Reactivity of Ruthenium(II) Complexes with 1-Hydroxymethyl- or 1-Benzyl-3,5-dimethylpyrazole and Similar Functionalized Bipyrazoles. *X*-Ray Crystal Structure of Carbonylchlorohydrido(3,5-dimethylpyrazole-N^2)-bis(triphenylphosphine)ruthenium(II)†

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The complexes $[RuCl_2(PPh_3)_3]$, $[RuClH(PPh_3)_3]$, and $[Ru(CO)ClH(PPh_3)_3]$ react with 1-hydroxymethyl-3,5-dimethylpyrazole to give in all cases carbonylchlorohydrido(3,5-dimethylpyrazole-N^2)bis(triphenylphosphine)ruthenium(II) (**1a**) as product. The substitution of the 1-hydroxymethyl group by hydrogen in the pyrazole ring is characteristic of these reactions. Similar reactions take place with 1,1′-di(hydroxymethyl)-3,3′,5,5′-tetramethyl-4,4′-bipyrazole and -methylenedipyrazole to give binuclear bipyrazole-bridged complexes $[\{Ru(CO)ClH(PPh_3)_2\}_2(\mu\text{-}L')]$ [L′ = 3,3′,5,5′-tetramethyl-4,4′-bipyrazole or -methylenedipyrazole respectively]. No reaction occurs with 1-benzyl-3,5-dimethylpyrazole nor with the corresponding 1,1′-dibenzylbipyrazole. We have determined the crystal structure of $[Ru(CO)ClH(Hdmpz)(PPh_3)_2]$ (Hdmpz = 3,5-dimethylpyrazole). It crystallizes in the space group $P2_1n$ with a = 9.687(3), b = 16.244(6), c = 24.022(6) Å, β = 94.19(2)°, and Z = 4. Standard anisotropic least-squares refinement gave R = 0.060 for 3 920 observed reflections. The ruthenium atom is six-co-ordinated in a distorted octahedral geometry with the atom pairs (P,P), (Cl,H), and (C,N) in *trans* positions.

The co-ordination chemistry of substituted pyrazole and pyrazolate ligands is relatively recent[1,2] and for those containing $-CH_2OH$ groups as substituents at the N^1 atom in the pyrazole ring only Ni^{II} and Co^{II} derivatives of 1-hydroxymethyl-3,5-dimethylpyrazole have been described.[3]

There is little in the literature for ruthenium complexes with pyrazole and pyrazolate ligands and only three complexes, $[\{Ru_2H_2(cod)_2L\}(\mu\text{-}pz)_2]$[4] (Hpz = pyrazole; L = PMe_3 or Hpz; cod = cyclo-octa-1,5-diene) and $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4\text{-}CHMe_2)\}_2(pz)_2(OH)]BPh_4$,[5] have been reported.

In this work we describe the reactions of N-substituted pyrazole and bipyrazole ligands containing $-CH_2OH$ or benzyl groups as substituents with $[Ru(CO)ClH(PR_3)_3]$ (R = Ph or p-MeC_6H_4), $[RuClH(PPh_3)_3]$, and $[RuCl_2(PPh_3)_3]$.

Experimental

Starting Materials.—The complexes $[Ru(CO)ClH(PR_3)_3]$ (R = Ph or p-MeC_6H_4), $[RuClH(PPh_3)_3]$, and $[RuCl_2(PPh_3)_3]$ were synthesized as described in the literature.[6–8] The ligands were prepared by literature methods: 1-hydroxymethyl-3,5-dimethylpyrazole (hdmpz),[9] 1-benzyl-3,5-dimethylpyrazole,[10] 1,1′-di(hydroxymethyl)-3,3′,5,5′-tetramethyl-4,4′-bipyrazole,[11] 1,1′-di(hydroxymethyl)-3,3′,5,5′-tetramethyl-4,4′-methylenedipyrazole,[11] 1,1′-dibenzyl-3,3′,5,5′-tetramethyl-4,4′-bipyrazole.[11]

Preparation of Complexes.—The complexes can be synthesized by the following two methods.

