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Rhodium(I) complexes of 4-t-butylcyclohexyldiaziridine and adamantyldiaziridine: synthesis, structure and catalytic activity

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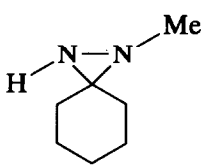
Abstract

Rhodium(I) complexes of the ligands adamantyldiaziridine and 4-t-butylcyclohexyldiaziridine have been prepared and characterised. The structure of [RhCl(cod)(4-t-butylcyclohexyldiaziridine)] has been established by an X-ray diffraction study. The rhodium is coordinated to the equatorial nitrogen atom of the diaziridine. The complexes are rather poor catalysts for hydrogenation or hydroformylation of alkenes.

1. Introduction

The coordination chemistry of diaziridines has been little investigated and to our knowledge no metal diaziridine complexes have been structurally characterised. Reaction of $[PdCl_2(PhCN)_2]$ with the substituted diaziridine, **1**, gave *trans*-$[PdCl_2L_2]$ as an inseparable mixture of diastereoisomers [1], and **2** coordi-



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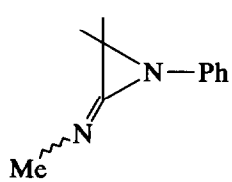

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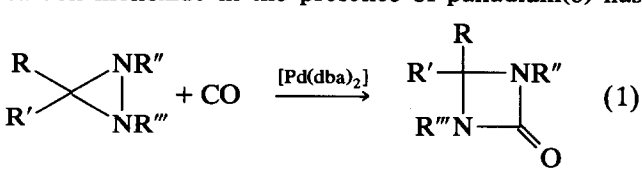
nates to palladium only at the more basic exocyclic nitrogen atom [2]. The reaction of diaziridines with carbon monoxide in the presence of palladium(0) has been studied (reaction (1)) but neither in this nor in a related cobalt catalysed process were any metal diaziridine complexes isolated [3].



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The coordination chemistry of diazirines, **3**, has received a little more attention, and the complex **4** has been structurally characterised [4]. **3** (R^1, R^2 = Me or $R^1R^2 = (CH_2)_5$) reacts with $[M(CO)_5(thf)]$ (M = Cr, Mo or W) to give mono- and bis-metallated species. Reaction with $[M(CO)_2(nbd)]$ (M = Mo or W) gave **5**, whilst $[MnCp(CO)_2(thf)]$ yielded **6** [5,6]. Related reactions were reported with $[Fe_2(CO)_9]$ [7].

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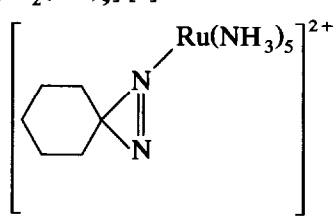

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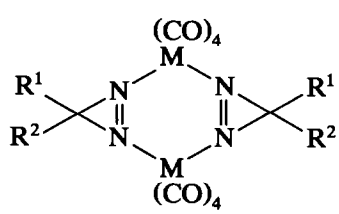

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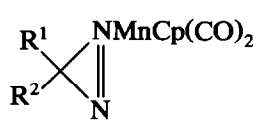

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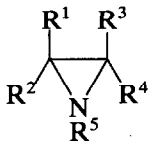
Metal complexes of aziridines, such as **7** [8,9], and the unsaturated analogue, **8** [10], have been more extensively investigated, as have metal-catalysed insertions into these three-membered rings [11–13].



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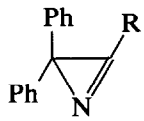

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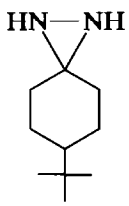
We now report the preparation and characterisation of a range of complexes of the diaziridines **9** and **10**, a study of their catalytic activity, and structural characterisation of one of them.



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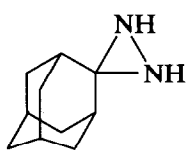

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2. Results and discussion

2.1. Ligand synthesis

The ligands **9** (^{t}BuCyDARD) and **10** (AdDARD) were prepared by the standard methods of reaction of the ketone with liquid ammonia and hydroxylamine-*O*-sulphonic acid [14].

