Synthesis and Reactions of Azido Complexes of Ruthenium

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Abstract

Sodium azide reacts with $\operatorname{RuH}_2(\operatorname{dmpe}_2(1a) (\operatorname{dmpe} = 1,2\operatorname{-bis}(\operatorname{dimethylphosphino})\operatorname{ethane})$ in methanol solution to form $\operatorname{RuH}(N_3)(\operatorname{dmpe}_2(2a))$, and reacts with $\operatorname{RuCl}_2(\operatorname{depe}_2(3b))$ (depe = 1,2-bis(diethylphosphino)ethane) to form the bis(azide) complex $\operatorname{Ru}(N_3)_2(\operatorname{depe}_2(4b))$. The crystal structures of $\operatorname{Ru}(\operatorname{Cl}_2(\operatorname{depe}_2(3b))$ and $\operatorname{Ru}(N_3)_2(\operatorname{depe}_2(4b))$ have been determined and indicate that the chloro groups in (3b) and the azido groups in (4b) are *trans* across the metal centre.

Introduction

The azide group (N_3^-) can be introduced relatively easily into transition metal complexes by substitution. Azide has been structurally characterized in metal complexes both as an η^1 -ligand and as a bridging ligand with end-to-end coordination or with a terminal nitrogen of the N₃ group bridging two or more metal centres.

In contrast to organic azides, the chemistry of metal-coordinated azides is only poorly explored. Organic azides react photochemically with scission of the N–N₂ bond to form reactive nitrenes, and thermally with alkenes and arenes to form heterocycles by a 1,3-dipolar addition.¹ In similar reactions, coordinated azides are known to undergo dipolar additions with CS₂, nitriles and isonitriles to form coordinated heterocycles,² and bound azide has been employed in the synthesis of triazoles by [3+2] cycloadditions with acetylenes.³

In the reaction of a cobalt azide with terminal acetylenes, the alkyne acts as an acid, and protonation of bound azide with subsequent replacement of HN_3 by acetylide occurs to form cobalt acetylides.³ Acetylide complexes of transition metals have been identified as potentially important precursors to

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¹ See for example: Wamhoff, H., in 'Comprehensive Heterocyclic Chemistry' (Eds A. Katritzky and C. W. Rees) Vol. 5, p. 669 (John Wiley and Sons: New York 1984); Lwowski, W., in 'The Chemistry of the Azido Group' (Ed. S. Patai) p. 331 (Interscience: London 1971).

² Dori, Z., and Ziolo, R. F., *Chem. Rev.*, 1973, **73**, 247, and references therein; Ziolo, R. F., and Dori, Z., *J. Am. Chem. Soc.*, 1968, **90**, 6560; Beck, W., Fehlhammer, W. P., Bock, H., and Bander, M., *Chem. Ber.*, 1969, **102**, 3637; Suzuki, H., Nakaya, C., and Matano, Y., *Tetrahedron Lett.*, 1993, **34**, 1055.

³ Kemmerich, T., Nelson, J. H., Takach, N. E., Boehme, H., Jablonski, B., and Beck, W., Inorg. Chem., 1982, 21, 1226.

materials with non-linear optical properties⁴ and the investigation of alternative synthetic approaches to acetylide-bridged organometallic dimers, trimers and polymers is a developing area of organometallic chemistry. We have previously demonstrated⁵ that metal bis(acetylide) complexes can be synthesized from $FeH_2(pp)_2$ (pp = $R_2PCH_2CH_2PR_2$, R = Me, dmpe; Et, depe; Pr, dprpe) by reaction with terminal acetylenes in alcohol solution, or from $Fe(N_3)_2(pp)_2$ by reaction with terminal acetylenes.⁶

We report here the synthesis and properties of two ruthenium azides, RuH(N₃)(dmpe)₂ (2a) and Ru(N₃)₂(depe)₂ (4b), the reaction of (4b) with phenylacetylene to form Ru(C \equiv CPh)₂(depe)₂ (5b), and the crystal structures of Ru(Cl)₂(depe)₂ (3b) and Ru(N₃)₂(depe)₂ (4b).