(1) To a suspension of $[Ru(CO)ClH(PR_3)_3]$ (R = Ph or p-MeC_6H_4) (0.10 mmol) in ethanol (40 cm^3) at *ca.* 40 °C, was added one equivalent of the ligand in the same solvent and the reaction mixture was stirred for 1 h. A clear solution was obtained after 15 min. After partial evaporation of solvent (to 10 cm^3) a white solid appeared which was filtered off, washed with ethanol and diethyl ether, and dried under vacuum.

(2) To a solution of $[RuClH(PPh_3)_3]$ or $[RuCl_2(PPh_3)_3]$ (0.10 mmol) in benzene (40 cm^3), was added one equivalent amount of the ligand in benzene (10 cm^3). In both cases a colourless solution was obtained. After 1 h stirring the solution was concentrated to *ca.* 10 cm^3 and the white precipitate which appeared was filtered off, washed with benzene, acetone, and diethyl ether, and dried under vacuum.

Crystal Structure.—Crystals of $[Ru(CO)ClH(Hdmpz)(PPh_3)_2]$ (Hdmpz = 3,5-dimethylpyrazole) were grown from a solution in CH_2Cl_2–MeOH (1 : 1).

Crystal data. $C_{42}H_{39}ClN_2OP_2Ru$, M = 786.26, monoclinic, a = 9.687(3), b = 16.244(6), c = 24.022(6) Å, β = 94.19(2)°, U = 3 769.8 $Å^3$, λ = 0.7107 Å, space group $P2_1/n$ (no. 14), Z = 4, D_c = 1.38 g cm^{-3}, $F(000)$ = 1 656, $\mu(Mo\text{-}K_\alpha)$ = 7.61 cm^{-1}. Crystal dimensions: 0.15 × 0.20 × 0.12 mm.

Data collection. CAD4 Diffractometer, ω–2θ scan mode with ω-scan width of (0.80 + 0.35 tanθ)°, graphite-monochromated Mo-K_α radiation; 8 905 reflections measured ($2 \leqslant \theta \leqslant 27°$, $\pm h,k,l$), 8 405 unique reflections. 4 485 with $I \leqslant 3\sigma(I)$ considered as unobserved. Absorption correction was not applied but crystal decay and instability of *X*-ray beam were taken into account [maximum variation of the standard reflection intensity from the mean was $3\sigma(I)$].

Structure analysis and refinement. Scattering factors for neutral atoms and anomalous dispersion factors for Ru, Cl, and P were taken from International Tables.[12] Normal heavy-atom procedures were followed by Fourier synthesis. Full-matrix least-squares refinement (in three blocks for final anisotropic cycles) was made. Unit weights were applied to every reflection. A ΔF Fourier synthesis was calculated to determine the positions of the H atoms which were located in the vicinity of

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† *Supplementary data available* (No. SUP 56651, 3 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

