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Bis(acetylacetonato)ruthenium(II) complexes containing bulky tertiary phosphines. Formation and redox behaviour of $Ru(acac)_2$ (PR₃) (R = ^{*i*}Pr, Cy) complexes with ethene, carbon monoxide, and bridging dinitrogen

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Dedicated to Professor Gordon Stone, FRS, on the occasion of his 80th birthday

Abstract

Reaction of cis-[Ru(acac)₂(η^2 -C₈H₁₄)₂] (1) (acac = acetylacetonato) with two equivalents of PⁱPr₃ in THF at -25 °C gives *trans*- $[Ru(acac)_2(P^iPr_3)_2]$, trans-3, which rapidly isomerizes to cis-3 at room temperature. The poorly soluble complex $[Ru(acac)_2(PCy_3)_2]$ (4), which is isolated similarly from cis-[Ru(acac)₂(η^2 -C₂H₄)₂] (2) and PCy₃, appears to exist in the *cis*-configuration in solution according to NMR data, although an X-ray diffraction study of a single crystal shows the presence of trans-4. In benzene or toluene 2 reacts with $P^{i}Pr_{3}$ or PCy_{3} to give exclusively *cis*-[Ru(acac)₂(η^{2} -C₂H₄)(L)] [L = $P^{i}Pr_{3}$ (5), PCy_{3} (6)], whereas in THF species believed to be either square pyramidal [Ru(acac)₂L], with apical L, or the corresponding THF adducts, can be detected by ³¹P NMR spectroscopy. Complexes 3-6 react with CO (1 bar) giving trans-[Ru(acac)₂(CO)(L)] [L = PⁱPr₃ (trans-8), PCy₃ (trans-9)], which are converted irreversibly into the cis-isomers in refluxing benzene. Complex 5 scavenges traces of dinitrogen from industrial grade dihydrogen giving a bridging dinitrogen complex, cis-[{Ru(acac)₂(PⁱPr₃)} ₂(μ -N₂)] (10). The structures of cis-3, trans-4, 5, 6 and 10 · C₆H₁₄ have been determined by single-crystal X-ray diffraction. Complexes trans- and cis-3, 5, 6, cis-8, and trans- and cis-9 each show fully reversible one-electron oxidation by cyclic voltammetry in CH₂Cl₂ at -50 °C with $E_{1/2}(Ru^{3+/2+})$ values spanning -0.14 to +0.92 V (versus Ag/AgCl), whereas for the vinylidene complexes $[Ru(acac)_2 (C=CHR)(P^iPr_3)]$ $[R = SiMe_3 (11), Ph (12)]$ the process is irreversible at potentials of +0.75 and +0.62 V, respectively. The trend in potentials reflects the order of expected π -acceptor ability of the ligands: $P^{i}Pr_{3}$, $PCy_{3} < C_{2}H_{4} < C = CHR < CO$. The UV-Vis spectrum of the thermally unstable, electrogenerated Ru^{III} ethene cation 6^+ has been observed at -50 °C. Cyclic voltammetry of the μ -dinitrogen complex 10 shows two, fully reversible processes in CH₂Cl₂ at -50 °C at +0.30 and +0.90 V (versus Ag/AgCl) corresponding to the formation of 10⁺ (Ru^{II,III}) and 10²⁺ (Ru^{III,III}). The former, generated electrochemically at -50 °C, shows a band in the near IR at ca. 8900 cm⁻¹ ($w_{1/2}$ ca. 3700 cm⁻¹) consistent with the presence of a valence delocalized system. The comproportionation constant for the equilibrium $10 + 10^{2+} \Rightarrow 2 \ 10^+$ at 223 K is estimated as $10^{13.6}$. © 2004 Elsevier B.V. All rights reserved.

Keywords: Ruthenium (II) complex; Acetylacetonato complex; Redox behaviour; X-ray crystal structure

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1. Introduction

Reduction of tris(acetylacetonato)ruthenium(III), [Ru(acac)₃], with zinc dust or zinc amalgam in the presence of a variety of ligands (L) provides a convenient synthesis of ruthenium(II) complexes of the type [Ru(acac)₂L₂]. The procedure was employed first by Satô and coworkers [1] to prepare the acetonitrile complex *cis*-[Ru(acac)₂(NCMe)₂] and has been extended both to complexes containing bidentate ligands such as S-BI-NAP [2], chelating dienes [3,4] and conjugated dienes [5–7], and to more labile complexes containing monoalkenes [cyclooctene (C₈H₁₄) and ethene (C₂H₄)] [4,8] and monodentate Group 15 donors such as triisopropylstibine (SbⁱPr₃) and triisopropylphosphine (PⁱPr₃) [9].

Werner and coworkers [9] have shown that one of the stibine ligands of cis-[Ru(acac)₂(Sb^{*i*}Pr₃)₂] is easily replaced to give the mixed ligand species cis-[Ru $(acac)_2(L)(Sb^iPr_3)$] (L = PⁱPr₃, PCy₃, C₂H₄, C=CHPh). We have reported [4] that many ligands (L) replace the labile alkenes in *cis*-[Ru(acac)₂(η^2 -alkene)₂] [alkene = C_8H_{14} (1), C_2H_4 (2)] to give, unexpectedly, the *trans*-isomers of $[Ru(acac)_2L_2]$ (L = PMe₃, PEt₃, PMe₂Ph, PMePh₂, P(OMe)₃, P(OPh)₃, ^tBuNC), which isomerize on heating to the more stable cis-complexes, probably via an undetected fluxional square pyramidal intermediate Ru(acac)₂L. With some ligands, it is possible to isolate mono-substitution products cis-[Ru $(acac)_2(\eta^2 - alkene)(L)]$ (alkene = C₈H₁₄, C₂H₄, L = SbPh₃, MeCN, NH₃; alkene = C_2H_4 , L = py) and, in two cases, (alkene = C_2H_4 , L = NH₃, py), intermediate trans-isomers have been identified [8]. Thus, the first substitution in *cis*-[Ru(acac)₂(η^2 -alkene)₂] probably also proceeds via a five-coordinate intermediate, Ru(a $cac)_2(\eta^2$ -alkene). However, the tertiary phosphines that

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we have used so far evidently replace the second alkene in **1** or **2** more rapidly than the first, since mono-substitution products could not be detected in these cases. It seemed possible that the second step could be slowed by use of bulky ligands such as $P'Pr_3$ and PCy_3 and we report here our results, which complement and extend those of Werner and coworkers [9].

2. Results

2.1. General

The chemistry to be described is summarized in Schemes 1–3. Elemental analyses and mass spectrometric data for the new bis(acac) complexes are listed in Table 1; selected IR and NMR data are collected in Tables 2 and 3. All the compounds show two or three intense bands in the regions of 1590–1570 and 1525–1510 cm⁻¹ of their IR spectra (Table 2), which are characteristic of O-bonded acac in its usual bidentate mode [10]. In general, the number of bands observed is unfortunately not diagnostic of the *cis-* or *trans*-arrangement of acac groups; this feature, however, is easily established from the ¹H and ¹³C NMR spectra (Table 3) [4,8].

2.2. $[Ru(acac)_2L_2]$ complexes

Addition of two equiv of P^iPr_3 to a solution of **1** in THF at -25 °C causes the precipitation within 1 h of *trans*-[Ru(acac)₂(P^iPr_3)₂] (*trans*-**3**) as a moderately airsensitive, rust-red solid, which can be isolated in ca. 45% yield (Scheme 1). The corresponding reaction with **2** is slower, no precipitate having formed after 1 h. As expected, the ¹H and ¹³C{¹H} NMR spectra of *trans*-**3**



Scheme 1.



Table 1				
Elemental analyses ^a	and mass spectra c	f Ru(acac) ₂ (PR ₃)	complexes (R =	= ^{<i>i</i>} Pr, Cy)

Complex	%C	%H	%P	m/z (% relative abundance, assignment)
<i>trans</i> -[Ru(acac) ₂ ($P^{i}Pr_{3}$) ₂] (3) ^b				460.2 (100, $M - P^{i}Pr_{3}$)
cis-[Ru(acac) ₂ (P ⁱ Pr ₃) ₂] (3)	54.26 (53.32)	8.38 (8.38)		620.0 (12, M), 519 (7, M - acac),
				459.9 (100, $M - P^{i}Pr_{3}$)
$[Ru(acac)_2(PCy_3)_2]$ (4)	64.23 (64.23)	9.37 (9.57)	7.20 (6.93)	860.5 (6, M), 580.2 (100, M – PCy ₃)
cis -[Ru(acac) ₂ (η^2 -C ₂ H ₄)(P ^{<i>i</i>} Pr ₃)] (5)	51.73 (51.10)	8.06 (7.61)		460.1 (100, $M - C_2H_4$), 359.1 [10, $Ru(acac)(P'Pr_3)$],
				300.0 [17, Ru(acac) ₂]
cis -[Ru(acac) ₂ (η^2 -C ₂ H ₄)(PCy ₃)] (6)	59.29 (57.78)	8.46 (8.11)		860.5 [2, $Ru(acac)_2(PCy_3)_2$], 580.3 (100, $M - C_2H_4$)
trans-[Ru(acac) ₂ (CO)(P ⁱ Pr ₃)] (8)	49.27 (49.10)	7.24 (7.25)	6.35 (6.36)	460.1 (100, M – CO)
cis-[Ru(acac) ₂ (CO)(P ⁱ Pr ₃)] (8)	49.27 (49.20)	7.24 (6.90)	6.35 (6.03)	488.2 (45, M), 460.2 (100, M - CO), 389.1 (24, M - acac)
trans-[Ru(acac) ₂ (CO)(PCy ₃)] (9)	57.31 (57.08)	7.79 (7.66)	5.10 (4.62)	580.1 (53, M – CO), 297.1 [50, Ru(acac) ₂]
<i>cis</i> -[Ru(acac) ₂ (CO)(PCy ₃)] (9)	57.31 (57.21)	7.79 (7.87)	5.10 (4.87)	608.3 (62, M), 580.2 (100, M - CO), 509.2 (31, M - acac)
$cis-[{Ru(acac)_2(P^iPr_3)}_2(\mu-N_2)]$ (10)	48.19 (48.07)	7.45 (7.61)	2.96 (2.63) (N)	950.2, 948.2 (M), 460.2 [100, Ru(acac) ₂ (P ⁱ Pr ₃)]

^a Found values in parentheses.