Results and Discussion

Synthesis and Characterization of Azido Complexes

Ruthenium dihydride complexes, $\operatorname{RuH}_2(\operatorname{pp})_2(1)$, provide precursors for a variety of metal complexes since, in methanol solution, the complexes are protonated to form $[\operatorname{RuH}(\operatorname{H}_2)(\operatorname{pp})_2]^+$, and displacement of the η^2 -bound hydrogen by better ligands occurs rapidly at room temperature.⁷ Reaction of $[\operatorname{RuH}(\operatorname{H}_2)(\operatorname{dmpe})_2]^+$, generated from $\operatorname{RuH}_2(\operatorname{dmpe})_2$ (1a), with N_3^- results in rapid formation of $\operatorname{RuH}(\operatorname{N}_3)(\operatorname{dmpe})_2$ (2a), Scheme 1. The *trans* bis(azide) complex, $\operatorname{Ru}(\operatorname{N}_3)_2(\operatorname{dmpe})_2$ (4a), does not appear to form from $\operatorname{RuH}(\operatorname{N}_3)(\operatorname{dmpe})_2$ (2a) under these conditions.



 $\operatorname{RuCl}_2(\operatorname{dmpe})_2$ (3a) is unchanged when treated with sodium azide in refluxing methanol. However, the ruthenium complex $\operatorname{RuCl}_2(\operatorname{depe})_2$ (3b) does react with excess azide in refluxing methanol to form $\operatorname{Ru}(N_3)_2(\operatorname{depe})_2$ (4b), Scheme 2. Clearly, subtle changes to the phosphine ligand modify the reactivity of the

⁵ Field, L. D., George, A. V., Hambley, T. W., Malouf, E. Y., and Young, D. J., *J. Chem. Soc., Chem. Commun.*, 1990, 931; Field, L. D., George, A. V., Malouf, E. Y., Slip, I. H. M., and Hambley, T. W., *Organometallics*, 1991, **10**, 3842.

⁶ Buys, I. E., Field, L. D., George, A. V., Hambley, T. W., and Pike, S. R., unpublished data.
⁷ Field, L. D., Hambley, T. W., and Yau, B. C. K., *Inorg. Chem.*, 1994, 33, 2009.

⁴ Pollagi, T. P., Stoner, T. C., Dallinger, R. F., Gilbert, T. M., and Hopkins, M. D., J. Am. Chem. Soc., 1991, **113**, 703; Myers, L. K., Langhoff, C., and Thompson, M. E., J. Am. Chem. Soc., 1992, **114**, 7560; Sun, Y., Taylor, N. J., and Carty, A. J., J. Organomet. Chem., 1992, **423**, C43; Lewis, J., Khan, M. S., Kakkar, A. K., Raithby, P. R., Fuhrmann, K., and Friend, R. H., J. Organomet. Chem., 1992, **433**, 135; Khan, M. S., Davis, S. J., Kakkar, A. K., Schwartz, D., Lin, B., Johnson, B. F. G., and Lewis, J., J. Organomet. Chem., 1992, **424**, 87; Johnson, B. F. G., Kakkar, A. K., Khan, M. S., and Lewis, J., J. Organomet. Chem., 1991, **409**, C12; Pirio, N., Touchard, D., Dixneuf, P. H., Fettouhi, M., and Ouahab, L., Angew. Chem. Int. Ed. Engl., 1992, **31**, 651.

metal centre. The increased steric requirement of the depe ligand compared with the dmpe ligand may make depe a more labile ligand which facilitates the substitution reaction.



The azido complexes (2a) and (4b) both show one singlet resonance in their ³¹P n.m.r. spectra, indicative of a *trans* complex in which the four phosphorus atoms of the chelating ligands are equivalent and occupy an equatorial plane around the metal atom.

