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REACTIONS OF S_4N_4 WITH PHOSPHINEIRIDIUM(I) COMPLEXES. SYNTHESIS AND CRYSTAL STRUCTURES OF $[(dppen)_2Ir(S_2N_2)](BPh_4) \cdot 0.5CH_3COCH_3$ AND $\{(dppen)_2Ir(S_2N_2)[W(CO)_5]\}(BPh_4) \cdot 0.5CH_2Cl_2$

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Summary

The iridium(I) complexes $[(diphos)_2Ir(CO)](BPh_4)$ react with S_4N_4 to give the octahedral derivatives $[(diphos)_2Ir(S_2N_2)](BPh_4)$, (diphos = bis(diphenylphosphino)ethylene, dppen, (**1**); diphos = bis(diphenylphosphino)methane, dppm, (**2**). Reaction of **1** with $W(CO)_6$ gave the carbonyl derivative $\{(dppen)_2Ir(S_2N_2)[W(CO)_5]\}(BPh_4)$, (**3**). The crystal structures of **1** and **3** have been determined by X-ray diffraction. In both compounds the iridium atom shows a distorted octahedral geometry, being surrounded by two bidentate phosphine ligands and by the sulfur and a nitrogen atom of the open-chain disulfur dinitride ligand. In **3** the nitrogen atom of the S_2N_2 group which is not coordinated to the iridium atom is linked to the tungsten atom of a $W(CO)_5$ residue. The ^{31}P NMR spectra of **1** and **3** are indicative of a rigid structure in solution at room temperature.

Introduction

The unusual electric properties of polymeric sulfur-nitride $(SN)_x$ [1] have recently given rise to much interest in sulfur nitrogen compounds. Particular attention has been devoted to the tetrasulfur tetranitride molecule, which has been shown to be readily attacked by organic nucleophiles]2]. Although several reactions involving S_4N_4, or closely related species and higher oxidation state transition metal halides have been reported [3], very few involve reactions of S_4N_4 with low oxidation state metal complexes. Moreover the few known organometallic sulfur-nitrogen derivatives were usually isolated in very low yield, as products of reactions under drastic conditions [4].

Our current interest in transition metal complexes containing unsubstituted V and/or VI Main Group atoms as ligands prompted us to investigate the reactions of S_4N_4 with organometallic species. As part of this study we recently prepared the dimeric complexes $[(PPh_3)M(\mu\text{-}S_2N_2)]_2$, M = Ni, Pd, Pt, by reaction of S_4N_4 with d^{10} metal(0) complexes [5]. The palladium and platinum dimers were subsequently reported [6].

We describe here the reactions of S_4N_4 with d^8 iridium complexes $[(diphos)_2Ir(CO)](BPh_4)$ (diphos = bis(diphenylphosphino)ethylene, dppen, bis(diphenylphosphino)methane, dppm,) under mild conditions, to give the monomeric complexes $[(diphos)_2Ir(S_2N_2)](BPh_4)$. The complex $[(dppen)_2Ir(S_2N_2)](BPh_4) \cdot 0.5\ (CH_3)_2CO$, (**1**), reacts with $W(CO)_6$ to form the heterodimetallic derivative $\{(dppen)_2Ir(S_2N_2)[W(CO)_5]\}(BPh_4) \cdot 0.5CH_2Cl_2$, (**3**).

Complexes **1** and **3** have been characterized by ^{31}P NMR spectroscopy and by X-ray structural studies.

A preliminary communication has appeared [7].

Experimental

Solvents were reagent-grade quality and were used without further purification. The reactions were carried out under oxygen-free nitrogen. The complexes $[(dppen)_2Ir(CO)](BPh_4)$ [8] and $[(dppm)_2Ir(CO)](BPh_4)$ [9] were prepared by previously published methods. Tetrasulfur tetranitride was prepared in the usual way [10] and crystallized several times from CH_2Cl_2 before use. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WX200 spectrometer at the University of Liverpool; CD_2Cl_2 was employed as solvent and 85% H_3PO_4 as external references. IR spectra were recorded as Nujol mulls on a Perkin–Elmer 283 spectrophotometer.

Synthesis of $[(diphos)_2Ir(S_2N_2)](BPh_4) \cdot x(solv)$ (diphos = dppen (1), dppm (2))

A solution of S_4N_4 (37.5 mg, 0.2 mmol) in tetrahydrofuran (THF) (20 ml) was added to a solution of $[(diphos)_2Ir(CO)](BPh_4)$ (0.4 mmol) in THF (30 ml) at 50°C and after ca. 2 h di-n-butyl ether was added. The solution was heated and orange-brown crystals separated out. They were filtered off, and washed with di-n-butyl-ether and petroleum ether. The dppen derivative was recrystallized from acetone/n-butanol.