2.2. Preparation and interconversion of the complexes

Addition of a stoicheiometric amount of diaziridine to a dichloromethane solution of $[\{RhCl(cod)\}_2]$ leads to the formation of [RhCl(cod)(diaziridine)] by cleavage of the chloride bridge. The complexes were isolated as yellow, relatively air-stable solids. Microanalytical, conductivity and IR spectroscopic data are shown in Tables 1 and 2. The IR spectra show the presence of the coordinated diene as well as bands for the free and coordinated NH groups of the coordinated diaziridine. ^{1}H NMR spectra of $CDCl_3$ solutions of the complexes show signals which may be assigned to the coordinated dienes ($\delta = 4.20$ and 3.88 for the complexes of **9** and **10** respectively). The conductivity data, measured in acetone solution, are in accord with the neutrality of the complexes.

FAB mass spectrometry of [RhCl(cod)(AdDARD)] resulted in a molecular ion at m/z 411 (M + 1) and a peak at 375, corresponding to the loss of chloride ion, indicating the mononuclear nature of the complexes. There is a strong peak at 360, which we assign to the loss of an NH moiety, in the light of the observation that there is an exactly analogous fragmentation in the related complex of ^{t}BuCyDARD. The peak at m/z 265 may be assigned to a loss of chloride and $codH_2$, whilst the fragment at m/z 211 is {Rh(cod)}. In the spectrum of the complex of ^{t}BuCyDARD the M + 1 peak is at m/z 415, and the M − Cl peak at m/z 379. There is a strong peak at m/z 364, which corresponds to a loss of NH, and the peak for {Rh(cod)} at m/z 211 is also clear. The peaks owing to NH loss are interesting and, so far as we are aware, unprecedented.

TABLE 1. Microanalytical and conductivity data for rhodium complexes

Complex	Anal. (Found (calc.)(%))			Conductivity (Ω^{-1} cm^2 mol^{-1})
	C	H	N	
[RhCl(^{t}BuCyDARD)(cod)]	51.9 (52.1)	7.7 (7.7)	6.6 (6.7)	1.96
[RhCl(AdDARD)(cod)]	52.4 (52.6)	6.9 (6.8)	6.6 (6.8)	0.80
$[RhCl(CO)_2(^t$BuCyDARD)]	40.0 (39.7)	5.7 (5.5)	7.9 (7.7)	5.2
$[RhCl(CO)_2$(AdDARD)]	40.1 (40.2)	4.8 (4.5)	7.9 (7.8)	0.5
$[Rh(^t$BuCyDARD)(cod)$(PPh_3)][ClO_4]$	58.1 (58.3)	6.3 (6.3)	3.9 (3.8)	115.2
$[Rh$(AdDARD)(cod)$(PPh_3)][ClO_4]$	58.4 (58.7)	5.8 (5.8)	3.6 (3.8)	113.9
$[Rh$(AdDARD)(cod)$][ClO_4]$	45.6 (45.5)	5.8 (5.9)	5.8 (5.9)	110.7
$[Rh(^t$BuCyDARD)(cod)$][ClO_4]$	45.3 (45.5)	6.3 (5.9)	5.0 (5.8)	110.4

TABLE 2. IR spectroscopic data for the complexes [a]

Complex	ν(NH)	ν(CO) [b] cm^{-1}	ν(ClO_4)
[RhCl(^{t}BuCyDARD)(cod)]	3203(s), 3168(s)		
[RhCl(AdDARD)(cod)]	3166(s), 3137(sh)		
[RhCl$(CO)_2$(^{t}BuCyDARD)]	3200(s), 3180(s)	2089, 2016	
[RhCl$(CO)_2$(AdDARD)]	3210(s), 3200(sh)	2089, 2014	
[Rh(^{t}BuCyDARD)(cod)(PPh_3)][ClO_4]	3210(w)		
[Rh(AdDARD)(cod)(PPh_3)][ClO_4]	3210(w)		
[Rh(AdDARD)(cod)][ClO_4]	3220(w)		1091(s), 626(m)
[Rh(^{t}BuCyDARD)(cod)][ClO_4]	3220(w), 3200(w)		1091(s), 625(m)

[a] All the complexes showed C–H stretches in the range 2280–2290 cm^{-1}, and C–N stretches in the range 1110–1225 cm^{-1}. [b] Measured in CH_2Cl_2, all strong.