The ¹H n.m.r. spectra of the azido complexes reflect the symmetry of the ligand environment; a more complex spectrum is observed in the case of the azido hydrido complex (2a) than in the symmetrically substituted bis(azido) complex (4b). The α methylene hydrogens of the ethyl groups of the depe ligand in (4b) are diastereotopic and give rise to multiplet patterns in the ¹H n.m.r. spectrum on complexation with the metal. The hydride ligand in Ru(H)(N₃)(dmpe)₂ (2a) is very shielded (δ -20.58) and the signal appears as a quintet (²J_{P,H} 20.9 Hz) which collapses to a singlet resonance on ³¹P decoupling.

The stretching frequency of the azide ion is shifted approximately 15 cm^{-1} to lower energy on binding to the metal. A similar shift is observed when azide is bound to iron(II) in the complexes $\text{Fe}(N_3)_2(\text{dmpe})_2$ and $\text{Fe}(N_3)_2(\text{depe})_2$.⁶

The coordinated azido ligands are replaced by acetylide in an alcohol solvent. Thus, the bis(phenylacetylide) complex, $\operatorname{Ru}(C \equiv CPh)_2(\operatorname{depe})_2$ (5b) can be prepared from $\operatorname{Ru}(N_3)_2(\operatorname{depe})_2$ (4b) by refluxing a methanol solution of the complex with phenylacetylene in the presence of sodium methoxide.

X-Ray Crystal Structure of $RuCl_2(depe)_2$ (3b) and $Ru(N_3)_2(depe)_2$ (4b)

The crystal structure of RuCl₂(depe)₂ (3b) (Fig. 1) shows the two chlorine atoms to be *trans* to one another (Tables 1 and 2). The length of the Ru–Cl bond $(2 \cdot 427(1) \text{ Å})$ is similar to that determined for Ru(Cl)₂(dppm)₂ $(2 \cdot 426(1) \text{ Å}; dppm = 1,2$ -bis(diphenylphosphino)methane)⁸ and shorter than in either Ru(Cl)₂(dppe)₂ $(2 \cdot 436(1) \text{ Å}; dppe = 1,2$ -bis(diphenylphosphino)ethane)⁹ or Ru(Cl)₂(dppp)₂ $(2 \cdot 435(1) \text{ Å}; dppp = 1,2$ -bis(diphenylphosphino)propane).¹⁰ In contrast, in (3b) the metal–phosphorus bonds are slightly shorter than those in any of the related complexes Ru(Cl)₂(dppm)₂, Ru(Cl)₂(dppe)₂ or Ru(Cl)₂(dppp)₂, (Table 3^{6,8–11}).

The crystal structure of $Ru(N_3)_2(depe)_2$ (4b) (Fig. 2) shows the three nitrogen atoms of each azide group to be approximately linear and form a Ru–N–N₂ angle of $132.9(3)^{\circ}$ (Tables 4 and 5). The observed Ru–N–N₂ angle compares with the angle

⁸ Chakravarty, A. R., Cotton, F. A., and Schwotzer, W., Inorg. Chim. Acta, 1984, 84, 179.

⁹ Lobana, T. S., Singh, R., and Tiekink, E. R. T., J. Coord. Chem., 1990, 21, 225.

¹⁰ Fontes, M. R. M., Oliva, G., Cordeiro, L.-A. C., and Batista, A. A., J. Coord. Chem., 1993, 30, 125.

¹¹ Baker, M. V., Field, L. D., and Hambley, T. W., Inorg. Chem., 1988, 27, 2872.



Fig. 1. View of the complex trans-RuCl₂(depe)₂ (3b) showing atom labelling.