$[(dppen)_2Ir(S_2N_2)](BPh_4) \cdot 0.5(CH_3)_2CO$. Found: C, 64.74; H, 5.05; N, 1.82; S, 4.25; Ir, 11.4. $C_{77.5}H_{67}N_2BIrO_{0.5}P_4S_2$ calcd.: C, 65.29; H, 4.74; N, 1.96; S, 4.50; Ir, 13.48%; Yield: 300 mg (50%).

$[(dppm)_2Ir(S_2N_2)](BPh_4)$. Found: C, 63.74; H, 4.62; N, 2.18; S, 4.90. $C_{74}H_{64}N_2BIrP_4S_2$ calcd.: C, 64.77, H, 4.70; N, 2.04; S, 4.66%. Yield: 390 mg (70%).

Synthesis of $\{(dppen)_2Ir(S_2N_2)[W(CO)_5]\}(BPh_4) \cdot 0.5CH_2Cl_2$ (3)

A solution of $[(dppen)_2Ir(S_2N_2)](BPh_4)$ (700 mg, 0.5 mmol) in CH_2Cl_2 (50 ml) was added, under nitrogen, to an excess of solid $W(CO)_6$ in a quartz vessel. The mixture was refluxed and irradiated with UV light for 2 h. Di-n-butyl ether (20 ml) was added to the filtrate, and after concentration at 50°C orange crystals separated out. They were filtered off, washed with di-n-butyl ether and petroleum ether, and dried. Yield: 500 mg (30%). Found: C, 54.08; H, 3.57; N, 1.75. $C_{81.5}H_{65}N_2BClO_5P_4IrS_2W$, calcd.: C, 55.55; H, 3.72; N, 1.59%.

Data collection, solution and structure refinement

Diffraction data for both compounds were collected at room temperature on a

TABLE 1

POSITIONAL PARAMETERS ($\times 10^4$) FOR $[(\mathrm{dppen})_2\mathrm{Ir}(\mathrm{S}_2\mathrm{N}_2)](\mathrm{BPh}_4)\cdot 0.5(\mathrm{CH}_3)_2\mathrm{CO}$

Atom	*x*	*y*	*z*
Ir	70(1)	1948(1)	2051(1)
P(1)	741(2)	2022(3)	1061(4)
P(2)	739(2)	1695(2)	3616(4)
P(3)	10(2)	2917(2)	2387(5)
P(4)	−636(2)	2114(2)	512(4)
S(1)	−523(3)	1734(4)	3223(7)
S(2)	−355(4)	754(4)	2218(8)
N(1)	−30(4)	1009(5)	1614(10)
N(2)	−661(5)	1162(6)	3090(11)
C(1)	1343(7)	1878(9)	2083(15)
C(2)	1344(7)	1695(8)	3115(15)
C(3)	−481(8)	3217(8)	1206(18)
C(4)	−749(7)	2873(8)	452(17)
C(11)	849(4)	2684(6)	403(10)
C(21)	1323(4)	2965(6)	689(10)
C(31)	1397(4)	3468(6)	144(10)
C(41)	997(4)	3691(6)	−687(10)
C(51)	523(4)	3411(6)	−973(10)
C(61)	450(4)	2907(6)	−429(10)
C(12)	829(6)	1502(5)	−24(12)
C(22)	937(6)	1675(5)	−1056(12)
C(32)	1050(6)	1274(5)	−1817(12)
C(42)	1057(6)	702(5)	−1545(12)
C(52)	950(6)	529(5)	−512(12)
C(62)	836(6)	929(5)	248(12)
C(13)	729(5)	974(6)	4146(10)
C(23)	946(5)	540(6)	3619(10)
C(33)	962(5)	−8(6)	4051(10)
C(43)	763(5)	−122(6)	5009(10)
C(53)	546(5)	313(6)	5536(10)
C(63)	529(5)	860(6)	5105(10)
C(14)	873(4)	2103(7)	4928(13)
C(24)	471(4)	2288(7)	5420(13)
C(34)	580(4)	2599(7)	6426(13)
C(44)	1092(4)	2726(7)	6940(13)
C(54)	1494(4)	2541(7)	6448(13)
C(64)	1385(4)	2229(7)	5442(13)
C(15)	−287(5)	3164(7)	3550(15)
C(25)	−16(5)	3501(7)	4429(15)
C(35)	−249(5)	3667(7)	5312(15)
C(45)	−753(5)	3496(7)	5317(15)
C(55)	−1024(5)	3159(7)	4438(15)
C(65)	−792(5)	2994(7)	3555(15)
C(16)	565(5)	3392(7)	2527(12)
C(26)	527(5)	3930(7)	2048(12)
C(36)	953(5)	4292(7)	2264(12)
C(46)	1418(5)	4114(7)	2958(12)
C(56)	1456(5)	3576(7)	3437(12)
C(66)	1030(5)	3214(7)	3221(12)
C(17)	−615(5)	1894(6)	−929(11)
C(27)	−396(5)	1379(6)	−1134(11)
C(37)	−392(5)	1217(6)	−2246(11)
C(47)	−606(5)	1569(6)	−3151(11)

