica gel (1 g) was added. After removal of the solvent the mixture of products was chromatographed. Using light petroleum (b.p. 40–60 °C) as the eluent 100 mg of unreacted $[Ru_3(CO)_{12}]$ were obtained as confirmed by its IR spectrum.[16] Compounds **1** and **2** could not be separated by chromatography and were obtained in a combined yield of 210 mg as a yellow band using light petroleum–$CH_2Cl_2$ (10 : 1) as the eluent. With light petroleum–$CH_2Cl_2$ (3 : 1) a red band containing 60 mg of **3** was eluted. At last using light petroleum–$CH_2Cl_2$ (1 : 1) a small deep red band containing 20 mg of **4** was obtained. Compounds **1** and **2** can be separated by slow crystallization from light petroleum as orange (Found: C, 44.6; H, 2.8; N, 2.5. Calc. for $C_{21}H_{13}NO_6Ru_2$: C, 43.7; H, 2.3; N, 2.4%) and yellow crystals (Found: C, 37.4; H, 2.5; N, 2.4. Calc. for $C_{24}H_{15}NO_9Ru_3$: C, 37.7; H, 2.0; N, 1.8%) at −30 °C. Compounds **3** (Found: C, 49.3; H, 2.9; N, 3.3. Calc. for $C_{36}H_{24}N_2O_6Ru_3$: C, 48.9; H, 2.7; N, 3.2%) and **4** (Found: C, 44.7; H, 3.0; N, 2.5. Calc. for $C_{40}H_{24}N_2O_{10}Ru_4$: C, 43.8; H, 2.2; N, 2.55%) were recrystallized at −30 °C from light petroleum–$CH_2Cl_2$ (10 : 1 and 4 : 1 respectively). Yields {calculated on the basis of reacted $[Ru_3(CO)_{12}]$}: **1**, 30; **2**, 39; **3**, 15; **4**, 4%; those of **1** and **2** were calculated from the integrals of a $^1$H NMR spectrum of the mixture of both compounds obtained from chromatography.

**Table 7** Atomic coordinates ( × $10^4$) for compound **1**

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ru(1) | 1374(1) | 2292(1) | 3646(1) |
| Ru(2) | 3227(1) | 2853(1) | 5088(1) |
| C(1) | 375(4) | 1090(3) | 3059(2) |
| O(1) | −259(3) | 373(2) | 2751(2) |
| C(2) | 2087(4) | 2840(3) | 2766(2) |
| O(2) | 2558(3) | 3163(3) | 2289(2) |
| C(3) | −207(4) | 3188(3) | 3296(2) |
| O(3) | −1182(3) | 3683(3) | 3066(2) |
| C(4) | 2743(4) | 3924(3) | 5769(2) |
| O(4) | 2483(3) | 4543(3) | 6189(2) |
| C(5) | 4822(4) | 2476(3) | 6010(3) |
| O(5) | 5729(3) | 2258(3) | 6561(2) |
| C(6) | 3790(4) | 3957(3) | 4472(2) |
| O(6) | 4134(4) | 4611(3) | 4101(2) |
| N | 3252(3) | 1561(2) | 4280(2) |
| C(7) | 3046(4) | 685(3) | 4838(2) |
| C(8) | 2212(4) | 1279(3) | 5283(2) |
| C(9) | 1209(4) | 1967(3) | 4822(2) |
| C(10) | 150(4) | 2349(3) | 5190(2) |
| C(11) | −380(4) | 1636(3) | 5661(2) |
| C(12) | −1301(4) | 2002(4) | 6054(3) |
| C(13) | −1696(4) | 3069(4) | 6008(3) |
| C(14) | −1212(4) | 3779(4) | 5532(3) |
| C(15) | −310(4) | 3421(3) | 5123(2) |
| C(16) | 4276(4) | 1313(3) | 3879(2) |
| C(17) | 5508(4) | 1852(4) | 4086(3) |
| C(18) | 6473(5) | 1600(4) | 3693(3) |
| C(19) | 6222(5) | 789(4) | 3102(3) |
| C(20) | 5004(5) | 245(4) | 2895(3) |
| C(21) | 4017(4) | 503(3) | 3276(2) |