^b Elemental analyses not obtained owing to thermal instability of compound.

in d⁸-toluene at -35 °C show one sharp singlet each for the acac methyl and methine groups and the ¹³C{¹H} NMR spectrum contains just one C=O resonance; however, the ¹H and ¹³C resonances of the isopropyl groups are broad, possibly because of restricted rotation about the Ru–P bonds. Rotamers arising from hindered rotation about M–P bonds have been observed at low temperature for a variety of four- and five-coordinate complexes containing bulky ligands such as *t*-butylphosphines and PCy_3 [11–16].

When a solution of *trans*-**3** in d⁸-toluene is warmed from -35 to +5 °C, quantitative *trans*- to *cis*-isomerization occurs, as is evident from the disappearance of the ${}^{31}P{}^{1}H{}$ NMR singlet at δ 29.6 and its replacement by a M.A. Bennett et al. | Inorganica Chimica Acta 358 (2005) 1692-1708

Table 2 Characteristic IR and NMR data for $Ru(acac)_2(PR_3)$ complexes (R = ^{*i*}Pr, Cy)

Complex	$IR (cm^{-1})^a$	NMR (δ) ^b
3	1565, 1507 (acac)	
4	1563, 1506 (acac)	
5	1583, 1514 (acac)	¹ H: 4.00–4.60 (m, C_2H_4); ¹³ C: 69.6 (s, C_2H_4)
6	1585, 1512 (acac)	¹ H: 3.78–4.38 (m, C_2H_4); ¹³ C: 69.5 (s, C_2H_4)
trans-8	1565, 1517 (acac), 1931 (C=O)	¹³ C: 206.5 (d, J _{PC} 120, CO)
cis-8	1588, 1573, 1516 (acac), 1928 (C=O)	¹³ C: 209.4 (d, <i>J</i> _{PC} 20, C=O)
trans-9	1572, 1510 (acac), 1950 (C=O)	13 C: 206.8 (d, J_{PC} 120, CO)
cis-9	1589, 1575, 1520 (acac), 1944 (CO)	¹³ C: 209.6 (d, J_{PC} 18, C \equiv O)
10	1582, 1512 (acac), 2089 (N≡N) ^c	

^a Bands refer to KBr disks, except where stated.

^b In C₆D₆, coupling constants J are in Hertz.

^c Raman.

singlet at δ 47.7. The *cis*-isomer is also formed by direct reaction of **1** or **2** with two equivalents of P^{*i*}Pr₃ at room temperature and can be isolated as an orange solid, identical with the product reported by Werner and coworkers [9]. The *cis*-configuration is evident from the ¹H and ¹³C{¹H} NMR spectra, which show two acac methyl singlets and one methine singlet; in addition, there are two C=O resonances in the ¹³C{¹H} NMR spectrum. The structure of *cis*-**3** has been confirmed by X-ray crystallography (see below).

Addition of two equiv of PCy₃ to a solution of **1** or **2** in THF at room temperature gives a rust-red solid of empirical formula [Ru(acac)₂(PCy₃)₂] (**4**), which can be isolated in ca. 80% yield. At room temperature it is almost insoluble in benzene or toluene and only slightly soluble in THF, but on warming it dissolves completely in all three solvents to give orange-brown solutions. The NMR spectra of the red-brown solid that crystallizes from toluene are identical with those of the original solid and the X-ray structure of a single crystal selected from the batch shows it to be the *trans*-isomer (see below). However, the ¹H and ¹³C{¹H} NMR spectroscopic data (two acac CH₃ singlets, one acac methine singlet, and two C=O resonances) are consistent with the presence of *cis*-**4** as the main species in solution.

The ³¹P{¹H} NMR chemical shift also agrees better with a *cis*-formulation, although the evidence is not decisive. The spectrum in d⁸-toluene at room temperature consists of a very broad peak (half-width 145 Hz) at δ 38.5, which sharpens on warming to 100 °C and separates into two peaks of unequal intensity at δ 37.7 and 36.9 at -65 °C. At the lowest temperature the ¹H and ¹³C resonances of the cyclohexyl groups were broad and provided no information. Similar behaviour has been observed for *cis*-[Ru(O₂CMe)₂(PCy₃)₂] [9], *trans*-[W(CO)₃(PCy₃)₂] [14], and *trans*-[Re(CO)₃(PCy₃)₂]⁺ [15], and, in the last two cases, was attributed to the presence of rotamers. Shaw and coworkers [16–18] have shown that the ³¹P shifts caused by coordination in a series of tertiary phosphine complexes, such as *trans*- $[PdX_2L_2]$, *cis*- $[PdX_2L_2]$, and *trans*- $[RhCl(CO)L_2]$, are related linearly to the chemical shifts of the free phosphines. We find the same to hold for the complexes *cis*- and *trans*- $[Ru(acac)_2L_2, ^1$ the equations for the best straight lines being given in Eqs. (1) and (2):

$$cis: \Delta \delta = 50.3 - 0.72 \delta_{\rm P}({\rm ligand}),$$
 (1)

$$trans: \Delta \delta = 31.4 - 0.71 \delta_{\rm P}(\text{ligand}), \tag{2}$$

where

 $\Delta \delta = \delta_{\rm P}(\text{complex}) - \delta_{\rm P}(\text{ligand}).$

On this basis the ³¹P chemical shifts calculated for *cis*and *trans*-4 are +43.9 and +26.0, respectively, and the observed value is clearly closer to that expected for *cis*-4. The similarity between the observed values for the ³¹P chemical shifts for 4 and *cis*-[Ru(acac)₂(η^2 -C₂H₄)(PCy₃)] (see below) also supports this assignment. The matter could perhaps be settled by solid-state ³¹P NMR spectroscopic measurements but these have not been carried out.

There was no reaction between 1 and an excess of $P'Bu_3$, even after a week at room temperature.

2.3. $[Ru(acac)_2(L)(L')]$ complexes

The reactions of complex **2** with one equiv of P^iPr_3 or PCy_3 are solvent-dependent, as shown by ³¹P NMR spectroscopy (Scheme 1). For P^iPr_3 in THF at -35 °C the first detectable product is the bis(ligand) complex *trans*-**3** (δ_P 29.6), but when the solution is allowed to warm to ca. 10 °C this disappears and is replaced by singlets at δ 87.3, 50.5 and 19.2, the last being due to free P^iPr_3 . Similarly, addition of one equiv of PCy₃ to **2** in THF at -35 °C gives initially a singlet at δ 21.0, whose chemical shift suggests that it may be due to *trans*-**4** (see above), together with a peak at δ 8.9 due to free PCy₃. When the solution is brought to ca. 0 °C for 30 min, a

¹ The ³¹P chemical shifts are provided as supplementary material.

Complex	acac					PR ₃		
	¹ H		¹³ C			¹ H	¹³ C	³¹ P
	CH ₃	СН	CH ₃	СН	C=0			
trans-3 ^b	1.75	5.10	27.4	100.5	184.1	1.32 (br, CH ₃), 2.30 (br, CH)	20.0 (br, CH ₃), 24.8 (br, CH)	29.6
cis-3	1.78, 1.91	5.30	27.8, 27.9	99.8	183.6, 186.8	1.24, 1.37 (each dd, J _{PH} 11, J _{HH} 7.2, CH ₃), 2.46 (m, CH)	27.6 (d, J _{PC} 9, CH ₃), 38.0 (br, CH)	47.7
4	1.82, 1.94	5.28	27.7 (d, <i>J</i> _{PC} 2.2), 28.0	100.3	183.5, 186.7	1.15–1.45, 1.60–2.10, 2.20–2.40 (each m, CH ₂ , CH)	27.5, 29.1 (m), 30.2 (br, CH ₂), 38.0 (br, CH)	38.5 (br)
5	1.84, 1.86, 1.88, 1.94	5.30, 5.35	27.2, 27.5, 28.1 (d, J _{PC} 5.6), 28.3	98.1, 99.8	184.7, 185.0, 185.5 (d, J _{PC} 2.2), 187.7	1.08, 1.23 (each dd, J_{PH} 12, J_{HH} 7.2, CH ₃), 2.45 (m, CH)	19.0, 19.4 (CH ₃), 24.8 (d, J _{PC} 19, CH)	50.5
6	1.83, 1.86, 1.87, 1.98	5.30, 5.40	27.6, 27.7, 28.1 (d, J _{PC} 5.6), 28.4	98.2, 99.8	184.5, 184.9, 185.6 (d, J _{PC} 2.2), 187.7	1.10–2.25 (br m, CH ₂ , CH)	27.2, 28.5, 28.6, 28.7, 28.9, 29.2 (CH ₂), 35.4 (d, J _{PC} 19, CH)	40.0
7	1.62, 1.64, 1.88, 1.96	5.07, 6.45	27.3, 28.0, 28.2, 28.3 (d, J _{PC} 6.0)	98.9, 99.2	184.2, 185.8, 186.0, 186.8	7.04–7.06 (m, <i>m</i> -, <i>p</i> -arom), 7.62–7.68 (m, <i>o</i> -arom)	nm	54.7
trans-8	1.70	5.08	27.0	100.8	189.1	1.23 (dd, <i>J</i> _{PH} 12, <i>J</i> _{HH} 7.1, CH ₃), 2.25 (m, CH)	19.1 (CH ₃), 23.1 (d, J _{PC} 20, CH)	18.9
<i>cis</i> - 8	1.71, 1.79, 1.85, 1.91	5.16, 5.34	27.2, 27.7, 27.8, 28.0	99.1, 100.2	186.0, 186.5, 187.8, 189.1	1.13, 1.25 (each dd, J_{PH} 13, J_{HH} 7.0, CH ₃), 2.25 (m, CH)	18.8, 19.4 (CH ₃), 24.7 (d, J _{PC} 22, CH)	61.5
trans -9	1.73	5.09	27.0	100.6	188.9	1.05–1.40, 1.50–2.30 (br m, CH ₂ , CH)	27.1, 28.6 (d, <i>J</i> _{PC} 8.8), 29.1 (CH ₂), 33.3 (d, <i>J</i> _{PC} 10, CH)	8.4
cis-9	1.73, 1.86, 1.86, 1.98	5.17, 5.40	27.3, 27.8 (d, <i>J</i> _{PC} 5.4), 27.9, 28.1	99.2, 100.3	186.0, 186.4, 187.9, 189.0	1.10–1.30, 1.50–2.00, 2.10–2.30 (br m, CH ₂ , CH)	27.0, 28.2 (d, J_{PC} 2), 28.4 (d, J_{PC} 3), 29.0 (d, J_{PC} 2), 29.5 (CH ₂), 35.1 (d, J_{PC} 21, CH)	52.3
10 ΔΔ/ΛΛ	1.81, 1.83, 1.85, 2.03	5.26, 5.33	27.2, 27.6, 27.8, 28.3 (d, J _{PC} 5.6)	98.5, 100.3	184.6, 185.7, 186.4, 187.5	1.29, 1.40 (each dd, J _{PH} 12.5, J _{HH} 7.5, CH ₃), 2.47 (m, CH)	19.2, 19.5 (CH ₃), 24.6 (d, J_{PC} 20, CH)	60.6
10 ΔΛ/ΛΔ	1.80, 1.87, 2.08	5.29, 5.35	27.2, 27.6, (d, J _{PC} 5.6)	98.6, 100.3	184.5, 185.8, 187.6	1.29, 1.40 (each dd, J _{PH} 12.5, J _{HH} 7.5, CH ₃), 2.47 (m, CH)	19.1, 19.4 (CH ₃), 24.6 (d, <i>J</i> _{PC} 20, CH)	60.5

