Crystal structure of [bis 1,2-(diphenylphosphino)ethane]bis(pyridine-2-thiolato)ruthenium(II)

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The Ru atom in the title compound, $[\text{Ru}(\text{dppe})(2\text{-pyS})_2]$ exists in a distorted octahedral geometry defined by a dppe ligand and two 2-pyS anions which function as bidentate ligands via their N— and S— atoms. Important interatomic parameters are Ru—P 2.240(3), 2.256(3); Ru—N 2.131(8), 2.136(8); Ru—S 2.413(3), 2.428(3) Å; P—Ru—P 84.1(1), S—Ru—S 155.0(1) and N—Ru—N 87.5(3)°. Crystals are monoclinic, space group $P2_1/c$, with unit cell dimensions a = 10.342(1), b = 31.145(6), c = 11.107(2) Å, $\beta = 113.80(1)^{\circ}$ and Z = 4. The structure was refined to final R = 0.064 for 3057 reflections with $I \ge 2.5\sigma(I)$.

Introduction

This communication reports the crystal structure analysis of the title compound, hereafter [Ru(dppe)(2pyS)₂]; where dppe is 1,2-bis(diphenylphosphino)ethane, Ph₂PCH₂CH₂PPh₂, and 2-pyS is the anion derived from 2-mercaptopyridine. Ruthenium complexes of 2-pyS are well known in the literature (e.g., Alteparmakian et al., 1985; Constable and Lewis, 1983; Powell, 1974; Rosete et al., 1979). In addition, three crystal structures are known, namely, that of [Ru(PPh₃)₂(2-pyS)₂] (Fletcher and Skapski, 1972) and of $[Ru(PPh_3)(CO)_2(2-pyS)_2]$ and $[Ru(PPh_3)(CO)(2-pyS)_2]$ pyS_{2} (Mura *et al.*, 1985). Thus far, however, there are no reports of ruthenium complexes containing both 2pyS and bidentate phosphines such as dppe. The title compound was prepared recently and it was found that this complex was more stable in diffuse- and sun light than is the PPh₃ analog, $[Ru(PPh_3)_2(2-pyS)_2]$ which is known to change from an orange to a green color in solution. As a prelude to a detailed photochemical study of these compounds, an X-ray study of the dppe compound was undertaken in order to determine whether there were any obvious differences between the compounds in the solid state.

Experimental

Materials

 $[Ru(PPh_3)_2(2-pyS)_2]$ was prepared according to the literature method (Fletcher and Skapski, 1972).

Preparation of $[Ru(dppe)(2-pyS)_2]$: To a solution of dppe (39.8 mg, 0.1 mmol) in toluene (20 cm³) was added a solution of $[Ru(PPh_3)_2(2-pyS)_2]$ (84.5 mg, 0.1 mmol) in toluene (20 cm³). The solution was refluxed for 48 hr, the volume reduced to about one third of its initial volume and petroleum ether (60–80°C) added. The orange crystals that separated were washed with diethylether and recrystallized from a benzene/hexane solution of the compound yielding crystals suitable for the X-ray study. The compound was soluble in CH₂Cl₂, CHCl₃ and benzene and sparingly soluble in methanol and ethanol.

Intensity data were measured at 295 K on an Enraf-Nonius CAD4F diffractometer fitted with graphite monochromatized Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å. The $\omega: 2\theta$ scan technique was employed to measure 6710 reflections on a crystal 0.21, 0.06, 0.16 mm up to a

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maximum Bragg angle of 25° . The data were corrected for Lorentz and polarization effects and for absorption with the use of an analytical procedure (Sheldrick, 1976). Of the 5737 unique reflections, 3057 satisfied the $I \ge 2.5 \sigma(I)$ criterion of observability and were used in the subsequent analysis.

Crystal data [Ru(dppe)(2-pyS)₂], C₃₆H₃₂N₂P₂S₂Ru, M = 719.8, monoclinic, space group $P2_1/c$, a = 10.342(1), b = 31.145(6), c = 11.107(2) Å, $\beta = 113.80(1)^\circ$, V = 3273.3 Å³, Z = 4, $D_c = 1.461$ g cm⁻³, F(000) = 1472, $\mu = 6.80$ cm⁻¹, max and min transmission factors: 0.959 and 0.902.