TABLE 1 (continued)

Atom	x	y	z
C(57)	−825(5)	2085(6)	−2946(11)
C(67)	−830(5)	2247(6)	−1835(11)
C(18)	−1259(6)	1828(5)	644(13)
C(28)	−1609(6)	2179(5)	1031(13)
C(38)	−2095(6)	1974(5)	1103(13)
C(48)	−2232(6)	1419(5)	788(13)
C(58)	−1883(6)	1068(5)	402(13)
C(68)	−1396(6)	1273(5)	330(13)
C(19)	3480(5)	752(7)	4010(11)
C(29)	3729(5)	465(7)	4987(11)
C(39)	4258(5)	358(7)	5174(11)
C(49)	4540(5)	537(7)	4383(11)
C(59)	4292(5)	823(7)	3406(11)
C(69)	3762(5)	931(7)	3219(11)
C(110)	2713(7)	1434(6)	2921(15)
C(210)	2667(7)	1373(6)	1751(15)
C(310)	2632(7)	1850(6)	1060(15)
C(410)	2642(7)	2387(6)	1537(15)
C(510)	2688(7)	2448(6)	2706(15)
C(610)	2723(7)	1971(6)	3398(15)
C(111)	2667(5)	991(6)	5013(11)
C(211)	2199(5)	779(6)	5191(11)
C(311)	2044(5)	896(6)	6203(11)
C(411)	2357(5)	1225(6)	7037(11)
C(511)	2825(5)	1437(6)	6859(11)
C(611)	2981(5)	1320(6)	5847(11)
C(112)	2522(5)	285(7)	3187(11)
C(212)	2709(5)	−242(7)	3598(11)
C(312)	2426(5)	−728(7)	3227(11)
C(412)	1955(5)	−687(7)	2445(11)
C(512)	1767(5)	−160(7)	2035(11)
C(612)	2051(5)	326(7)	2406(11)
B	2844(10)	859(11)	3788(22)
O	2330(18)	3590(19)	8420(37)
C(5)	2746(28)	3700(30)	8867(56)
C(6)	3175(26)	3412(28)	9331(55)
C(7)	2761(29)	4226(34)	8625(64)

Philips PW 1100 diffractometer. Unit cell parameters were determined by least-squares refinement of the setting angles of 24 and 20 carefully centered reflections for **1** and **3**, respectively. All calculations were carried out using the SHELX76 [11] and ORTEP [12] programs on a SEL32/77 computer. Atomic scattering factors for non-hydrogen atoms were taken from ref. 13 and those for hydrogen atoms from ref. 14. Both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all non-hydrogen atoms [15]. The refinements were based on F_o, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$.

$[(dppen)_2Ir(S_2N_2)](BPh_4) \cdot 0.5CH_3COCH_3$ (1). Crystal data: $C_{77.5}H_{67}BIrN_2O_{0.5}P_4S_2$, $M = 1425.4$; monoclinic; space group $P2_1/n$: a 26.458(12), b 23.688, c 12.045(6) Å; β 102.36(5)°; U 7374.1 Å^3; D_{calcd} 1.284 g cm^{-3}; $Z = 4$; μ(Mo-K_α) 19.83 cm^{-3}; R 0.065 for 4185 observed reflections. Owing to the disorder affecting

TABLE 2

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR $[(\mathrm{dppen})_2\mathrm{Ir}(\mathrm{S}_2\mathrm{N}_2)](\mathrm{BPh}_4)\cdot 0.5(\mathrm{CH}_3)_2\mathrm{CO}$

Ir–P(1)	2.347(5)	Ir–N(1)	2.289(12)
Ir–P(2)	2.370(5)	S(1)–N(2)	1.40(2)
Ir–P(3)	2.341(5)	N(2)–S(2)	1.75(2)
Ir–P(4)	2.367(5)	S(2)–N(1)	1.38(2)
Ir–S(1)	2.379(9)		
P(1)–Ir–P(2)	84.6(2)	P(3)–Ir–S(1)	91.6(3)
P(1)–Ir–P(3)	95.9(2)	P(3)–Ir–N(1)	169.6(3)
P(1)–Ir–P(4)	98.4(2)	P(4)–Ir–S(1)	89.4(2)
P(1)–Ir–S(1)	169.7(2)	P(4)–Ir–N(1)	87.0(3)
P(1)–Ir–N(1)	91.1(3)	S(1)–Ir–N(1)	82.5(4)
P(2)–Ir–P(3)	100.2(2)	Ir–S(1)–N(2)	109.0(8)
P(2)–Ir–P(4)	174.3(2)	S(1)–N(2)–S(2)	117.4(10)
P(2)–Ir–S(1)	87.1(2)	N(2)–S(2)–N(1)	119.7(9)
P(2)–Ir–N(1)	88.1(3)	S(20–N(1)–Ir	111.1(8)
P(3)–Ir–P(4)	84.3(2)		

the S_2N_2 group, which could not be resolved, the results are not wholly satisfactory, so only the main features of the coordination geometry of **1** are discussed. Table 1 lists final positional parameters and selected bond distances and angles are given in Table 2.

