DALTON
FULL PAPER

Syntheses and structures of novel zerovalent ruthenium monodentate amine complexes†

Toshiaki Suzuki, Masashi Shiotsuki, Kenji Wada, Teruyuki Kondo and Take-aki Mitsudo *

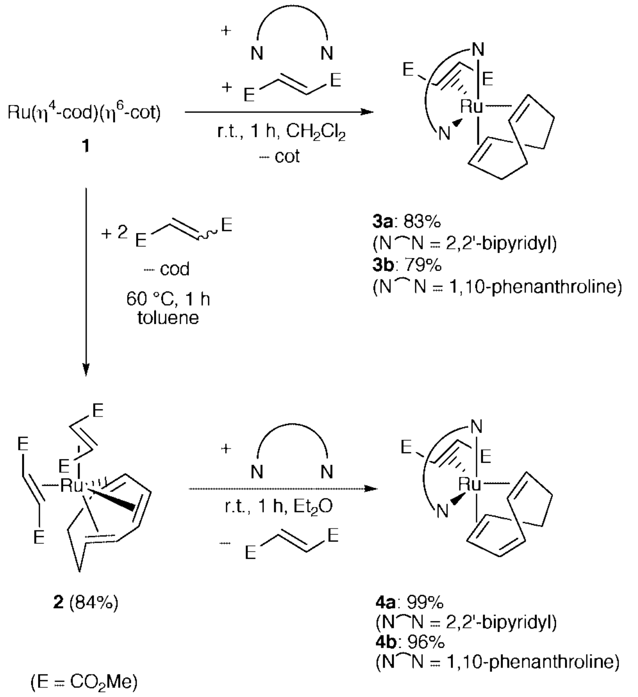
Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan. E-mail: mitsudo@scl.kyoto-u.ac.jp

Received 10th September 1999, Accepted 13th October 1999

Novel ruthenium(0) monodentate amine (primary, secondary, and tertiary) and pyridine complexes, [Ru(η^6-cot)(η^2-dmfm)(L)] (cot = cycloocta-1,3,5-triene, dmfm = dimethyl fumarate; L = propylamine, benzylamine, dimethylamine, morpholine or pyridine), were prepared by the reaction of [Ru(η^6-cot)(η^2-dmfm)$_2$] with the corresponding amine in high yields. The structures of three of the complexes were determined by X-ray analyses and the co-ordination geometry around the central ruthenium atom is a highly distorted trigonal bipyramid. The nitrogen atom and one carbon–carbon double bond of the cyclooctatriene occupy the two axial positions, and the other two olefinic bonds of the cyclooctatriene and dimethyl fumarate the equatorial positions. The propylamine complex is in equilibrium with [Ru(η^4-cot)(η^2-dmfm)(PrNH$_2$)$_2$] in the presence of an excess of propylamine. The structure of this complex was confirmed by X-ray analysis. The position of the second amine is equatorial and the cyclooctatriene co-ordinated in a 1–2 : 5–6-η bonding mode. When it was dissolved in CD$_2$Cl$_2$, propylamine at the equatorial position was dissociated, changing the η^4-cyclooctatriene to the η^6 mode to give [Ru(η^6-cot)(η^2-dmfm)(PrNH$_2$)].

Ruthenium complexes containing amine ligands have been the focus of recent studies in the field of organometallic chemistry.[1] A number of monodentate amine complexes of Ru^{II} and Ru^{III} are well known. For example, [RuH(X)L$_{3-n}$(amine)$_n$] (X = halide; L = CO, phosphine and/or dimethyl sulfoxide; n = 1 or 2),[2,3] [RuX$_2$L$_{3-n}$(amine)$_n$] (X = halide or PhCOS$^-$; L = CO, phosphine, arsine and/or nitrile; n = 1–3),[3–6] [Ru(amine)$_6$]$^{2+}$,[7] [Ru(NH$_3$)$_{6-n}$(L)$_n$]$^{2+\text{ or }3+}$ (L = amine or amino acid derivative; n = 1 or 2),[8] *etc.*[5,9,10] have been reported. Some of them play important roles in several catalytic processes, including *N*-alkylation of amines employing alcohols[2,6,11] and the oxidation of amines to nitriles.[5,10,12] As for bidentate amine complexes, many ruthenium(II) complexes with pyridyl ligands such as 2,2′-bipyridyl or 1,10-phenanthroline have been reported, and much attention has been focused on the photo- and electrochemistry of these complexes.[13] Moreover, a wide range of divalent ruthenium complexes with bidentate,[14,15] tridentate[16,17] and tetradentate[18–20] nitrogen ligands has been used in catalytic reactions, such as enantioselective hydrogenation of ketones catalysed by Ru^{II} with ethylenediamine derivatives,[14] asymmetric cyclopropanation of olefins catalysed by Ru^{II} with bis(oxazolinyl)pyridine (‘pybox’)[16] and epoxidation of alkenes with Ru^{II} with porphyrin derivatives.[18]

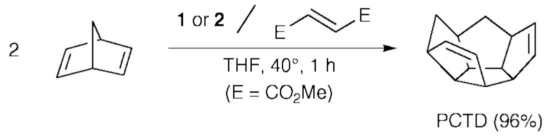
On the other hand, few zerovalent ruthenium complexes with amine or pyridine ligands have been reported[21,22] and these complexes have not been isolated, except for [Ru(bipy)$_2$(CO)(CO$_2$)][21] and [Ru(CO)$_3$(py)$_2$].[22] The structure of [Ru(bipy)$_2$(CO)(CO$_2$)] has been confirmed by X-ray analysis,[21] and the complex may be formulated as six-co-ordinated 18-electron [Ru^{II}(bipy)$_2$(CO)(η^1-CO$_2$$^{2-}$)] rather than 20-electron [Ru^0(bipy)$_2$(CO)(CO$_2$)].[23] It has been reported that [Ru(CO)$_3$(py)$_2$] was prepared, but the product could not be perfectly purified.[1c,22] Thus, to our knowledge, no mononuclear 18-electron ruthenium(0) complex with amine or pyridine ligands had been isolated, until we quite recently reported the first example with bidentate nitrogen ligands (L$_2$) such as 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen), [Ru(η^4-cod)(dmfm)(L$_2$)] **3** and [Ru(η^4-cot)(dmfm)(L$_2$)] **4** (η^4-cod = 1,2 : 5,6-η-cycloocta-1,5-diene, η^4-cot = 1,2 : 5,6-η-cycloocta-1,3,5-triene, dmfm = dimethyl fumarate, L$_2$ = bipy or phen),[24] which are easily derived from [Ru(η^4-cod)(η^6-cot)] **1** and [Ru(η^6-cot)(dmfm)$_2$] **2**[25] (η^6-cot = 1–6-η-cyclooctatriene), respectively (Scheme 1). The complex **2**, which showed excellent catalytic activity in the unusual dimerization of bicyclo[2.2.1]hepta-2,5-diene to give pentacyclo[6.6.0^{2,6}.0^{3,13}.0^{10,14}]tetradeca-4,11-diene (PCTD) involving carbon–carbon bond cleavage and reconstruction of



Scheme 1 Novel ruthenium(0) complexes derived from [Ru(η^4-cod)(η^6-cot)] **1**.