Table	1.	Final	atomic	coordinates	for	trans-RuCl ₂ (depe) ₂	(3b)	with	estimated	standard
				de	eviat	ions in parentheses				

Atom	$10^4 x$	$10^{4}y$	$10^{4}z$
Ru	0	0	0
Cl(1)	1073(1)	1744(1)	1242(1)
P(1)	-2033(1)	1055(1)	-361(1)
P(2)	-538(1)	-1022(1)	1334(1)
C(1)	-2835(5)	308(7)	489(5)
C(2)	-1846(5)	-37(6)	1518(4)
C(3)	-2143(8)	2833(8)	-26(8)
C(4)	-1653(9)	3751(9)	-516(9)
C(5)	-3321(5)	838(6)	-1627(4)
C(6)	-4709(5)	1219(8)	-1753(5)
C(7)	677(5)	-1108(7)	2647(4)
C(8)	233(6)	-1349(9)	3554(4)
C(9)	-1225(7)	-2711(6)	1102(5)
C(10)	-2165(8)	-3201(8)	1568(6)

Table 2. Selected bond lengths and bond angles in trans-RuCl₂(depe)₂ (3b) Superscript i refers to the transformation -x, -y, -z

	Distar	ices (A)			
P(1)–Ru	$2 \cdot 338(1)$	P(2)–Ru	$2 \cdot 340(1)$		
Cl(1)–Ru	$2 \cdot 427(1)$	P(1)-C(1)	$1 \cdot 840(6)$		
C(1) - C(2)	$1 \cdot 483(7)$	P(1)-C(3)	1.847(8)		
P(1)-C(5)	$1 \cdot 820(5)$	C(5)-C(6)	$1 \cdot 506(7)$		
	Angles	(degrees)			
P(1)-Ru-P(2)	$83 \cdot 40(4)$	$P(1)$ -Ru- $P(2)^{i}$	96.60(4)		
P(1)-Ru- $Cl(1)$	89.36(5)	$P(1)$ -Ru- $Cl(1)^{i}$	90.64(5)		
P(2)-Ru- $Cl(1)$	$92 \cdot 63(4)$	$P(2)$ -Ru- $Cl(1)^{i}$	$87 \cdot 37(4)$		
Ru-P(1)-C(1)	$107 \cdot 8(2)$	P(1)-C(1)-C(2)	110.5(4)		
Ru-P(1)-C(5)	$120 \cdot 1(2)$	P(1)-C(5)-C(6)	$118 \cdot 8(4)$		

<u></u>			M Cl	N. NT(1)	N(1) N(0)	Def
Complex	M-P(1)	M-P(2)	M-CI	M-N(1)	N(1) - N(2)	Rei.
$Fe(dmpe)_2Cl_2$	$2 \cdot 241(1)$	$2 \cdot 230(1)$	$2 \cdot 352(1)$			11
$Fe(depe)_2Cl_2$	$2 \cdot 256(2)$	$2 \cdot 264(2)$	$2 \cdot 344(1)$			11
$Ru(depe)_2Cl_2$	$2 \cdot 338(1)$	$2 \cdot 340(1)$	$2 \cdot 427(1)$			this work
$Ru(dppm)_2Cl_2$	$2 \cdot 340(1)$	$2 \cdot 367(1)$	$2 \cdot 426(1)$			8
$Ru(dppe)_2Cl_2$	$2 \cdot 369(1)$	$2 \cdot 389(1)$	$2 \cdot 436(1)$			9
$Ru(dppp)_2Cl_2$	$2 \cdot 416(1)$	$2 \cdot 441(1)$	$2 \cdot 435(1)$			10
$Fe(dmpe)_2(N_3)_2$	$2 \cdot 239(1)$	$2 \cdot 242(1)$		$2 \cdot 024(3)$	$1 \cdot 162(5)$	6
$\operatorname{Ru}(\operatorname{depe})_2(\operatorname{N}_3)_2$	$2 \cdot 354(1)$	$2 \cdot 343(1)$		$2 \cdot 124(2)$	$1 \cdot 180(5)$	this work

Table 3. Comparison of bond lengths (Å) for iron and ruthenium phosphine complexes

Table 4. Final atomic coordinates for trans- $Ru(N_3)_2(depe)_2$ (4b) with estimated standard deviations in parentheses