**Table 8** Atomic coordinates ( × $10^4$) for compound **2**

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ru(1) | 2064(1) | 814(1) | 1712(1) |
| Ru(2) | 1658(1) | 3404(1) | 927(1) |
| Ru(3) | 4151(1) | 2589(1) | 1503(1) |
| C(1) | 395(6) | 127(5) | 2291(4) |
| O(1) | −577(5) | −273(4) | 2622(4) |
| C(2) | 1850(7) | −220(6) | 465(5) |
| O(2) | 1728(5) | −808(5) | −276(4) |
| C(3) | 3221(6) | −414(6) | 2270(5) |
| O(3) | 3889(5) | −1175(5) | 2578(4) |
| C(4) | 1331(8) | 2985(6) | −556(6) |
| O(4) | 1152(8) | 2762(6) | −1384(4) |
| C(5) | 2304(7) | 5158(6) | 716(4) |
| O(5) | 2675(7) | 6214(5) | 624(4) |
| C(6) | −133(7) | 3781(6) | 1240(5) |
| O(6) | −1206(5) | 3990(5) | 1473(4) |
| C(7) | 5293(7) | 4191(7) | 1620(5) |
| O(7) | 5946(5) | 5141(5) | 1666(5) |
| C(8) | 5565(7) | 1482(7) | 1852(5) |
| O(8) | 6433(5) | 836(5) | 2036(4) |
| C(9) | 4296(8) | 2271(7) | 99(5) |
| O(9) | 4398(6) | 2024(6) | −764(4) |
| C(10) | 1838(5) | 5984(3) | 5282(3) |
| C(11) | 2059(5) | 7021(4) | 5996(2) |
| C(12) | 1962(5) | 8298(3) | 5700(3) |
| C(13) | 1645(5) | 8537(3) | 4690(3) |
| C(14) | 1425(4) | 7500(3) | 3976(2) |
| C(15) | 1522(4) | 6223(3) | 4272(2) |
| C(16) | 1350(6) | 5117(6) | 3493(5) |
| C(17) | 2709(6) | 4747(6) | 3066(4) |
| C(18) | 2504(5) | 3529(5) | 2373(4) |
| N | 2744(4) | 2343(4) | 2762(3) |
| C(19) | 1944(3) | 2121(4) | 4489(2) |
| C(20) | 2188(3) | 2029(4) | 5529(2) |
| C(21) | 3520(4) | 2035(5) | 5919(2) |
| C(22) | 4609(3) | 2133(6) | 5267(3) |
| C(23) | 4365(3) | 2224(5) | 4226(2) |
| C(24) | 3033(3) | 2218(4) | 3837(2) |

**Table 9** Atomic coordinates ( × $10^4$) for compound **3**

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ru(1) | 5 767(1) | 2 500 | 9 093(1) |
| Ru(2) | 7 443(1) | 1 142(1) | 8 463(1) |
| C(1) | 9 429(5) | 1 314(4) | 9 022(5) |
| O(1) | 10 633(4) | 1 399(4) | 9 283(5) |
| C(2) | 7 986(7) | 1 329(4) | 6 965(4) |
| O(2) | 8 386(6) | 1 427(3) | 6 108(4) |
| C(3) | 7 483(4) | −140(4) | 8 419(4) |
| O(3) | 7 440(4) | −908(3) | 8 396(4) |
| C(4) | 6 746(5) | 1 668(4) | 12 036(4) |
| C(5) | 7 433(6) | 1 595(4) | 13 151(4) |
| C(6) | 8 633(6) | 1 042(5) | 13 393(3) |
| C(7) | 9 145(5) | 563(4) | 12 520(4) |
| C(8) | 8 457(6) | 636(4) | 11 404(4) |
| C(9) | 7 258(6) | 1 189(4) | 11 162(3) |
| C(4X) | 7 447(6) | 864(4) | 12 084(5) |
| C(5X) | 8 328(8) | 887(5) | 13 129(5) |
| C(6X) | 9 555(7) | 1 423(5) | 13 262(4) |
| C(7X) | 9 901(5) | 1 935(4) | 12 349(5) |
| C(8X) | 9 020(6) | 1 911(4) | 11 304(4) |
| C(9X) | 7 793(6) | 1 376(4) | 11 171(4) |
| N(1) | 6 689(4) | 1 312(3) | 10 026(3) |
| C(10) | 5 209(5) | 1 304(4) | 9 979(5) |
| C(11) | 4 441(5) | 1 306(3) | 8 895(6) |
| C(12) | 5 232(4) | 1 322(3) | 8 010(4) |
| C(13) | 2 951(6) | 1 715(4) | 6 834(4) |
| C(14) | 2 090(5) | 1 666(4) | 5 781(5) |
| C(15) | 2 498(7) | 1 122(5) | 4 919(4) |
| C(16) | 3 766(7) | 628(4) | 5 110(4) |
| C(17) | 4 626(5) | 678(4) | 6 163(5) |
| C(18) | 4 219(5) | 1 221(4) | 7 025(4) |
| C(13X) | 3 540(6) | 820(4) | 6 314(4) |
| C(14X) | 2 904(6) | 820(4) | 5 180(5) |
| C(15X) | 3 428(6) | 1 385(5) | 4 391(4) |
| C(16X) | 4 588(6) | 1 952(4) | 4 736(4) |
| C(17X) | 5 223(5) | 1 952(4) | 5 870(4) |
| C(18X) | 4 699(6) | 1 387(4) | 6 659(3) |

