Notes

Hydrido(benzochalcogenadiazole) Complexes of Ruthenium: Crystal Structure of $[RuCl(H)(CO)(PPh_3)_2(SN_2C_6H_4)]$†

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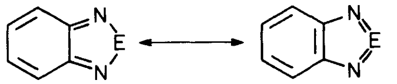
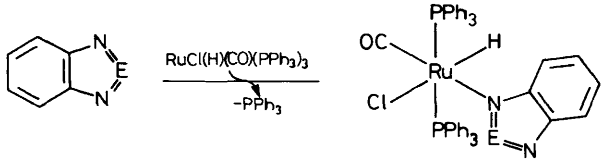
The complex $[RuCl(H)(CO)(PPh_3)_3]$ reacts with 2,1,3-benzothiadiazole ($C_6H_4N_2S$) or 2,1,3-benzoselenadiazole ($C_6H_4N_2Se$) to provide the compounds $[RuCl(H)(CO)(PPh_3)_2(EN_2C_6H_4)]$ (E = S or Se). An *X*-ray diffraction study of *trans*-$[RuCl(H)(CO)(PPh_3)_2(SN_2C_6H_4)]$ established the mode of heterocycle co-ordination as being through one nitrogen atom and *cis* to the hydrido ligand. The crystal structure also shows an unusual four-centre interaction between the unco-ordinated N–S multiple bonds of the two molecules of the asymmetric unit.

The co-ordination of di-imino-λ^4-sulphuranes to transition metals often results in disruption of the tetravalent-sulphur-based heterocumulene spine (ref. 1 and references therein). An exception to this is provided in the case of 2,1,3-benzothiadiazole ($C_6H_4N_2S$) which contains a –N=S=N– linkage somewhat deactivated by conjugation into the benzo π system (Scheme 1).[1] As with alicyclic di-imino-λ^4-sulphuranes, a number of modes of co-ordination are conceivable, however there has been no structural study to establish which mode is actually adopted in these complexes. We report herein the synthesis of ruthenium complexes of $C_6H_4N_2S$ and its selenium analogue, 2,1,3-benzoselenadiazole ($C_6H_4N_2Se$) and an *X*-ray diffraction study of one such complex.



Scheme 1. 2,1,3-Benzochalcogenadiazole



Scheme 2. Synthesis of complexes of $C_6H_4N_2E$ (E = S or Se)

Results and Discussion

The reactivity of the ruthenium hydrido complex $[RuCl(H)(CO)(PPh_3)_3]$[2] centres around the lability of one phosphine ligand, the compound thereby serving as a convenient source of the fragment '$RuCl(H)(CO)(PPh_3)_2$.' The treatment of a suspension of this complex in dichloromethane with $C_6H_4N_2S$ leads to the formation of a bright yellow solution from which the bis(phosphine) complex $[RuCl(H)(CO)(PPh_3)_2(SN_2C_6H_4)]$ may be isolated in high yield upon addition of ethanol. A similar reaction is observed when the selenium analogue, $C_6H_4N_2Se$ is employed (Scheme 2). Spectroscopic data for the complexes indicate that the triphenylphosphine ligands adopt a *trans* arrangement, *i.e.* the signal due to the hydrido ligand in the ^1H n.m.r. spectrum of $[RuCl(H)(CO)(PPh_3)_2(SN_2C_6H_4)]$ appears as a triplet due to *cis* coupling to two chemically equivalent phosphorus nuclei [δ –13.19, t, *J*(PH) 16.3 Hz]. The i.r. activity due to the carbonyl ligand is split in the solid state, appearing at 1 931vs and 1 922vs cm^{-1} when measured as a Nujol mull. The presence of a ruthenium hydrido ligand is confirmed by peaks at 2 048w and 2 027 cm^{-1} in the i.r. spectrum. In a similar manner the $C_6H_4N_2Se$ complex gives rise to a solid-state splitting with two ν(CO) and two ν(RuH) absorbances in the solid state (1 918vs, 1 924vs and 2 024w, 2 052w cm^{-1}, respectively). Solution i.r. spectra, however, indicate only one isomer is present [*e.g.* in CH_2Cl_2: ν(CO) 1 938vs, ν(RuH) 2 042w cm^{-1}] consistent with the ^1H n.m.r. data ($CDCl_3$) (Experimental section).