Similar apparent losses of {NH} are noted for the free ligands. It seems likely that nitrenes or nitrene complexes are being formed in these fragmentations, but this requires more extensive investigation.

Reaction of [RhCl(cod)(DARD)] with triphenylphosphine led to the formation of [RhCl(cod)(PPh_3)] with displacement of diaziridine. When carbon monoxide was bubbled through dichloromethane solutions of the complexes at room temperature, the species [RhCl$(CO)_2$(DARD)] were obtained by displacement of the diene, as yellow solids that could be isolated by addition of diethyl ether. IR spectroscopy, both in the solid state and in $CHCl_3$ solution showed two carbonyl stretching bands in the 2100–2000 cm^{-1} region, characteristic of mononuclear *cis*-dicarbonyl complexes [15]. Microanalytical, conductivity and IR spectroscopic data are shown in Tables 1 and 2.

We considered it to be of interest to study the reaction of the [RhCl(cod)(diaziridine)] complexes with Ag[ClO_4], to attempt to prepare cationic species. However, starting material was recovered from these reactions.

The cationic complexes [Rh(cod)(diaziridine)][ClO_4] were prepared by reaction of [Rh$(cod)_2$][ClO_4] with the diaziridine in CH_2Cl_2. IR spectroscopy (Table 2) showed bands that could be assigned to the coordinated diene, and uncoordinated perchlorate ions (1091(s) and 625(m) cm^{-1}). Conductivity data in acetone solution were in agreement with the characterisation of the complexes as 1 : 1 electrolytes. Microanalytical, conductivity and IR spectroscopic data are given in Tables 1 and 2, but the complexes were less stable than those in the neutral series.

The structure of [RhCl(cod)(^{t}BuCyDARD)] (*vide infra*) shows that the rhodium atom is coordinated to only one of the two nitrogen atoms of the diaziridine. However, in the cationic species in which we have shown the perchlorate ion to be uncoordinated, it is necessary to postulate that both of the nitrogen atoms are rhodium bound. This would necessitate a change in the normal stable *trans*-geometry noted for diaziridines to a more strained *cis*-structure. To the best of our knowledge there is no precedent for a diaziridine complex in which both nitrogen atoms are coordinated to the same metal centre, but there are no obvious alternatives. The low stability noted for the complexes may reflect the fact that this arrangement is not energetically very favourable. Treatment of [Rh(cod)(DARD)][ClO_4] with PPh_3 gave [Rh(cod)(DARD)(PPh_3)][ClO_4]. However, IR and ^{1}H NMR spectroscopic data do not allow us to distinguish between a planar four-coordinate complex with a monodentate diaziridine, and a square pyramidal species, in which the diaziridine ligand is bidentate. Attempts to grow crystals of the cationic complexes for X-ray diffraction studies have so far been unsuccessful.

Carbonylation of [Rh(cod)(DARD)][ClO_4] gave species which showed solution IR spectra characteristic of *cis*-dicarbonyl complexes, but these were too unstable to be isolated in a pure form.

2.3. Catalytic activity

It has been reported that rhodium(I) complexes of the type [Rh(diene)L_2]$^+$, in which L is a nitrogen ligand, may catalyse hydrogenation and/or hydroformylation under relatively mild conditions [16], but rhodium diaziridine complexes have not previously been tested in this context.

