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The coordination chemistry of 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole. Complexes of ruthenium, osmium and iridium

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Abstract

The reactions of $[MCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2]$ (M = Ru, Os) and $[IrCl_2H(PPh_3)_3]$ with 2,1,3-benzothiadiazole (BTD) result in quantitative formation of the adducts $[MCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2(BTD)]$ and $[IrCl_2H(PPh_3)_2(BTD)]$, respectively. Similar reactions with 2,1,3-benzoselenadiazole (BSD) provide the corresponding selenium analogues. The thiocarbonyl complex $[OsCl_2(CS)(PPh_3)_2$-(BSD)] is obtained by replacement of one phosphine in $[OsCl_2(CS)(PPh_3)_3]$. The BSD and BTD ligands in the complexes are labile; $[OsCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2$-(BSD)] reacts with carbon monoxide and *N,N*-dimethylthionitrosamine to give $[OsCl(C_6H_4Me\text{-}4)(CO)_2(PPh_3)_2]$ and $[OsCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2(SNNMe_2)]$, respectively. The IR, ^1H, and $^{31}P\text{-}\{^1H\}$ NMR data for the new complexes are reported and discussed.

Introduction

The first diiminosulphurane to be isolated, 2,1,3-benzothiadiazole (BTD) [1], contains a somewhat deactivated N=S=N cumulene system owing to extensive conjugation with the aromatic π-system of the arene ring (Scheme 1).

The π-delocalisation into the heterocyclic ring and concomitant perturbation of the arene ring have been structurally established [2] both for BTD and the selenium analogue, 2,1,3-benzoselenadiazole (BSD), and confirmed for several other 2,1,3-chalcogenadiazoles (see ref. 3 for a compilation of structural data). The SN and SeN bond lengths are intermediate between those of typical single and double bonds [3].

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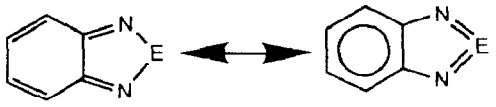


E = S (BTD): $d_{(SN)}$ 160(3), $d_{(NC)}$ 134(3) pm [2]
E = Se (BSD): $d_{(SeN)}$ 183(4), $d_{(NC)}$ 130(4) pm [2]

Scheme 1. 2,1,3-Benzochalcogenadiazoles.

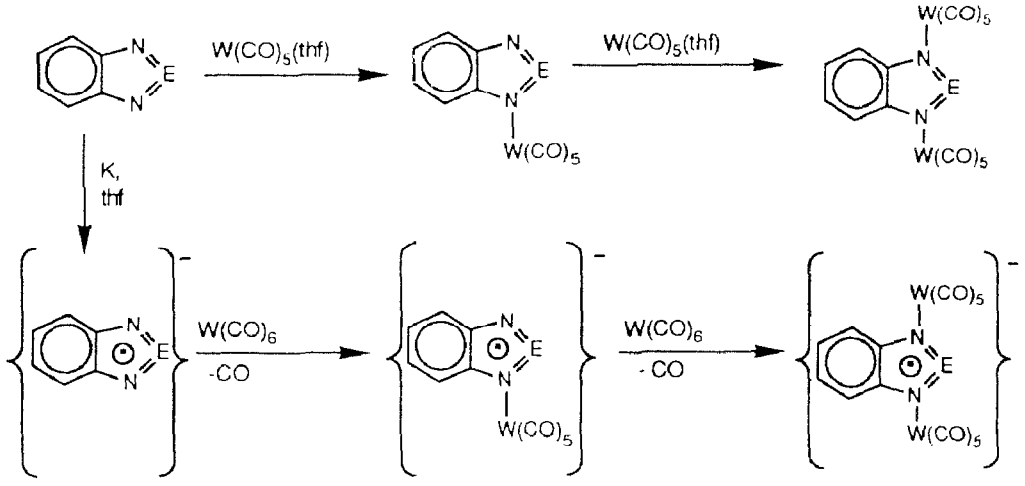
Studies by Vrieze and co-workers [4] have shown that 5,6-dimethyl-2,1,3-benzothiadiazole, like open chain diiminosulphuranes, may become coordinated to group 6 pentacarbonylmetal fragments $M(CO)_5$ (M = Cr, Mo, W) through one of the nitrogen atoms. The stepwise addition of two $M(CO)_5$ fragments to both nitrogen atoms of BSD and BTD has been investigated by Kaim [5]. Complex formation is considerably facilitated [6] by one-electron reduction of the heterocycles BSD and BTD, to the more nucleophilic radical anions (Scheme 2).