Table 1. Atomic co-ordinates for (**1a**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru	0.670 84(8)	0.268 88(5)	0.734 35(3)
Cl	0.791 62(27)	0.128 33(16)	0.732 06(12)
P(1)	0.684 26(23)	0.266 06(17)	0.832 14(10)
P(2)	0.646 16(24)	0.278 74(16)	0.636 72(10)
C(1)	0.816 20(115)	0.339 65(73)	0.735 76(47)
O	0.901 48(102)	0.388 11(63)	0.736 45(39)
N(1)	0.477 18(80)	0.200 73(49)	0.730 27(33)
N(2)	0.476 10(84)	0.117 38(51)	0.726 80(37)
C(2)	0.347 67(108)	0.086 43(70)	0.724 22(45)
C(3)	0.259 43(104)	0.152 46(68)	0.726 23(50)
C(4)	0.342 46(93)	0.222 96(66)	0.729 38(38)
C(5)	0.318 83(146)	−0.005 33(70)	0.721 25(69)
C(6)	0.298 71(116)	0.312 33(66)	0.733 56(53)
C(101)	0.613 82(100)	0.171 90(56)	0.860 30(41)
C(102)	0.698 42(106)	0.108 24(65)	0.880 57(55)
C(103)	0.638 78(150)	0.033 85(77)	0.895 66(65)
C(104)	0.498 92(147)	0.022 90(75)	0.890 77(57)
C(105)	0.413 41(112)	0.086 66(80)	0.871 57(48)
C(106)	0.471 11(101)	0.161 04(66)	0.857 65(43)
C(111)	0.595 30(98)	0.349 99(58)	0.867 36(42)
C(112)	0.534 63(128)	0.336 70(72)	0.917 54(51)
C(113)	0.473 91(132)	0.403 35(95)	0.943 17(51)
C(114)	0.536 40(130)	0.492 57(73)	0.872 35(60)
C(115)	0.477 71(134)	0.480 37(85)	0.920 66(63)
C(116)	0.597 80(107)	0.428 87(60)	0.843 24(46)
C(121)	0.861 50(89)	0.272 23(65)	0.867 39(37)
C(122)	1.102 16(111)	0.244 33(80)	0.863 51(51)
C(123)	0.968 69(95)	0.241 63(73)	0.838 46(43)
C(124)	1.128 20(122)	0.277 64(87)	0.916 62(54)
C(125)	0.886 99(109)	0.303 08(72)	0.920 29(43)
C(126)	1.020 21(129)	0.306 39(76)	0.944 56(49)
C(201)	0.563 04(94)	0.187 03(61)	0.603 55(38)
C(202)	0.642 53(120)	0.119 35(71)	0.593 11(46)
C(203)	0.583 68(142)	0.046 05(72)	0.576 02(55)
C(204)	0.441 45(172)	0.041 29(81)	0.567 38(56)
C(205)	0.361 43(127)	0.108 13(92)	0.578 87(60)
C(206)	0.421 86(120)	0.181 59(66)	0.597 09(48)
C(211)	0.808 20(91)	0.286 77(60)	0.600 23(40)
C(212)	1.050 12(111)	0.255 47(84)	0.600 72(50)
C(213)	1.056 51(118)	0.293 07(80)	0.550 44(49)
C(214)	0.810 02(113)	0.322 75(68)	0.548 55(43)
C(215)	0.928 84(100)	0.253 63(69)	0.626 88(43)
C(216)	0.936 30(122)	0.325 73(75)	0.523 74(45)
C(221)	0.541 16(92)	0.365 25(59)	0.607 50(44)
C(222)	0.460 51(133)	0.504 20(71)	0.615 89(65)
C(223)	0.537 70(113)	0.436 69(63)	0.637 43(52)
C(224)	0.389 74(143)	0.500 26(93)	0.566 81(70)
C(225)	0.468 32(114)	0.361 43(78)	0.555 42(51)
C(226)	0.393 54(123)	0.429 57(91)	0.535 41(56)
H(1)	0.560	0.340	0.730
H(2)	0.560	0.065	0.725