TABLE 3

CRYSTAL DATA AND DATA COLLECTION DETAILS FOR $\{(\mathrm{dppen})_2\mathrm{Ir}(\mathrm{S}_2\mathrm{N}_2)[\mathrm{W(CO)}_5]\}(\mathrm{BPh}_4)\cdot 0.5\mathrm{CH}_2\mathrm{Cl}_2$

Formula	$C_{81.5}H_{65}BClIrN_2O_5P_4S_2W$
Mol. wt.	1762.77
a (Å)	43.158(30)
b (Å)	13.236(8)
c (Å)	25.515(14)
β (deg)	92.94(5)
V (Å^3)	14556.0
Space group	$C2/c$
Z	8
d_{calcd} (g cm^{-3})	1.608
Habit	truncated polyhedron
Dimensions (mm)	0.17 × 0.17 × 0.03
Linear abs coeff (cm^{-1})	36.63
Abs corr range	1.00–1.35
Radiation (Å)	Mo-K_α $\lambda = 0.7107$
Monochromator	graphite crystal
Method	$\omega - 2\theta$
Scan speed (deg/s)	0.03
Scan width (deg)	$0.6 + 0.3\tan\theta$
Background time	half the scan time
Standards	3 every 120 min
Maximum deviation of standards (%)	5
2θ limits (deg)	$5 \leqslant 2\theta \leqslant 40$
Number of data with $I \geqslant 3\sigma(I)$	3122
Final number of variables	293

TABLE 4

POSITIONAL PARAMETERS ($\times 10^4$) FOR $\{(\text{dppen})_2\text{Ir}(\text{S}_2\text{N}_2)[\text{W(CO)}_5]\}(\text{BPh}_4)\cdot 0.5\text{CH}_2\text{Cl}_2$

Atom	*x*	*y*	*z*
Ir	1463(1)	−731(1)	766(1)
W	2691(1)	−1038(1)	1288(1)
P(1)	1040(1)	−685(5)	140(2)
P(2)	1598(2)	841(5)	383(3)
P(3)	1180(2)	−210(5)	1476(3)
P(4)	1359(2)	−2374(5)	1088(3)
S(1)	1924(2)	−648(5)	1319(2)
S(2)	2096(2)	−1472(5)	362(3)
Cl	243(2)	3357(6)	2904(4)
O(1)	2884(4)	−3242(15)	940(8)
O(2)	2990(4)	−473(14)	210(8)
O(3)	3340(5)	−785(15)	1820(8)
O(4)	2549(5)	1212(16)	1651(8)
O(5)	2471(6)	−1769(18)	2403(11)
N(1)	1757(4)	−1387(12)	207(7)
N(2)	2208(4)	−1077(12)	945(6)
C(1)	1084(5)	464(17)	−264(9)
C(2)	1315(5)	1059(15)	−154(8)
C(3)	1005(5)	−1316(16)	1773(8)
C(4)	1081(5)	−2240(17)	1636(9)
C(5)	2791(7)	−2469(22)	1081(11)
C(6)	2893(6)	−672(22)	591(12)
C(7)	3082(6)	−942(20)	1603(10)
C(8)	2598(7)	414(23)	1522(12)
C(9)	2537(7)	−1568(22)	1998(13)
C(10)	0	4074(30)	2500
B	4211(7)	2154(22)	1668(12)
C(1,1)	1007(3)	−1597(12)	−396(6)
C(2,1)	731(3)	−2114(12)	−516(6)
C(3,1)	710(3)	−2780(12)	−939(6)
C(4,1)	965(3)	−2929(12)	−1244(6)
C(5,1)	1241(3)	−2413(12)	−1125(6)
C(6,1)	1262(3)	−1747(12)	−701(6)
C(1,2)	655(4)	−574(9)	385(6)
C(2,2)	530(4)	−1372(9)	662(6)
C(3,2)	236(4)	−1281(9)	859(6)
C(4,2)	66(4)	−392(9)	778(6)
C(5,2)	191(4)	406(9)	501(6)
C(6,2)	486(4)	315(9)	305(6)
C(1,3)	1956(4)	868(11)	31(4)
C(2,3)	2235(4)	1194(11)	276(4)
C(3,3)	2501(4)	1260(11)	−9(4)
C(4,3)	2489(4)	1002(11)	−540(4)
C(5,3)	2210(4)	677(11)	−785(4)
C(6,3)	1944(4)	610(11)	−500(4)
C(1,4)	1634(3)	2003(12)	766(5)
C(2,4)	1473(3)	2858(12)	583(5)
C(3,4)	1497(3)	3761(12)	864(5)
C(4,4)	1682(3)	3809(12)	1328(5)
C(5,4)	1842(3)	2954(12)	1512(5)
C(6,4)	1818(3)	2051(12)	1231(5)
C(1,5)	867(3)	767(13)	1433(6)
C(2,5)	895(3)	1575(13)	1008(6)