Studies of the mononuclear complexes in the case of the neutral compounds by ^{1}H NMR [4,6] and in the case of the radical anions by EPR spectroscopy [5] have revealed that the heterocycles BSD and BTD are generally bound through nitrogen, and this was established by X-ray structure analysis for the 1/1 adduct of BSD with AsF_5 [7]. However, the radical anion $[W(CO)_5(BSD)]^-$ showed an EPR spectrum consistent with C_{2v} symmetry, and a possible interpretation [5] is that the BSD ligand may be coordinated through selenium. In order to extend knowledge of the coordination chemistry of the 2,1,3-benzochalcogenadiazoles BSD and BTD, we have identified the products formed in the reactions with some soft late-transition metal complexes.

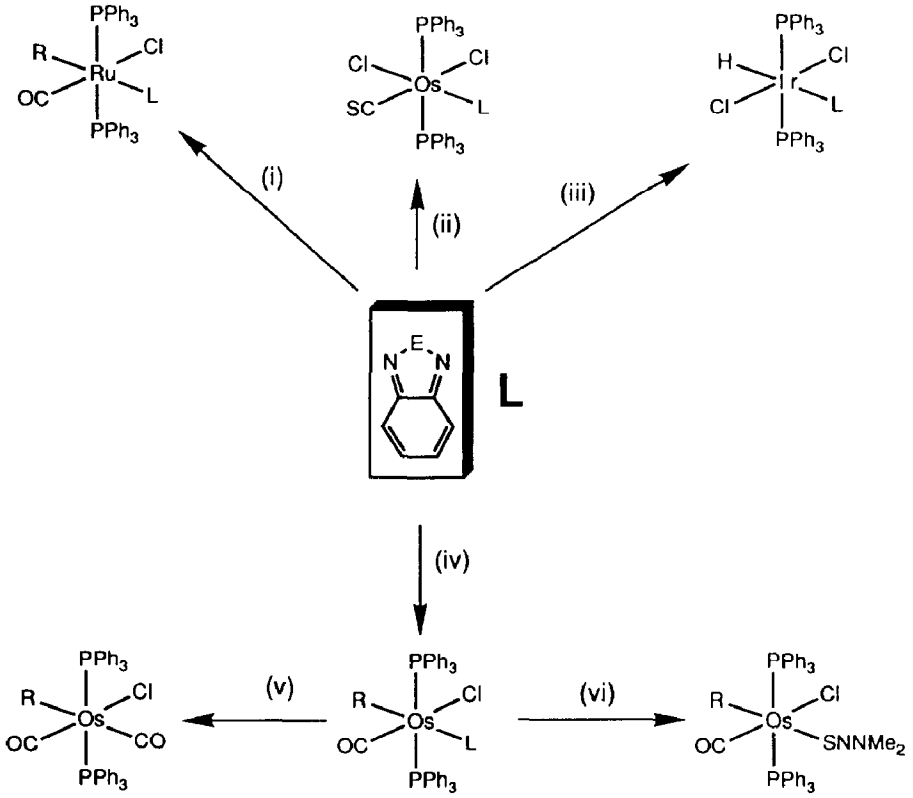
Results and discussion

Complexes of ruthenium and osmium

The 16-electron *p*-tolyl complexes $[MCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2]$ (M = Ru (**1**), M = Os (**2**)) readily accept ligands [8–12] to give coordinatively saturated com-



Scheme 2. 2,1,3-Benzochalcogenadiazole complexes (E = S, Se) of tungsten [5,6] (reactions in thf).



Scheme 3. Synthesis of benzochalcogenadiazole complexes. R = C_6H_4Me-4; E = S, Se; (i) $RuCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2$; (ii) $OsCl_2(CS)(PPh_3)_3$, $-PPh_3$; (iii) $IrCl_2H(PPh_3)_3$, $-PPh_3$; (iv) $OsCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2$; (v) $+CO$, $-L$; (vi) $+SNNMe_2$, $-L$.

pounds. Not surprisingly, therefore, suspensions of **1** and **2** in dichloromethane react with BTD, dissolving slowly to yield solutions of the brightly coloured 1/1 adducts $[MCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2(BTD)]$ (M = Ru (**3**), M = Os (**4**)) (Scheme 3).