Table 3 NMR data for acac and PR₃ in Ru(acac)₂(PR₃) complexes (R = i Pr, Cy)^a

^a Measured in C₆D₆ at 20.5 °C, except where stated otherwise; resonances are singlets, except as indicated; coupling constants (*J*) in Hertz. ^b In d⁸-toluene at -40 °C.

new species is formed that shows a singlet at δ 74.7, and at 25 °C a second species of unknown origin characterized by a singlet at δ 39.7 appears. The compounds responsible for the highly deshielded resonances at δ 87.3 (L = P'Pr₃) and 74.7 (L = PCy₃) are likely to be either the five-coordinate, probably square pyramidal species [Ru(acac)₂L], or possibly six-coordinate solvent adducts [Ru(acac)₂(L)(THF)]; similar deshielded resonances have been observed for apical PPh3 in well-established square pyramidal ruthenium(II) complexes such as $[RuCl_2(PPh_3)_3]$ (δ_P 75.7) [19], [RuX(NN'N)(P-Ph₃)]OTf [δ_P 86.6 (X=Cl), 74.5 (X=OTf); NN'N= 2,6-[bis(dimethylamino)methyl]pyridine] [20], and $[Ru{N(SPR_2)_2}(PPh_3)] [\delta_P 75.1 (R = {}^{i}Pr), 77.8 (R=Ph)]$ [21].

The same highly deshielded resonances appear in solutions of **3** and **4** in THF at room temperature, together with those for the original compounds and the free ligands, evidently owing to ligand dissociation (Scheme 1). Moreover, the ¹H NMR spectrum of **4** in THF shows two additional singlets at δ 1.75 and 5.20, consistent with the presence of a species having *trans*-acac groups; correspondingly, the ¹³C{¹H} NMR spectrum shows additional signals at δ 27.4 (acac methyl), 100.2 (acac methine) and 183.8 (acac C=O).

The reactions of **2** with P^iPr_3 or PCy_3 (one equiv) in C_6D_6 are slower than those in THF and the only detectable ³¹P NMR resonances are the singlets at δ 50.5 and 49.0, respectively; the highly deshielded singlets ascribed to $[Ru(acac)_2L]$ are absent. The ¹H NMR resonances due to acac consist of four methyl and two methine singlets, characteristic of a *cis*-[Ru(acac)_2] fragment attached to two different ligands, and there is also a symmetrical 4H-multiplet due to coordinated ethene in the region δ 3.7–4.8, the pattern being similar to that observed in the complexes *cis*-[Ru(acac)_2(\eta^2-C_2H_4)(L)] (L = SbPh_3, NH_3, MeCN).² Thus, in C_6D_6, the complexes *cis*-[Ru(acac)_2(\eta^2-C_2H_4)(L)] [L = PⁱPr_3 (**5**), PCy_3 (**6**)] are the exclusive products of reaction of **2** with one equiv of the ligands (Scheme 1).

Complexes 5 and 6 can be isolated as, respectively, red crystalline and yellow microcrystalline solids in 65-70% yield from the reactions of 2 with the ligands in benzene or toluene at room temperature over a period of hours. The ¹H and ³¹P{¹H} NMR spectra are identical with those measured in situ and the structures have been confirmed by X-ray crystallography (see below). The ${}^{13}C{}^{1}H$ NMR spectra support the structural assignment: there are four C=O resonances in the region of δ 190, two methine resonances at δ ca. 100, and four acac methyl singlets at δ 27–28, together with a singlet at δ ca. 69.5 due to coordinated ethene. At -95 °C the ethene proton multiplets broaden but the ¹³C resonance remains sharp. Hence, as for other members of this class [8,9], we do not know whether ethene rotation is fast even at low temperature or whether the asymmetry induced by the cis-[Ru(acac)₂] fragment is insufficient to distinguish between the ethene carbon atoms. The ethene C=C stretching bands could not be located in the IR spectra of 5 and 6, probably because they are hidden beneath the intense acac absorption in the 1500–1600 cm^{-1} region. The complexes turn green on exposure to air over several weeks but are apparently stable indefinitely under argon at room temperature. Ethene is not lost when a benzene solution of 6 is heated in vacuo or under argon. However, although the elemental analysis for 5 was satisfactory, that for 6corresponded best with the empirical formula [Ru(acac)₂(PCy₃)], possibly because ethene was lost before combustion was complete. The most abundant ion in the FAB-mass spectra of 5 and 6 corresponds in each case to $[M - C_2H_4]^+$, no molecular ion peak being detected. Also, in THF, the ³¹P{¹H} NMR spectra of 5 and 6 show the same highly deshielded resonances observed in THF solutions of 3 and 4 (see above). Evidently ethene is only weakly bound in 5 and 6.

In benzene, complex 2 also reacts with PPh_3 (one equiv) to give cis-[Ru(acac)₂(η^2 -C₂H₄)(PPh₃)] (7) as the main product, which was identified by its ¹H, ¹³C and $^{31}P{^{1}H}$ NMR spectra (Table 3). It is noteworthy that the ³¹P chemical shifts in C_6D_6 of *cis*-[Ru(acac)₂(PPh₃)₂] and 7 are very close (53.7 and 54.7, respectively); the same is true for their PPr_3^i analogues, *cis*-3 and 5, and for their PCy₃ counterparts (cis-4 and 6). In THF at -20 °C the first species detectable by ³¹P NMR spectroscopy when PPh₃ (one equiv) is added to 2 is trans-[Ru(acac)₂(PPh₃)₂], but at room temperature this is replaced by a singlet at δ 54.7, due either to *cis*-[Ru $(acac)_2(PPh_3)_2$ or 7, and a less intense singlet at δ 83.9. The latter is the only signal observed when a large excess of 1 (ca. 10 equiv) is added to a solution of PPh_3 in THF at room temperature. It probably belongs to the pyramidal species $[Ru(acac)_2(PPh_3)]$ or to its octahedral THF adduct.

2.4. Reactions of $[Ru(acac)_2L_2]$

The *trans*-isomers of $[Ru(acac)_2L_2]$ $[L = P'Pr_3$ (3), PCy₃ (4)], and the *cis*-ethene derivatives $[Ru(acac)_2(\eta^2-C_2H_4)(L)]$ $[L = P'Pr_3$ (5), PCy₃ (6)] react readily with CO (1 bar) to give monocarbonyl complexes *trans*- $[Ru(acac)_2(CO)(L)]$ $[L = PPr_3^i$ (8), PCy₃ (9)], which have been isolated as yellow solids in yields of 50–70% (Scheme 2). The carbonylation of *trans*-3 was performed at -20 °C to prevent competing isomerization to *cis*-3. The latter also reacts with CO (3 bar) over a period of days to give *trans*-8. Both *trans*-8 and *trans*-9 form the corresponding *cis*-isomers when they are heated in benzene. This behaviour is generally similar to that observed in the triphenylphosphine series, except that *cis*- $[Ru(acac)_2(PPh_3)_2]$ is completely unreactive toward CO (1–3 bar) [4]. Also, in contrast with the lability of ethene in **5** and **6**, the alkene in the triphenylstibine complexes cis-[Ru(acac)₂(η^2 -alkene)(SbPh₃)] (alkene = C₈H₁₄ [4], C₂H₄ [8]) is not replaced by CO after several days at room temperature.

The structures of the isomers of **8** and **9** follow unequivocally from the number of acac resonances in the ¹H and ¹³C{¹H} NMR spectra (Table 2). The IR spectra contain a single, intense v(CO) band in the region of 1950–1925 cm⁻¹ whose position does not differ significantly for the *cis*- and *trans*-isomers. The highest identifiable peak in the FAB-mass spectra of the *trans*-isomers corresponds to the loss of one carbonyl ligand, whereas a parent ion peak is observed in the case of the *cis*isomers.

In an attempt to generate either the five-coordinate species $[Ru(acac)_2(P'Pr_3)]$ or its dihydrogen adduct, we heated a benzene solution of the ethene complex 5 under industrial grade hydrogen (3 bar) for 3 days. Unexpectedly, the product, isolated in ca. 90% yield, was the yellow, crystalline, binuclear dinitrogen complex cis- $[{Ru(acac)_2(P'Pr_3)}_2(\mu-N_2)]$ (10), which presumably was formed from the small amount of nitrogen (ca. 100 ppm) present in the hydrogen gas. The presence of nitrogen in 10 was confirmed by elemental analysis. Complex 10 also resulted from an attempt to crystallize 5 in a nitrogen-filled "inert atmosphere" box over a period of several weeks. The displacement of ethene by nitrogen is reversible, 5 being re-formed from 10 in the presence of C₂H₄ (1 bar) in C₆D₆ at 25 °C. Complex 10 also reacts readily with CO (1 bar) giving trans-8, and with phenylacetylene to give the known phenylvinylidene complex cis-[Ru(acac)₂(=C=CHPh)(PⁱPr₃)] (11) [9].