We now report the use of [RhCl(^{t}BuCyDARD)(cod)], [RhCl$(CO)_2$(^{t}BuCyDARD)] and [Rh(^{t}BuCyDARD)(cod)][ClO_4]/PPh_3, and the related complexes of the adamantyl diaziridine, as catalyst precursors for the hydrogenation and hydroformylation of 1-hexene. Ethanol solutions of the cyclooctadiene containing systems showed low activity for 1-hexene hydrogenation (25°C, 1 atm), but [RhCl(AdDARD)$(CO)_2$]/PPh_3 was inactive.

The complexes [RhCl(^{t}BuCyDARD)(cod)], [Rh(^{t}BuCyDARD)(cod)][ClO_4]/PPh_3 and [RhCl(AdDARD)$(CO)_2$]/PPh_3 were used as catalyst precursors

TABLE 3. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Rh	3519.0(3)	2033.9(3)	2007.3(4)	39(1)
Cl	4001.2(11)	3673.4(10)	2798.1(13)	54(1)
N1	4630(3)	1981(3)	1027(4)	40(2)
N2	5375(3)	2791(3)	1118(4)	50(2)
C1	5629(4)	1781(4)	1608(5)	39(2)
C2	5920(4)	1559(4)	3057(5)	46(3)
C3	6979(4)	1781(4)	3590(5)	49(3)
C4	7620(4)	1228(4)	2858(5)	45(2)
C5	7261(4)	1454(4)	1380(5)	46(3)
C6	6211(4)	1210(4)	843(5)	42(2)
C7	8699(4)	1419(5)	3430(6)	63(3)
C8	9279(5)	792(8)	2662(8)	97(5)
C9	8967(6)	2512(7)	3367(9)	118(5)
C10	9021(5)	1082(7)	4853(7)	86(4)
C11	2807(4)	835(5)	853(6)	62(3)
C12	3455(5)	457(4)	1951(7)	66(3)
C13	3232(6)	63(6)	3204(8)	92(4)
C14	2590(5)	749(6)	3755(7)	86(4)
C15	2673(4)	1836(5)	3397(6)	64(3)
C16	2138(4)	2311(6)	2260(6)	69(4)
C17	1410(5)	1813(8)	1147(8)	103(5)
C18	1752(5)	861(6)	685(8)	90(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 4. Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) Bonds			
Rh–Cl	2.376(1)	Rh–N1	2.107(4)
Rh–C11	2.109(6)	Rh–C12	2.101(5)
Rh–C15	2.136(7)	Rh–C16	2.104(6)
Rh–M1 [a]	1.988	Rh–M2	2.000
N1–N2	1.508(6)	N1–C1	1.442(6)
N2–C1	1.454(7)		
(b) Angles			
M1–Rh–M2	88.3	M1–Rh–Cl	178.2
M1–Rh–N1	90.1	M2–Rh–Cl	91.2
M2–Rh–N1	176.4	Cl–Rh–N1	90.5(1)
Rh–N1–N2	124.1(3)	Rh–N1–C1	126.9(3)
N1–N2–C1	58.2(3)	N2–N1–C1	59.0(3)
N1–C1–N2	62.8(3)		

[a] M1 and M2 are the mid-points of the C11–C12 and C15–C16 bonds.

for the hydroformylation of 1-hexene, under mild conditions (5 atm, $Co:H_2 = 1:1$, $T^a = 80°C$). Only with [Rh(ᵗBuCyDARD)(cod)][ClO_4]/PPh_3 was any significant reaction noted. After 330 min there was 26% conversion to aldehydes, with an *n:iso* ratio of 1.7:1.

It may be concluded that these types of complexes are not good catalysts for hydrogenation or hydroformylation of alkenes under mild conditions. The activities observed are considerably lower than those noted in related rhodium(I) complexes of nitrogen-containing ligands [16].

2.4. *Structure of [RhCl(cod){spiro(4-t-butylcyclohexane)diaziridine)}]*

This is, to the best of our knowledge, the first structural study of a metal diaziridine complex. There have been isolated reports of studies on diazirine complexes such as **4** [4] and some reports on aziridine complexes, particularly of zinc [17,18] and iron [19,20].