Table 2. Analytical* and i.r. spectroscopic data for the complexes

		Analysis (%)			ν/cm^{-1}			
Compound	R	C	H	N	NH	RuH	CO	CN
(**1a**)	Ph	63.90	4.80	3.50	3 193m	2 030w	1 932vs	1 565m
		(64.15)	(5.00)	(3.55)				
(**1b**)	*p*-MeC_6H_4	66.10	5.75	3.30	3 198m	2 038w	1 930vs	1 576m
		(66.25)	(5.90)	(3.20)				
(**2a**)	Ph	64.05	4.85	3.65	3 170m	2 018w	1 920vs	1 590m
		(64.25)	(4.90)	(3.55)				
(**2b**)	*p*-MeC_6H_4	66.20	5.85	3.15	3 178m	2 025w	1 923vs	1 598m
		(66.30)	(5.80)	(3.20)				
(**3a**)	Ph	64.20	5.00	3.55	3 160m	2 012w	1 929vs,	1 587m
		(64.45)	(4.95)	(3.55)			1 907 (sh)	
(**3b**)	*p*-MeC_6H_4	66.50	5.95	3.05	3 165m	2 020w	1 935vs,	1 592m
		(66.45)	(5.85)	(3.20)			1 915 (sh)	

* Required values are given in parentheses.

the calculated positions. Their co-ordinates were held invariant in the last least-squares refinement. However, the hydride ligand, located in the ΔF Fourier synthesis at (0.06,0.16,0,23) and separated 1.58(10) Å from the Ru atom, was allowed to vary freely, resulting in a great shortening of the Ru–H bond length (1.33 Å) as was the case in the refinement of [$\{Ru_2H_2(cod)_2L\}(\mu$-$pz)_2$].[4] The final bond lengths and angles involving H(1) were calculated on the basis of its ΔF Fourier co-ordinates. The final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.060$ for observed reflections only. The final atomic co-ordinates are collected in Table 1. Most of the calculations were performed with the *X*-RAY 70 system of crystallographic programs.[13]

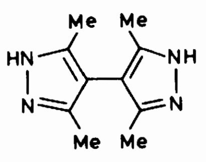
Results

General.—Analytical data and the principal i.r. frequencies for the new complexes are given in Table 2; ^1H n.m.r. spectroscopic data are given in Table 3.

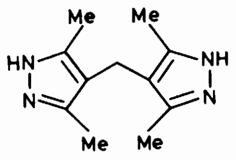
The reactions of [$Ru(CO)ClH(PR_3)_3$] (R = Ph or *p*-MeC_6H_4) with hdmpz in ethanol lead to complexes of composition [$Ru(CO)ClH(Hdmpz)(PR_3)_2$], (**1a**) and (**1b**), as can be deduced from analytical, i.r., and ^1H n.m.r. data. The i.r. spectra show no characteristic bands of OH groups; instead, a ν(NH) stretching band appears at 3 193 cm^{-1}, suggesting the substitution of the $-CH_2OH$ group at the N^1 atom of the pyrazole ring by H. The ^1H n.m.r. spectra (Table 3) are in agreement with these results, which have also been confirmed by the *X*-ray structure determination of (**1a**).

No substitution of Cl takes place even with an excess of hdmpz and in the presence of $NaClO_4$. This behaviour differs from that observed when the reactions take place in an excess of pyridine (py) and acetonitrile; in which cases, complexes of composition [$Ru(CO)H(PR_3)_2L_2$]ClO_4 (L = py or MeCN, R = Ph or *p*-MeC_6H_4) are formed.[14]

Similar reactions occur with the N,N′-substituted bipyrazoles, in which the binuclear bridged [$\{Ru(CO)ClH(PR_3)_2\}_2(\mu$-tmbipz)] (tmbipz = 3,3′5,5′-tetramethyl-4,4′-bipyrazole), (**2a**) and (**2b**), and [$\{Ru(CO)ClH(PR_3)_2\}_2(\mu$-tmmdpz)]



tmbipz



tmmdpz

(tmmdpz = 3,3′5,5′-tetramethyl-4,4′-methylenedipyrazole), (**3a**) and (**3b**) are formed. However, no reaction occurs in the case of *N*-substituted pyrazoles and bipyrazoles with benzyl groups as substituents.