---

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4231/



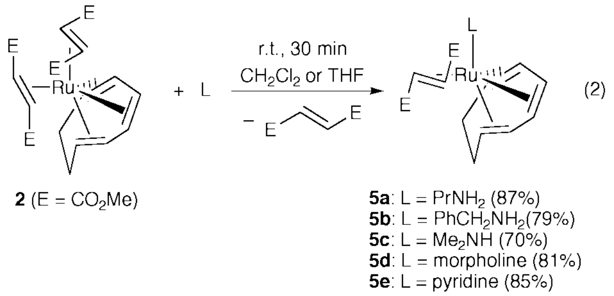
(1)

a novel carbon skeleton under very mild conditions, eqn. (1),[25] is expected to be a versatile starting material for preparation of various ruthenium(0) complexes. The reactions of **2** with monodentate amines are much more complicated than those with bipy or phen. Furthermore, the products were air sensitive while the complexes **3** and **4** were stable in air for 24 h. We finally succeeded in isolation of a series of novel zerovalent ruthenium complexes with monodentate amines, and the full details of the results will be described.

Results and discussion

[Ru(η^6-cot)(dmfm)(L)] 5

The complex [Ru(η^6-cot)(dmfm)$_2$] **2** readily reacted with monodentate amines or pyridine in CH_2Cl_2 or THF at room temperature to give [Ru(η^6-cot)(dmfm)(L)] (L = $PrNH_2$ **5a**, $PhCH_2NH_2$ **5b**, Me_2NH **5c**, morpholine **5d** or pyridine **5e**) in high yields by the substitution of one of the dimethyl fumarates with L, eqn. (2). The reactions of **2** with trialkylamines, such as triethylamine and *N*-methylpiperidine, in CH_2Cl_2 did not give the analogues of **5** under similar conditions but in 1,4-dioxane at 80 °C afforded corresponding amine complexes, which were identified by ^{1}H NMR. However, isolation of them was not successful because they were in equilibrium with **2** in the solution and **2** was more easily crystallized from the solution than **5**. Fine microcrystals of complexes **5a**–**e** are very air-sensitive, but relatively large crystals of them could be handled in air for a few minutes. Concerning the substitution of the olefinic ligand with amine on a ruthenium complex, it has been reported that [$RuCl_2(CO)(\eta^2\text{-}CH_2{=}CH_2)(PMe_2Ph)_2$] reacts with benzylamine to give [$RuCl_2(CO)(PMe_2Ph)_2(PhCH_2NH_2)$].[4a]



(2)

The complexes **5** are the first examples of mononuclear *zerovalent* ruthenium complexes co-ordinated by a monodentate amine or pyridine ligand which were isolated purely and well characterized. It is considered that a combination of monodentate amine ligand as σ-donor ligands and dimethyl fumarate as a π-acceptor ligand would stabilize this new type of ruthenium(0) complexes. The structures of **5a**–**e** were deduced on the basis of ^{1}H, ^{13}C NMR, and IR spectra, and those of **5a**, **5d**, and **5e** confirmed by X-ray analyses.

The structures of complexes **5a**, **5d** and **5e** are shown in Figs. 1, 2, and 3, respectively. These structures are represented by a highly distorted trigonal bipyramid, and quite similar to that of **2**.[25] The protons of the amine were found on the nitrogen atom. In these reactions the dimethyl fumarate ligand on the axial position of complex **2** is apparently substituted by the *N*-donor ligand. Selected bond distances and angles are provided in Tables 1 and 2, respectively.

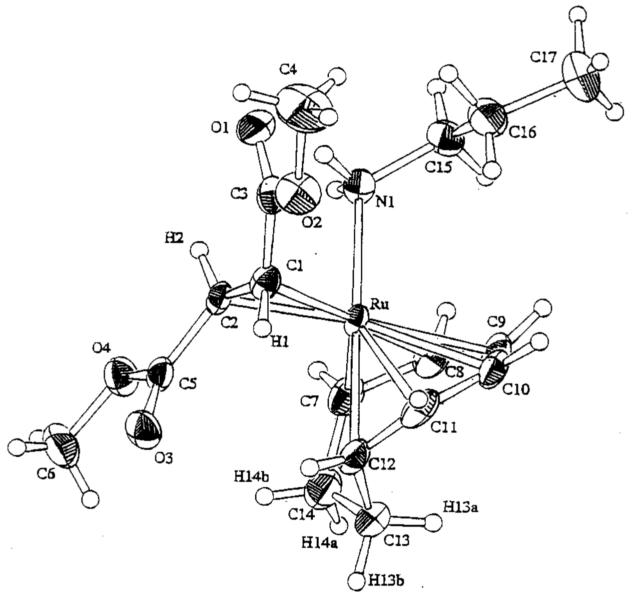


Fig. 1 An ORTEP[26] drawing of the structure of complex **5a**. Thermal ellipsoids (in all Figures) are shown at the 30% probability level.

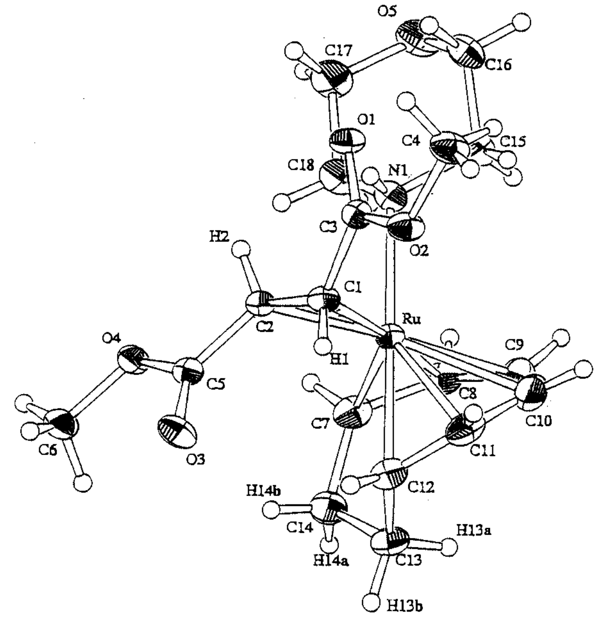


Fig. 2 An ORTEP drawing of the structure of complex **5d**.

The distances between ruthenium and the axial nitrogen, Ru–N(1), are between 2.175(3) and 2.229(3) Å, and in the range of those observed for Ru–N (amine) σ bonds.[4b,9a,b,14a] The Ru–C(1) bond is longer than Ru–C(2), pointing to a slightly unsymmetrical co-ordination of the olefinic ligands.[27a] This feature is probably related to their relative position with respect to the cyclooctatriene ligand. The distances between ruthenium and the olefinic carbons of the cot at the axial positions (C(11) and C(12)) are shorter than those of **2** (2.256(6) and 2.261(6) Å)[25] due to the *trans* influence of the σ-donor nitrogen ligand or the electron-withdrawing dimethyl fumarate ligand. Concerning the distances between ruthenium and the olefinic carbons of the cot at the equatorial positions, Ru–C(7) is shorter than those in **2** (2.285(6) Å), although Ru–C(8), Ru–C(9) and Ru–C(10) did not show significant differences. The angles N(1)–Ru–Ctr(11–12), where Ctr(11–12) is the center of C(11) and C(12), are between 160.8 and 163.2°, which implies that the co-ordinated N(1) of the σ-donor ligand and C(11)–C(12) of the cyclooctatriene occupy the axial position and the structures are highly distorted by the co-ordination of the tridentate cyclooctatriene.