The structure of [RhCl(cod){spiro(4-t-butylcyclohexane)diaziridine)}] consists of monomeric neutral molecules. Atomic coordinates are given in Table 3 and selected bond distances and angles in Table 4. A view of the structure with atomic numbering is shown in Fig. 1.

The rhodium atom is in a slightly distorted square planar environment, coordinated to the carbon–carbon double bonds of the cyclooctadiene, chloride and one of the nitrogen atoms of the diaziridine. The cyclohexyl ring adopts an approximate chair geometry with both the tert-butyl group and the coordinated nitrogen atom equatorial. The hydrogen atoms attached to the nitrogen atoms of the diaziridine ring (which were located from a difference map and their positions refined) are *trans*, as expected.

There are a few data on structures of uncoordinated diaziridines, though most of these are highly substituted. The best data for comparison derive from the structures of **11** [21] and **12** [22]. Comparing the structural parameters for the diaziridine ring in **11** (N–N = 1.506, N^1–C = 1.505, N^2–C = 1.458 Å) with those in our complex suggest that there is little change on complexation. In this structure the N–H hydrogens were not directly located, so comparison with our data on these is not useful. The structure of **12** is relatively similar although the bond lengths are longer (N–N = 1.58, N^1–C = 1.57, N^2–C = 1.58 Å), but the data are of relatively poor quality. Electron diffraction data on **13**

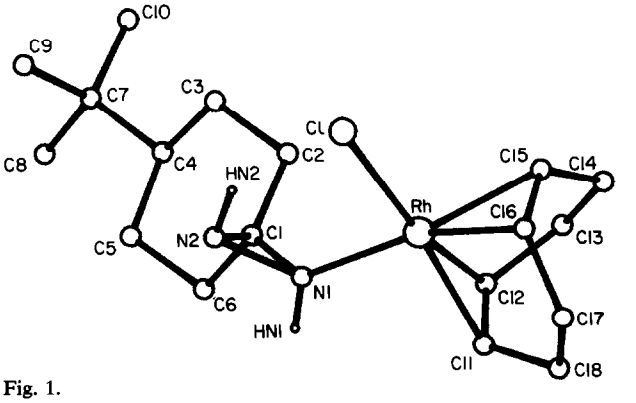
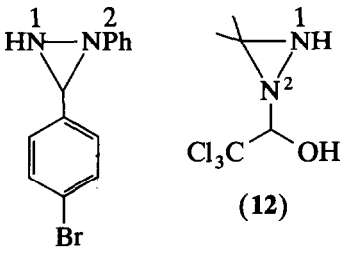


Fig. 1.

gave rather shorter bond lengths (N–N = 1.468, C–N = 1.479 Å) [23]. The hydrogen atoms were located from the difference map in the structure of the cation, **14** [24], but their positions were not refined, so detailed comparison is unwarranted.



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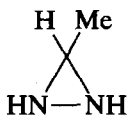

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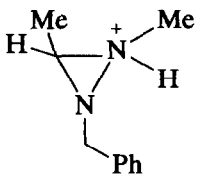

(14)

The structure of *trans*-$[RhI_2(az)_4]I$ (az = aziridine) has been established [25]. The authors comment that the bond lengths (C–N = 1.47(4), C–C = 1.36(5) Å) are significantly different from those in the free ligand, but the errors in the bond lengths are high. The rhodium–nitrogen bond length is shorter (1.99(2)) than in our complex, though this may in part reflect the difference in oxidation state between the two complexes. The structure of $[Co(NO_2)_2(az)_4]Br \cdot 2H_2O \cdot LiBr$ has recently been established [9]. The C–C bond in the complexes ligand is somewhat shorter than in the free ligand, as for the rhodium derivative. Data from $[PtCl_2(az)_2]$ are of too poor quality to make a useful comparison.