TABLE 4 (continued)

Atom	*x*	*y*	*z*
C(3,5)	679(3)	2359(13)	1080(6)
C(4,5)	435(3)	2336(13)	1418(6)
C(5,5)	407(3)	1528(13)	1764(6)
C(6,5)	624(3)	743(13)	1771(6)
C(1,6)	1409(3)	268(12)	2045(6)
C(2,6)	1395(3)	1288(12)	2179(6)
C(3,6)	1573(3)	1654(12)	2610(6)
C(4,6)	1765(3)	999(12)	2907(6)
C(5,6)	1779(3)	−21(12)	2772(6)
C(6,6)	1601(3)	−387(12)	2342(6)
C(1,7)	1183(3)	−3295(11)	651(5)
C(2,7)	910(3)	−3779(11)	780(5)
C(3,7)	777(3)	−4511(11)	445(5)
C(4,7)	917(3)	−4759(11)	−18(5)
C(5,7)	1190(3)	−4274(11)	−147(5)
C(6,7)	1323(3)	−3542(11)	188(5)
C(1,8)	1688(4)	−3069(11)	1402(5)
C(2,8)	1920(4)	−3456(11)	1098(5)
C(3,8)	2168(4)	−3987(11)	1335(5)
C(4,8)	2185(4)	−4132(11)	1878(5)
C(5,8)	1953(4)	−3746(11)	2182(5)
C(6,8)	1705(4)	−3214(11)	1944(5)
C(1,9)	3834(4)	2060(11)	1433(6)
C(2,9)	3751(4)	1601(11)	954(6)
C(3,9)	3439(4)	1522(11)	788(6)
C(4,9)	3210(4)	1901(11)	1102(6)
C(5,9)	3293(4)	2360(11)	1581(6)
C(6,9)	3605(4)	2439(11)	1747(6)
C(1,10)	4449(4)	1684(12)	1204(5)
C(2,10)	4617(4)	788(12)	1264(5)
C(3,10)	4814(4)	485(12)	878(5)
C(4,10)	4843(4)	1077(12)	431(5)
C(5,10)	4675(4)	1973(12)	370(5)
C(6,10)	4478(4)	2276(12)	757(5)
C(1,11)	4311(3)	3384(13)	1748(6)
C(2,11)	4094(3)	4164(13)	1693(6)
C(3,11)	4189(3)	5165(13)	1761(6)
C(4,11)	4500(3)	5387(13)	1884(6)
C(5,11)	4717(3)	4608(13)	1939(6)
C(6,11)	4622(3)	3606(13)	1872(6)
C(1,12)	4252(4)	1468(11)	2200(8)
C(2,12)	4483(4)	1670(11)	2587(8)
C(3,12)	4522(4)	1034(11)	3022(8)
C(4,12)	4329(4)	197(11)	3069(8)
C(5,12)	4097(4)	−4(11)	2682(8)
C(6,12)	4058(4)	631(11)	2247(8)

$\{(dppen)Ir(S_2N_2)[W(CO)_5]\}(BPh_4) \cdot 0.5CH_2Cl_2$ (3). An irregularly shaped red crystal of approximate dimensions 0.17 × 0.17 × 0.03 mm was used for the data collection. The crystals belong to monoclinic system, space group *C*2/*c*. Crystal data and details of the data collection collection are given in Table 3. Intensities

data were processed [16], using the value of 0.03 for the instability factor *k*. The intensity data were corrected for Lorentz-polarization effects and for absorption.

The structure was solved by the heavy-atom method: the iridium position

TABLE 5

SELECTED BOND DISTANCES (Å) AND ANGLES (DEG) WITH ESTIMATED STANDARD DEVIATIONS FOR $\{(\mathrm{dppen})_2\mathrm{Ir}(\mathrm{S}_2\mathrm{N}_2)[\mathrm{W}(\mathrm{CO})_5]\}(\mathrm{BPh}_4)\cdot0.5\mathrm{CH}_2\mathrm{Cl}_2$