**Table 10** Atomic coordinates ( × $10^4$) for compound **4**

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ru(1) | 961(1) | 3119(1) | 3139(1) |
| Ru(2) | 309(1) | 4326(1) | 1061(1) |
| N(1) | −1450(9) | 4448(8) | 2614(6) |
| C(1) | 487(9) | 2063(7) | 1956(6) |
| C(2) | −1153(11) | 2673(9) | 1522(7) |
| C(3) | −3026(12) | 7976(9) | 3564(7) |
| C(15) | −1993(11) | 6845(9) | 3115(7) |
| C(16) | 3427(12) | 2081(10) | 3263(7) |
| O(1) | −2189(9) | 3941(9) | 1880(7) |
| C(4) | 1548(10) | 727(9) | 1686(6) |
| C(5) | 821(12) | −373(10) | 1714(8) |
| C(6) | 1871(14) | −1691(10) | 1481(9) |
| C(7) | 3606(13) | −1889(10) | 1184(8) |
| C(8) | 4301(12) | −799(10) | 1177(7) |
| C(9) | 3286(11) | 515(9) | 1400(7) |
| C(10) | −2523(9) | 5673(9) | 3080(6) |
| C(11) | −4166(11) | 5683(10) | 3498(7) |
| C(12) | −5219(12) | 6836(11) | 3960(8) |
| C(13) | −4667(12) | 7971(10) | 3990(7) |
| C(14) | 4873(9) | 1563(8) | 3362(6) |
| C(17) | 223(11) | 2111(9) | 4409(7) |
| O(2) | −331(10) | 1527(8) | 5151(6) |
| C(18) | 1387(10) | 4479(9) | 3896(7) |
| O(3) | 1667(8) | 5255(7) | 4324(5) |
| C(19) | 2461(10) | 4595(9) | 1050(7) |
| O(4) | 3802(8) | 4723(8) | 1022(6) |
| C(20) | 858(10) | 3644(9) | −413(6) |
| O(5) | 1530(8) | 2538(7) | −666(5) |

## Mass spectrometry

**Compound 1.** Electron impact (EI): $m/z$(%) 578 (3, $M^+$), 550 (12, $M^+$ – CO), 522 (6, $M^+$ – 2 CO), 494 (1, $M^+$ – 3CO), 466 (41, $M^+$ – 4CO), 438 (11, $M^+$ – 5 CO), 410 (23, $M^+$ – 6 CO), 408 (27, $Ru_2C_3NPh_2^+$), 380 (16, $Ru_2C_8H_3Ph^+$), 331 (6, $Ru_2C_3NPh^+$), 306 (25, $Ru_2C_2HPh^+$), 233 (22, $Ru_2CH_3N^+$), 204 (100, $Ru_2^+$), 191 (23, $RuC_7H_5^+$), 178 (11, $RuC_6H_4^+$), 165 (7, $RuC_5H_3^+$), 152 (4, $RuC_4H_2^+$), 140 (3, $RuC_3H_2^+$), 127 (5, $RuC_2H^+$), 115 (7, $RuCH^+$), 104 (20, $C_2H_3Ph^+$), 77 (28, $Ph^+$) and 51 (8, $C_4H_3^+$).

**Compound 2.** EI: $m/z$ (%) 766 (3, $M^+$), 738 (2, $M^+ - CO$), 710 (1, $M^+ - 2\ CO$), 681 (11, $M^+ - 3\ CO - H$), 653 (10, $M^+ - 4\ CO - H$), 625 (20, $M^+ - 5\ CO - H$), 623 [23, $Ru_3(CO)_4C_3HNPh_2^+$], 595 [12, $Ru_3(CO)_3C_3HNPh_2^+$], 567 [12, $Ru_3(CO)_2C_3HNPh_2^+$], 539 [13, $Ru_3(CO)C_3HNPh_2^+$], 511 (12, $Ru_3C_3HNPh_2^+$), 480 [18, $Ru_3(CO)_2C_2H_3NPh^+$], 466 (20, $Ru_3C_5H_9NPh^+$), 436 [5, $Ru_2(CO)_3C_4H_9NPh^+$], 408 [19, $Ru_2(CO)_2C_4H_9NPh^+$], 380 [11, $Ru_2(CO)C_4H_9NPh^+$], 352 (5, $Ru_2C_4H_9NPh^+$), 283 (20, $RuC_7H_6NPh^+$), 270 (21, $RuC_6H_5NPh^+$), 255 (34, $RuC_5H_2NPh^+$), 241 (32, $RuC_{10}H_5N^+$), 209 [69, $PhN{=}CH(CH_2)_2Ph^+$], 204 (29, $Ru_2^+$), 131 (24, $C_3H_4NPh^+$), 117 (89, $C_2H_2NPh^+$), 107 (60, $C_7H_9N^+$), 91 (100, $C_7H_7^+$), 77 (72, $Ph^+$), 65 (28, $C_5H_5^+$), 58 (25, $C_3H_8N^+$), 51 (24, $C_4H_3^+$) and 44 (31, $C_2H_6N^+$).