3. Experimental details

All preparations of organometallic complexes were carried out under dry nitrogen using Schlenck techniques. Solvents were distilled and degassed prior to use. Elemental analyses were carried out with a Perkin Elmer 240B microanalyser. IR spectra were recorded on a Nicolet 5ZDX-FT or a Perkin Elmer 1430 spectrometer and are referenced to polystyrene. ^1H and ^{31}P NMR spectra were recorded using Varian XL200 or Bruker WM360 spectrometers with Me_4Si and 85% H_3PO_4 respectively as references.

3.1. Preparation of spiro(4-t-butylcyclohexane)diaziridine

4-t-Butylcyclohexanone (30.8 g, 0.2 mol) was dissolved in methanol (100 ml), contained in a three-necked 500 ml flask fitted with a gas inlet and a dry-ice condenser. The solution was cooled to −15°C and ammonia gas (200 ml) condensed into the flask, with vigorous stirring. Stirring was continued under nitrogen for 2 h. The gas inlet was then replaced by a pressure-equalising funnel containing a solution of hydroxylamine-*O*-sulphonic acid (25 g) in methanol (150 ml), which was added over 15 min. The mixture was stirred for 2 h at −15°C, and after being allowed to warm slowly to room temperature, for a further 14 h at 25°C, the partially dissolved residue was poured into water (400 ml) and extracted with CH_2Cl_2 (5 × 50 ml). The combined organic layers were extracted with 1 M sulphuric acid (3 × 100 ml), and the free diaziridine precipitated from the latter by the addition of 5 M NaOH solution (100 ml). This was re-extracted into CH_2Cl_2 (3 × 100 ml), the combined layers dried ($Mg[SO_4]$), and the solvent removed under reduced pressure to give the crude diaziridine (3.1 g, 11%) as a colourless solid which was used without further purification. Pure *spiro*(4-t-butylcyclohexane)diaziridine) could be obtained by recrystallisation ($CHCl_3$/heptane) as colourless needles, m.p. 107–108°C.

Microanalysis. Found: C, 71.3; H, 11.9; N, 16.5. $C_{10}H_{20}N_2$ calc.: C, 71.4; H, 12.0; N, 16.6%. IR (KBr): 3197 (N–H), 3184 (N–H), 2955, 2943, 2911, 2851, 1365, 1212, 1182, 1169, 1115, 1102, 882 cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 0.86 (9H, s, CMe_3); 1.05 (1H, t of t, J = 12, 3 Hz, H^4); 1.14 (3H, m); 1.37 (1H, m); 1.51 (1H, d, J = 6.5 Hz, NH); 1.67 (1H, d, J = 7 Hz, NH); 1.83 (3H, m); 2.12 (1H, t of d, J = 14, 3.7 Hz, H^{2a}). ^{13}C NMR ($CDCl_3$, 270 K): δ 57.5 (C^1); 47.0 (C^4); 36.6, 35.8 (C^2, $C^{2'}$); 32.3 (CMe_3); 27.5 (CMe_3); 25.8, 25.4 (C^3, $C^{3'}$). MS (+ve FAB): 169 (MH^+); 154 ($MH^+ - NH$); 57 (Me_3C^+).

3.2. Preparation of spiro(adamantane-2)diaziridine [26]

A 250 ml three-necked flask fitted with a pressure equalising funnel, gas inlet, dry-ice condenser, dring tube and magnetic follower was cooled to −78°C. Liquid NH_3 (11 ml) was condensed into the flask, and 2-adamantanone (4.5 g, 30 mmol) and methanol (85 ml) were added. A solution of hydroxylamine-*O*-sulphonic acid (4.2 g, 30 mmol) in methanol (36 ml) was then added dropwise to the vigorously stirred reaction mixture. After stirring at −78°C for 4 h, the mixture was allowed to warm slowly to room temperature overnight. The white solid residue obtained was dissolved in a mixture of 1 M H_2SO_4 (100 ml) and CH_2Cl_2 (400 ml). This was separated and the organic layer extracted further with 1 M H_2SO_4 (4 × 50 ml). The combined acid extract was made alkaline with 5 M NaOH solution, precipitating the crude product as a white solid. This was re-extracted with CH_2Cl_2 (5 × 40

ml) and the combined extracts dried [$K_2[CO_3]$], filtered through Celite and the solvent removed under reduced pressure to afford the diaziridine (3.9 g, 80%) as a colourless solid which was used without further purification.