The spectroscopic data fail to distinguish between the co-ordination isomerism possible within the molecular *meso* plane. Thus it is neither possible to say whether the $C_6H_4N_2S$ ligand co-ordinates *cis* or *trans* to the hydrido ligand, nor whether nitrogen or sulphur is the donor atom of the $C_6H_4N_2S$ ligand. In view of the absence of any structural studies on transition-metal complexes of benzochalcogenadiazoles, $[RuCl(H)(CO)(PPh_3)_2(SN_2C_6H_4)]$ was chosen for a single-crystal *X*-ray diffraction structure analysis. The results are summarised in Tables 1 and 2 and Figures 1 and 2.

The co-ordination geometry about ruthenium is distorted pseudo-octahedral (*trans* phosphines) with the heterocycle bound *cis* to the hydrido ligand and *trans* to the carbonyl group. The heterocumulene binds in this instance *via* nitrogen as was established for the arsenic pentafluoride adduct[3] and proposed for the complex $[W(CO)_5(SN_2C_6H_2Me_2\text{-}3,4)]$.[4] Co-ordination induces some minor deformation of the heterocycle from ideal C_{2v} symmetry with a significant shortening of the nitrogen–sulphur bond not directly involved in co-ordination to ruthenium [N(12)–S(1)] relative to that ligating ruthenium [N(11)–S(1)]. The nitrogen bound to ruthenium appears to be bound slightly less strongly to carbon [C(12)] than is the free imino nitrogen to C(14). These albeit slight distortions are consistent with a resonance contribution from the canonical form (**B**) in Scheme 3. A similar resonance form was invoked for the NSN cumulene of alkylated imino-oxo-λ^4-sulphuranes.[5]

Two further structural features are noteworthy. First, a major

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† *trans*-(Benzothiadiazole-*N*)carbonylchlorohydridobis(triphenylphosphine)ruthenium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

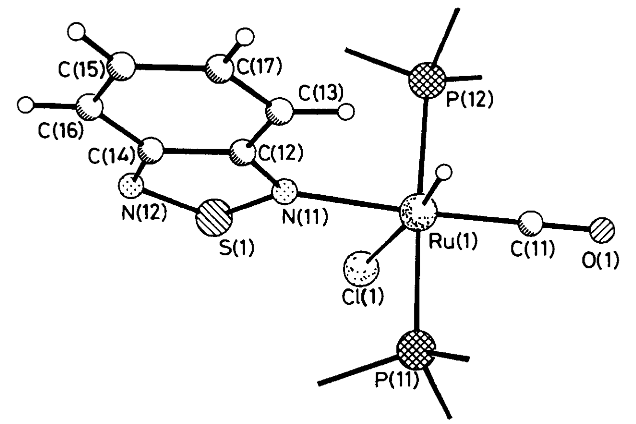


Figure 1. Molecular structure of $[RuCl(H)(CO)(PPh_3)_2(SN_2C_6H_4)]$. Phenyl hydrogen and carbon atoms omitted

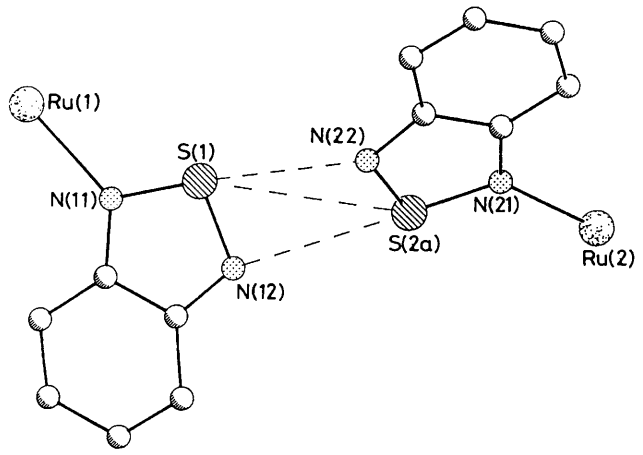
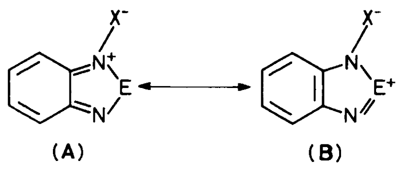