A single-crystal X-ray diffraction study of a *n*-hexane solvate of 10, discussed in detail below, shows the presence of two cis-[Ru(acac)₂(P'Pr₃)] units bridged symmetrically by linearly bonded dinitrogen (Scheme 3). When the molecule is viewed down the Ru-N₂-Ru axis, the PⁱPr₃ ligands appear to be mutually orthogonal. The Raman spectrum of 10 contains a strong band at 2089 cm^{-1} assigned to the symmetric v(NN) mode, similar to those found for the symmetrical binuclear cations $[{Ru(NH_3)_5}_2(\mu-N_2)]^{4+}$ (2100 cm⁻¹) [22] and $[{Ru(-1)}_2(\mu-N_2)]^{4+}$ $H_2O_{5}_{2}(\mu-N_2)^{4+}$ (2080 cm⁻¹) [23]. The 2089 cm⁻¹ band does not appear in the IR spectrum of 10, either in the solid state or in benzene solution. Hence, the amount of any mononuclear dinitrogen complex present in equilibrium with 10 (Eq. (3)) is too small to be detected by IR spectroscopy

$$\begin{split} & [\{\operatorname{Ru}(\operatorname{acac})_2(\operatorname{P}^{i}\operatorname{Pr}_3)\}_2(\mu-\operatorname{N}_2)] \\ & \rightleftharpoons [\operatorname{Ru}(\operatorname{acac})_2(\operatorname{N}_2)(\operatorname{P}^{i}\operatorname{Pr}_3)] + [\operatorname{Ru}(\operatorname{acac})_2(\operatorname{P}^{i}\operatorname{Pr}_3)] \quad (3) \end{split}$$

The most abundant ion in the FAB-mass spectrum is at m/z 460.2 corresponding to the fragment [Ru(acac)₂ (PⁱPr₃)]. A parent ion peak at m/z 948.2 is observed,

but this is accompanied by a peak at m/z 950.2 of unknown origin.

The NMR spectra of 10 reveal the presence of two isomers in solution, which are probably the homochiral $(\Delta\Delta/\Lambda\Lambda)$ and heterochiral $(\Delta\Lambda/\Lambda\Delta)$ species arising from the two chiral cis-[Ru(acac)₂] fragments (Scheme 3). Only the former is found in the solid state structure (see below). Thus, the ¹H NMR spectrum measured ca. 10 min after dissolution of a solid sample in C_6D_6 shows, as expected, four acac methyl and two methine singlets belonging to the major isomer; the corresponding signals of the minor isomer are similar except that two of the acac methyl singlets overlap. The isomer ratio under these conditions is ca. 4:1 but this changes steadily with time to ca. 2:1 after 14 h and 3:2 after 62 h. The ³¹P{¹H} NMR spectrum, measured after 62 h, shows two distinct singlets, at δ 60.6 and 60.5, also in a ratio of ca. 3:2, and in the ${}^{13}C{}^{1}H{}$ NMR spectrum there are seven acac methyl, four methine, and seven C=O resonances, the odd numbers presumably arising from accidental overlap of a pair of signals. The isomer ratio in a solution of 10, measured directly in situ by ¹H NMR spectroscopy after the reaction of 5 with dinitrogen, is ca. 1:1. Thus, the homochiral species must crystallize preferentially and transform slowly in solution to the diastereomeric mixture, possibly via the equilibrium shown in Eq. (3). A similar one-ended dissociation of bridging dinitrogen has been observed in the nickel(0) complex [{Ni(PCy₃)₂} $_{2}(\mu$ -N₂)], the mononuclear species in this case, $[Ni(PCy_3)_2(N_2)]$, being detectable by IR spectroscopy [24]. Diastereomers of the binuclear osmium(II) complex cis-[{OsCl(bipy)}_2]_2(μ -N₂)] have also been observed by ¹H NMR spectroscopy [25].

2.5. X-ray structures

The molecular structures of *cis*-3, *trans*-4, 5, 6 and $10 \cdot C_6 H_{14}$, determined by single-crystal X-ray diffraction, are shown in Figs. 1-5; selected bond lengths and angles are collected in Tables 4-8. The coordination geometries are essentially octahedral, as expected. In trans-4 the interbond angles are close to 90°, whereas in *cis*-3 the P–Ru–P angle opens out to 105°, presumably because of steric repulsion between the mutually cis- $P^{i}Pr_{3}$ ligands; similar angles have been observed in $[Rh(acac)(PCy_3)_2]$ [26], $[Rh(\eta^2 - O_2CMe)(P^iPr_3)_2]$ [27], cis-[Mo(CO)₄(PCy₃)₂] [28], and cis-[Mo(CO)₄(PPh₃)₂] [29]. In 5 the C=C vector of the coordinated ethene eclipses the plane defined by the metal atom and the mutually trans oxygen atoms O(1) and O(3); this orientation is perpendicular to that found in cis-[Ru $(acac)_2(\eta^2-C_2H_4)(NH_3)]^2$ and is presumably adopted to minimize steric repulsion between ethene and the bulky P'Pr₃ ligand. Surprisingly, however, the ethene ligand in 6, containing the even bulkier PCy₃ ligand, displays two mutually perpendicular orientations, the slightly more



Fig. 1. Molecular structure of cis-[Ru(acac)₂(PⁱPr₃)₂], cis-3, with selected atom labelling. Displacement ellipsoids show 30% probability levels. Hydrogen atoms have been omitted for clarity.



Fig. 2. Molecular structure of *trans*-[Ru(acac) $_2(PCy_3)_2$], *trans*-4, with selected atom labelling. Displacement ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity.

abundant one (ca. 55% occupation) being the same as in **5**; in the minor one the C=C vector eclipses the plane defined by Ru(1), P(1) and O(2). The Ru–C(C₂H₄) distances in **5** and **6** are in the range 2.15–2.21 Å found in members of the series containing less bulky co-ligands, *viz.*, *cis*-[Ru(acac)₂(η^2 -C₂H₄)(L)] (L = C₂H₄, NH₃) and *trans*-[Ru(acac)₂(η^2 -C₂H₄)(py)] [8], and the C=C bond lengths are only ca. 0.02 Å greater than that of free ethene [1.333(2) Å] [30].

In complex $10 \cdot C_6 H_{14}$ the Ru–N \equiv N–Ru unit is almost linear, the Ru–N \equiv N angle being 174°. The N \equiv N distance [1.135(8) Å] is slightly greater than that in free dinitrogen [1.0977 Å] [30] and is similar to those observed in other μ -dinitrogen ruthenium(II) complexes



Fig. 3. Molecular structure of cis-[Ru(acac)₂(η^2 -C₂H₄)(PⁱPr₃)], **5**, with selected atom labelling. Displacement ellipsoids show 30% probability levels. Hydrogen atoms have been omitted except those on the ethene group, which are drawn as circles of small radii.



Fig. 4. Molecular structure of cis-[Ru(acac)₂(η^2 -C₂H₄)(PCy₃)], **6**, with selected atom labelling, showing the major orientation of coordinated ethene. Displacement ellipsoids show 50% probability levels. Hydrogen atoms have been omitted except those on the ethene group, which are drawn as circles of small radii.

such as $[{Ru(NH_3)_5}_2(\mu-N_2)]^{4+}$ [1.124(15) Å] [31], [${mer, trans-RuCl_2(NN'N)}_2(\mu-N_2)$] [1.110(3) Å] [20], [$\{CpRu(dippe)\}_2(\mu-N_2)$]²⁺ [dippe = 1,2-bis-(disopropylphosphino)ethane] [1.118(3)Å] [32], [$\{CpRu(PEt_3)_2\}_2(\mu-N_2)$]²⁺ [1.114(5) Å] [32], and [$\{RuH_2-$

Table 6



Fig. 5. Molecular structure of *cis*-[{Ru(acac)₂(P^{*i*}Pr₃)}(μ -N₂)], **10**, with selected atom labeling. Asterisks indicate atoms generated by the symmetry operation (2 – *x*, *y*, 3/2 – *z*). Displacement ellipsoids show 30% probability levels. Only the major orientation of the disorder of atoms C(17) and C(19) is shown. Hydrogen atoms have been omitted for clarity.

 Table 4

 Selected metrical parameters for complex *cis*-3

Selected methodi pe	Selected metrical parameters for complex <i>cus</i> 5					
Ru(1)–O(1)	2.068(2)	Ru(1)–O(4)	2.104(2)			
Ru(1)–O(2)	2.088(2)	Ru(1) - P(1)	2.3525(9)			
Ru (1)–O(3)	2.059(2)	Ru(1)–P(2)	2.3467(8)			
O(1)-Ru(1)-O(2)	90.46(8)	O(2)–Ru(1)–P(2)	87.25(6)			
O(1)–Ru(1)–O(3)	174.02(7)	O(3)-Ru(1)-O(4)	90.50(8)			
O(1)-Ru(1)-O(4)	85.28(8)	O(3) - Ru(1) - P(1)	93.86(6)			
O(1)-Ru(1)-P(1)	90.20(6)	O(3)-Ru(1)-P(2)	88.73(6)			
O(1)-Ru(1)-P(2)	94.43(6)	O(4) - Ru(1) - P(1)	87.57(6)			
O(2)–Ru(1)–O(3)	84.62(8)	O(4) - Ru(1) - P(2)	167.01(6)			
O(2)-Ru(1)-O(4)	79.77(8)	P(1)-Ru(1)-P(2)	105.42(3)			
O(2)-Ru(1)-P(1)	167.23(6)					

Table 5

Ru(1)–O(1) Ru(1)–O(2)	2.0677(13) 2.0658(12)	Ru(1)–P(1)	2.4273(4)
$O(1)-Ru(1)-O(1)^*$	180.0	P(1)-Ru(1)-O(1)	90.94(4)
O(1)-Ru(1)-O(2)	91.87(5)	$P(1)-Ru(1)-O(1)^*$	89.06(4)
$O(2)-Ru(1)-O(2)^*$	180.0	P(1)-Ru(1)-O(2)	91.06(4)
$P(1)-Ru(1)-P(1)^*$	180.0	$P(1)-Ru(1)-O(2)^*$	88.94(4)

Atoms generated by the symmetry operation (1 - x, 1 - y, 1 - z).