The structure was solved from the interpretation of the Patterson synthesis and refined by a full-matrix leastsquares procedure based on F (Sheldrick, 1976). All nonhydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the model at their calculated positions (C-H 0.97 Å). After the inclusion of a weighting scheme of the form, $w = k/[\sigma^2(F) + g|F|^2]$, the refinement was continued until convergence; R = 0.064, k = 3.52, g = 0.0004, and $R_w = 0.061$. The analysis of variance showed no special features. Fractional atomic coordinates are listed in Table 1 and the numbering scheme employed is shown in Fig. 1 drawn with ORTEP (Johnson, 1976) at 15% probability ellipsoids. Scattering factors for neutral Ru, corrected for f' and f'', were from the International Tables (Ibers and Hamilton, 1974) and those for the remaining atoms were as incorporated in the SHELX76 program (Sheldrick, 1976). Calculations were performed on a SUN 4/280 computer.

Results and discussion

The molecular structure of $[Ru(dppe)(2-pyS)_2]$ is shown in Fig. 1 and selected interatomic parameters are given in Table 2. The crystal structure is comprised of discrete molecular units of $[Ru(dppe)(2-pyS)_2]$, there being no close intermolecular contacts in the lattice. The Ru atom exists in a distorted octahedral geometry defined by a chelating dppe ligand and two bidentate 2pyS anions such that there is a N₂P₂S₂ donor set. The S atoms occupy positions approximately *trans*- to each other and the two pairs of P and N atoms are *trans*- to each other. Distortions from the ideal geometry arise as a result of the restricted bite distances of both types of ligands but in particular the 2-pyS ligands; P-Ru-P 84.1(1) and N-Ru-S 67.6(2) and 67.0(2)°.

Within the 2-pyS ligands in [Ru(dppe)(2-pyS)₂] the

Table 1. Fractional atomic coordinates and B_{eq} values (Å²): $B_{eq} = 8\pi^2 (U_{11} + U_{22} + U_{33})/3$

| Atom | <i>x</i> | у | Ζ | $B_{\rm eq}$ |
|--------|-------------|------------|-------------|--------------|
| Ru | 0.03489(8) | 0.10557(3) | 0.23706(8) | 2.21 |
| N(11) | 0.1535(8) | 0.0500(3) | 0.2335(8) | 2.88 |
| C(21) | 0.2866(11) | 0.0618(3) | 0.3128(11) | 3.32 |
| S(21) | 0.2843(3) | 0.1142(1) | 0.3690(3) | 3.16 |
| C(31) | 0.4003(12) | 0.0345(4) | 0.3381(13) | 4.76 |
| C(41) | 0.3748(14) | -0.0046(4) | 0.2813(14) | 5.96 |
| C(51) | 0.2397(14) | -0.0174(4) | 0.2005(12) | 4.73 |
| C(61) | 0.1313(12) | 0.0110(3) | 0.1801(11) | 3.70 |
| N(12) | -0.0156(9) | 0.0737(3) | 0.3829(8) | 2.74 |
| C(22) | -0.1397(10) | 0.0548(3) | 0.3096(10) | 2.71 |
| S(22) | -0.1860(3) | 0.0661(1) | 0.1444(3) | 3.14 |
| C(32) | -0.2167(11) | 0.0317(3) | 0.3655(12) | 3.83 |
| C(42) | -0.1625(15) | 0.0295(4) | 0.5025(14) | 5.44 |
| C(52) | -0.0363(14) | 0.0484(4) | 0.5761(12) | 4.91 |
| C(62) | 0.0368(11) | 0.0698(3) | 0.5152(11) | 3.43 |
| P(1) | 0.0499(3) | 0.1372(1) | 0.0620(3) | 2.67 |
| P(2) | -0.0237(3) | 0.1719(1) | 0.2792(3) | 2.53 |
| C(1) | 0.0852(11) | 0.1945(3) | 0.0970(10) | 3.19 |
| C(2) | -0.0158(12) | 0.2110(3) | 0.1562(10) | 3.71 |
| C(111) | -0.1058(11) | 0.1379(3) | -0.0949(10) | 2.92 |
| C(112) | -0.0995(12) | 0.1412(4) | -0.2147(11) | 5.05 |
| C(113) | -0.2156(13) | 0.1426(5) | -0.3286(12) | 6.30 |
| C(114) | -0.3496(12) | 0.1413(5) | -0.3285(12) | 5.07 |
| C(115) | -0.3597(11) | 0.1386(4) | -0.2118(11) | 3.92 |
| C(116) | -0.2405(10) | 0.1368(3) | -0.0949(11) | 3.27 |
| C(121) | 0.1884(10) | 0.1186(3) | 0.0105(9) | 2.60 |
| C(122) | 0.3088(12) | 0.1414(4) | 0.0300(11) | 4.81 |
| C(123) | 0.4162(13) | 0.1230(5) | 0.0007(13) | 6.15 |
| C(124) | 0.4024(15) | 0.0825(5) | -0.0466(13) | 6.21 |
| C(125) | 0.2835(14) | 0.0587(5) | -0.0669(13) | 6.15 |
| C(126) | 0.1778(12) | 0.0776(4) | -0.0386(11) | 4.96 |
| C(211) | -0.1850(9) | 0.1873(3) | 0.2968(10) | 2.56 |
| C(212) | -0.2831(11) | 0.1559(3) | 0.2965(11) | 3.59 |
| C(213) | -0.3977(11) | 0.1671(4) | 0.3204(11) | 4.31 |
| C(214) | -0.4211(12) | 0.2075(4) | 0.3486(12) | 4.88 |
| C(215) | -0.3286(12) | 0.2388(4) | 0.3485(14) | 5.69 |
| C(216) | -0.2108(11) | 0.2293(4) | 0.3241(13) | 4.76 |
| C(221) | 0.1080(10) | 0.1910(3) | 0.4381(10) | 2.74 |
| C(222) | 0.0935(11) | 0.1791(3) | 0.5510(10) | 3.31 |
| C(223) | 0.1990(12) | 0.1874(4) | 0.6725(12) | 4.07 |
| C(224) | 0.3187(11) | 0.2093(4) | 0.6823(12) | 3.97 |
| C(225) | 0.3319(11) | 0.2235(4) | 0.5700(13) | 4.39 |
| C(226) | 0.2284(11) | 0.2145(4) | 0.4486(11) | 4.01 |
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C-S bond distances of 1.75(1) and 1.74(1) Å are significantly longer than 1.62 Å, being the distance expected for a C=S double bond (Pauling, 1960), indicating the S atoms are coordinating the Ru atom more as thiolate atoms rather than as thione functions. Extensive delocalization of π -electron density within the heterocyclic rings is indicated by a high degree of multiple bond character in the N-C and C-C bonds as evi-