The C(1)–C(2) bond lengths of the co-ordinated dimethyl fumarate are in agreement with the values generally observed

Table 1 Selected bond distances (Å) for complexes **5a**, **5d**, **5e** and **6a**

	5a	**5d**	**5e**	**6a**
Ru–N(1)	2.200(3)	2.229(3)	2.175(3)	2.199(4)
Ru–N(2)				2.257(4)
Ru–C(1)	2.149(3)	2.136(3)	2.134(3)	2.201(5)
Ru–C(2)	2.109(3)	2.113(3)	2.122(3)	2.128(5)
Ru–C(7)	2.204(4)	2.219(3)	2.231(3)	2.143(5)
Ru–C(8)	2.197(3)	2.221(3)	2.223(3)	2.140(5)
Ru–C(9)	2.265(3)	2.266(4)	2.257(3)	
Ru–C(10)	2.266(3)	2.266(4)	2.267(4)	
Ru–C(11)	2.136(3)	2.136(4)	2.143(3)	2.168(5)
Ru–C(12)	2.206(3)	2.188(4)	2.199(3)	2.182(5)
C(1)–C(2)	1.448(4)	1.443(4)	1.438(4)	1.434(7)
C(7)–C(8)	1.401(5)	1.422(6)	1.415(5)	1.421(8)
C(8)–C(9)	1.426(5)	1.427(6)	1.433(5)	1.481(8)
C(9)–C(10)	1.399(5)	1.407(6)	1.424(5)	1.309(8)
C(10)–C(11)	1.426(5)	1.424(6)	1.417(5)	1.470(8)
C(11)–C(12)	1.394(5)	1.385(6)	1.402(5)	1.403(7)
C(12)–C(13)	1.490(5)	1.510(5)	1.515(4)	1.520(7)
C(13)–C(14)	1.506(6)	1.498(6)	1.502(5)	1.503(8)
C(14)–C(7)	1.491(6)	1.507(6)	1.510(5)	1.510(8)

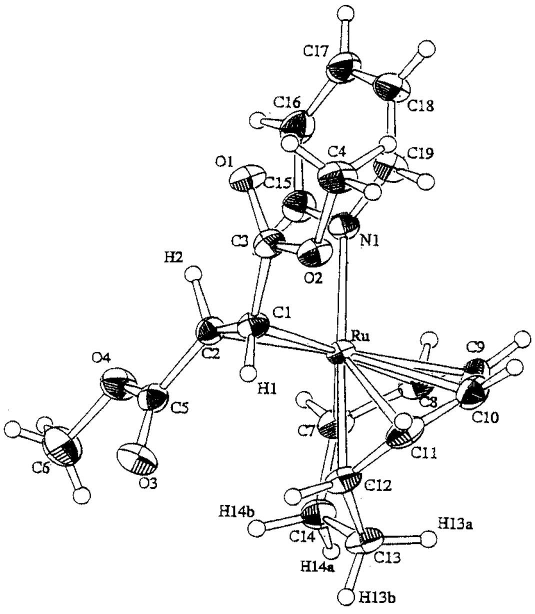


Fig. 3 An ORTEP drawing of the structure of complex **5e**.

Table 2 Selected bond angles (°) for complexes **5a**, **5d**, **5e** and **6a**[a]

	5a	**5d**	**5e**	**6a**
N(1)–Ru–N(2)				80.2(2)
N(1)–Ru–C(1)	91.1(1)	91.6(1)	94.2(1)	91.1(2)
N(1)–Ru–C(2)	85.1(1)	83.1(1)	84.6(1)	82.8(2)
N(1)–Ru–C(7)	100.4(1)	102.3(1)	100.8(1)	91.8(2)
N(1)–Ru–C(8)	86.3(1)	88.5(1)	85.5(1)	91.8(2)
N(1)–Ru–C(9)	94.0(1)	94.9(1)	91.4(1)	
N(1)–Ru–C(10)	113.3(1)	113.5(1)	111.1(1)	
N(1)–Ru–C(11)	144.3(1)	143.2(1)	141.8(1)	158.9(2)
N(1)–Ru–C(12)	176.8(1)	179.4(1)	177.3(1)	163.0(2)
N(2)–Ru–C(1)				101.8(2)
N(2)–Ru–C(2)				136.3(2)
N(2)–Ru–C(7)				121.5(2)
N(2)–Ru–C(8)				83.3(2)
N(2)–Ru–C(11)				79.6(2)
N(2)–Ru–C(12)				116.7(2)
C(1)–Ru–C(2)	39.8(1)	39.7(1)	39.5(1)	38.6(2)
C(1)–Ru–C(7)	136.0(1)	136.1(1)	135.3(1)	136.5(2)
C(1)–Ru–C(8)	171.4(1)	173.0(2)	171.6(1)	174.5(2)
C(1)–Ru–C(9)	151.3(1)	149.8(2)	151.0(1)	
C(1)–Ru–C(10)	117.2(1)	115.0(2)	115.9(1)	
C(1)–Ru–C(11)	90.2(1)	87.3(1)	88.1(1)	98.8(2)
C(1)–Ru–C(12)	91.7(1)	88.6(1)	88.5(1)	85.4(2)
C(2)–Ru–C(7)	98.7(1)	100.4(1)	100.2(1)	99.0(2)
C(2)–Ru–C(8)	131.7(1)	133.5(1)	132.3(1)	137.4(2)
C(2)–Ru–C(9)	168.9(1)	170.5(2)	169.3(1)	
C(2)–Ru–C(10)	153.2(1)	152.4(2)	153.6(1)	
C(2)–Ru–C(11)	116.9(1)	116.7(1)	118.4(1)	116.3(2)
C(2)–Ru–C(12)	96.0(1)	96.7(1)	97.8(1)	84.2(2)
C(7)–Ru–C(8)	37.1(1)	37.4(1)	37.0(1)	38.8(2)
C(7)–Ru–C(9)	70.6(1)	70.9(2)	70.8(1)	
C(7)–Ru–C(10)	97.1(1)	97.3(2)	97.4(1)	
C(7)–Ru–C(11)	103.3(1)	103.8(1)	104.0(1)	93.6(2)
C(7)–Ru–C(12)	76.5(1)	77.2(1)	77.5(1)	79.5(2)
C(8)–Ru–C(9)	37.2(1)	37.1(2)	37.3(1)	
C(8)–Ru–C(10)	71.4(1)	71.2(2)	71.8(1)	
C(8)–Ru–C(11)	96.8(1)	96.8(2)	97.3(1)	79.9(2)
C(8)–Ru–C(12)	90.7(1)	91.3(1)	91.9(1)	90.4(2)
C(9)–Ru–C(10)	36.0(1)	36.2(2)	36.7(1)	
C(9)–Ru–C(11)	69.6(1)	70.0(2)	70.4(1)	
C(9)–Ru–C(12)	84.4(1)	85.1(2)	86.0(1)	
C(10)–Ru–C(11)	37.6(1)	37.6(2)	37.3(1)	
C(10)–Ru–C(12)	66.8(1)	66.8(2)	67.1(1)	
C(11)–Ru–C(12)	37.4(1)	37.3(1)	37.7(1)	37.6(2)
N(1)–Ru–Ctr(1–2)	88.0	87.2	89.4	86.9
N(1)–Ru–Ctr(7–8)	93.5	95.6	93.3	91.9
N(1)–Ru–Ctr(9–10)	104.1	104.8	101.7	
N(1)–Ru–Ctr(11–12)	163.2	162.1	160.8	176.6
N(2)–Ru–Ctr(1–2)				119.1
N(2)–Ru–Ctr(7–8)				102.4
N(2)–Ru–Ctr(11–12)				98.2
Ctr(1–2)–Ru–Ctr(7–8)	135.2	136.5	135.6	137.5
Ctr(1–2)–Ru–Ctr(9–10)	153.5	151.9	153.1	
Ctr(1–2)–Ru–Ctr(11–12)	99.4	97.8	98.8	96.6
Ctr(7–8)–Ru–Ctr(9–10)	68.5	68.5	68.8	
Ctr(7–8)–Ru–Ctr(11–12)	91.9	92.4	92.8	85.4
Ctr(9–10)–Ru–Ctr(11–12)	63.3	63.6	63.9	

[a] Definitions: Ctr(1–2), the center of C(1) and C(2); Ctr(7–8), the center of C(7) and C(8); Ctr(9–10), the center of C(9) and C(10); Ctr(11–12), the center of C(11) and C(12).

for co-ordinated fumarate or maleate C=C bonds.[24,25,27] The co-ordinated triene moiety of the η^6-C_8H_{10} ligand is characterized by C–C bond lengths that do not significantly differ from each other. A similar bonding pattern indicating substantial electron delocalization within the conjugated π system has previously been observed for the triene moieties of **1**[28] and **2**,[25] which likewise do not exhibit a marked C–C/C=C change in carbon–carbon bond lengths. The triene fragments are slightly deviated from the plane; the deviations of the olefinic carbon from the least-squares plane C(7)/C(8)/C(9)/C(10)/C(11)/C(12) are within 0.162(3) Å for **5a**, 0.169(3) Å for **5d** and 0.163(4) Å for **5e**.