 $(\eta^1-N_2)(P'Pr_3)_2\}_2(\mu-N_2)$] [1.113(2) Å for bridging N₂, 1.105(2) Å for terminal N₂] [33], consistent with $d(\pi) \rightarrow \pi^*$ Ru–N₂ back-bonding [31,34,35]. The Ru–N distance to the nitrogen atom of N₂ in 10·C₆H₁₄ [1.919(14) Å] is slightly shorter than those found in the first two compounds cited above [1.928(6), 1.953(2) Å, respectively] and significantly shorter than those observed in the last three [1.980(1), 1.977(3) and 2.050(2) Å (average), respectively], possibly reflecting the

Selected metrical para	Selected metrical parameters for complex 5				
Ru(1)–O(1)	2.079(3)	Ru(2)–O(5)	2.082(3)		
Ru(1)–O(2)	2.077(3)	Ru(2)–O(6)	2.079(3)		
Ru (1)–O(3)	2.071(3)	Ru(2)–O(7)	2.064(3)		
Ru(1)–O(4)	2.094(3)	Ru(2)–O(8)	2.089(3)		
Ru(1) - P(1)	2.321(1)	Ru(2) - P(2)	2.322(1)		
Ru(1)–C(11)	2.172(5)	Ru(2)–C(32)	2.180(6)		
Ru(1)–C(12)	2.181(5)	Ru(2)–C(33)	2.185(5)		
C(11)–C(12)	1.350(9)				
O(1)-Ru(1)-O(2)	89.1(1)	O(5)-Ru(2)-O(6)	89.5(1)		
O(1)–Ru(1)–O(3)	167.4(1)	O(5)-Ru(2)-O(7)	168.1(1)		
O(1)-Ru(1)-O(4)	81.4(1)	O(5)-Ru(2)-O(8)	81.4(1)		
O(1)-Ru(1)-P(1)	95.68(9)	O(5)-Ru(2)-P(2)	95.93(9)		
O(2)-Ru(1)-O(3)	79.9(1)	O(6)-Ru(2)-O(7)	80.3(1)		
O(2)-Ru(1)-O(4)	85.4(1)	O(6)-Ru(2)-O(8)	84.7(1)		
O(2)-Ru(1)-P(1)	91.63(9)	O(6)-Ru(2)-P(2)	91.14(9)		
O(3)-Ru(1)-O(4)	91.6(1)	O(7)-Ru(2)-O(8)	91.5(1)		
O(3)-Ru(1)-P(1)	90.70(9)	O(7)-Ru(2)-P(2)	90.48(9)		
O(4)-Ru(1)-P(1)	175.9(1)	O(8)-Ru(2)-P(2)	175.01(9)		
C(11)-Ru(1)-C(12)	36.1(2)	C(32)-Ru(2)-C(33)	36.0(2)		
P(1)-Ru(1)-C(11)	99.7(2)	P(2)-Ru(2)-C(32)	100.5(2)		
P(1)-Ru(1)-C(12)	91.3(2)	P(2)-Ru(2)-C(33)	91.0(2)		

Table 7					
Selected	metrical	parameters	for	complex	6

percenter methoda p		i vompien v	
Ru(1)–O(1)	2.06(2)	Ru(1)–C(121)	2.148(2)
Ru(1)–O(2)	2.10(2)	C(110)-C(111) ^a	1.005
Ru(1)–O(3)	2.07(2)	$C(110)-C(120)^{a}$	1.344
Ru(1)–O(4)	2.074(18)	C(110)-C(121) ^a	0.987
Ru(1) - P(1)	2.356(7)	C(111)-C(120) ^a	1.097
Ru(1)–C(110)	2.167(2)	$C(111)-C(121)^{a}$	1.356
Ru(1)–C(120)	2.190(2)	C(120)-C(121) ^a	0.738
Ru(1)–C(111)	2.151(2)		
O(1)–Ru(1)–O(2)	90.9(8)	O(3)–Ru(1)–P(1)	89.2(6)
O(1)–Ru(1)–O(3)	89.2(6)	O(4) - Ru(1) - P(1)	94.4(6)
O(1)–Ru(1)–O(4)	173.1(8)	C(110)-Ru(1)-C(120) ^a	35.94(3)
O(1)-Ru(1)-P(1)	90.2(6)	P(1)-Ru(1)-C(110)	116.33(18)
O(2)–Ru(1)–O(3)	82.9(9)	P(1)-Ru(1)-C(120)	80.40(17)
O(2)–Ru(1)–O(4)	83.9(8)	$C(111)-Ru(1)-C(121)^{a}$	36.78(3)
O(2)-Ru(1)-P(1)	171.9(8)	P(1)-Ru(1)-C(111)	99.29(17)
O(3)-Ru(1)-O(4)	90.2(8)	P(1)-Ru(1)-C(121)	93.92(17)
-			

^a The atoms C(110), C(111), C(120) and C(121) were restrained during refinement.

relatively unhindered coordination environment provided by two acac ligands and only one tertiary phosphine. The two octahedra in $10 \cdot C_6 H_{14}$ adopt a mutually orthogonal orientation which, as suggested also for the second and fourth of the compounds cited above, may help to maximize $d(\pi)$ back-donation into the orthogonal sets of empty π^* -orbitals on N₂.

The lability of complexes **3** and **4** can be correlated with the Ru–P bond lengths. Thus, the Ru–P distance in *trans*-**4**, 2.4273(4) Å, is significantly greater than in *trans*-[Ru(acac)₂(PMePh₂)₂] [2.343(1), 2.346(1) Å for independent molecules] [4]; the same trend is evident in a comparison of *cis*-**3** [2.3525(9), 2.3467(8) Å for independent molecules] with *cis*-[Ru(acac)₂(PMePh₂)₂]

Table 8 Selected metrical parameters for complex $10 \cdot C_6 H_{14}$

Ru(1)–O(1)	2.046(4)	Ru(1) - P(1)	2.312(2)
Ru(1)–O(2)	2.035(4)	Ru(1)-N(1)	1.919(4)
Ru(1)–O(3)	2.050(4)	$N(1)-N(1)^{a}$	1.135(8)
Ru(1)–O(4)	2.107(4)		
O(1)-Ru(1)-O(2)	92.4(2)	O(2)-Ru(1)-N(1)	174.2(2)
O(1)-Ru(1)-O(3)	173.8(2)	O(3)-Ru(1)-O(4)	91.3(2)
O(1)-Ru(1)-O(4)	82.5(2)	O(3)-Ru(1)-P(1)	90.2(1)
O(1)-Ru(1)-P(1)	96.0(1)	O(3)-Ru(1)-N(1)	90.0(2)
O(1)-Ru(1)-N(1)	90.3(1)	O(4) - Ru(1) - P(1)	177.9(1)
O(2)–Ru(1)–O(3)	86.8(1)	O(4)-Ru(1)-N(1)	88.9(2)
O(2)–Ru(1)–O(4)	86.4(1)	P(1)-Ru(1)-N(1)	92.6(1)
O(2)-Ru(1)-P(1)	92.3(1)	$Ru(1)-N(1)-N(1)^{a}$	174.2(4)

^a Atoms generated by the symmetry operation (2-x, y, 3/2-z).

[2.2765(9) Å] [4]. Replacement of one of the P^iPr_3 ligands in *cis*-3 by C_2H_4 or N_2 causes a contraction of ca. 0.04 Å in the Ru–P distance.

2.6. Electrochemistry

The half-wave potentials $E_{1/2}(Ru^{3+/2+})$ of the complexes studied in this work are listed in Table 9. The trans- and cis-isomers of 3 each show fully reversible redox couples, the former being the more easily oxidized by ca. 140 mV. Differences of a similar order have been observed for *trans*- and *cis*-[Ru(acac)₂(NCMe)₂] (120 mV) and [Ru(acac)₂(AsPh₃)₂] (190 mV) [36,37]. We could not measure the $E_{1/2}$ -value for 4 because of the insolubility of this compound in CH2Cl2 at room temperature. Replacement of one of the PⁱPr₃ ligands in cis-3 by ethene shifts the redox potential by ca. 400 mV in favour of Ru^{II}, presumably because of the weaker σ -donor/stronger π -acceptor ability of ethene. The $E_{1/2}$ values of 5 and 6 (+0.42, +0.43 V, respectively) are slightly greater than that of cis-[Ru(acac)₂(η^2 - C_2H_4 (NH₃)] (+0.38 V),² but, surprisingly, are considerably less than those for the corresponding acetonitrile and SbPh₃ complexes (+0.56, +0.59 V, respectively). Substitution of CO for one of the PⁱPr₃ ligands in *cis*-3 causes an even larger shift in favour of Ru^{II} than does C₂H₄, clearly reflecting the preferred binding of the strong π -acceptor to the d⁶ ion. The effect is most marked for cis-8 and cis-9, which are less easily oxidized to the Ru^{III} level than their *trans*-isomers by ca. 300 mV, in accord with the usual trend for substituted carbonyl complexes [38,39]. The couples are fully reversible for both cis- and trans-isomers.

The vinylidene complexes $[Ru(acac)_2(=C=CHR)-(P^iPr_3)]$ [R = Ph (11), SiMe₃ (12)] [9] ² exhibit irreversible cyclic voltammograms, even at -50 °C with scan

Table 9	
Reduction potentials $E_{1/2}(Ru^{3+/2+})$	for complexes $[Ru(acac)_2(L)(L')]^{a,b}$

Complex	$E_{1/2}$	Complex	$E_{1/2}$
trans-3	-0.14	cis-3	+0.02
cis-5	+0.42	cis-6	+0.43
trans-8	nm	cis-8	+0.92
trans-9	$+0.64^{\circ}$	cis- 9	$+0.89^{\circ}$
11	$+0.75^{d}$	12	$+0.62^{d}$
10	+0.30, +0.90		

^a $L' = P^{i}Pr_{3}$, $L = P^{i}Pr_{3}$ (3), $C_{2}H_{4}$ (5), CO (8), 1/2 N₂ (10), C=CHPh (11), C=CHSiMe₃ (12); L'=PCy₃, $L = C_{2}H_{4}$ (6), CO (9).

^b Measured in CH₂Cl₂ vs. Ag/AgCl at ca. -50 °C, except where stated.

^c Measured at ca. 20 °C.

^d Irreversible process (see text).

rates up to 500 mVs⁻¹, presumably because of the instability of the oxidation products. The anodic potentials are +0.75 and +0.62 V, respectively. Although these values are not strictly comparable with the $E_{1/2}$ -values for C_2H_4 and CO, the trend is similar to the order $C_2H_4 < C=CPh_2 < CO$ observed for *trans*-RhCl(L)(PPr_3^i)_2], which is believed to reflect primarily the π -acceptor ability of these ligands [40].