Spectroscopic data for the complexes are collected in Table 1. The appearance of only one singlet resonance in the $^{31}P\text{-}\{^1H\}$ NMR spectra of the adducts **3** (26.5) and **4** (-2.3 ppm) indicates that the two phosphine ligands occupy *trans* positions in the pseudooctahedral complex. The coordination of *N,N*-dimethylthionitrosamine to the complexes **1** and **2** occurs *trans* to the strongly *trans*-directing σ-organyl ligand, as established crystallographically [11]. Similarly, SO_2 in the adduct $[Os(C_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2(SO_2)]$ is coordinated *trans* to the σ-tolyl ligand [10]. It is therefore likely that a similar coordination geometry is present in the case of the BTD complex. The $\nu(CO)$ absorptions in the infrared spectra of **3** (1921) and **4** (1898 cm^{-1}) suggest that the BTD ligand has $\sigma + \pi$ donor properties comparable with those of the thionitroso ligand [10].

The selenium analogues of **3** and **4** are prepared in a completely analogous manner. Spectroscopic data (Table 1) for the compounds $[MCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2(BSD)]$ (M = Ru (**5**), Os (**6**)), confirm the structural similarity to the complexes **3** and **4**, whilst infrared data suggest that, at least in the case of the ruthenium complexes, the BSD ligand is a slightly better donor than BTD.

Table 1

Spectroscopic data for the 2,1,3-benzochalcogenadiazole complexes

Compound (L = PPh_3, R = *p*-tolyl)	Infrared (Nujol) [a] (cm^{-1})		NMR ($CDCl_3$) (ppm)	
	ν(CO/CS)	Other	$\delta(^1H)$ [b]	$\delta(^{31}P)$ [c]
BTD complexes				
(3) $RuCl(R)(CO)L_2$(BTD) (red/orange)	1921	1529, 1336, 1313, 1278, 1042, 1016, 922, 870, 853, 825	2.16 (s, 3H, CH_3)	26.5
(4) $OsCl(R)(CO)L_2$(BTD) (red)	1898	1336, 1315, 1048, 924, 875, 854, 823	2.20 (s, 3H, CH_3)	−2.3
(10) $IrCl_2(H)L_2$(BTD) (yellow)	–	2249(Ir–H), 1529, 1336, 1315, 1278, 929, 908, 884, 832, 803, 319(Ir–Cl)	−20.7 (t, 1H, Ir–*H*) ^2J(PH) 13.2 Hz	−2.3
BSD complexes				
(5) $RuCl(R)(CO)L_2$(BSD) (red)	1913	1511, 1312, 1284, 805	2.16 (s, 3H, CH_3)	25.6
(6) $OsCl(R)(CO)L_2$(BSD) (violet)	1900	1512, 1313, 1280, 806, 791	2.17 (s, 3H, CH_3)	−2.8
(8) $OsCl_2(CS)L_2$(BSD) (orange)	1279	1514, 814, 774		−14.0
(11) $IrCl_2(H)L_2$(BSD) (yellow)	–	2190(Ir–*H*), 1512, 1292, 814, 788	−23.7 (t, 1H, Ir–*H*) ^2J(PH) 13.7 Hz	−6.6

[a] Nujol mulls of the complexes between KBr disks, range 4000–400 cm^{-1}. [b] Saturated solutions in $CDCl_3$, 25 °C, chemical shifts rel. to internal $SiMe_4$; the signals of the aromatic protons of the PPh_3 groups and of the C_6H_4 units are not amenable to analysis (Jeol FX 90Q). [c] ^{31}P-{^1H} data obtained from saturated solutions in $CDCl_3$, 25 °C, and reported rel. to external H_3PO_4/D_3PO_4.

The thiocarbonylosmium complex $[OsCl_2(CS)(PPh_3)_3]$ (**7**) [13] owes its reactivity to the lability of one phosphine ligand, a feature deriving from steric pressure associated with octahedral coordination of three bulky triphenylphosphines. Treatment of solution of **7** in dichloromethane with BSD gives the orange complex $[OsCl_2(CS)(PPh_3)_2(BSD)]$ (**8**) in good yield. The infrared spectrum of **8** features a strong absorption at 1279 cm^{-1}, a value typical of the thiocarbonyl ligand when coordinated to divalent osmium [13].

Complexes of iridium

Treatment of solutions of pale yellow $[IrCl_2H(PPh_3)_3]$ (**9**) [14] with BSD or BTD caused a deepening of the yellow colour, but the expected displacement of a PPh_3 ligand did not go to completion, and upon work-up, mixtures of **9** with the benzochalcogenadiazole complexes $[IrCl_2H(PPh_3)_2(BTD)]$ (**10**) and $[IrCl_2H(PPh_3)_2(BSD)]$ (**11**), respectively, were obtained. This problem was overcome by adding methyl iodide to the reaction mixture in order to trap the liberated triphenylphosphine as $[PMePh_3]I$ and drive the equilibrium towards the desired complexes.