Figure 2. Intermolecular association of co-ordinated 2,1,3-benzothiadiazole ligands in the crystal of $[RuCl(H)(CO)(PPh_3)_2(SN_2C_6H_4)]$; extraneous ligands and hydrogen atoms omitted. Angles between the planes defined by N(21)–N(22)–S(2a) (1), N(22)–S(1)–S(2a) (2), N(12)–S(1)–S(2a) (3), and N(11)–N(12)–S(1) (4) are given by (1)–(2) 18.6, (1)–(3) 47.4, (2)–(3) 55.3, (3)–(4) 20.4°



Scheme 3. 2,1,3-Benzochalcogenadiazole–Lewis acid formation

deviation from octahedral geometry is apparent when the molecular *meso* plane is viewed along one of the ruthenium–phosphorus vectors. The carbon–ruthenium and ruthenium–nitrogen bonds are essentially collinear, however the ruthenium–chlorine bond lies at an angle of 103.3(2)° to the Ru(1)–C(11) vector such that the chlorine to sulphur distance is 2.996 Å (covalent radii sum 2.02 Å).

Secondly, the two distinct molecules in the asymmetric unit are apparently linked intermolecularly by an unusual arrangement of two sulphur and two nitrogen atoms of the benzothiadiazole ligands (Figure 2). The secondary bonding is clearly weak [S(1) ••• S(2a) 3.61, S(1) ••• N(22) 3.08, S(2a) ••• N(12) 3.12 Å; covalent radii sums N–S 1.77, S–S 2.04 Å] however it should be pointed out that the complex is very sterically cluttered and this may be limiting the interaction. Intermolecular interactions in the solid state between sulphur and nitrogen or sulphur in sulphur–nitrogen compounds are not uncommon and in particular thiadiazoles as a class often show this feature;[6] however it is less common in co-ordination complexes and clearly weak in this case.

Experimental

All manipulations were carried out under an inert atmosphere of prepurified nitrogen employing conventional Schlenk-tube techniques. The ligands $C_6H_4N_2S$ and $C_6H_4N_2Se$ were obtained commercially and used as received. Satisfactory elemental microanalytical data were obtained for the new complexes.

$[RuCl(H)(CO)(PPh_3)_2(SN_2C_6H_4)]$.—A solution of $[RuCl(H)(CO)(PPh_3)_3]$ (0.95 g, 1.0 mmol) in tetrahydrofuran

Table 1. Selected internuclear distances (Å) and angles (°) for $[RuCl(H)(CO)(PPh_3)_2(SN_2C_6H_4)]$ (molecule 1) with estimated standard deviations in parentheses