The electronic spectra recorded at -50 °C for the one-electron oxidation of cis-[Ru(acac)₂(η^2 - C_2H_4 (PCy₃)] (6) are similar to those reported previously for cis-[Ru(acac)₂(η^2 -C₂H₄)(L)] (L = C₂H₄, NH₃, SbPh₃) [8] and for chelate alkene-amine complexes such as $[Ru(acac)_2(o-CH_2=CHC_6H_4NMe_2)]$ and [Ru(acac)₂(2-CH₂=CHC₅H₄N)] [41]. On electrooxidation of 6, a band at 29600 cm⁻¹ (ε 6500), which probably arises from charge transfer transitions within the Ru(acac)₂ unit, is replaced by absorptions at 14700 cm⁻¹ (ϵ 1300) and 17600 cm⁻¹ (ϵ 1300), due to acac(π) \rightarrow Ru^{III} transitions in **6**⁺, and by a band at 29400 cm^{-1} (ϵ 4700). The band in **6** at 36700 cm⁻¹ (ϵ 14600), which probably arises from acac $\pi \to \pi^*$ transitions, shifts only slightly in position and intensity on electro-oxidation. These changes can be completely reversed at -50 °C by applying a potential of ca. 300 mV less than the $E_{1/2}(Ru^{3+1/2+})$ value. Isosbestic points are observed during both oxidation and reduction processes showing that only two absorbing species are present in solution. Addition of one equiv of $AgPF_6$ to a cold solution of 6 gives a deep blue solution whose CV trace $(6^+ \rightarrow 6)$ is superimposable on that of $6 \rightarrow 6^+$. Hydrodynamic voltammetric results show that, for 6, no current is detected between 0 and +0.4 V (versus Ag/AgCl) but, as the potential passes between +0.4 and +0.5 V, a positive current passes through the solution corresponding to the oxidation of the complex; above +0.5 V a limiting current is reached. The potential at half-current height is ca. +0.45 V, in good agreement with the value measured by cyclic voltammetry. After addition of a slight excess of AgPF₆, a negative

² Complex **12** was prepared similarly to **11** by treatment of *cis*-**3** with trimethylsilylacetylene.

current is found between 0 and +0.4 V; above +0.5 V no current is passing through the solution. The potential at half-current height is again ca. +0.45 V, indicating the presence of 6^+ in solution.³

The cyclic and AC voltammograms of the binuclear μ -dinitrogen complex 10 show two reversible oxidation potentials, at +0.30 and + 0.90 V (versus Ag/AgCl) at -50 °C in CH₂Cl₂. All of the Ru(acac)₂ complexes containing π -acceptor ligands studied so far [8,36,37,41] show just one one-electron oxidation in the potential range 0–1.5 V and show no $Ru^{III} \rightarrow Ru^{IV}$ oxidation. Hence, the two couples for 10 probably correspond to sequential oxidation of the two metal centres, i.e., $Ru^{II,II} \rightarrow Ru^{II,III}$ and $Ru^{II,III} \rightarrow Ru^{III,III}$. At 25 °C the first oxidation is still fully reversible whereas the second is irreversible. The difference in $E_{1/2}$ -values for the two oxidation couples is similar to that found for $[{Ru(NH_3)_5}_2(\mu-N_2)]^{4+}$, which undergoes a reversible one-electron oxidation at $E_{1/2}$ + 0.73 V (versus NHE) and a second, irreversible oxidation at ca. +1.2 V (versus NHE) [42]. The electronic spectrum of 10 is very similar to that of **6** and of the other $Ru(acac)_2(C_2H_4)$ complexes [8]; application of a potential of ca. +1.2 V (versus Ag/ AgCl) at -50 °C generates the spectrum typical of a Ru^{III}(acac)₂ complex (Table 10) and is consistent with the presence of the doubly oxidized Ru^{III,III} species $cis-[{Ru(acac)_2(P^iPr_3)}_2(\mu-N_2)]^{2+}$, 10²⁺. This process is fully reversible at -50 °C. Application of a potential of +0.60 V (versus Ag/AgCl) at -50 °C generates a spectrum that differs from those of 10 and 10^{2+} mainly in the presence of a weak, broad, asymmetric near-IR band at ca. 8900 cm^{-1} (Table 10); again, the process is completely reversible at -50 °C and isosbestic points are observed, as shown in Fig. 6. The species responsible for this spectrum is likely to be the half-oxidized Ru^{II,III} cation 10^+ ; similar near IR-bands have been reported for the mixed valence species $[{Ru(NH_3)_5}_2(\mu-N_2)]^{5+}$ [42] and for the Creutz-Taube ion containing bridging pyrazine, $[{Ru(NH_3)_5}_2(\mu-pyz)]^{5+}$ [43,44].

Since the potentials for the stepwise oxidation of **10** differ by more than 250 mV [45], the value for the comproportionation constant K (Eq. (4)) at 223 K can be estimated simply from the difference in $E_{1/2}$ values (Eq. (5)):

$$\mathbf{10} + \mathbf{10}^{2+} \rightleftharpoons \mathbf{2} \ \mathbf{10}^{+} \tag{4}$$

$$\log_{10} K = 22.65(\Delta E_{1/2}). \tag{5}$$

The resulting value, $10^{13.6}$, can be compared with the values at 298 K of ca. 10^8 for $[{Ru(NH_3)_5}_2(\mu-N_2)]^{5+}$ and 4.10^6 for $[{Ru(NH_3)_5}_2(\mu-pyz)]^{5+}$ [46,47]. The near

Table 10

Principal electronic band maxima (cm^{-1}) and molar absorptivities $(M^{-1} cm^{-1})$ for Ru^{II} and in situ electrogenerated Ru^{III} complexes

Complex	MLCT or LMCT	acac $\pi \rightarrow \ acac \ \pi^*$	
6	29600 (6500)	36700 (14600)	
10	27 500 (16 900)	37400 (53500)	
6 ⁺	14700 (1300),	36600 (12700)	
	17600 (1300)		
10 ⁺	8900 (2900), 16300 (1800),	38 200 (38 800)	
	17700 (1800), 30100 (15500)		
10 ²⁺	13900 (3000), 17800 (3000),	37600 (35700)	
	30000 (16700)		

IR band in 10^+ ($w_{1/2}$ ca. 3700 cm⁻¹) is broader than that in [{Ru(NH₃)₅}₂(μ -N₂)]⁵⁺ ($w_{1/2}$ ca. 2630 cm⁻¹) but the half-width is less than 4750 cm⁻¹, the value predicted by Hush's theory [48] for localized mixed-valence systems. Hush [49] has also suggested that fully delocalized systems will show asymmetric bands. All these observations are consistent with the notion that 10^+ belongs to the class of fully delocalized mixed-valence ions (class III of the Robin–Day classification).

3. Discussion

The tertiary phosphines P'Pr₃ and PCy₃, like their less bulky analogues, replace both alkenes from 1 or 2 to give cis-[Ru(acac)₂L₂] as the final product. In contrast with the behaviour of the less bulky ligands, however, the half-substituted intermediates cis-[Ru(acac)₂(η^2 - $C_2H_4(L)$ [L = P^{*i*}Pr₃ (3), PCy₃ (4)] can be isolated from 2, provided that the reaction is carried out in a poorly coordinating solvent such as benzene. These compounds may be formed via their *trans*-isomers, as is the case for the corresponding compounds with $L = NH_3$ or py, but we have no strong supporting evidence. Although the Ru–C(C_2H_4) and C=C bond lengths in 3 and 4 are normal, the ethene appears to be weakly bound, being displaced readily by CO, N₂ and even to some extent by solvent THF; under the same conditions the analogues cis-[Ru(acac)₂(η^2 -C₂H₄)(L)] (L = NH₃, py, SbPh₃) are inert towards these reagents.

We attribute this difference to the accessibility and relative stability of the formally five-coordinate, 16-electron fragments $Ru(acac)_2L$ ($L = P^iPr_3$, PCy_3), which can be detected, possibly in the form of their weakly stabilized THF adducts, by their characteristic, highly deshielded ³¹P NMR resonances. The exclusive formation of the *trans*-isomers of the carbonyl complexes **8** and **9** as the kinetic products of reaction of CO with the *cis*-ethene complexes **5** and **6** is consistent with a square pyramidal geometry, with L in the apical position, for the 16-electron fragment. A similar explanation was advanced previously to account for the formation of the kinetic products *trans*-[Ru(acac)₂L₂]

³ The current is slightly greater after addition of the oxidant, possibly because of a slight concentration of the solution during the measurement, the presence of colloidal silver on the electrodes, or the slight excess of Ag^+ .



Fig. 6. Electronic spectra recorded during the one-electron oxidation of cis-[{Ru(acac)₂(PⁱPr₃)} ₂(μ -N₂)] (10) in 0.5 M [Bu₄ⁿN]PF₆/CH₂Cl₂ at ca. -50 °C ($E_{appl} = + 0.60$ V vs. Ag/AgCl).

from the reactions of the *cis*-complex 1 with two equivalents of L [4]. Square pyramidal geometry is favoured for a five-coordinate d⁶-metal complex according to the-oretical calculations [50,51] and has been observed for several five-coordinate ruthenium(II) complexes, e.g., [RuCl₂(PPh₃)₃] [19,52], [RuY(NN'N)(PPh₃)]OTf (Y = Cl, OTf) [20], and [Ru{N(SPR₂)}₂(PPh₃)] (R = Ph, ^{*i*}Pr) [21]. The proposed intermediate Ru(a-cac)₂L (L = P^{*i*}Pr₃, PCy₃) may be further stabilized by weak intramolecular Ru···H–C interactions, as observed in [RuCl₂(PPh₃)₃] [52].

Complexes **3** and **4** undergo *trans* to *cis* isomerization far more readily than their counterparts containing smaller Group 15 donor ligands, a feature that can also be traced both to the relative stability of the fragment Ru(acac)₂L and to the long (and presumably weak) Ru–L bonds in the *trans*-isomers. Thermochemical measurements of ligand exchange reactions of [RuCl₂(η^6 -*p*-cymene)(PR₃)] [53] and ([RuCl(η^5 -C₅R'₅)-(PR₃)] (R' = H, Me) [54,55] have shown that PⁱPr₃ or PCy₃ form weaker bonds, by ca. 45 kJ mol⁻¹, than PMe₃, for example. Despite the steric crowding inherent in the *cis*-arrangement of two such bulky ligands, the competition between two strong σ -donors for the same metal-based orbital evidently disfavours the *trans*arrangement.