The reaction of [$RuClH(PPh_3)_3$] and [$RuCl_2(PPh_3)_3$] with hdmpz gave in both cases [$Ru(CO)ClH(Hdmpz)(PPh_3)_2$] (**1a**). Similarly, when [$RuClH(PPh_3)_3$] reacts with the 1,1′-di(hydroxymethyl)bipyrazoles, the same products, (**2a**) and (**3a**), are obtained as in the reactions with [$Ru(CO)ClH(PPh_3)_3$].

Discussion

The molecular structure of (**1a**) is shown in the Figure. The interatomic distances and angles are collected in Table 4.

Table 3. ^1H Chemical shift data* for the complexes

Compound	
(**1a**)	1.52 (3 H, s, CH_3), 1.70 (3 H, s, CH_3), 5.20 (1 H, s, CH), 7.15—7.40 (20 H, m, 4 C_6H_5), 7.40—7.60 (10 H, m, 2 C_6H_5), 11.45 (1 H, s, NH), −13.46 [1 H, t, *J*(PH) 19.8, H^-]
(**1b**)	1.59 (3 H, s, CH_3), 1.66 (3 H, s, CH_3), 2.28 (12 H, s, 4 CH_3), 2.37 (6 H, s, 2 CH_3), 5.16 (1 H, s, CH), 7.07—7.12 (16 H, m, 4 C_6H_4), 7.24—7.43 (8 H, m, 2 C_6H_4), 11.33 (1 H, s, NH), −13.57 [1 H, t, *J*(PH) 22, H^-]
(**2a**)	1.40 (6 H, s, 2 CH_3), 1.44 (6 H, s, 2 CH_3), 7.20—7.60 (60 H, m, 12 C_6H_5), 11.40 (2 H, s, 2 NH), −13.55 [2 H, t, *J*(PH) 21.2, 2 H^-]
(**2b**)	1.30 (6 H, s, 2 CH_3), 1.33 (6 H, s, 2 CH_3), 2.20 (18 H, s, 6 CH_3), 2.28 (18 H, s, 6 CH_3) 6.88—7.45 (48 H, m, 12 C_6H_4), 11.28 (2 H, s, 2 NH), −13.6 [2 H, t, *J*(PH) 19.2, 2 H^-]
(**3a**)	1.42 (6 H, s, 2 CH_3), 1.47 (6 H, s, 2 CH_3), 2.40 (2 H, s, CH_2), 7.16—7.48 (60 H, m, 12 C_6H_5), 11.37 (2 H, s, 2 NH), −13.44 [2 H, t, *J*(PH) 20, $2H^-$]
(**3b**)	1.42 (6 H, s, 2 CH_3), 1.49 (6 H, s, 2 CH_3), 2.21 (18 H, s, 6 CH_3), 2.30 (18 H, s, 6 CH_3), 2.45 (2 H, s, CH_2), 6.90—7.40 (48 H, m, 12 C_6H_4), 11.20 (2 H, s, 2 NH), −13.5 [2 H, t, *J*(PH) 18, 2 H^-]

* Solvent $CDCl_3$, 360 MHz, standard $SiMe_4$; δ/p.p.m., *J* values in Hz.

This structure determination confirmed the absence of the $-CH_2OH$ group which had been substituted by a H atom forming the N^1–H bond. The molecular structure seems to persist in $CDCl_3$ solution as deduced from the ^1H n.m.r. data. Signals appeared for the hydride ligand as a triplet at *ca.* −13 p.p.m. [*J*(PH) 20 Hz], corresponding to a P–H–P coupling, with both phosphine molecules being *cis*-co-ordinated with respect to it; for N^1–H, δ *ca.* 11—12 p.p.m. Similar structures are expected for all these compounds of this type.

The results above allow us to establish that all the reagents used, *i.e.* [$RuCl_2(PPh_3)_3$], [$RuClH(PPh_3)_3$], and [$RuCl_2(PPh_3)_3$], react with the pyrazole hdmpz, leading to (**1a**) as the final reaction product.