Ir–P(1)	2.362(7)	P(1)–C(1,2)	1.81(2)
Ir–P(2)	2.384(7)	P(2)–C(2)	1.81(2)
Ir–P(3)	2.342(8)	P(2)–C(1,3)	1.82(2)
Ir–P(4)	2.376(7)	P(2)–C(1,4)	1.82(2)
Ir–S(1)	2.383(7)	P(3)–C(3)	1.83(2)
Ir–N(1)	2.14(2)	P(3)–C(1,5)	1.87(2)
W–N(2)	2.22(2)	P(3)–C(1,6)	1.83(2)
W–C(5)	2.02(4)	P(4)–C(4)	1.90(3)
W–C(6)	2.08(4)	P(4)–C(1,7)	1.80(2)
W–C(7)	1.83(3)	P(4)–C(1,8)	1.84(2)
W–C(8)	2.06(4)	C(1)–C(2)	1.29(3)
W–C(9)	2.08(4)	C(3)–C(4)	1.32(3)
S(1)–N(2)	1.69(2)	C(5)–O(1)	1.16(3)
S(2)–N(1)	1.50(2)	C(6)–O(2)	1.11(3)
S(2)–N(2)	1.63(2)	C(7)–O(3)	1.23(3)
P(1)–C(1)	1.85(3)	C(8)–O(4)	1.13(3)
P(1)–C(1,1)	1.82(2)	C(9)–O(5)	1.12(4)
P(1)–Ir–P(2)	84.1(3)	Ir–S(1)–N(2)	104.9(7)
P(1)–Ir–P(3)	95.7(3)	N(1)–S(2)–N(2)	117.1(11)
P(1)–Ir–P(4)	96.0(3)	Ir–N(1)–S(2)	117.3(11)
P(1)–Ir–S(1)	172.6(3)	S(1)–N(2)–S(2)	115.9(11)
P(1)–Ir–N(1)	91.4(5)	S(1)–N(2)–W	117.6(10)
P(2)–Ir–P(3)	102.0(3)	S(2)–N(2)–W	126.6(11)
P(2)–Ir–P(4)	174.5(3)	Ir–P(1)–C(1)	107.5(9)
P(2)–Ir–S(1)	89.3(3)	Ir–P(1)–C(1,1)	121.2(6)
P(2)–Ir–N(1)	85.1(5)	Ir–P(1)–C(1,2)	117.3(6)
P(3)–Ir–P(4)	83.5(3)	C(1)–P(1)–C(1,1)	97.6(10)
P(3)–Ir–S(1)	88.9(3)	C(1)–P(1)–C(1,2)	104.3(10)
P(3)–Ir–N(1)	170.4(5)	C(1,1)–P(1)–C(1,2)	105.9(8)
P(4)–Ir–S(1)	90.3(3)	Ir–P(2)–C(2)	106.1(8)
P(4)–Ir–N(1)	89.4(5)	Ir–P(2)–C(1,3)	116.7(6)
S(1)–Ir–N(1)	84.7(5)	Ir–P(2)–C(1,4)	122.1(6)
N(2)–W–C(5)	94.8(10)	C(2)–P(2)–C(1,3)	100.4(10)
N(2)–W–C(6)	95.4(10)	C(2)–P(2)–C(1,4)	107.8(10)
N(2)–W–C(7)	176.1(10)	C(1,3)–P(2)–C(1,4)	101.4(8)
N(2)–W–C(8)	86.6(11)	Ir–P(3)–C(3)	109.1(8)
N(2)–W–C(9)	89.9(11)	Ir–P(3)–C(1,5)	124.2(6)
C(5)–W–C(6)	83.7(13)	Ir–P(3)–C(1,6)	115.7(6)
C(5)–W–C(7)	88.6(13)	C(3)–P(3)–C(1,5)	105.5(10)
C(5)–W–C(8)	178.1(14)	C(3)–P(3)–C(1,6)	99.6(10)
C(5)–W–C(9)	89.6(13)	C(1,5)–P(3)–C(1,6)	99.6(8)
C(6)–W–C(7)	86.8(12)	Ir–P(4)–C(4)	107.9(9)
C(6)–W–C(8)	97.3(13)	Ir–P(4)–C(1,7)	119.2(6)
C(6)–W–C(9)	171.8(13)	Ir–P(4)–C(1,8)	116.9(6)
C(7)–W–C(8)	89.9(13)	C(4)–P(4)–C(1,7)	104.9(10)
C(7)–W–C(9)	88.3(13)	C(4)–P(4)–C(1,8)	103.3(10)
C(8)–W–C(9)	89.2(14)	C(1,7)–P(4)–C(1,8)	102.9(8)

parameters were obtained from a three-dimensional Patterson map. All the non-hydrogen atoms were located from successive Fourier syntheses. A ΔF Fourier map, calculated at this stage, revealed the presence of a methylene chloride solvent molecule, lying on a twofold axis. The refinement was carried out by using full-matrix least-squares techniques anisotropic thermal parameters being attributed to tungsten, iridium, phosphorus, sulfur and nitrogen atoms. During the refinement the phenyl rings were treated as rigid bodies of D_{6h} symmetry and the hydrogen atoms, introduced into their calculated positions, were not refined. At convergence the R and R_w factors were 0.054 and 0.048, respectively. Final positional parameters are reported in Table 4 and bond distances and angles in Table 5. Lists of thermal parameters and structure factors for this compound and compound **1** are available from the authors.