Ru(1)–Cl(1)	2.522(2)	Ru(1)–P(11)	2.339(2)	Ru(1)–P(12)	2.359(2)
Ru(1)–N(11)	2.177(5)	Ru(1)–C(11)	1.818(7)	S(1)–N(11)	1.637(6)
S(1)–N(12)	1.606(6)	C(11)–O(1)	1.152(8)	C(21)–O(2)	1.142(8)
N(11)–C(12)	1.356(10)	N(12)–C(14)	1.333(11)	N(21)–C(22)	1.347(9)
N(22)–C(27)	1.344(11)	C(17)–C(13)	1.345(12)	C(17)–C(15)	1.411(12)
C(27)–C(22)	1.425(8)	C(27)–C(26)	1.425(10)	C(12)–C(13)	1.405(11)
C(12)–C(14)	1.424(9)	C(14)–C(16)	1.416(12)	C(15)–C(16)	1.329(14)
C(22)–C(23)	1.406(11)	C(23)–C(24)	1.356(11)		
Ru(1)–H(1)	1.50	Ru(2)–H(2)	1.60		
S(1) ••• S(2a)	3.605	S(1) ••• N(22)	3.082	S(2a) ••• N(12)	3.122
Cl(1)–Ru(1)–P(11)	91.0(1)	Cl(1)–Ru(1)–P(12)	94.0(1)	P(11)–Ru(1)–P(12)	175.0(1)
Cl(1)–Ru(1)–N(11)	83.7(2)	P(11)–Ru(1)–N(11)	91.4(1)	P(12)–Ru(1)–N(11)	90.1(1)
Cl(1)–Ru(1)–C(11)	103.3(2)	P(11)–Ru(1)–C(11)	88.6(2)	P(12)–Ru(1)–C(11)	103.3(2)
N(11)–Ru(1)–C(11)	172.9(3)	N(11)–S(1)–N(12)	99.4(3)	Ru(1)–N(11)–S(1)	122.3(3)
Ru(1)–N(11)–C(12)	130.9(4)	S(1)–N(11)–C(12)	106.8(4)	Ru(1)–N(11)–C(12)	130.9(4)
S(1)–N(1)–C(12)	106.8(4)	S(1)–N(12)–C(14)	107.0(4)	Ru(1)–C(11)–O(1)	177.2(6)
N(11)–C(12)–C(13)	128.2(6)	N(11)–C(12)–C(14)	112.3(7)	C(13)–C(12)–C(14)	119.5(7)
C(17)–C(13)–C(12)	118.3(7)	N(12)–C(14)–C(12)	113.7(7)	N(12)–C(14)–C(16)	126.2(6)
C(12)–C(14)–C(16)	120.0(7)	C(17)–C(15)–C(16)	121.9(9)	C(14)–C(16)–C(15)	118.2(7)

The planes defined by S(1)–N(22)–S(2a) and S(1)–N(12)–S(2a) intersect at an angle of 55.3°.

Table 2. Atomic positional parameters (fractional co-ordinates × 10^4) for $[RuCl(H)(CO)(PPh_3)_2(SN_2C_6H_4)]$ with estimated standard deviations in parentheses