The ^1H and ^{13}C NMR data of complexes **5**, summarized in Tables 3 and 4, respectively, showed that none of the protons and carbons of the cyclooctatriene is equivalent. The patterns of the peaks of the protons of the cyclooctatriene are similar to those of **2**. The signal at δ −0.46 for complex **2**,[25] which was assigned to one of the methylene protons of the cyclooctatriene moiety, shifts to slightly higher field for **5**. This shift of one of the methylene protons, H^7, is interpreted reasonably by the magnetic anisotropy of the η^6-triene plane.[24,25,29] The signals of the two olefinic protons of the cycloocta-1,3,5-triene of **5**, H^1 and H^6, appeared at higher field than those of **2** (δ 5.84 and 3.88),[25] and the ^{13}C NMR spectra of **5** showed a high-field shift of signals of C^1, C^2, C^5 and C^6 of the cot compared with those of **2** (δ 100.6, 114.4, 102.3 and 92.7).[25] The values of $\Delta\delta$ of C^1, C^2, C^5 and C^6 are *ca.* 20, 24, 13 and 26 ppm, respectively. These results correspond to the shortening of Ru–C(7), Ru–C(11) and Ru–C(12) due to the increase of the electron densities on the ruthenium atom. The Ru–C(8) bond was not shortened, perhaps due to steric influence, in spite of the electronic effect. The signals of H^3 and H^4, and C^3 and C^4, of the cot in **5** were observed at almost the same region as those in **2**.

Some NMR spectra of ruthenium complexes bearing an amine ligand have been reported. For $[RuH(Cl)(CO)(PPh_3)_2(NH_2Pr)]$[2c] the signals of the protons of NH_2 and those of α-protons of the amine are observed at δ 1.30 and 1.99, respect-

Table 3 ^{1}H NMR Data of complexes **5** (δ)[a]

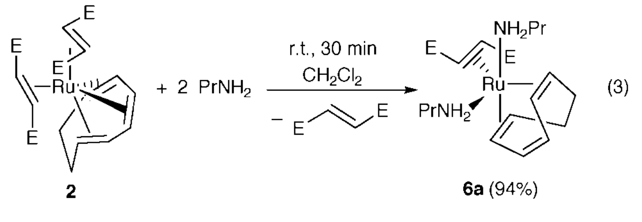
	5a	**5b**	**5c**	**5d**	**5e**
Dimethyl fumarate					
=CH	2.56 (d, 8.8)	2.78 (d, 8.3)	2.57 (d, 8.8)	2.54 (d, 8.8)	2.86 (d, 8.8)
	2.47 (d, 8.8)	2.59 (d, 8.3)	2.30 (d, 8.8)	2.33 (d, 8.8)	2.65 (d, 8.8)
Me	3.72 (s)	3.77 (s)	3.73 (s)	3.73 (s)	3.76 (s)
	3.49 (s)	3.57 (s)	3.48 (s)	3.49 (s)	3.15 (s)
Cycloocta-1,3,5-triene					
H^1	5.18 (ddd, 9.8, 5.4, 3.9)	5.30 (br)	5.38 (br d, 9.8)	5.38 (br d, 9.3)	5.37 (ddd, 9.3, 5.4, 3.4)
H^2	4.13 (dd, 9.8, 8.8)	4.27 (br t)	4.29 (dd, 9.8, 8.8)	4.34 (dd, 9.3, 8.8)	3.73 (dd, 9.3, 8.3)
H^3	5.87 (dd, 8.8, 8.3)	5.97 (t, 8.5)	5.89 (t, 8.8)	5.92 (t, 8.8)	5.59 (t, 8.3)
H^4	6.41 (dd, 8.3, 5.9)	6.45 (t, 8.5)	6.43 (dd, 8.8, 5.9)	6.44 (dd, 8.8, 5.9)	6.45 (dd, 8.3, 5.9)
H^5	4.92 (dd, 7.3, 5.9)	5.00 (br t)	4.98 (dd, 7.3, 5.9)	5.00 (dd, 7.3, 5.9)	5.17 (dd, 7.8, 5.9)
H^6	2.53 (dt, 8.8, 7.3)	2.59 (br)	2.12 (dt, 8.8, 7.3)	2.17 (m)	2.48 (dt, 8.8, 7.8)
H^7	1.08 (ddt, 12.7, 7.3, 3.9)	1.13 (br)	0.85 (m)	0.86 (m)	1.09 (m)
	−0.64 (tdd, 12.7, 8.8, 3.9)	−0.59 (br)	−0.98 (tdd, 13.2, 8.8, 3.9)	−0.95 (tdd, 13.2, 8.8, 4.4)	−0.63 (tdd, 12.7, 8.8, 4.4)
H^8	2.05 (dddd, 13.7, 12.7, 5.4, 3.9)	2.13 (m)	2.15 (tdd, 13.2, 5.9, 3.3)	2.14 (tdd, 13.2, 5.9, 3.4)	2.13 (dddd, 13.7, 12.7, 5.4, 3.9)
	1.69 (dq, 13.7, 3.9)	1.78 (br d, 11.2)	1.92[b]	1.92 (br d, 13.2)	1.77 (ddt, 13.7, 4.4, 3.4)
Amine					
NH	1.40 (br)	1.90 (br t)	2.30 (br)	2.62 (br)	
	1.18 (br)	1.65 (br)			
α-H	2.17 (m)	3.37 (br t, 11.5)	1.94 (d, 3H, 5.9)	2.53 (m)	
	1.88 (m)	3.03 (br t, 11.5)	1.90 (d, 3H, 5.9)	2.45 (br d, 13.2)	
				2.25 (ddd, 13.2, 12.2, 2.9)	
				1.95 (br d, 12.2)	
Others					
	1.24 (m)	7.3–7.1 (m, 5 H)		3.58 (br d, 12.2)	8.06 (d, 2 H, 4.9)
	1.18 (m)			3.50 (m)	7.52 (t, 7.8)
	0.75 (t, 3 H, 7.3)			3.23 (td, 12.2, 2.9)	6.97 (dd, 2 H, 7.8, 4.9)
				3.16 (td, 12.2, 2.4)	

[a] Measured in CD_2Cl_2 solution at room temperature and 400 MHz. s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Figures in parentheses are the values of the coupling constants, J_{H-H} (in Hz). [b] The signal is overlapped with those of the methyl protons of Me_2NH.

ively. For $[Ru(CO)_2(NH_2CH_2Ph)_2(SiMe_2Ph)I]$[9b] the protons of NH_2 appear at δ 1.66 and 2.05 and α-protons of the amine are observed at δ 3.15 and 4.13, respectively, and ^{13}C NMR showed the signal of the α-carbon of benzylamine at δ 52.34. These results are similar to those of **5a** and **5b**.