Results and discussion

Tetrasulfur tetranitride in a THF or benzene solution, reacts with solutions of iridium(I) complexes $[(\text{diphos})_2\text{Ir(CO)}](\text{BPh}_4)$ (diphos = dppm, dppen), at 50 °C to give the iridium(III) derivatives $[(\text{diphos})_2\text{Ir}(\text{S}_2\text{N}_2)](\text{BPh}_4)$ in yields of up to 70% *.

$$2[(\text{diphos})_2\text{Ir(CO)}]^+ + \text{S}_4\text{N}_4 \rightarrow 2[(\text{diphos})_2\text{Ir}(\text{S}_2\text{N}_2)]^+ + 2\text{CO}$$

(**1**, diphos = dppen;
2, diphos = dppm)

The complexes are air stable in the solid state and in solution. Compound **1** is moderately soluble in CH_2Cl_2 in which it behaves as a 1/1 electrolyte. The dppm derivative is practically insoluble. The IR spectra of **1** and **2** (Nujol mulls) are complicated by the presence of numerous absorptions due to the diphosphine ligands and the BPh_4^- anion. However the bands at 1075 (1065) and 660 (660) cm^{-1} may be attributed to ν(NS) vibrations (the values in parentheses refer to compound **2**) [19].

The molecular structure of **1** consists of $[(\text{dppen})_2\text{Ir}(\text{S}_2\text{N}_2)]^+$ cations and BPh_4^- anions with acetone molecules interspersed in the lattice. The metal atom is coordinated by the four phosphorus atoms, of the two dppen ligands, and by a sulfur and a nitrogen of the N_2S_2 group, in a slightly distorted octahedral geometry. Figure 1 shows a perspective view of the complex cation **1**.

In order to examine the nucleophilic properties of the N_2S_2 chain in these complexes, compound **1** was treated with tungsten hexacarbonyl. The substitution derivative $\{[\text{dppen})_2\text{Ir}(\text{S}_2\text{N}_2)][\text{W(CO)}_5]\}(\text{BPh}_4)\cdot 0.5\text{CH}_2\text{Cl}_2$ (**3**) was readily isolated with the formation of the cation proceeding as follows:

$$[(\text{dppen})_2\text{Ir}(\text{S}_2\text{N}_2)]^+ + \text{W(CO)}_6 \xrightarrow[\text{CH}_2\text{Cl}_2]{h\nu} \{[(\text{dppen})_2\text{Ir}(\text{S}_2\text{N}_2)][\text{W(CO)}_5]\}^+ \qquad (2)$$

Even when a large excess of $W(CO)_6$ was used, only complex **3** was isolated. This complex is air stable and moderately soluble in CH_2Cl_2, in which it behaves as a

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* Analogous procedures with the complexes $[(\text{diphos})_2\text{Ir(CO)}]^+$, diphos ≠ dppen, dppm, led only to the recovery of the starting materials.

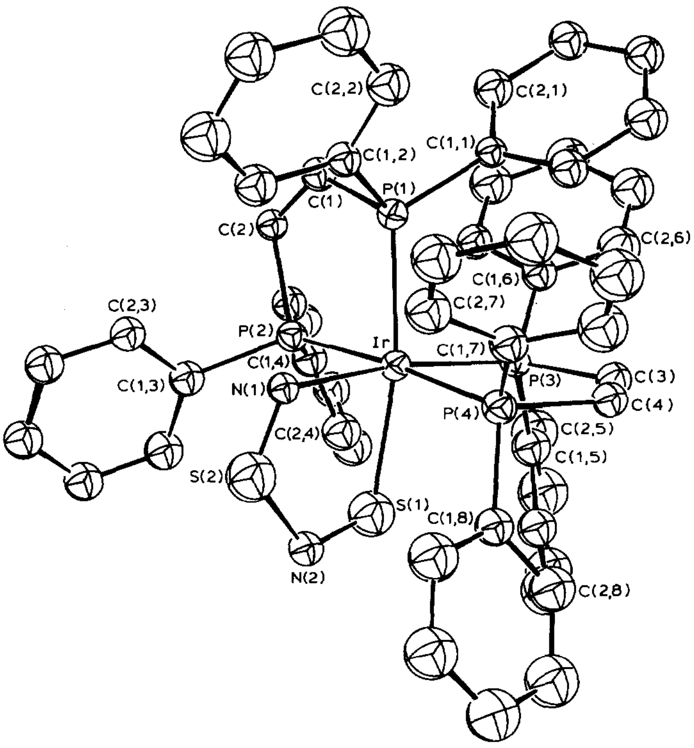

Fig. 1. Perspective view of the complex cation $[(\text{dppen})_2\text{Ir}(S_2N_2)]^+$. ORPEP drawing with 30% probability ellipsoids.

1/1 electrolyte. The IR spectrum of 3 (CH_2Cl_2 solution) shows bands in the CO stretching region at 2065w, 1930s, 1885m cm^{-1}, characteristic of a $M(CO)_5$ group.