Atom	$10^4 x$	10^4y	$10^{4}z$
Ru	5000	0	0
P(1)	4274(1)	1196(1)	-1397(1)
P(2)	3886(1)	607(1)	-159(1)
N(1)	4572(2)	-2334(4)	-541(2)
N(2)	5996(2)	3041(4)	785(2)
N(3)	3456(2)	-3793(6)	-1026(3)
C(1)	3307(2)	1721(5)	-1765(3)
C(2)	3088(2)	653(5)	-1331(3)
C(3)	3541(2)	-679(5)	283(3)
C(4)	2748(3)	-240(7)	1(5)
C(5)	3803(3)	2637(5)	141(3)
C(6)	4275(3)	2945(6)	1089(3)
C(7)	4075(5)	81(5)	-2312(4)
C(8)	3461(3)	-1230(6)	-2701(3)
C(9)	4625(3)	3116(6)	-1481(3)
C(10)	4129(4)	4042(7)	-2300(4)



Fig. 2. View of the complex $trans-\operatorname{Ru}(N_3)_2(\operatorname{depe})_2$ (4b) showing atom labelling.

of $116 \cdot 7(7)^{\circ}$ for the complex $[Ru(N_2)(N_3)(en)_2]^+$, ¹² $125 \cdot 4(5)^{\circ}$ for Cu–N–N₂ in the complex $[Cu(Br)(N_3)(Et_2NCH_2CH_2N(H)CH_2CH_2NEt_2)_2]$,¹³ and angles of between $121 \cdot 4(6)$ and $129 \cdot 9(5)^{\circ}$ for Mo–N–N₂ in the complex [Mo(N₃)₄(NO)(H₂NO)].¹⁴ The N–N bond lengths are 1.180(5) and 1.170(5) Å for RuN–N and NN–N respectively, and these are similar to 1.179(10) and 1.146(11) Å for the corresponding bond lengths in the ruthenium complex $[Ru(N_2)(N_3)(en)_2]^+$.¹² The N-N bond lengths in HN₃ are 1.240(3) and 1.134(3) Å,¹⁵ and in N₃⁻¹ 1.15(2) Å.¹⁶ The azide groups in (4b) are disposed *anti* with respect to one another in the crystal. There is only a small change in Ru-P bond lengths when the chloride ligands are exchanged for azide ligands. The Ru-P and Ru-L $(L = Cl, N_3)$ bond lengths are longer than the corresponding bond lengths in the analogous iron complex $Fe(N_3)_2(dmpe)_2$ (Table 3).

	Distances (Å)						
P(1)–Ru	$2 \cdot 354(1)$	P(2)-Ru	$2 \cdot 343(1)$				
N(1)-Ru	$2 \cdot 124(2)$	N(3) - N(2)	$1 \cdot 170(5)$				
N(2) - N(1)	1.180(5)	P(1)-C(1)	$1 \cdot 847(3)$				
C(1) - C(2)	1.530(4)	P(1) - C(9)	$1 \cdot 852(3)$				
P(1) - C(7)	$1 \cdot 825(4)$	$\mathbf{C}(7) - \mathbf{C}(8)$	1.534(5)				
	Angles	(degrees)					
P(1)-Ru- $P(2)$	$82 \cdot 3(0)$	$P(1)$ -Ru- $P(2)^{i}$	$97 \cdot 8(1)$				
P(1)-Ru- $N(1)$	$91 \cdot 8(1)$	P(1)-Ru-N(1) ⁱ	$87 \cdot 7(1)$				
P(2)-Ru- $N(1)$	$91 \cdot 4(1)$	P(2)-Ru-N(1) ⁱ	$88 \cdot 3(1)$				
N(2)-N(1)-Ru	$132 \cdot 9(3)$	N(1)-N(2)-N(3)	$177 \cdot 4(5)$				
Ru-P(1)-C(9)	$116 \cdot 8(1)$	Ru-P(1)-C(7)	120.7(1)				
P(2)-C(3)-C(4)	$115 \cdot 8(3)$	P(1)-C(1)-C(2)	$110 \cdot 1(2)$				

Table 5. Selected bond lengths and bond angles in $trans-Ru(N_3)_2(depe)_2$ (4b) Superscript i refers to the transformation $1 - \pi - \mu = -\pi$