**Compound 3.** EI: $m/z$ (%) 885 (4, $M^+$), 857 (8, $M^+ - CO$), 829 (4, $M^+ - 2\ CO$), 801 (8, $M^+ - 3\ CO$), 773 (22, $M^+ - 4\ CO$), 745 (15, $M^+ - 5\ CO$), 717 (27, $M^+ - 6\ CO$), 612 [14, $Ru_3(C_5H_2NPh)_2^+$], 582 [11, $Ru_3(C_{10}H_4N)_2^+$], 506 [12, $Ru_3(C_7H_2N)_2^+$], 358 (46, $Ru_2C_5H_3NPh^+$), 209 (84, $RuC_7H_9N^+$), 132 (32, $C_3H_5NPh^+$), 117 (100, $C_2H_2NPh^+$), 84 (92, $C_5H_{10}N^+$) and 42 (76, $C_2H_4N^+$).

**Compound 4.** Field desorption: $m/z$ 1098 ($M^+$).

## References

1 J. Evans, *Chem. Soc. Rev.*, 1981, **10**, 159; E. L. Muetterties, *Angew. Chem.*, 1978, **90**, 577; *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 545; G. Ertl, *Nachr. Chem. Tech. Lab.*, 1983, **31**, 178; G. A. Somorjai, *Chem. Soc. Rev.*, 1984, **13**, 321; K. Knoll and G. Huttner, *Angew. Chem.*, 1987, **99**, 725; *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 743.

2 G. Whyman, in *Transition Metal Clusters*, ed. B. F. G. Johnson, Wiley, New York, 1980; E. L. Muetterties and M. J. Krause, *Angew. Chem.*, 1983, **95**, 135; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 135; P. C. Ford, *Acc. Chem. Res.*, 1981, **14**, 31.

3 R. Mahé, Y. Sasaki, C. Bruneau and P. H. Dixneuf, *J. Org. Chem.*, 1989, **54**, 1518; Y. Sasaki and P. H. Dixneuf, *J. Chem. Soc., Chem Commun.*, 1986, 790; R. Mahé, P. H. Dixneuf and S. Lécolier, *Tetrahedron Lett.*, 1986, 633; Y. Sasaki and P. H. Dixneuf, *J. Org. Chem.*, 1987, **52**, 314; C. Bruneau, P. H. Dixneuf and S. Lécolier, *J. Mol. Catal.*, 1988, **44**, 175; J. Hofer, H. Doucet, C. Bruneau and P. H. Dixneuf, *Tetrahedron Lett.*, 1991, **32**, 7409.

4 (*a*) D. Walther, S. Geβler, U. Ritter, A. Schmidt, K. L. Hamza, W. Imhof, H. Görls and J. Sieler, *Chem. Ber.*, 1995, **128**, 281; (*b*) D. Walther and V. Herzog, *Z. Chem.*, 1987, **27**, 373; (*c*) V. Herzog, *Z. Chem.*, 1989, **29**, 146; (*d*) D. Walther, U. Ritter, R. Kempe, J. Sieler and B. Undeutsch, *Chem. Ber.*, 1992, **125**, 1529.