Atom	x	y	z
Ru(1)	3 204(1)	2 281(1)	1 420(1)
Ru(2)	7 857(1)	2 461(1)	1 010(1)
Cl(1)	3 699(1)	1 814(1)	629(1)
Cl(2)	8 475(1)	1 880(1)	381(1)
S(1)	3 243(1)	492(1)	1 135(1)
S(2)	7 088(1)	1 191(1)	−189(1)
P(11)	4 292(1)	2 238(1)	2 350(1)
P(12)	2 073(1)	2 381(1)	544(1)
P(21)	7 347(1)	3 360(1)	153(1)
P(22)	8 277(1)	1 643(1)	1 941(1)
O(1)	3 358(2)	3 885(2)	1 402(3)
O(2)	8 914(3)	3 508(3)	1 901(3)
N(11)	3 031(2)	1 131(2)	1 536(2)
N(12)	2 978(3)	−207(3)	1 399(3)
N(21)	7 027(2)	1 717(3)	396(2)
N(22)	6 359(3)	782(3)	−453(3)
H(1)	2 901(26)	2 465(27)	1 911(26)
H(2)	7 358(25)	2 717(26)	1 347(25)
C(17)	2 159(4)	676(5)	2 612(4)
C(27)	6 036(3)	1 042(3)	− 86(3)
C(11)	3 299(3)	3 262(4)	1 393(3)
C(111)	4 317(3)	2 724(3)	3 098(3)
C(112)	4 729(3)	3 331(4)	3 363(4)
C(113)	4 694(4)	3 732(4)	3 895(4)
C(114)	4 254(4)	3 518(4)	4 170(3)
C(115)	3 828(4)	2 931(4)	3 896(3)
C(116)	3 859(3)	2 548(4)	3 370(3)
C(12)	2 729(3)	796(3)	1 895(3)
C(121)	5 024(3)	2 625(3)	2 238(3)
C(122)	4 929(3)	3 060(3)	1 684(3)
C(123)	5 501(4)	3 369(4)	1 631(4)
C(124)	6 146(4)	3 231(4)	2 112(4)
C(125)	6 248(4)	2 784(4)	2 653(4)
C(126)	5 694(3)	2 480(4)	2 726(3)
C(13)	2 441(3)	1 115(4)	2 303(3)
C(131)	4 583(3)	1 311(3)	2 619(3)
C(132)	4 850(3)	915(4)	2 248(4)
C(133)	5 018(4)	187(4)	2 379(4)
C(134)	4 908(4)	−153(4)	2 876(5)
C(135)	4 638(4)	217(5)	3 250(5)
C(136)	4 475(4)	946(4)	3 123(4)
C(14)	2 709(3)	26(4)	1 816(3)
C(141)	1 984(3)	3 057(3)	−112(3)
C(142)	1 387(4)	3 454(4)	−442(3)
C(143)	1 359(5)	3 987(4)	−916(4)
C(144)	1 906(5)	4 110(4)	−1 057(4)
C(145)	2 472(5)	3 717(5)	−744(4)
C(146)	2 524(4)	3 184(4)	−275(4)
C(15)	2 130(4)	−86(5)	2 522(4)
C(151)	1 414(3)	2 658(3)	825(3)
C(152)	1 586(3)	3 156(3)	1 351(3)
C(153)	1 093(3)	3 403(4)	1 554(3)
C(154)	426(4)	3 123(4)	1 248(4)
C(155)	258(3)	2 639(4)	729(4)
C(156)	739(3)	2 412(4)	509(3)
C(16)	2 393(4)	−412(4)	2 139(4)
C(161)	1 731(3)	1 549(3)	64(3)
C(162)	1 529(3)	982(4)	360(3)
C(163)	1 330(4)	320(4)	19(4)
C(164)	1 316(4)	223(4)	−608(5)
C(165)	1 491(4)	789(4)	−913(4)
C(166)	1 707(3)	1 449(4)	−573(3)
C(21)	8 512(4)	3 110(4)	1 543(3)
C(211)	6 781(3)	2 976(3)	−683(3)
C(212)	6 114(3)	2 750(4)	−821(4)
C(213)	5 727(4)	2 378(4)	−1 414(4)
C(214)	5 983(5)	2 230(5)	−1 874(4)
C(215)	6 630(5)	2 456(4)	−1 746(4)
C(216)	7 036(4)	2 819(3)	−1 163(3)
C(22)	6 411(3)	1 586(3)	401(3)
C(221)	6 797(4)	4 029(3)	318(4)
C(222)	6 243(4)	4 362(4)	−198(5)
C(223)	5 868(5)	4 884(5)	−55(6)
C(224)	6 055(6)	5 075(5)	618(7)
C(225)	6 586(6)	4 757(5)	1 131(6)
C(226)	6 966(4)	4 233(4)	987(4)
C(23)	6 126(3)	1 922(3)	804(3)
C(231)	7 924(3)	3 952(3)	−60(3)
C(232)	7 690(4)	4 594(4)	−416(3)
C(233)	8 122(5)	4 995(4)	−593(4)
C(234)	8 784(5)	4 789(4)	−417(4)
C(235)	9 011(4)	4 170(5)	−70(4)
C(236)	8 594(4)	3 743(4)	114(4)
C(24)	5 488(4)	1 697(4)	707(4)
C(241)	9 060(3)	1 121(3)	2 104(3)
C(242)	9 180(4)	431(4)	2 404(3)
C(243)	9 794(4)	84(4)	2 559(4)
C(244)	10 295(4)	400(5)	2 415(5)
C(245)	10 181(4)	1 082(5)	2 120(5)
C(246)	9 569(4)	1 441(4)	1 969(3)
C(25)	5 098(3)	1 154(4)	223(4)
C(251)	7 646(3)	946(3)	1 882(3)
C(252)	7 506(4)	403(3)	1 391(3)
C(253)	7 005(4)	−108(4)	1 274(4)
C(254)	6 631(4)	−83(5)	1 651(5)
C(255)	6 748(4)	448(5)	2 132(4)
C(256)	7 262(3)	964(4)	2 253(3)
C(26)	5 367(3)	835(4)	−163(4)
C(261)	8 503(3)	2 049(3)	2 783(3)
C(262)	8 090(4)	2 604(4)	2 846(4)
C(263)	8 221(5)	2 888(4)	3 485(5)
C(264)	8 762(5)	2 463(5)	4 054(5)
C(265)	9 182(5)	2 116(5)	4 002(4)
C(266)	9 041(4)	1 824(4)	3 371(4)