Conclusions

Two azido complexes of ruthenium (2a) and (4b) have been synthesized and characterized. The azido ligands of $Ru(N_3)_2(depe)_2$ (4b) may be replaced by phenylacetylido ligands by refluxing a solution of (4b) in excess phenylacetylene. The crystal structures of $Ru(Cl)_2(depe)_2$ (3b) and $Ru(N_3)_2(depe)_2$ (4b) have been determined and indicate that the four phosphorus atoms of the chelating bisphosphine ligands lie in one plane, with the two non-phosphorus ligands of each complex adopting a geometry *trans* to one another.

¹² Davis, B. R., and Ibers, J. A., Inorg. Chem., 1970, 9, 2768.

¹³ Ziolo, R. F., Allen, M., Titus, D. D., Gray, H. B., and Dori, Z., Inorg. Chem., 1972, 11, 3044.

¹⁴ Wieghardt, K., Backes-Dahmann, G., Swiridoff, W., and Weiss, J., Inorg. Chem., 1983, 22, 1221. ¹⁵ Amkle, E., and Dailey, B. P., J. Chem. Phys., 1950, 18, 1422.

¹⁶ Evans, B. L., Yoffe, A. D., and Gray, P., Chem. Rev., 1959, 59, 515.

Experimental

Tetrahydrofuran was distilled from benzophenone ketyl under nitrogen prior to use. Acetone was dried by distillation from calcium sulfate, and methanol was dried by distillation from magnesium methoxide.¹⁷ Sodium azide and phenylacetylene were obtained from Aldrich, and phenylacetylene was distilled before use. The phosphorus ligands dmpe and depe were obtained from Strem, and RuCl₂(PPh₃)₃ was synthesized by literature methods.¹⁸ Deuterated solvents were obtained from Merck and Aldrich and used as received. ¹H (400 · 1 MHz), ^{31}P (162.0 MHz) and ^{13}C (100.6 MHz) n.m.r. spectra were recorded on a Bruker AMX-400 spectrometer in the solvents indicated. ^{31}P n.m.r. spectra were referenced to neat, external $P(OMe)_3$, taken as δ 140.85; ¹H and ¹³C n.m.r. spectra were referenced to solvent residuals. U.v.-visible spectra were recorded on a Hitachi 150–20 spectrophotometer with tetrahydrofuran as the solvent. Infrared spectra were recorded on a Perkin Elmer 1600 F.t.i.r. spectrometer with the sample in a Nujol mull. Electron impact mass spectra were obtained by using an AEI-MS30 mass spectrometer. Microanalyses were performed by the University of New South Wales Analytical Chemistry Laboratories and the National Analytical Laboratories. Nitrogen (>99.5%) was obtained from Commonwealth Industrial Gases (C.I.G.) and used as received.

Crystallography

Cell constants were determined by a least-squares fit to the θ values of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4-F diffractometer with a graphite monochromator. Data were reduced and Lorentz, polarization and decomposition corrections were applied by using the Enraf-Nonius Structure Determination Package.¹⁹ The structure of (3b) was solved by heavy atom methods and was refined by full-matrix least-squares analysis with Texsan.²⁰ Neutral atom scattering factors were obtained from Cromer and Waber.²¹ The structure of (4b) was solved by direct methods and was refined by full-matrix least-squares analysis with SHELX-76.²² Pertinent results are given in Figs 1 and 2 and Tables 1-5. Material deposited comprises atomic coordinates, bond lengths and angles, thermal parameters and structure factors (copies are available from the Australian Journal of Chemistry, P.O. Box 89, East Melbourne, Vic. 3002).