$[Ru(\eta^4\text{-cot})(dmfm)(PrNH_2)_2]$ 6a

As described above, $[Ru(\eta^6\text{-cot})(dmfm)_2]$ **2** reacts with an excess of propylamine to give $[Ru(\eta^6\text{-cot})(dmfm)(PrNH_2)]$ **5a**. However, the recrystallization of **5a** in the presence of a large excess of propylamine gave $[Ru(\eta^4\text{-cot})(dmfm)(PrNH_2)_2]$ **6a**, eqn. (3).



(3)

Syntheses of other $[Ru(\eta^4\text{-cot})(dmfm)(L)_2]$ were unsuccessful. The structure of **6a** was also confirmed by X-ray analysis.

The structure of complex **6a** is shown in Fig. 4. It is represented by a distorted trigonal bipyramid and quite similar to that of $[Ru(\eta^4\text{-cot})(dmfm)(L_2)]$ (L_2 = 2,2′-bipyridyl **4a** or 1,10-phenanthroline **4b**).[24] Selected bond distances and angles are provided in Tables 1 and 2, respectively.

The distance between ruthenium and the axial nitrogen, Ru–N(1), is in agreement with the value observed for **5a**; Ru–N(2) is longer than Ru–N(1), due to steric interaction with the cyclooctatriene ligand, or the decrease of electron density at the Ru atom by the dimethyl fumarate ligand in the equatorial position. Compared with the 2,2′-bipyridyl and the 1,10-phenanthroline complexes **4**, both Ru–N(1) and Ru–N(2) of **6a** are longer than those of **4** (2.084(5) and 2.096(3) Å for Ru–N(1); 2.178(5) and 2.194(3) Å for Ru–N(2)),[24] where the propylamine ligand is a weaker σ donor than the bipy and the phen.

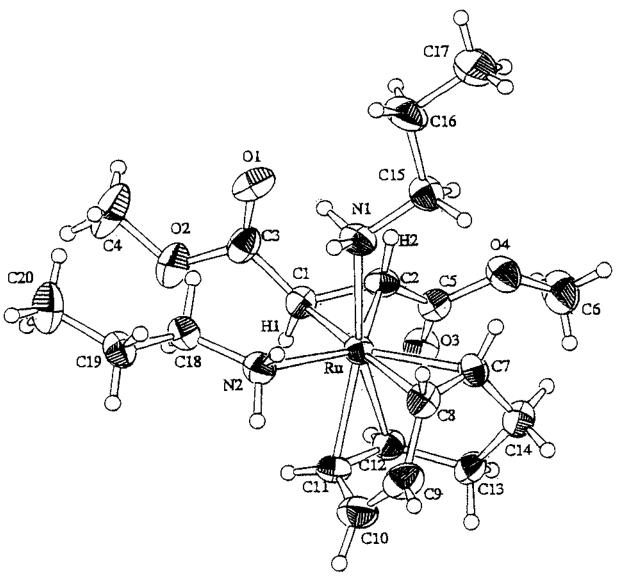


Fig. 4 An ORTEP drawing of the structure of complex **6a**.

The distances between ruthenium and the equatorial olefinic carbons of the cyclooctatriene ligands in complex **6a**, Ru–C(7) and Ru–C(8), are shorter than those in **5a** due to the influence of the σ-donor nitrogen ligand in the equatorial position or the

Table 4 ^{13}C NMR data of complexes **5** (δ)[a]

	5a	**5b**[b]	**5c**	**5d**	**5e**
Dimethyl fumarate					
C=O	179.3	179.12	179.0	178.9	179.4
	178.1	178.2	178.1	178.5	175.9
=CH	44.9 (153)	45.1	46.3 (151)	46.4	45.2 (154)
	39.2 (158)	39.3	40.0 (158)	39.7	41.3 (153)
Me	51.2 (145)	51.2	51.2 (145)	51.4	50.6 (145)
	50.7 (145)	50.7	50.7 (145)	50.7	50.3 (145)
Cycloocta-1,3,5-triene					
C^1	80.8 (147)	81.0	82.1 (156)	81.8	82.6 (149)
C^2	90.7 (160)	90.6	90.5 (158)	91.1	93.9 (160)
C^3	107.0 (155)	107.1	109.8 (158)	109.3	107.0 (158)
C^4	95.4 (162)	95.3	94.3 (165)	94.4	96.2 (164)
C^5	89.5 (162)	89.5	89.1 (158)	89.3	92.0 (164)
C^6	68.0 (164)	67.9	65.6 (158)	65.9	66.2 (156)
C^7	25.1 (125)	24.9	23.5 (125)	23.5	25.0 (123)
C^8	35.1 (127)	35.1	36.2 (129)	36.1	35.0 (125)
Amine					
	48.7 (136)	51.1	44.1 (136)	69.2	153.0 (182)
	26.5 (127)		42.2 (136)	68.9	136.5 (164)
	11.4 (125)			52.5	124.2 (165)
				50.0	

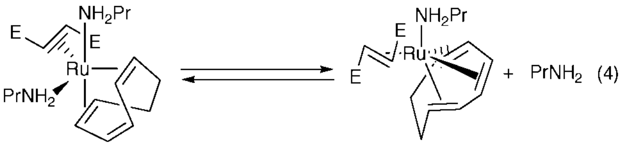
[a] Measured in CD_2Cl_2 solution at room temperature and 100 MHz. Figures in parentheses are the values of the coupling constants, J_{C-H} (in Hz). [b] Signals for aromatic carbons were at δ 140.7, 129.0, 128.7, 127.83, 127.76 and 127.3

steric influence of the dissociation of the central double bond of the cyclooctatriene ligand, and in agreement with values observed in complex **4** (2.145(4)–2.169(6) Å).[24] The angle of N(1)–Ru–Ctr(11–12) in **6a** is 176.6°, which implies a strain-free configuration compared with that of **5a**.

The co-ordinated triene moiety of the cyclooctatriene ligand is characterized by C–C bond lengths that significantly differ from each other. The central double bond, C(9)–C(10), is shorter than C(7)–C(8) and C(11)–C(12). The shortening of the carbon–carbon double bond compared with that of the free olefin (1.34 Å) is also observed in complex **4** (1.31(1) and 1.315(6) Å).[24] The triene moiety of **6a** is far from the plane; the dihedral angles C(7)–C(8)–C(9)–C(10) and C(9)–C(10)–C(11)–C(12) are −73.8(9) and 63.9(8)°, respectively. This result is similar to that for **4** and quite different from those in **2**[25] and **5a**. A bonding pattern indicating substantial electron delocalization within the conjugated π system is not observed for the triene moiety in **6a**, which exhibits a marked C–C/C=C change in its carbon–carbon bond lengths, in contrast with those in **1**, **2** and **5a**.

When the complex **6a** was dissolved in CD_2Cl_2, ^{1}H and ^{13}C NMR data showed the signals of **5a**, not those of **6a**, and liberated propylamine. On the other hand, the solid state high resolution CPMAS ^{13}C NMR spectrum showed the signals of **6a**; the two signals of the non-co-ordinated olefinic carbons (δ 140.5 and 135.3), assigned to the carbons at 3 and 4 positions of the cyclooctatriene moiety, which are in agreement with values observed for **4**.[24] In this region no signal was observed for **2** and **5**. Equilibria of ruthenium complexes with amines have been observed between $[RuH(Cl)(CO)(PPh_3)_3]$ and $[RuH(Cl)(CO)(PPh_3)_2(Et_2NH)]$,[2a] $[RuH(Cl)(PPh_3)_3]$ and $[RuH(Cl)(PPh_3)_2(EtNH_2)_2]$,[3] and $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(PPh_3)_2(EtNH_2)_2]$.[3] However, no equilibrium involving the dissociation and co-ordination of amines and olefins is known for ruthenium complexes, eqn. (4).