IR (KBr): 3218, 2927, 2904, 2852, 1655, 1449, 1258, 1147, 897 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.28 (br s, 2H); 1.9 (m, 12H); 2.55 (br s, 1H); 2.7 (br t, 1H); 3.3 (br m, 1H); 3.6 (br s, 1H). ^{13}C NMR ($CDCl_3$): δ 26.6 (C^4); 35.4 (C^4); 36.65 (C^5); 38.3 (C^3); 63.0 (C^1). MS (EI): 165 (MH^+); 150 ($MH^+ - NH$).

3.3. Preparation of [RhCl(cod){spiro(4-t-butylcyclohexane)diaziridine}]

To a solution of di-μ-chloro bis(cyclooctadiene)dirhodium (319.6 mg, 0.6 mmol) in CH_2Cl_2 (2 ml) was added *spiro*(4-t-butylcyclohexane)diaziridine (201.2 mg, 1.2 mmol). The bright yellow suspension was stirred for 15 min and then poured into diethylether. The yellow suspension was cooled in ice, the solid collected by filtration, washed (Et_2O, 25 ml) and dried under reduced pressure to give [RhCl(cod){*spiro*(4-t-butylcyclohexane)diaziridine}] (233 mg, 86.7%).

IR (KBr): 3204, 3171, 2965, 1266, 1123, 811, 292 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.93 (s, 9H, $C(CH_3)_3$); 1.2 (m, 2H); 1.7–2.2 (m, 11H); 2.45 (m, 4H, CH_2 of cod); 4.20 (br s, 4H, C*H*=C). ^{13}C NMR ($CDCl_3$); δ 25.36, 25.45 (C^3, $C^{3'}$ diaziridine); 27.51 ($C(CH_3)_3$); 30.63 (CH_2, cod); 32.39 ($C(CH_3)_3$); 33.77, 34.89 (C^2, $C^{2'}$, diaziridine); 46.56 (C^4, diaziridine); 63.5 (C^1, diaziridine); 79.55 (br, *C*H=C, cod). MS (FAB): 415 (M + 1); 379 (M − Cl); 364 (M − Cl − NH); 211 ({Rh(cod)}).

3.4. Preparation of [RhCl(cod){spiro(adamantane-2)diaziridine}]

To a solution of di-μ-chloro bis(cyclooctadiene)dirhodium (56 mg, 0.11 mmol) was added *spiro*(adamantane-2)diaziridine (44.7 mg, 0.27 mmol), and the pale yellow solution was stirred for 15 min. Addition of diethyl ether caused the precipitation of a pale yellow solid, which was washed (hexane, 2 × 2 ml), collected by filtration and dried *in vacuo* to give the desired complex (90 mg, 82%) as a pale yellow powder.

^1H NMR ($CDCl_3$): δ 1.25 (m, 1H); 1.93 (m, 12H); 2.03 (br s, 2H); 2.44 (m, 8H, CH_2 of cod); 3.88 (m, 4H, C*H*=C). MS (FAB): 411 (M + 1); 375 (M − Cl); 360 (M − Cl − NH); 310; 265 (M − Cl − codH_2); 211 ({Rh(cod)}).

3.5. Preparation of [Rh(cod){spiro(4-t-butylcyclohexanediaziridine)}][ClO_4]

Spiro(4-t-butylcyclohexanediaziridine) (17 mg, 0.1 mmol) was added to a solution of [$Rh(cod)_2$][ClO_4] (50 mg, 0.12 mmol), and the solution stirred for 15 min. Addition of an excess of diethyl ether gave a yellow precipitate which was collected by filtration, washed (hexane, 2 × 2 ml) and dried *in vacuo* to give the required complex (31 mg, 64%).