The ability of the 16-electron fragment to form complex 10 by scavenging dinitrogen from industrial grade dihydrogen, itself a potential competitor ligand, indicates the high affinity of the fragment for N_2 . We have no evidence for the existence of a mononuclear species, $[Ru(acac)_2(\eta^1-N_2)(P^iPr_3)]$, under the reaction conditions, although it may be an intermediate in the formation of 10 and, as noted above, in the interconversion of the corresponding diastereomers. The high affinity of $Ru(acac)_2(P'Pr_3)$ for N₂ is reminiscent of the ability of the 16-electron fragments $[RuCpL_2]^{2+}$ (L₂ = dippe, $2PEt_3$, $2PMe'Pr_2$) [32], $Mo(CO)(Et_2PCH_2CH_2PEt_2)_2$ [56], and $Ru\{P(CH_2CH_2PPh_2)_3\}$ [57] to scavenge traces of dinitrogen from commercial argon or helium; we have not attempted to generate $Ru(acac)_2(P^iPr_3)$ under these gases. The apparently low affinity of $Ru(acac)_2(P^iPr_3)$ for dihydrogen contrasts with the ability of numerous 16-electron fragments, such as $[RuCpL_2]^{2+}$, $[RuH_2L_n]$ L = various tertiary phosphines; n = 2,3), and $[Os(NH_3)_5]^{2+}$, to bind both η^1 -N₂ and H₂ (either as η^2 -H₂ or a dihydride) '[58,59]; moreover, η^2 -H₂ and η^1 -N₂ are supposed to have similar π -acceptor ability [60]. The closest analogue to $Ru(acac)_2(P'Pr_3)$ may be $[Ru(H_2O)_5]^{2+}$, which reversibly binds both N₂ and H₂ to give $[Ru(H_2O)_5(\eta^1-N_2)]^{2+}$ and $[Ru(H_2O)_5(\eta^2-H_2)]^{2+}$, respectively [61,62]. In both cases the back-bonding interactions are thought to be weak [62,63] and the η^{1} - N_2 complex readily decomposes to the μ - N_2 species $[{Ru(H_2O)_5}_2(\mu-N_2)]^{2+}$ [23,62]. Clearly, further work directed to the detection or isolation of the mononuclear entities $[Ru(acac)_2(\eta^2-H_2)(P^iPr_3)]$ and $[Ru(acac)_2(\eta^1 N_2$ ($P^i Pr_3$)] is warranted.

The ruthenium(III)–ethene cation 6^+ , like the analogous complexes $[Ru(acac)_2(\eta^2-C_2H_4)(L)]^+$ (L = NH₃, SbPh₃) [8], is stable indefinitely in solution at -50 °C but decomposes at room temperature, consistent with weaker binding of ethene to the metal atom in its higher oxidation state. Solutions of the half- and fully-oxidized μ -dinitrogen complexes, 10^+ and 10^{2^+} , also are stable at -50 °C. Evidently Ru^{III}–N₂ bonds have some stability in the absence of competing donor solvents, despite the poor π -donor ability of the trivalent metal ion; for the ammine cation analogous to 10^+ , [{Ru(NH₃)₅}₂(μ -N₂)]⁵⁺, the half-life for aquation at 0 °C is only 3.4 min [42].

4. Experimental

4.1. General procedures

All operations were carried out under argon, unless stated otherwise, with use of standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen. NMR spectra were recorded at 20.5 °C (unless otherwise indicated) on Varian Gemini 300 BB or Varian VXR 300 spectrometers (¹H at 300 MHz, ¹³C at 75.4 MHz, ³¹P at 121.4 MHz) spectrometers. Variable temperature NMR spectra were recorded on the Varian VXR 300 instrument. Chemical shifts (δ) for ¹H and ¹³C are given in ppm referenced to the residual protons and the carbon atoms of the deuterated solvents, ³¹P chemical shifts are referenced to external 85% H_3PO_4 . Coupling constants (J) are given in Hertz. IR spectra were recorded on either Perkin-Elmer 1800 FT or Perkin-Elmer Spectrum One instruments with use of KBr disks or 0.1 mm path length KBr cells. Fast Atom Bombardment (FAB) mass spectra were measured on a VG ZAB2-SEQ mass spectrometer using either 3-nitrobenzyl alcohol or (3-nitrophenyl)octylether as the matrix. Microanalyses were performed in-house.

Electrochemical measurements in CH₂Cl₂ at various temperatures were carried out on a Princeton Applied Research 170 system as described in previous papers [8,41,64]. At room temperature $E_{1/2}$ for the [FeCp₂]^{+/0} couple was +0.55 V versus a non-aqueous reference electrode consisting of Ag/AgCl/CH₂Cl₂, 0.05 M [Bu₄N]Cl, 0.45 M [Bu₄N]PF₆. Electronic spectra in the range 6000– 45000 cm⁻¹ were collected in a cryogenically controlled OTTLE cell placed in the beam of either a Perkin-Elmer Lambda 9 or a Cary 5E UV–Vis–NIR spectrometer as described earlier.

4.2. In situ ³¹P NMR studies

Aliquots of freshly prepared solutions of 1 or 2 in C_6D_6 , or in THF containing a small amount of d_8 -toluene, contained in sealed NMR tubes were cooled in a

dry-ice/acetone slush bath. Standard solutions of the appropriate tertiary phosphine in d_8 -toluene were prepared similarly. The solutions were mixed, placed immediately in a NMR probe cooled to -40 °C, and the ${}^{31}P{}^{1}H{}$ NMR spectra recorded immediately.

4.3. Preparations

4.3.1. $[Ru(acac)_2(P^iPr_3)_2]$ (3)

A solution of 1, prepared from [Ru(acac)₃] (800 mg, ca. 2.0 mmol) in THF (30 ml), was cooled to ca. -25 °C and PⁱPr₃ (0.78 ml, 4.08 mmol) was added from a gas-tight syringe. After the solution had been stirred for 1 h, a fine solid had formed. The volume of solvent was reduced in vacuo by about half and cold hexanes were added by cannula. The mixture was stirred for ca. 5 min, the solid was allowed to settle, and the supernatant was decanted. The process was repeated several times with cold pentane until the supernatant was almost colorless. Filtration gave trans-3 as a rust-red solid (0.58 g, ca. 45%), which was stable in an inert atmosphere at ca. -20 °C but decomposed slowly on exposure to air. The complex was converted into cis-3 in toluene over 1 h at room temperature. The product isolated from this solution by removal of solvent in vacuo was identical to that obtained independently by Werner and coworkers [9] by reduction of $[Ru(acac)_3]$ with Zn/Hg in the presence of P'Pr₃ or by treatment of $[Ru(acac)_2(Sb'Pr_3)_2]$ with an excess of $P^i Pr_3$.

4.3.2. $[Ru(acac)_2(PCy_3)_2]$ (4)

A solution of **2**, prepared from $[Ru(acac)_3]$ (300 mg, 0.75 mmol) in THF (15 ml), was stirred with PCy₃ (500 mg, 1.78 mmol) at room temperature. After the solution had been stirred for 30 min, a fine brown solid had formed. The mixture was stirred for another 6 h and set aside overnight. The supernatant was removed by decantation and the brown solid was washed with pentane. The yield of **4** was 530 mg (82%). The solid is air-stable and insoluble in benzene and toluene at room temperature, though it is soluble in the hot solvents. It is partly soluble in THF at room temperature and decomposes in CH₂Cl₂.

4.3.3. Cis-[$Ru(acac)_2(\eta^2 - C_2H_4)(P^iPr_3)$] (5)

A magnetically stirred solution of **2** (freshly prepared from [Ru(acac)₃] (1.0 g, 2.51 mmol) in benzene (40 ml)) was treated with P^iPr_3 (0.48 ml, 2.51 mmol) at room temperature and set aside overnight, causing the colour to change from yellow to orange. Solvent was removed in vacuo and the orange residue was redissolved in pentane (ca. 5 ml). The solution was cooled to -20 °C to give a red, crystalline solid. The supernatant was removed by decantation and evaporated to ca. half-volume in vacuo to give a second crop of red solid. Both crops were washed by decantation with cold pentane. The yield of **5** was 676 mg (55%). X-ray quality crystals were selected from the first crop. The solid is stable indefinitely under argon at 25 °C and is very soluble in benzene or toluene to give yellow solutions that turn green immediately on exposure to air.

4.3.4. $cis-[Ru(acac)_2(\eta^2-C_2H_4)(PCy_3)]$ (6)

A solution of **2** (freshly prepared from $[Ru(acac)_3]$ (420 mg, 1.05 mmol) in benzene (40 ml)) was treated dropwise with a solution of PCy₃ (292 mg, 1.04 mmol) in benzene (10 ml) at room temperature. After 1 h the colour had changed from yellow to orange. The mixture was stirred overnight and worked up as for **5** to give **6** as a yellow, microcrystalline solid (641 mg, 68%). Its properties are similar to those of **5**. X-ray quality crystals were obtained by slow evaporation of the supernatant after the first crop of solid.

4.3.5. $trans-[Ru(acac)_2(CO)(P^tPr_3)]$ (trans-8)

(i) A solution of *trans*-3 (246 mg, 0.40 mmol) in toluene (2 ml) and hexanes (5 ml) at -70 °C was allowed to warm to room temperature under CO (1 bar). When the temperature had reached -15 °C, the solution had become yellow. Solvents were removed in vacuo leaving a yellow solid, which was treated with pentane (5 ml). The resulting solution was evaporated to ca. 2 ml and set aside at -20 °C to give a yellow solid, which was separated by filtration and washed with cold pentane (2 ml). The yield of *trans*-8 was 105 mg (52%). The solid turns green in air over several months and is readily soluble in benzene, toluene, and THF.

(ii) A solution of *cis*-**3** (197 mg, 0.32 mmol) in benzene (10 ml) was stirred for 3 days under CO (3 bar) in a medium pressure vessel behind a safety shield. Monitoring by ${}^{31}P{}^{1}H{}$ NMR spectroscopy showed the products to be *trans*-**8** and free P^{*i*}Pr₃, together with a small amount of *cis*-**8**.

