Ditertiary Phosphine Rhodium and Iridium Complexes Containing the Molecular Unit S_2 or Se_2 as a Ligand

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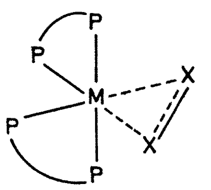
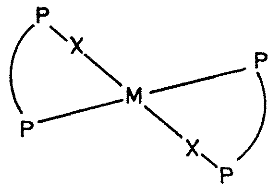
Summary Cyclo-octasulphur and cyclo-octaselenium react with $[Ir(dppe)_2]Cl$ and $[Rh(dmpe)_2]Cl$ (dppe = $Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2$ and dmpe = $Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2$) to form the complexes $[Ir(S_2)(dppe)_2]Cl$ (**1**), $[Ir(Se_2)(dppe)_2]Cl$ (**2**), and $[Rh(S_2)(dmpe)_2]Cl$ (**3**).

THE iridium and rhodium oxygen complexes $[Ir(O_2)(dppe)_2]^+$ (dppe = $Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2$), $IrX(O_2)CO[PPh_3]_2$ (X = Cl, or I), and $[Rh(O_2)(dppe)_2]^+$ have O_2 molecules linked to the metal atom in the "π-bonding" manner.[1–3] We report analogous S_2 and Se_2 complexes (**1**), (**2**), and (**3**). Unlike O_2, the free S_2 and Se_2 molecules do not exist at room temperature; in the complexes they are stabilized by co-ordination to the metal atom. Transition-metal complexes with nonbridging molecular Se_2 were previously unknown. The recently reported[4] niobium complexes $(\pi\text{-}C_5H_5)_2Nb(S_2)X$ (X = Cl, Br, I, or SCN), the O_2 analogues of which are not known, contain a nonbridging S_2 molecule; shown by *X*-ray methods[5] to be attached to the metal atom in the "π-bonding" manner with an S–S distance of 1·73 Å in the chloride (*cf.*, d_{S-S} = 1·92 Å in the free S_2 molecule[6].



X = O,S,Se
M = Rh,Ir
(A)



X = S,Se
M = Rh,Ir
(B)

Properties of the new S_2 and Se_2 complexes are listed in the Table. The compounds were formed by treating the appropriate iridium and rhodium bis-diphosphine complexes with cyclo-octasulphur or cyclo-octaselenium as indicated in reactions (1), (2), and (3). The reactions were carried out under N_2 in dry, degassed solvents. Treatment of (**3**) with aqueous NH_4PF_6 precipitated (**4**).

$$[Ir(dppe)_2]Cl + S_8 \xrightarrow[C_6H_6\text{–}CH_2Cl_2]{25°,\ 16\ h.} (\mathbf{1}) \qquad (1)$$

$$[Ir(dppe)_2]Cl + Se_8 \xrightarrow[CH_2Cl_2]{20°,\ 3\ days} (\mathbf{2}) \qquad (2)$$

$$[Rh(dmpe)_2]Cl + S_8 \xrightarrow[C_6H_6\text{–}THF]{25°,\ 16\ h.} (\mathbf{3}) \qquad (3)$$

Complexes (**1**), (**2**), and (**4**) appear to be unchanged on exposure to air in the solid state, but (**3**) is hygroscopic. Compound (**1**) was recovered unchanged from a methylene chloride solution through which O_2 had been passed for 12 h. Conductivity measurements in acetonitrile show the complexes to be monomeric 1 : 1 electrolytes, and we suggest that they have the structure A similar to that found by *X*-ray analysis[1] for the O_2 complexes $[Ir(O_2)(dppe)_2]PF_6$ and $[Rh(O_2)(dppe)_2]PF_6$.