Fig. 1. Molecular structure and crystallographic numbering scheme employed for $[Ru(dppe)(2-pyS)_2]$ drawn with 15% probability ellipsoids with ORTEP (Johnson, 1976).

| Table 2. | Selected interatomic parameters | (Å; | deg) | foi |
|----------|---------------------------------|-----|------|-----|
| | [Ru(dppe)(2-pyS) ₂] | | | |

| Ru-S(21) | 2.413(3) | Ru-S(22) | 2.428(3) |
|--------------------------|----------|-----------------------------|----------|
| Ru - P(1) | 2.240(3) | Ru - P(2) | 2.256(3) |
| Ru = N(11) | 2.131(8) | Ru - N(12) | 2.136(8) |
| N(11)C(21) | 1.35(1) | N(21) - C(22) | 1.35(1) |
| S(21)-C(21) | 1.75(1) | S(22) - C(22) | 1.74(1) |
| C(21)-C(31) | 1.38(1) | C(22)-C(32) | 1.39(1) |
| C(31) - C(41) | 1.35(2) | C(32) - C(42) | 1.40(2) |
| C(41)-C(51) | 1.38(2) | C(42) - C(52) | 1.36(2) |
| C(51)-C(61) | 1.37(1) | C(52)-C(62) | 1.37(2) |
| C(61)N(11) | 1.35(1) | C(62)-N(21) | 1.35(1) |
| P(1) - C(1) | 1.83(1) | P(2) - C(2) | 1.85(1) |
| P(1)-C(111) | 1.83(1) | P(2)-C(211) | 1.820(9) |
| P(1)-C(121) | 1.84(1) | P(2)-C(221) | 1.84(1) |
| C(1) - C(2) | 1.53(1) | | |
| | | | |
| S(21) - Ru - S(22) | 155.0(1) | S(21) = Ru = P(1) | 92.7(1) |
| S(21) - Ru - P(2) | 94.7(1) | S(21) = Ru = N(11) | 67.6(2) |
| S(21) - Ru - N(12) | 96.9(2) | S(22) = Ru = P(1) | 103.8(1) |
| S(22)-Ru-P(2) | 105.5(1) | S(22) = Ru = N(11) | 91.7(2) |
| S(22) = Ru = N(12) | 67.0(2) | P(1)-Ru- $P(2)$ | 84.1(1) |
| P(1) - Ru - N(11) | 95.6(2) | P(1) - Ru - N(12) | 170.4(2) |
| P(2) - Ru - N(11) | 162.4(2) | P(2) - Ru - N(12) | 95.7(2) |
| N(11) - Ru - N(12) | 87.5(3) | | |
| $R_{H} = S(21) = C(21)$ | 81 1(4) | $R_{11} - S(22) - C(22)$ | 81.0(3) |
| $R_{II} = N(11) = C(21)$ | 102.1(6) | $R_{\rm H} = N(12) = C(22)$ | 102.1(6) |
| Ru = N(11) = C(61) | 138.8(7) | Ru = N(12) = C(62) | 138.9(7) |
| Ru - P(1) - C(1) | 108.7(3) | $R_{u} - P(2) - C(2)$ | 110.6(4) |
| $R_{u} - P(1) - C(111)$ | 119.2(3) | $R_{u} - P(2) - C(211)$ | 126.7(3) |
| Ru - P(1) - C(121) | 117.9(3) | Ru - P(2) - C(221) | 109.8(3) |
| C(1) - P(1) - C(111) | 102.3(5) | C(2) - P(2) - C(211) | 102.8(5) |
| C(1) - P(1) - C(121) | 105.0(4) | C(2) - P(2) - C(221) | 105.0(5) |
| C(111) - P(1) - C(121) | 101.8(4) | C(211) - P(2) - C(221) | 99.7(4) |
| | | | |