(iii) Carbon monoxide was bubbled gently through a solution of **5** (ca. 15 mg, 0.03 mmol) in C_6D_6 (0.4 ml) for 30 min. Monitoring by ¹H and ³¹P{¹H} NMR spectroscopy showed that *trans*-**8** had been formed quantitatively after several hours.

4.3.6. $cis-[Ru(acac)_2(CO)(P^iPr_3)]$ (cis-8)

A solution of *trans*-8 (150 mg, 0.31 mmol) in benzene (10 ml) was heated under reflux for 1 h, causing the colour to fade. The solution was evaporated almost to dryness and the residue was treated with pentane (2 ml). The solution was set aside at -20 °C for 2 days, and the resulting pale yellow, crystalline solid was separated by filtration and washed with cold pentane. The yield of *cis*-8 was 85 mg (57%). The solid is air-stable for several weeks and readily soluble in aromatic solvents.

4.3.7. $trans-[Ru(acac)_2(CO)(PCy_3)]$ (trans-9)

A suspension of 4 (200 mg, 0.23 mmol) in benzene (10 ml) was stirred under CO (1 bar). A clear orange solution was formed within 30 min. Most of the solvent was removed in vacuo, the yellow residue was stirred with pentane (5 ml), and the solution was evaporated to a volume of ca. 2 ml in vacuo. The yellow solid that precipitated was washed with ca. 2 ml of pentane. The yield of *trans*-9 was 101 mg (72%). The properties of the solid are similar to those of *trans*-8.

4.3.8. $cis - [Ru(acac)_2(CO)(PCy_3)]$ (cis-9)

A solution of *trans*-**9** (200 mg, 0.33 mmol) in benzene (10 ml) was heated under reflux for 1 h. The solution was evaporated almost to dryness and pentane (ca. 3 ml) was added to the yellow residue. The light yellow solid that formed overnight was separated by filtration. The yield of *cis*-**9** was 123 mg (62%).

4.3.9. $cis-[{Ru(acac)_2(P^iPr_3)}_2(\mu-N_2)]$ (10)

Benzene (10 ml) was added to *cis*-3 (167 mg, 0.34 mmol) in a medium pressure vessel under industrial grade hydrogen gas (1 bar), which probably contains at least 100 ppm N₂ (this level is specified in Grade 3.8 high purity hydrogen). The pressure was increased to 3 bar and the yellow solution was heated at 60 °C for 2 days. The solution was allowed to cool to room temperature and the hydrogen pressure reduced to 1 bar. The solution was cannulated into a Schlenk flask under hydrogen and the solvent was removed in vacuo. The yellow residue was dissolved in a small volume of hexanes or pentane and the solution was set aside at -20 °C for 2 days. The yellow crystals were separated by filtration under argon and washed with small aliquots of hexanes or pentane. The yield of **10** was 149 mg (92%).

The solid compound is stable to air for short periods but is best stored under argon. It forms thermally stable solutions in benzene or toluene that immediately turn green in air. Solutions in CH_2Cl_2 immediately turn red. The products of these decompositions have not been identified.

4.4. X-ray crystallography

Crystal data and details of data collection are given in Table 11. The data for complexes *cis*-3 and 5 were collected on a Rigaku AFC6R diffractometer with graphite-monochromated CuK α radiation ($\lambda = 1.54178$ Å) and a rotating anode generator, those for 6 on a Rigaku AFC6S diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å), and those for *trans*-4 and 10 on a Nonius Kappa CCD area detector with graphite-monochromated Mo K α radiation. The structures of *cis*-3, 5 and 6 were solved by direct methods [65] and those of *trans*-4 and 10 by heavy atom Patterson methods [66]. Least-squares refinements were Table 11

Crystal and refinement data for cis-[Ru(acac)₂(PⁱPr₃)₂] (cis-3), trans-[Ru(acac)₂(PCy₃)₂] (trans-4), cis-[Ru(acac)₂(η^2 -C₂H₄)(PⁱPr₃)] (5), cis-[Ru(acac)₂(η^2 -C₂H₄)(PCy₃)] (6), and cis-[{Ru(acac)₂(η^2 -C₂H₄)(PCy₃)] (7), cis-[Ru(acac)₂(η^2 -C₂H₄)(PCy₃)] (7), cis-[$(\vec{P'Pr_3})_2(\mu - N_2)] (10 \cdot C_6 H_{14})^a$

	cis-3	trans-4	5	6	$10 \cdot C_6 H_{14}$
Empirical formula	C ₂₈ H ₅₆ O ₄ P ₂ Ru	$C_{46}H_{80}O_4P_2Ru$	C ₂₁ H ₃₉ O ₄ PRu	$C_{30}H_{51}O_4PRu$	$C_{44}H_{84}N_2O_8P_2Ru_2$
Formula weight	619.77	860.16	487.58	607.78	1033.24
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ <i>n</i> (No. 14)	<i>P</i> 2 ₁ <i>n</i> (No. 14)	<i>P</i> 1̄ (No. 2)	<i>P</i> 2 ₁ <i>c</i> (No. 14)	<i>C</i> 2/ <i>c</i> (No. 15)
Crystal colour, habit	orange, block	brown, plate	orange, wedge	orange, triangular fragment	orange, block
a (Å)	10.660(3)	9.56650(10)	9.747(1)	13.699(4)	20.087(1)
b (Å)	19.825(3)	17.8085(3)	15.645(2)	11.780(4)	14.562(1)
<i>c</i> (Å)	15.504(3)	13.6210(2)	17.270(2)	19.130(3)	18.065(1)
α (°)			66.391(7)		
β (°)	98.89(2)	109.4660(10)	81.03(1)	92.94(2)	106.538(4)
γ (°)			89.79(1)		
$V(\text{\AA}^3)$	3237(1)	2187.90(5)	2378.5(5)	3076(2)	5065.5(5)
Ζ	4	2	4	4	4
$D_{\text{calc}} (\text{g cm}^{-3})$	1.272	1.306	1.362	1.31	1.355
$\mu (\mathrm{cm}^{-1})$	50.76	4.70	62.70	5.90	7.07
<i>T</i> (K)	193	200	243	296	200
Crystal dimensions (mm)	$0.22 \times 0.18 \times 0.15$	$0.27 \times 0.14 \times 0.11$	$0.30 \times 0.16 \times 0.10$	$0.50 \times 0.30 \times 0.18$	$0.20 \times 0.10 \times 0.10$
<i>F</i> (000)	1320.00	924.00	1024.00	1284.00	2176.00
$2\theta_{\max}$ (°)	120.1	66.3	120.1	50.1	55.1
Number of reflections measured	6272	45663	7548	5995	9739
Number of unique reflections (R_{int})	4813 (0.026)	8233 (0.047)	7064 (0.046)	5743 (0.018)	5751 (0.051)
Number of observations	4295 $[I > 2\sigma(I)]$	5758 $[I > 3\sigma(I)]$	5865 $[I > 2\sigma(I)]$	4319 $[I > 3\sigma(I)]$	$3093 \ [I > 3\sigma(I)]$
Number of variables	317	241	511	358	254
<i>p</i> -Factor	0.030	0.355; 0.156; 0.106 ^b	0.020	1.97; 0.322; 1.49 ^b	0.040
$R; R_W$	0.028; 0.034	0.035; 0.038	0.036; 0.044	0.028; 0.034	0.050; 0.059
S	1.71	1.407	1.88	1.22	1.44
$\rho_{\rm max}, \rho_{\rm min} ({\rm e}^{-3})$	0.75, -0.52	0.46, -0.92	0.78, -0.74	0.28, -0.46	0.62, -0.55

^a Definitions: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_W = \left[\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2\right]^{1/2}$; $w = [\sigma^2(F_o) + 0.25p^2F_o^2]^{-1}$; GOF = $\left[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)\right]^{1/2}$; N_o = number of observations, N_v = number of observations. variables. ^b 3-Term Chebychev polynomial: J.R. Carruthers, D.J. Watkin, Acta Crystallogr., Sect. A 35 (1979) 698.

carried out with use of the crystallographic software packages teXsan [67] (for *cis*-3, 5 and 10) and CRYS-TALS [68] (for *trans*-4 and 6).

The non-hydrogen atoms of cis-3, trans-4 and 5 were refined anisotropically, methyl groups being aligned to best-fit peaks in difference electron-density maps. For cis-3 and 5, the hydrogen atoms were included at geometrically determined positions which were periodically recalculated but not refined; for trans-4 the hydrogen atoms rode on the carbon atom to which they were attached. In 6 the coordinated ethene was disordered over two sites with occupancies of 55(4) and 45(4)% (see text). The optimal refinement required the imposition of restraints on the Ru-C distances, which were based on those of the closely related complexes 2 and 5. Consequently the e.s.d.s of the geometrical parameters of the Ru-ethene fragment are underestimated and no e.s.d.s are reported for these carbon atom positional parameters. The remaining atoms were refined similarly to those of cis-3, trans-4 and 5.

In **10** a region of electron density around the twofold axis at 0.50, *y*, 0.75 (*y* ca. 0.76) was modelled as a disordered molecule of *n*-hexane with restraints on distances and angles. Elongated ellipsoids on C(17) and C(19) implied that these atoms also were disordered; each was split over two sites and relative occupancies were refined. All ordered non-hydrogen atoms were refined anisotropically; disordered atoms were refined isotropically. Hydrogen atoms of the solvate and of the minor conformation for the disordered P^iPr_3 were omitted; other hydrogen atoms were included at calculated positions.

Neutral atom scattering factors [69], the anomalous dispersion terms ($\Delta f'$ and $\Delta f''$) [70], and the mass attenuation coefficients [71] were taken from the appropriate references.

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Appendix A. Supporting information available

Tabulation of ³¹P NMR chemical shifts for *cis*- and *trans*-[Ru(acac)₂(PR₃)₂] and plots of $\Delta\delta_P$ versus δ_P (free ligand); tables giving X-ray data for *cis*-3, *trans*-4, 5, 6 and 10. This information is available free of charge from the Internet at http://pubs.acs.org. Supplementary data

associated with this article can be found, in the online version, at doi:10.1016/j.ica.2004.07.062.

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