$Bis[1,2-bis(diethylphosphino)ethane]dichlororuthenium(II) (3b)^{23}$

A solution of depe $(2 \cdot 6 \text{ g}, 12 \cdot 6 \text{ mmol})$ in dry acetone (5 ml) was added to a suspension of $RuCl_2(PPh_3)_3$ (5.0 g, 5.2 mmol) in dry acetone (100 ml). The solution was refluxed for 3 h, cooled to room temperature and filtered, and the solvent was removed under vacuum to give a yellow residue. The residue was washed with hexane $(2 \times 10 \text{ ml})$ and dried under vacuum to give trans-RuCl₂(depe)₂ as a bright yellow, crystalline *solid* which was recrystallized from acetone (2.26 g, 74%), m.p. 230°C (dec.) (Found: C, 41.6; H, 8.2. C₂₀H₄₈Cl₂P₄Ru requires C, 41.1; H, 8.3%). ³¹P{¹H} n.m.r. δ [(D₆)benzene] 48.0. ¹H{³¹P} n.m.r. δ [(D₆)benzene] 1.28, m, 24H, 8×CH₃; 1.88, s, 8H, 4×CH₂; 2.00, m, 8H, 8×CHHCH₃; 2.56, m, 8H, 8×CHHCH₃. ¹³C{³¹P,¹H} n.m.r. δ [(D₆)benzene] 9.9, CH₃; 18.0, CH₂; 21.4, CH₂. The crystals were yellow in colour, the specimen chosen for study having the dimensions 0.28 by 0.05 by 0.57 mm. C₂₀H₄₈Cl₂P₄Ru, *M* 584.47, monoclinic, space group, P_{2_1}/n , *a* 10.865(2), *b* 9.978(2), *c* 13.710(2) Å, β 110.55(1)°, *V* 1391.71 Å³, λ (Mo K α) 0.71069, *Z* 4, *D*_{calc} 2.79, F(000) 1224, μ 19.82 cm⁻¹, R 0.036, R' 0.038 for 1997 reflections with $I > 2.5\sigma(I)$. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at calculated sites.

¹⁷ Perrin, D. D., and Armarego, W. L. F., 'Purification of Laboratory Chemicals' 3rd Edn (Pergamon Press: Oxford 1988).

¹⁸ Stephenson, T. A., and Wilkinson, G., J. Inorg. Nucl. Chem., 1966, 28, 945.

¹⁹ Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, Holland, 1985.

²⁰ Texsan, 'Crystal Structure Analysis Package' Molecular Structure Corporation, 1985. ²¹ Cromer, D. T., and Waber, J. T., 'International Tables for X-Ray Crystallography' Vol. 4

(Kynoch Press: Birmingham, 1974). ²² Sheldrick, G. M., SHELX-76, 'A Program for X-Ray Crystal Structure Determination', University of Cambridge, 1976.

²³ Chatt, J., and Hayter, R. G., J. Chem. Soc., 1961, 896.

Bis/1, 2-bis(dimethylphosphino)ethane/dichlororuthenium(II) (3a)²³

trans-RuCl₂(dmpe)₂ was prepared by a method directly analogous to that used for RuCl₂(depe)₂ and employed RuCl₂(PPh₃)₃ (3.6 g, 3.8 mmol) to give an 87% yield of RuCl₂(dmpe)₂ as a pale yellow solid, m.p. 250–255°C (dec.) (lit.²³ 294°). ³¹P{¹H} n.m.r. δ [(D₆)benzene] 38.7. ¹³C{³¹P,¹H} n.m.r. δ [(D₆)benzene] 12.7, CH₃; 29.3, CH₂.

Bis[1,2-bis(dimethylphosphino)ethane]azidohydridoruthenium(II) (2a)