denced by the shortening of the N-C and C-C bond distances compared to their normal single bond values (Pauling, 1960); Table 2. Bond lengths and angles defining the dppe ligand are as expected.

The main purpose of this study was to ascertain whether there were any obvious structural differences existing between [Ru(dppe)(2-pyS)₂] and its PPh₃ analogue [Ru(PPh₃)₂(2-pyS)₂] (Fletcher and Skapski, 1972). Whereas the Ru-N bond distances in both complexes are equal within experimental error, the Ru-P distances in [Ru(dppe)(2-pyS)₂] of 2.240(3) and 2.256(3) Å are shorter than the Ru-P distances in the PPh_3 compound (2.319(2) and 2.332(2) Å). There are no obvious trends in the Ru-S bond distances, however, with one Ru-S bond distance in [Ru(dppe)(2 pyS_{2} being shorter (2.413(3) Å) than the other (2.428(3) Å) and at the same time being shorter than the Ru-S bond distances in $[Ru(PPh_3)_2(2-pyS)_2]$ of 2.434(2) and 2.437(2) Å (Fletcher and Skapski, 1972). Despite these differences there is a remarkable constancy in the S-Ru-S angles in the two complexes; i.e., 155.0(1) and $154.7(1)^{\circ}$, respectively. Also, the N-Ru-S angles are also equal within experimental error in both compounds. The restricted bite distance of the dppe ligand which imposes a P-Ru-P angle of 84.1(1) in the $[Ru(dppe)(2-pyS)_2]$ compound, c.f. 96.8(1)° in the PPh₃ compound, is reflected in the N-Ru-N angles however; this angle is significantly greater in the dppe compound 87.5(3) c.f. 80.9(3)°.

An interesting comparison may also be made with the compound $[Ru(PPh_3)(CO)(2-pyS)_2]$, the other Ru compound of this type that has been structurally characterized (Mura *et al.*, 1985). In this compound one P donor atom has been substituted by a carbonyl ligand and hence one would anticipate less steric strain in this complex compared to the dppe compound. In fact the P-Ru-C angle of 90.9(1)° is intermediate between the P-Ru-P angles found in the dppe and PPh₃ compounds. Interestingly, the N-Ru-N angle of 82.4(1)° is also intermediate between the N-Ru-N angles found in the other compounds although in this latter example the S-Ru-S angle has opened up somewhat to 157.96(3)° (Mura *et al.*, 1985).

Thus, in conclusion, except for the obvious differences in the Ru atom geometries imposed by the steric requirements of the dppe ligand in $[Ru(dppe)(2-pyS)_2]$ over the PPh₃ ligands in $[Ru(PPh_3)_2(2-pyS)_2]$, there are no outstanding differences between the solid state structures which may explain the apparently different photochemical behavior exhibited in this pair of compounds.

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Structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication No. 60716 (18 pages).