In conclusion, a combination of amines as σ-donor ligands and dimethyl fumarate as a π-acceptor ligand is good choice to stabilize new types of ruthenium(0) complexes. Moreover, the central carbon–carbon double bond of cycloocta-1,3,5-triene can dissociate and co-ordinate easily under mild conditions, and it is possible to obtain a vacant co-ordination site. The complexes **5** and **6** are expected to be widely used as versatile zerovalent ruthenium complexes, and may provide useful catalytic systems.



6a **5a** (4)

Experimental

Materials and methods

All manipulations were performed under an argon atmosphere using standard Schlenk techniques. The complexes [Ru(η^4-cod)(η^6-cot)][30] and [Ru(η^6-cot)(dmfm)$_2$][25] were synthesized as described. All solvents were distilled under argon over appropriate drying reagents (sodium, calcium hydride, sodium–benzophenone or calcium chloride). All new compounds are characterized below.

Physical and analytical measurements

The NMR spectra were recorded on a JEOL EX-400 (FT, 400 MHz (^{1}H), 100 MHz (^{13}C)) spectrometer. Chemical shift values (δ) for ^{1}H and ^{13}C are referenced to internal solvent resonances and reported relative to $SiMe_4$. The solid state high resolution CPMAS ^{13}C NMR spectrum was recorded on a JEOL GSX-270 spectrometer, and IR spectra using a Nicolet Impact 410 FT-IR spectrometer. Melting points were determined under argon on a Yanagimoto micro melting point apparatus. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Preparation of the amine complexes

[Ru(η^6-cot)(dmfm)(PrNH$_2$)] 5a and [Ru(η^4-cot)(dmfm)(PrNH$_2$)$_2$] 6a. To a solution of 0.25 g (0.50 mmol) of [Ru(η^6-cot)(dmfm)$_2$] **2** in 2.5 cm^3 of CH_2Cl_2 was added 0.18 g (3.0 mmol) of propylamine, and the mixture stirred at room temperature for 30 min, then chromatographed on alumina (Merck 1097). Elution with hexane–propylamine (90:10) gave a yellow solution, from which the solvent was evaporated. To remove the excess of propylamine completely, the light yellow residue was dissolved in 1,2-dichloroethane and the solvent removed *in vacuo*. The orange residue was recrystallized from Et_2O–pentane to give complex **5a** (0.18 g, 87%), mp 70–71 °C (decomp.) (Found: C, 49.45; H, 6.64; N, 3.46. $C_{17}H_{27}NO_4Ru$ requires C, 49.74; H, 6.63; N, 3.41%); $\tilde{\nu}$/cm^{-1} 3287s, 3234w, 3165w, 2940m, 2876w, 2830w, 1680vs, 1651vs, 1610m, 1459s, 1430m, 1302s, 1155vs, 1098w, 1044s and 870w (KBr).

On the other hand, when the eluent with hexane–propylamine was concentrated and cooled at −78 °C yellow needle microcrystals were formed. The product was separated by filtration, washed with pentane, and dried under vacuum to give complex **6a** (0.22 g, 94%), mp 53–54 °C (decomp.) (Found: C, 50.88; H, 7.93; N, 6.02. $C_{20}H_{36}N_2O_4Ru$ requires C, 51.16; H, 7.73; N, 5.97%); $\tilde{\nu}$/cm^{-1} 3327w, 3279m, 3232w, 3139w, 2964m, 2937m, 2876w, 1660vs, 1644vs, 1465m, 1434m, 1310s, 1178s, 1156vs, 1046s, 881w and 800w (KBr); δ_C (67.8 MHz; CPMAS) 183.1 and 180.9 (2 CO), 140.5 and 135.3 (2 non-co-ordinated olefinic carbons of the cot), 88.6, 76.9, 75.1 and 69.8 (4 co-ordinated olefinic carbons of the cot), 51.4 (MeO and NCH_2), 49.8 (MeO), 45.8 (NCH_2 and CH of dmfm), 38.2 (CH of dmfm), 35.9 (CH_2 of cot), 31.1 (CH_2Me), 29.8 (CH_2 of cot), 27.5 (CH$_2$Me), 13.8 and 12.8 (CH_2*Me*).

Table 5 Summary of crystal data, collection data, and refinement of complexes **5a**, **5d**, **5e** and **6a**

	5a	**5d**	**5e**	**6a**
Formula	$C_{17}H_{27}NO_4Ru$	$C_{18}H_{27}NO_5Ru$	$C_{19}H_{23}NO_4Ru$	$C_{20}H_{36}N_2O_4Ru$
Formula weight	410.47	438.49	430.46	469.59
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	7.736(4)	9.252(3)	9.303(4)	13.294(6)
b/Å	11.418(3)	13.898(7)	13.772(7)	12.141(7)
c/Å	21.239(4)	7.749(3)	7.379(3)	14.240(4)
α/°		94.97(4)	99.29(4)	
β/°	97.35(3)	101.27(3)	101.56(3)	94.95(3)
γ/°		73.03(3)	86.71(4)	
V/Å^3	1860(1)	934.1(7)	913.8(7)	2289(1)
Z	4	2	2	4
T/°C	23.0	23.0	23.0	23.0
μ(Mo-Kα)/cm^{-1}	8.60	8.66	8.81	7.10
No. measured reflections	4574	4601	4451	5485
No. unique reflections	4263	4285	4193	5264
R_{int}	0.053	0.022	0.015	0.048
R	0.028	0.029	0.026	0.037

[Ru(η^6-cot)(dmfm)(PhCH$_2$NH$_2$)] 5b. To a solution of 0.25 g (0.50 mmol) of [Ru(η^6-cot)(dmfm)$_2$] **2** in 2.5 cm^3 of CH_2Cl_2 was added 0.26 g (2.5 mmol) of benzylamine, and the mixture stirred at room temperature for 30 min, then chromatographed on alumina. Elution with Et_2O gave a yellow solution, from which the solvent was evaporated. The orange residue was recrystallized from Et_2O–pentane to give complex **5b** (0.18 g, 79%), mp 76–77 °C (decomp.) (Found: C, 55.03; H, 5.82; N, 3.22. $C_{21}H_{27}NO_4Ru$ requires C, 55.02; H, 5.94; N, 3.06%); ν/cm^{-1} 3272m, 3119w, 3004w, 2990w, 2942m, 2878w, 2831w, 1658vs, 1637vs, 1458s, 1435s, 1304vs, 1159vs, 1040s, 987w, 884w, 756w and 698m (KBr).

[Ru(η^6-cot)(dmfm)(Me$_2$NH)] 5c. To a solution of 0.25 g (0.50 mmol) of [Ru(η^6-cot)(dmfm)$_2$] **2** in 1.25 cm^3 of THF were added 1.25 cm^3 of 2.0 M dimethylamine (2.5 mmol) in THF and the mixture was stirred at room temperature for 30 min, then chromatographed on alumina. Elution with hexane–2.0 M dimethylamine in THF (85:15) gave a yellow solution, from which the solvent was evaporated. The orange residue was recrystallized from Et_2O–pentane to give complex **5c** (0.14 g, 70%), mp 90–91 °C (decomp.) (Found: C, 48.31; H, 6.47; N, 3.41. $C_{16}H_{25}NO_4Ru$ requires C, 48.47; H, 6.36; N, 3.53%); $\tilde{\nu}$/cm^{-1} 3199m, 2983w, 2968m, 2940m, 2897w, 2878w, 2839w, 1693vs, 1647vs, 1448s, 1433s, 1298vs, 1170 (sh), 1147vs, 1076w, 1034s, 908w, 877m and 765w (KBr).