^1H NMR spectrum ($CDCl_3$): δ 0.92 (s, 9H, $C(CH_3)_3$); 1.72–2.5 (broad peaks, 17H); 3.8–4.50 (br m, 4H, C*H*=C).

3.6. Preparation of [Rh(cod){spiro(adamantane-2)diaziridine)}][ClO_4]

Spiro(adamantane-2)diaziridine (30 mg, 0.18 mmol) was added to a solution of [$Rh(cod)_2$][ClO_4] (50 mg, 0.12 mmol) in CH_2Cl_2. Addition of Et_2O caused the precipitation of a yellow solid which was collected by filtration, washed (hexane, 2 × 2 ml) and dried *in vacuo* to give the desired complex (60 mg, 70%).

^1H NMR ($CDCl_3$): δ 1.31 (m, 1H, H_α); 1.90 (m, 12H); 2.55 (m, 8H, CH_2, cod); 3.57 (m, 1H, H_α); 4.00 (m, 4H, C*H*=C*H*).

3.7. Preparation of [RhCl(CO)$_2$(diaziridine)] complexes

Carbon monoxide (1 atm) was bubbled at room temperature through a CH_2Cl_2 solution of [RhCl(cod)(diaziridine)]. A yellow solid was precipitated by addition of Et_2O, washed (cold hexane, 2 × 2 ml) and dried *in vacuo* to give the desired complexes in approximately 80% yield.

[RhCl(^{t}BuCyDARD)$(CO)_2$]. ^1H NMR ($CDCl_3$): δ 0.92 (s, 9H, $C(CH_3)_3$); 1.18 (m, 1H, H^{3e}); 1.22 (t, 2H, H^{3a}); 1.42 (m, 1H, H^{3e}); 1.70 (m, 1H, H^{2e}); 1.82 (m, 2H, H^{2a}); 2.20 (m, 1H, H^4).

3.8. Structure of [RhCl(cod){spiro(4-t-butylcyclohexane)diaziridine)}]

Suitable crystals were grown by slow diffusion of ether into a dichloromethane solution of the complex. Data were collected using a crystal *ca.* 0.4 × 0.2 × 0.05 mm on an Enraf Nonius CAD-4 diffractometer in the θ–2θ mode, with $\Delta\theta = (0.8 + 0.35 \tan\theta)°$, and a maximum scan time of 1 min. A total of 3596 reflections were measured in the range $2 < \theta < 25°$, h 0 → 12, k 0 → 15, l −17 → 17, and 2024 reflections with $|F^2| > 3\sigma(F^2)$ where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$ were used in the refinement. There was no significant change in three standard reflections measured every hour, and no correction was made for absorption. Lorentz and polarisation corrections were made. The structure was solved by routine heavy atom methods using SHELXS-86 [27] with refinement by full matrix least squares using SDP-PLUS programs [28] with non-hydrogen atoms anisotropic. Hydrogen atoms were located on the difference map and refined isotropically, with the exception of H16 which had to be fixed in position from the map. The weighting scheme was $\omega = 1/\sigma^2(F)$, with

$\Sigma\sigma(|F_o| - |F_c|)^2$ minimised, and the final residuals were $R = 0.031$, $R' = 0.032$, $s = 1.6$, $(\Delta/\sigma)_{max} = 0.35$, $\Delta\rho_{max,min} = 0.44$, -0.37 e Å^{-3}. Atomic scattering factors were taken from International Tables for Crystallography. Programs from the Enraf-Nonius SDP-PLUS package were run on a MicroVAX II computer.

The crystal was monoclinic, space group $P2_1/c$, $a = 14.408(2)$, $b = 13.312(2)$, $c = 10.484(4)$ Å, $\beta = 104.36(2)°$, $U = 1947.9$ Å^3, $Z = 4$, $D_c = 1.41$ g cm^{-3}, $F(000) = 860$. Monochromated Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 10.0$ cm^{-1}. A complete table of bond lengths and angles, tables of thermal parameters and hydrogen atom coordinates are available from PBH.

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