The stereochemistry of substitution can be inferred from the spectroscopic data (Table 1): The observation of one band attributable to ν(IrCl) indicates that the chloride ligands are *trans* to one another. The *trans* arrangement of the two

phosphine ligands is evident from the appearance of only a singlet in the $^{31}P-\{^1H\}$ NMR spectra of **10** (−2.3) and **11** (−6.6 ppm), and this is confirmed by the triplets observed to high field in the ^1H NMR spectra (**11** −23.7 t, J(PH) 13.7; **10** −20.7 ppm, t, J(PH) 13.2 Hz) arising from coupling of the hydride proton to two chemically equivalent phosphorus nuclei.

The apparent competition observed in the reactions of the fragment $IrCl_2H(PPh_3)_2$ with triphenylphosphine and BSD or BTD, as evident in the synthesis of **10** and **11**, suggests that the coordinated benzochalcogenadiazole ligands are kinetically very labile. Preliminary results with the complexes **3** and **4** appear to support this (Scheme 3): Treatment of (**4**) with either carbon monoxide or *N*,*N*-dimethylthionitrosamine rapidly gives the known complexes $[OsCl(C_6H_4Me\text{-}4)(CO)(PPh_3)L]$ (L = CO [8], $SNNMe_2$ [10,11]). Since the $SNNMe_2$ ligand in the latter has itself been shown to be comparatively labile [11], the BSD and BTD co-ordination must be very weak.

It could not be established spectroscopically whether the ligands in these complexes are bound to the metal through nitrogen or sulphur *. Comparison with the complexes described earlier [4–7] indicates that *N*-coordination is likely, but this must await structural confirmation. It is interesting to note in this connection that the corresponding pyridine and pyrazole adducts of $[RuCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2]$, both necessarily nitrogen-bound, are colourless or pale yellow [15], whereas the BTD and BSD complexes are very brightly coloured (see Table 1).

Experimental

General experimental procedures and instrumentation [16] and the synthesis of the parent compounds **1**, **2** [8], **7** [13] and **9** [14] are described elsewhere. The ligands BSD and BTD were obtained commercially (Fluka and Aldrich).

Complexes of ruthenium and osmium

$[MCl((C_6H_4Me\text{-}4)CO)(PPh_3)_2L]$ (L = BTD, M = Ru (3), Os (4); L = BSD, M = Ru (5), Os (6)). A suspension of $[MCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2]$ (0.50 mmol) and BSD or BTD (0.60 mmol) in dichloromethane (50 cm^3) was stirred until all the complex had dissolved (5 min, 12 h). Ethanol was then added and the solvent volume reduced (rotary evaporator). Additional ethanol was added and the brightly coloured crystals filtered off, washed with ethanol (2 × 10 cm^3) and hexane (10 cm^3), and dried in vacuo. **3**: 0.43 g (94%), m.p. 180 °C decomp. **4**: 0.44 g (96%), m.p. 169 °C decomp. Anal. Found: C, 59.43; N, 2.78; S, 3.18. $C_{50}H_{41}ClN_2OOsP_2S$ calcd.: C, 59.72; N, 2.79; S, 3.19%.

$[OsCl_2(CS)(PPh_3)_2(BSD)]$. A solution of $[OsCl_2(CS)(PPh_3)_3]$ (0.50 g, 0.46 mmol) and BSD (0.11 g, 0.60 mmol) in dichloromethane (30 cm^3) was stirred for 20 minutes and the solvent was the removed under reduced pressure. The orange residue was recrystallised from dichloromethane/ethanol as orange needles. 0.37 g (85%), m.p. 166 °C.

* Since this paper was submitted, a preliminary X-ray diffraction analysis of the compound $[RuClH(CO)(PPh_3)_2(BTD)]$ indicates that the heterocycle is bound to ruthenium through nitrogen.

Complexes of iridium

A solution of $[IrCl_2H(PPh_3)_3]$ (0.50 g, 0.48 mmol), the ligand BTD or BSD (0.60 mmol), and methyl iodide (1 cm^3) in dichloromethane (50 cm^3) was stirred for 2 h and the solvent then removed in vacuo. The residue was then dissolved in a minimum of dichloromethane and chromatographed on a water-cooled column (2 × 20 cm) filled with silica gel, with dichloromethane as eluent. The yellow eluate was collected, concentrated under reduced pressure, and treated with ethanol to induce the formation of bright yellow crystals of the complexes. **10**: 0.38 g (81%), m.p. 211°C decomp. **11**: 0.35 g (78%), m.p. 225°C decomp.

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