The transformation experienced by the hdmpz molecule is as expected in the cases of reactions with [$RuClH(PPh_3)_2$] or with [$RuCl_2(PPh_3)_3$].[15–17] However, it is surprising that the same product is obtained when the reaction takes place with [$Ru(CO)ClH(PPh_3)_3$] in which hydride and carbonyl are already present as ligands. The behaviour of the Ru complexes towards hdmpz contrasts with that observed for some Co^{II} and Ni^{II} complexes reported earlier.[3]

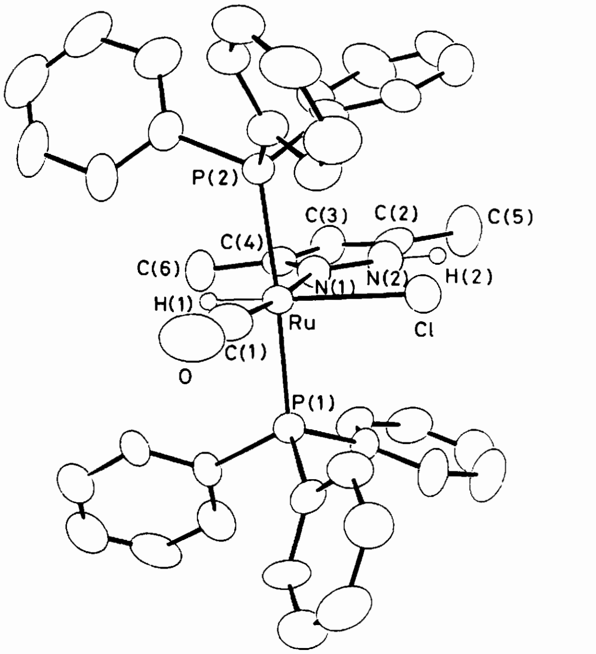


Figure. ORTEP Drawing of the molecule of (**1a**), showing the octahedral co-ordination around the Ru atom. Only the H(1) and H(2) hydrogen atoms are shown

Table 4. Selected bond distances (Å) and angles (°) for (**1a**)

Ru–Cl	2.568(3)	Ru–H(1)	1.58(10)	N(2)–C(2)	1.339(13)	C(4)–C(6)	1.518(15)
Ru–P(1)	2.344(3)	N(1)–N(2)	1.356(11)	C(2)–C(3)	1.375(15)	C(1)–O	1.140(15)
Ru–P(2)	2.345(3)	N(1)–C(4)	1.353(12)	C(2)–C(5)	1.517(16)	Mean P–C	1.847(10)
Ru–N(1)	2.174(8)	N(2)–H(2)	1.186(8)	C(3)–C(4)	1.398(15)	Mean C–C	1.380(17)
Ru–C(1)	1.816(11)						

Cl–Ru–P(1)	90.7(1)	P(1)–Ru–N(1)	91.2(2)	N(1)–Ru–H(1)	77.8(10)
Cl–Ru–P(2)	93.0(1)	P(1)–Ru–H(1)	93.8(10)	N(1)–N(2)–C(2)	112.4(8)
Cl–Ru–C(1)	102.1(4)	P(2)–Ru–C(1)	89.9(4)	N(1)–N(2)–C(4)	105.2(8)
Cl–Ru–N(1)	86.5(2)	P(2)–Ru–N(1)	88.0(2)	N(1)–C(3)–C(4)	109.4(9)
Cl–Ru–H(1)	162.8(10)	P(2)–Ru–H(1)	82.1(10)	N(2)–C(2)–C(3)	106.5(9)
P(1)–Ru–P(2)	176.13(9)	C(1)–Ru–N(1)	171.2(4)	C(2)–C(3)–C(4)	106.5(9)
P(1)–Ru–C(1)	90.4(4)	C(1)–Ru–H(1)	93.4(10)		
Mean C–P–C	103.1(4)	Mean C–C–C	120(1)	Mean Ru–P–C	115.3(3)

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