($20\ cm^3$) was treated with 2,1,3-benzothiadiazole (0.27 g, 0.2 mmol) and the mixture heated under reflux for 5 min. The yellow solution was allowed to cool to room temperature and ethanol ($50\ cm^3$) added. Upon concentration of the mixture under reduced pressure, yellow *microcrystals* of the complex precipitated which were isolated by filtration, washed with ethanol ($10\ cm^3$) and hexane ($10\ cm^3$), and dried *in vacuo*. Yield 0.66 g (80%). Infrared (Nujol): 2 048w and 2 027w [ν(RuH)], 1 931vs and 1 922vs [ν(CO)], 1 333w, 1 309w, 1 276w, 926m, 877w, and 846w cm^{-1}. ^1H N.m.r. ($CDCl_3$, 220 MHz, 25 °C): δ −13.19 [t, 1 H, J(PH) 16.3 Hz, Ru–H].

$[RuCl(H)(CO)(PPh_3)_2(SeN_2C_6H_4)]$.—A solution of $[RuCl(H)(CO)(PPh_3)_3]$ (0.95 g, 1.0 mmol) in dichloromethane ($20\ cm^3$) was treated with 2,1,3-benzoselenadiazole (0.2 g, 0.11 mmol) and the mixture stirred for 15 min and then ethanol ($50\ cm^3$) added. Upon concentration of the mixture under reduced pressure, yellow *microcrystals* of the complex precipitated which were isolated by filtration, washed with ethanol ($10\ cm^3$) and hexane ($10\ cm^3$), and dried *in vacuo*. Yield 0.86 g (98%). Infrared (Nujol): 2 052w and 2 024w [ν(RuH)], 1 924vs and 1 918vs [ν(CO)], 1 309w, 1 290w, 845m, 813w, 605m; (CH_2Cl_2) 2 038w, 1 938vs cm^{-1}. ^1H N.m.r. ($CDCl_3$, 220 MHz, 25 °C): δ −13.57 [t, 1 H, J(PH) 16.3 Hz, Ru–H].

Crystal Structure Determination.—Yellow prisms of the complex $[RuCl(H)(CO)(PPh_3)_2(SN_2C_6H_4)]$ were grown from acetone–ethanol. That chosen for data collection (*ca.*

0.2 × 0.2 × 0.3 mm) was mounted (epoxy adhesive) on a glass fibre. Diffracted intensities were collected (θ—2θ scans) at 298 K in the range $3.0 < 2\theta < 50.0°$, on a Syntex $P2_1$ four-circle diffractometer. Of 13 628 unique reflections, 8 110 had $F \geqslant 4\sigma(F)$, and only these data were used in the solution and refinement of the structure. Corrections were applied for Lorentz, polarisation and *X*-ray absorption effects, the last using ABSCOR.[7]

Crystal data. $C_{43}H_{35}ClN_2OP_2RuS$, $M = 826.3$, monoclinic, $a = 21.460(6)$, $b = 18.371(6)$, $c = 21.639(7)$ Å, $\beta = 115.44(3)$ °, $U = 7\,704(4)$ Å^3, $Z = 8$, $D_c = 1.42$ g cm^{-3}, $F(000) = 3\,376$, space group = $P2_1/n$ (no. 14), Mo-K_α *X*-radiation ($\lambda = 0.710\,69$ Å, graphite monochromator), μ(Mo-K_α) = 0.64 mm^{-1}.

The structure was solved, and all non-hydrogen atoms and the ruthenium hydride atoms located, by conventional heavy-atom and Fourier difference methods. Phenyl and phenylene hydrogen atoms were included in calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters. All non-hydrogen atoms were refined anisotropically (blocked-cascade least squares), the refinement converging at $R = 0.055$ ($R' = 0.047$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\,326|F|^2]$. The final electron-density difference synthesis showed no residual peaks of magnitude $\geqslant 0.43$ e Å^{-3}. Scattering factors and corrections for anomalous dispersion were taken from ref. 8. All calculations were carried out using a DEC micro-Vax II computer with the SHELXTL PLUS suite of programs.[9]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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