[Ru(η^6-cot)(dmfm)(OC$_4$H$_8$NH)] 5d. To a solution of 0.25 g (0.50 mmol) of [Ru(η^6-cot)(dmfm)$_2$] **2** in 2.5 cm^3 of CH_2Cl_2 was added 0.22 g (2.5 mmol) of morpholine, and the mixture stirred at room temperature for 30 min then was chromatographed on alumina. Elution with Et_2O gave a yellow solution, from which the solvent was evaporated. The orange residue was recrystallized from Et_2O–pentane to give **5d** (0.18 g, 81%), mp 79–80 °C (decomp.) (Found: C, 49.21; H, 6.39; N, 3.36. $C_{18}H_{27}NO_5Ru$ requires C, 49.31; H, 6.21; N, 3.19%); $\tilde{\nu}$/cm^{-1} 3151m, 3028w, 3009w, 2963m, 2942w, 2835m, 1682vs, 1655vs, 1451s, 1431s, 1303vs, 1160vs, 1122m, 1088m, 1030s, 886s and 760w (KBr).

[Ru(η^6-cot)(dmfm)(py)] 5e. To a solution of 0.25 g (0.50 mmol) of [Ru(η^6-cot)(dmfm)$_2$] **2** in 2.5 cm^3 of CH_2Cl_2 was added 0.21 g (2.6 mmol) of pyridine and the mixture stirred at room temperature for 30 min then chromatographed on alumina. Elution with hexane–pyridine (80:20) gave a yellow solution, from which the solvent was evaporated. The orange residue was recrystallized from Et_2O to give complex **5e** (0.18 g, 85%), mp 68–69 °C (decomp.) (Found: C, 52.80; H, 5.36; N, 3.31. $C_{19}H_{23}NO_4Ru$ requires C, 53.01; H, 5.39; N, 3.25%); $\tilde{\nu}$/cm^{-1} 3002w, 2980w, 2944m, 2864w, 2834m, 1692vs, 1686vs, 1448s, 1431s, 1292vs, 1143vs, 1037s, 868m, 755m and 695m (KBr).

Crystallographic study of complexes 5a, 5d, 5e and 6a

Single crystals of complexes **5a**, **5d** and **5e** obtained by recrystallization from Et_2O–pentane and **6a** from $PrNH_2$–hexane were subjected to X-ray crystallographic analyses. The crystal data and experimental details are summarized in Table 5. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) and a rotating anode generator. The structures were solved by direct methods using SIR 92[31a] for **5a**, **5e** and **6a** and SHELXS 86[31b] for **5d**, expanded using Fourier techniques, DIRDIF 94,[31c] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Hydrogen atoms were found except for the methoxy protons on C(6) for **5e** and the methyl protons of propylamines for **6a**. Hydrogens in **5a**, **5d** and **5e** were refined isotropically. Those in **6a** were not refined, and isotropic B values were refined. The calculations were performed on an IRIS Indigo and O_2 computer using the program system TEXSAN.[31d]

CCDC reference number 186/1697.

See http://www.rsc.org/suppdata/dt/1999/4231/ for crystallographic files in .cif format.

Acknowledgements

This work was supported in part by Grants-in-Aid for Scientific Research (Nos. 09238103, 1045341) from the Ministry of Education, Science, Sports and Culture, Japan.

References

1 For examples, see: (*a*) M. A. Bennett, M. I. Bruce and T. W. Matheson, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, E. W. Abel and F. G. A. Stone, Pergamon, Oxford, 1982, vol. 4, ch. 32.3, pp. 691–820; (*b*) E. A. Seddon and K. R. Seddon, in *The Chemistry of Ruthenium*, Elsevier, Amsterdam, 1984, ch. 8.14–8.21, pp. 221–284; ch. 9.10–9.18, pp. 366–487 and refs. therein; (*c*) E. A. Seddon and K. R. Seddon, in *The Chemistry of Ruthenium*, Elsevier, Amsterdam, 1984, ch. 11.4, p. 943.

2 (*a*) S. Ganguly and D. M. Roundhill, *Polyhedron*, 1990, **9**, 2517; (*b*) Y. Qu and N. Farrell, *Inorg. Chem.*, 1995, **34**, 3573; (*c*) K. Hiraki, T. Matsunaga and H. Kawano, *Organometallics*, 1994, **13**, 1878.

3 C. W. Jung, J. D. Fellmann and P. E. Garrou, *Organometallics*, 1983, **2**, 1042.

4 (*a*) M. Stephenson and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1981, 2112; (*b*) R. O. Gould, T. A. Stephenson and M. A. Thomson, *J. Chem. Soc., Dalton Trans.*, 1978, 769; (*c*) W. Heiber and P. John, *Chem. Ber.*, 1970, **103**, 2161; (*d*) P. John, *Chem. Ber.*, 1970, **103**, 2178 and refs. therein.

5 F. Porta, C. Crotti and S. Cenini, *J. Mol. Catal.*, 1989, **50**, 333; S. Cenini, F. Porta and M. Pizzotti, *J. Mol. Catal.*, 1982, **15**, 297; S. Cenini, M. Pizzotti, F. Porta and G. La Monica, *J. Organomet. Chem.*, 1977, **125**, 95.

6 Y. Watanabe, Y. Tsuji, H. Ige, Y. Ohsugi and T. Ohta, *J. Org. Chem.*, 1984, **49**, 3359.

7 W. R. McWhinnie, J. D. Miller, J. B. Watts and D. Y. Waddan, *Inorg. Chim. Acta*, 1973, **7**, 461.

8 S. Joss, H. B. Bürgi and A. Ludi, *Inorg. Chem.*, 1985, **24**, 949; K. Rieder, U. Hauser, H. Siegenthaler, E. Schmidt and A. Ludi, *Inorg. Chem.*, 1975, **14**, 1902; Y. Ilan and A. Kfir, *Inorg. Chim. Acta*, 1989, **156**, 221 and refs. therein.

9 (*a*) H. Kurosawa, H. Asano and Y. Miyaki, *Inorg. Chim. Acta*, 1998, **270**, 87; (*b*) B. J. Rappoli, K. J. McGrath, C. F. George and J. C. Cooper, *J. Organomet. Chem.*, 1993, **450**, 85; (*c*) W. Stüer, J. Wolf, H. Werner, P. Schwab and M. Schulz, *Angew. Chem.*, *Int. Ed. Engl.*, 1998, **37**, 3421; (*d*) J. A. Crayston, D. C. Cupertino and T. J. Dines, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 1603; (*e*) U. C. Sarma and P. K. Poddar, *Polyhedron*, 1988, **7**, 1737; (*f*) T. Rappert and A. Yamamoto, *Chem. Lett.*, 1994, 2211.

10 A. J. Bailey and B. R. James, *Chem. Commun.*, 1997, 505; 1996, 2343; F. R. Keene, D. J. Salmon and T. J. Meyer, *J. Am. Chem. Soc.*, 1976, **98**, 1884.

11 T. Naota and S.-I. Murahashi, *Synlett.*, 1991, 693; Y. Watanabe, Y. Morisaki, T. Kondo and T. Mitsudo, *J. Org. Chem.*, 1996, **61**, 4214; Y. Tsuji, S. Kotachi, K.-T. Huh and Y. Watanabe, *J. Org. Chem.*, 1990, **55**, 580; Y. Tsuji, Y. Yokoyama, K.-T. Huh and Y. Watanabe, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3456; J. A. Marsella, *J. Org. Chem.*, 1987, **52**, 467; A. Arcelli, B.-T. Khai and G. Porzi, *J. Organomet. Chem.*, 1982, **235**, 93; R. Grigg, T. R. B. Mitchell, S. Sutthivaiyakit and N. Tongpenyai, *J. Chem. Soc.*, *Chem. Commun.*, 1981, 611 and refs. therein.