^{31}P N.m.r. spectra of (**1**) and (**2**) (Table) show two sets of nonequivalent phosphorus atoms consistent with structure A or with structure B in which the S or Se atoms are placed between the metal and two of the phosphorus atoms. However, J_{P-P} for (**1**) and (**2**) are larger than J_{P-P} for the oxygen complex $[Ir(O_2)(dppe)_2]Cl$ (*cf.*, footnote e of the Table), and this excludes structure B, which would be expected to have a smaller J_{P-P} than A. The i.r. spectrum (CsI disk) of (**1**) also favours A. In the region 540—630 cm^{-1}, where $\nu(P{=}S)$ for a complex of type B would be expected, there is only a very weak band at 615 cm^{-1} due to the (dppe) ligand.

TABLE

S_2 *and* Se_2 *complexes with iridium and rhodium*[a]

				Conductivity in CH_3CN[c]			
						A theory	
	Formula	Colour	M.p.° C[b]	Λ_0	A	1 : 1	^{31}P n.m.r.[d,e]
(**1**)	$[Ir(S_2)(dppe)_2]Cl$	Orange	218—221	139	380	333	t, $\delta = -23{\cdot}8$; t, $\delta = -20{\cdot}4$; $J = 7{\cdot}2$ Hz[f]
(**2**)	$[Ir(Se_2)(dppe)_2]Cl$	Green	200—201	125	329	322	t, $\delta = -16{\cdot}5$; t, $\delta = -14{\cdot}9$; $J = 6{\cdot}7$ Hz[g]
(**3**)	$[Rh(S_2)(dmpe)_2]Cl$	Orange	154—155	Not measured			Not measured
(**4**)	$[Rh(S_2)(dmpe)_2]PF_6$	Orange	174—175	160	365	349	Not measured

[a] All compounds listed have satisfactory C, H, P, Cl, S, or Se analyses. [b] Uncorrected, in evacuated capillaries. [c] Measurements were made over the concentration range 10^{-2}—10^{-4}M at 25 °C. [d] In CH_2Cl_2 solution with ^1H decoupling. Shifts are in p.p.m. with reference to H_3PO_4; t stands for triplet. [e] For comparison, in CH_2Cl_2 solution, $[Ir(O_2)(dppe)_2]Cl$ shows t, $\delta = -20{\cdot}4$; t, $\delta = -13{\cdot}2$; $J = 4{\cdot}5$ Hz. [f] Measured at −60° with a PEt_3 reference and converted into H_3PO_4 reference using $\delta(PEt_3) = +20{\cdot}4$ p.p.m. [g] Measured at ambient temperature with H_3PO_4 reference.

The identifiable nonphosphine ligand frequencies of compounds (**1**)—(**4**) are of interest. A band at 525 cm^{-1} (m, i.r.) in the S_2 complexes (**3**) and (**4**) and at 310 cm^{-1} (vw, i.r.; s, Raman) in the Se_2 complex (**2**), are the highest frequencies observed that may be associated with, respectively, the S_2 and Se_2 groups. These bands presumably arise from a vibration of the same type as the 540 cm^{-1} band in $(\pi\text{-}C_5H_5)_2Nb(S_2)X$ (X = Cl, Br, I, or SCN) assigned as ν(S–S),[4] and the 858—862 cm^{-1} band in $IrX(O_2)(CO)(PPh_3)_2$ (X = Cl, or I) assigned as ν(O–O).[7] Both the latter are insensitive to the Y–Y (Y = O, or S) distance and so cannot be simple Y–Y stretching frequencies. A comparison of the 525 and 310 cm^{-1} bands with ν(S–S) and ν(Se–Se) in the free S_2 and Se_2 molecules does not indicate the S–S or Se–Se bond order in compounds (**1**)—(**4**). Whether the S–S distance in $[Ir(S_2)(dppe)_2]Cl$ changes like the O–O distance in $[Ir(O_2)(dppe)_2]Cl$ or the S–S distance in $(\pi\text{-}C_5H_5)_2Nb(S_2)Cl$, *i.e.* whether it expands or contracts relative to the free S_2 molecule, is being studied in an *X*-ray structure determination.[8]

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