Sodium (200 mg) was added to a solution of RuCl₂(dmpe)₂ (3a) (50 mg, 0.11 mmol) in propan-2-ol/tetrahydrofuran (10:90 v/v) and the mixture was stirred for 2 h. The solvent was removed under vacuum and the resulting residue was extracted with hexane (30 ml). Evaporation of the solvent left Ru(H)₂(dmpe)₂ (1a) as a white solid.⁷ The purity of the crude material was >98% by ³¹P n.m.r. spectroscopy and it was used without further purification. The crude Ru(H)₂(dmpe)₂ (1a) was dissolved in methanol (5 ml), and sodium azide (200 mg) was added with stirring. RuH(N₃)(dmpe)₂ (2a) started to form almost immediately and the reaction progress was monitored by ³¹P n.m.r. spectroscopy. After 2 h the solvent was removed under vacuum and the residue extracted with benzene (2×5 ml). The extracts were combined and filtered, and the solvent was removed to leave RuH(N₃)(dmpe)₂ (2a) as a cream-coloured, air-sensitive powder which was not further purified (28 mg, 60%) and which decomposed without melting at >280°C. ³¹P{¹H} n.m.r. δ [(D₆)benzene] 44·6. ¹H{³¹P} n.m.r. δ [(D₆)benzene] -20·58, s, 1H, RuH,²J_{P,H} 20·9 Hz; 1·28, s, 12H, 4×CH₃; 1·39, m, 4H, 4×CH₄; 1·63, s, 12H, 4×CH₃; 1·71, m, 4H, 4×CH₄. ¹³C{³¹P,¹H} n.m.r. δ [(D₆)benzene] 15·89, CH₃; 23·19, CH₃; 31·88, CH₂.

Bis/1, 2-bis(diethylphosphino)ethane/bis(azido)ruthenium(II) (4b)

RuCl₂(depe)₂ (115 mg, 0·19 mmol) and sodium azide (145 mg, 2·23 mmol) were dissolved in dry methanol (25 ml) and refluxed overnight. The solvent was removed under reduced pressure to leave a yellow residue. The residue was extracted with benzene and the solvent was removed under vacuum to give trans-Ru(N₃)₂(depe)₂ as a bright yellow solid (142 mg, 83%), m.p. 240°C (dec.) (Found: C, 40·3; H, 8·2; N, 14·5. C₂₀H₄₈N₆P₄Ru requires C, 40·0; H, 8·1; N, 14·1%). ν_{max}/cm^{-1} (Nujol) 2026 (N₃). ³¹P{¹H} n.m.r. δ [(D₆)acetone] 52·9. ¹H{³¹P} n.m.r. δ [(D₆)benzene] 1·21, m, 24H, 8×CH₃; 1·91, 2·19, m, 16H, 8×CH₂CH₃; 1·79 s, 8H, 4×CH₂P. ¹³C{³¹P,¹H} n.m.r. δ [(D₆)benzene] 9·1, CH₃; 19·0, **C**H₂CH₃; 21·1, CH₂P. Mass spectrum: m/z 598 (M, 55%), 556 (100), 514 (5). The crystals were yellow in colour, the specimen chosen for study having the dimensions 0·38 by 0·3 by 0·24 mm. C₂₀H₄₈N₆P₄Ru, $M = 597\cdot59$, monoclinic, space group C2/c, a 22·196(9), b 8·324(3), c 19·666(8) Å, β 129·13(4)°, V 2818·6, λ (Mo K α) 0·71069, Z = 4, D_{calc} 1·408, F(000) 1288, μ 7·9 cm⁻¹, R 0·049, R' 0·06 for 2216 reflections with $I > 2\cdot5\sigma(I)$. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were included at calculated sites.

Bis/1, 2-bis(diethylphosphino)ethane/bis(phenylacetylido)ruthenium(II) (5b)

RuCl₂(depe)₂ (50 mg, 86 μ mol) and sodium azide (50 mg, 770 μ mol) were dissolved in dry methanol (5 ml) and refluxed for 16 h. The resultant Ru(N₃)₂(depe)₂ was used without further purification. Phenylacetylene (c. 1 ml) and sodium metal (c. 100 mg) were added to the above reaction solution and refluxed for a further 16 h. The volume of the solution was reduced to approximately 2 ml and a pale solid precipitated from solution. The solid was filtered from the solution and dried under nitrogen to yield Ru(C=CPh)₂(depe)₂ (35 mg, 57%) which was identical in all respects to the complex previously characterized.²⁴

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 24 Buys, I. E., Field, L. D., George, A. V., Hambley, T. W., and Purches, G. R., unpublished data. \bullet