12 R. Tang, S. E. Diamond, N. Neary and F. Mares, *J. Chem. Soc.*, *Chem. Commun.*, 1978, 562.

13 S. I. Gorelsky, E. S. Dodsworth, A. B. P. Lever and A. A. Vlcek, *Coord. Chem. Rev.*, 1998, **174**, 469; V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Coord. Chem. Rev.*, 1996, **96**, 759; A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85 and refs. therein.

14 (*a*) H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, A. F. England, T. Ikariya and R. Noyori, *Angew. Chem.*, *Int. Ed*, *Engl.*, 1998, **37**, 1703; (*b*) T. Ohkuma, M. Koizumi, H. Doucet, T. Pham, M. Kozawa, K. Murata, E. Katayama, T. Yokozawa, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.*, 1998, **120**, 13529; (*c*) K. Mikami, T. Korenaga, M. Terada, T. Ohkuma, T. Pham and R. Noyori, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 495 and refs. therein.

15 A. J. Bailey, W. P. Griffith and P. D. Savage, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 3537; W.-H. Fung, W.-C. Cheng, W.-Y. Yu, C.-M. Che and T. C. W. Mak, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 2007; A. S. Goldstein, R. H. Beer and R. S. Drago, *J. Am. Chem. Soc.*, 1994, **116**, 2424; C. Augier, L. Malara, V. Lazzeri and B. Waegell, *Tetrahedron Lett.*, 1995, **36**, 8775.

16 H. Nishiyama, Y. Itoh, Y. Sugawara, H. Matsumoto, K. Aoki and K. Itoh, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 1247; S.-B. Park, N. Sakata and H. Nishiyama, *Chem. Eur. J.*, 1996, **2**, 303; H. Nishiyama, N. Soeda, T. Naito and Y. Motoyama, *Tetrahedron: Asymmetry*, 1998, **9**, 2865 and refs. therein.

17 H. Nishiyama, T. Shimada, H. Itoh, H. Sugiyama and Y. Motoyama, *Chem. Commun.*, 1997, 1863; W.-H. Fung, W.-Y. Yu and C.-M. Che, *J. Org. Chem.*, 1998, **63**, 7715; W.-C. Cheng, W.-Y. Yu, K.-K. Cheung and C.-M. Che, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1063.

18 C.-J. Liu, S.-G. Li, W.-Q. Pang and C.-M. Che, *Chem. Commun.*, 1997, 65; W.-H. Leung, C.-M. Che, C.-H. Yeung and C.-K. Poon, *Polyhedron*, 1993, **12**, 2331; J. T. Groves, M. Bonchio, T. Carofiglio and K. Shalyaev, *J. Am. Chem. Soc.*, 1996, **118**, 8961; J. T. Groves and R. Quinn, *J. Am. Chem. Soc.*, 1985, **107**, 5790; Z. Gross, S. Ini, M. Kapon and S. Cohen, *Tetrahedron Lett.*, 1996, **37**, 7325; H. Ohtake, T. Higuchi and M. Hirobe, *Tetrahedron Lett.*, 1992, **33**, 2521.

19 T. Higuchi, C. Satake and M. Hirobe, *J. Am. Chem. Soc.*, 1995, **117**, 8879; E. Galardon, P. Le Maux and G. Simonneaux, *Chem. Commun.*, 1997, 927; S.-M. Au, W.-H. Fung, M.-C. Cheng, C.-M. Che and S.-M. Peng, *Chem. Commun.*, 1997, 1665; W.-C. Lo, C.-M. Che, K.-F. Cheng and T. C. W. Mak, *Chem. Commun.*, 1997, 1205; M. Frauenkron and A. Berkessel, *Tetrahedron Lett.*, 1997, **38**, 7175.

20 K. Mizushima, M. Nakaura, S.-B. Park, H. Nishiyama, H. Monjushiro, K. Harada and M. Haga, *Inorg. Chim. Acta*, 1997, **261**, 175; H. Nishiyama, S.-B. Park, M. Haga, K. Aoki and K. Itoh, *Chem. Lett.*, 1994, 1111; W.-C. Cheng, W.-Y. Yu, C.-K. Li and C.-M. Che, *J. Org. Chem.*, 1995, **60**, 6840.

21 H. Tanaka, B.-C. Tzeng, S.-M. Peng and K. Tanaka, *Inorg. Chem.*, 1993, **32**, 1508.

22 E. F. Magoon, H. C. Volger, W. W. Spooncer, J. L. von Vinkle and L. H. Slaugh, *J. Organomet. Chem.*, 1975, **99**, 135.

23 Dr. K. Tanaka, personal communication.

24 T. Suzuki, M. Shiotsuki, K. Wada, T. Kondo and Take-aki Mitsudo, *Organometallics*, 1999, **18**, 3671.

25 T. Mitsudo, T. Suzuki, S.-W. Zhang, D. Imai, K. Fujita, T. Manabe, M. Shiotsuki, Y. Watanabe, K. Wada and T. Kondo, *J. Am. Chem. Soc.*, 1999, **121**, 1839.

26 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976

27 (*a*) M. von Wijnkoop, P. P. M. de Lange, H.-W. Frühauf, K. Vrieze, W. J. J. Smeets and A. L. Spek, *Organometallics*, 1995, **14**, 4781; (*b*) B. de Klerk-Engels, J. G. P. Delis, K. Vrieze, K. Goubitz and J. Fraanje, *Organometallics*, 1994, **13**, 3269; (*c*) B. de Klerk-Engels, J. G. P. Delis, J.-M. Ernsting, C. J. Elsevier, H.-W. Frühauf, D. J. Stufkens, K. Vrieze, K. Goubitz and J. Fraanje, *Inorg. Chim. Acta*, 1995, **240**, 273; (*d*) M. Helliwell, J. D. Vessey and R. J. Mawby, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 1193; (*e*) C. Bianchini, P. Frediani, D. Masi, M. Peruzzini and F. Zanobini, *Organometallics*, 1994, **13**, 4616; (*f*) F.-W. Grevels, J. G. A. Reuvers and J. Takats, *J. Am. Chem. Soc.*, 1981, **103**, 4069; (*g*) L. Kruczynski, J. L. Martin and J. Takats, *J. Organomet. Chem.*, 1974, **80**, C9.

28 K.-M. Frosin and L. Dahlenburg, *Inorg. Chim. Acta*, 1990, **167**, 83.

29 F. Bouachir, B. Chaudret, D. Neibecker and I. Tkatchenko, *Angew. Chem.*, *Int. Ed. Engl.*, 1985, **24**, 347; T. V. Ashworth, A. A. Chalmers, D. C. Liles, E. Meintjies and E. Singleton, *Organometallics*, 1987, **6**, 1543; J. W. Steed, D. A. Tocher and R. D. Rogers, *Chem. Commun.*, 1996, 1589; F. Bouachir, B. Chaudret and I. Tkatchenko, *J. Chem. Soc.*, *Chem. Commun.*, 1986, 94; F. Bouachir, B. Chaudret, F. Dahan, F. Agbossou and I. Tkatchenko, *Organometallics*, 1991, **10**, 455.

30 (*a*) K. Itoh, H. Nagashima, T. Ohshima, N. Oshima and H. Nishiyama, *J. Organomet. Chem.*, 1984, **272**, 179; (*b*) P. Pertici, G. Vitulli, M. Paci and L. Porri, *J. Chem. Soc.*, *Dalton Trans.*, 1980, 1961.

31 (*a*) SIR 92, A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435; (*b*) SHELXS 86, G. M. Sheldrick, in *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, Oxford, 1985, pp. 175–189; (*c*) DIRDIF 94, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1994; (*d*) TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corp., The Woodlands, TX, 1985 and 1992.

Paper 9/07333G