5 C. J. Elsevier, W. P. Mul and K. Vrieze, *Inorg. Chim. Acta*, 1992, **198–200**, 689.

6 (*a*) W. P. Mul, C. J. Elsevier, L. H. Polm, K. Vrieze, M. C. Zoutberg, D. Heijdenrijk and C. H. Stam, *Organometallics*, 1991, **10**, 2247; (*b*) W. P. Mul, C. J. Elsevier, K. Vrieze, W. J. J. Smeets and A. L. Spek, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 297; (*c*) W. P. Mul, C. J. Elsevier, W. J. J. Smeets and A. L. Spek, *Inorg. Chem.*, 1991, **30**, 4152; (*d*) M. Casarin, R. Bertoncello, A. L. Rizzi, C. J. Elsevier, W. P. Mul, K. Vrieze and A. Vittadini, *J. Organomet. Chem.*, 1990, **396**, 73; (*e*) L. H. Polm, W. P. Mul, C. J. Elsevier, K. Vrieze, M. J. N. Christophersen and C. H. Stam, *Organometallics*, 1988, **7**, 423; (*f*) W. P. Mul, J.-M. Ernsting, W. G. J. de Lange, M. D. M. van Straalen, K. Vrieze, C. J. Elsevier, M. de Wit and C. H. Stam, *J. Am. Chem. Soc.*, 1993, **115**, 980.

7 M. A. Andrews and H. D. Kaesz, *J. Am. Chem. Soc.*, 1979, **101**, 7238; M. A. Andrews, G. van Buskirk, C. B. Knobler and H. D. Kaesz, *J. Am. Chem. Soc.*, 1979, **101**, 7245; Z. Dawoodi, M. J. Mays and P. R. Raithby, *J. Organomet. Chem.*, 1981, **219**, 103.

8 R. D. Adams and N. M. Golembeski, *J. Am. Chem. Soc.*, 1979, **101**, 2579.

9 (*a*) R. D. Adams and G. Chen, *Organometallics*, 1993, **12**, 2070; (*b*) G. Süss-Fink, T. Jenke, H. Heitz, M. A. Pellinghelli and A. Tiripicchio, *J. Organomet. Chem.*, 1989, **379**, 311; (*c*) M. W. Day, S. Hajela, S. E. Kabir, M. Irving, T. McPhillips, E. Wolf, L. Milone, R. Gobetto and D. Osella, *Organometallics*, 1991, **10**, 2743; (*d*) M. W. Day, D. Espitia, K. I. Hardcastle, S. E. Kabir, E. Rosenberg, R. Gobetto, L. Milone and D. Osella, *Organometallics*, 1991, **10**, 3550; (*e*) M. W. Day, D. Espitia, K. I. Hardcastle, S. E. Kabir, T. McPhillips, E. Rosenberg, R. Gobetto, L. Milone and D. Osella, *Organometallics*, 1993, **12**, 2309; (*f*) M. P. Cifuentes, M. G. Humphrey, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1993, **458**, 211.

10 (*a*) C. C. Yin and A. J. Deeming, *J. Organomet. Chem.*, 1978, **133**, 123; (*b*) S. Aime, R. Gobetto, F. Padovan, M. Botta, E. Rosenberg and L. W. Gellert, *Organometallics*, 1987, **6**, 2074.

11 C. J. Adams, M. I. Bruce, O. Kühl, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1993, **445**, C6.

12 A. Basu, S. Bhaduri, K. Sharma and P. G. Jones, *J. Chem. Soc., Chem. Commun.* 1987, **1126**.

13 Y. Blum and Y. Shvo, *J. Organomet. Chem.*, 1984, **263**, 93; A. Basu, K. Bhaduri and K. Sharma, *J. Organomet. Chem.* 1987, **319**, 407; M. Bianchi, U. Maffeoli, P. Frediani, G. Menchi and F. Piacenti, *J. Organomet. Chem.* 1982, **240**, 59; M. Bianchi, U. Maffeoli, G. Menchi, P. Frediani, S. Pratesi, F. Piaceuti and C. Botteghi, *J. Organomet. Chem.*, 1980, **198**, 73.

14 Interatomic Distances Supplement, *Spec. Publ.*, The Chemical Society, London, 1965, 18; H. Böhme and H. G. Viehe, in *Imminium Salts in Organic Chemistry*, Wiley, New York, 1976, part 1, p. 89.

15 WIN-DAISY, a program system for simulation and iteration of high-resolution NMR spectra, Bruker, Karlsruhe, 1993.

16 C. R. Eady, P. F. Jackson, B. F. G. Johnson, J. Lewis, M. C. Malatesta, M. McPartlin and W. J. H. Nelson, *J. Chem. Soc., Dalton Trans.*, 1980, 383.

17 G. Sheldrick, SHELXS 86, Universität Göttingen, 1986; SHELXL 93, Universität Göttingen, 1993.

18 L. Zsolnai, XPMA, Universität Heidelberg, 1994; L. Zsolnai and H. Pritzkow, ZORTEP, Universität Heidelberg, 1994.

19 S. Parkin, B. Moezzi and H. Hope, *J. Appl. Crystallogr.*, 1995, **28**, 53.

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