The molecular structure of 3 consists of $\{(\text{dppen})_2\text{Ir}(S_2N_2)[W(CO)_5]\}^+$ cations and BPh_4^- anions, with methylene chloride solvent molecules interspersed in the lattice. Figure 2 shows a perspective view of the complex cation, and selected bond distances and angles are given in Table 5.

The coordination geometry around the metal atom closely resembles that in the mononuclear complex **1**. The iridium atom has a distorted octahedral geometry, being surrounded by the four phosphorus atoms of the two dppen ligands and by one sulfur and one nitrogen atom from the S_2N_2 group. The S_2N_2 chain, which chelates the metal to form a heterocyclic five-membered ring, is bonded through the nitrogen not coordinated to the metal, the tungsten atom of the $W(CO)_5$ fragment. The distortion from the limit octahedral geometry, evident from the axial angles, whose values 170.4(5), 172.6(3) and 174.5(3)°, seem to arise mainly from the steric requirements of the chelating rings.

The Ir–P bond distances, which range from 2.342(8) to 2.384(7) Å, are comparable with the corresponding values in the mononuclear compound **1** (range 2.347(5)–2.370(5) Å). As in **1**, the shorter Ir–P bond distances are those *trans* to the sulfur and nitrogen atoms of the S_2N_2 grouping. The Ir–N (2.14(2) Å) and Ir–S (2.383(7) Å) distances are significantly larger than the sum of their covalent radii

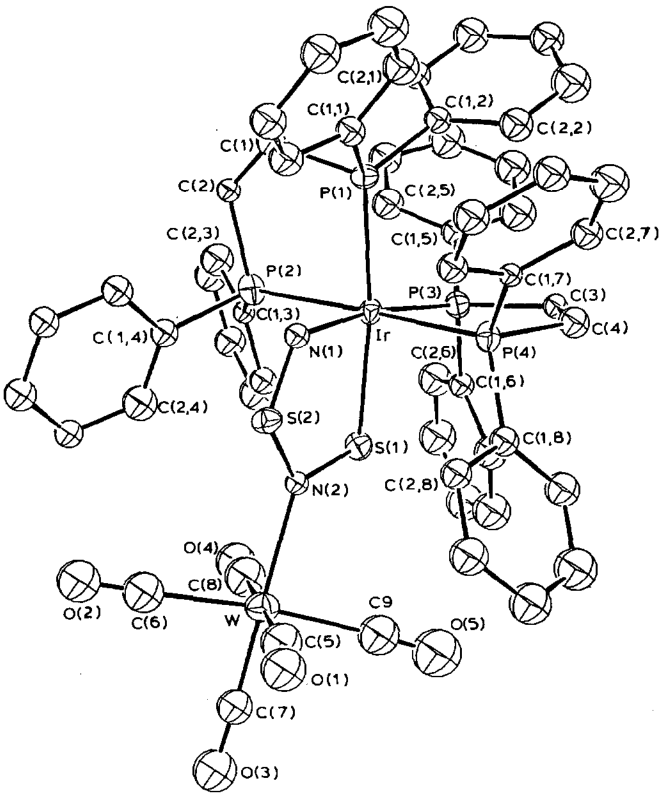

Fig. 2. Perspective view of the complex cation $\{(\text{dppen})_2\text{Ir}(S_2N_2)[\text{W(CO)}_5]\}^+$. ORTEP drawing with 30% probability ellipsoids.

(2.02 and 2.29 Å, respectively). Comparison with the bond lengths and angles involving the iridium center in the mononuclear compound **1**, could be made, comparison of the values within the S_2N_2 chain however is precluded by the marked disorder in the crystal of **1**. However the S_2N_2 electron distribution generally found in MS_2N_2 heterocycles (one longer and two shorter NS bonds) [4d, 17–19], may be assumed to apply in **3** also, account being taken of a probable lengthening of the bonds adjacent to the nitrogen atom attached to the $W(CO)_5$ residue. Changes in bond angles are not apparent; the values of the angles within the S_2N_2 group seem to be in good agreement with those noted in previous studies, and in particular are consistent with the values reported for the mononuclear compound $Pt(S_2N_2)(PPh_3)_2$ [19]. The $Ir-S_2N_2$ cycle is effectively planar, the largest deviation from the mean plane being 0.027 Å.

Within the $W(CO)_5$ grouping a considerable *trans* effect is evident: while the average of the lengths of the W–C bonds *cis* to the nitrogen atom is 2.06 Å (very close to the sum of covalent radii), that of the W–C bond *trans* to the nitrogen atom is significantly shortened; to 1.83(3) Å. In addition, the W–N bond, 2.20(2) Å, is significantly larger than the sum of covalent radii (2.02 Å). The CO group thus seems to compete with the nitrogen atom forming a partial multiple W–C bond.

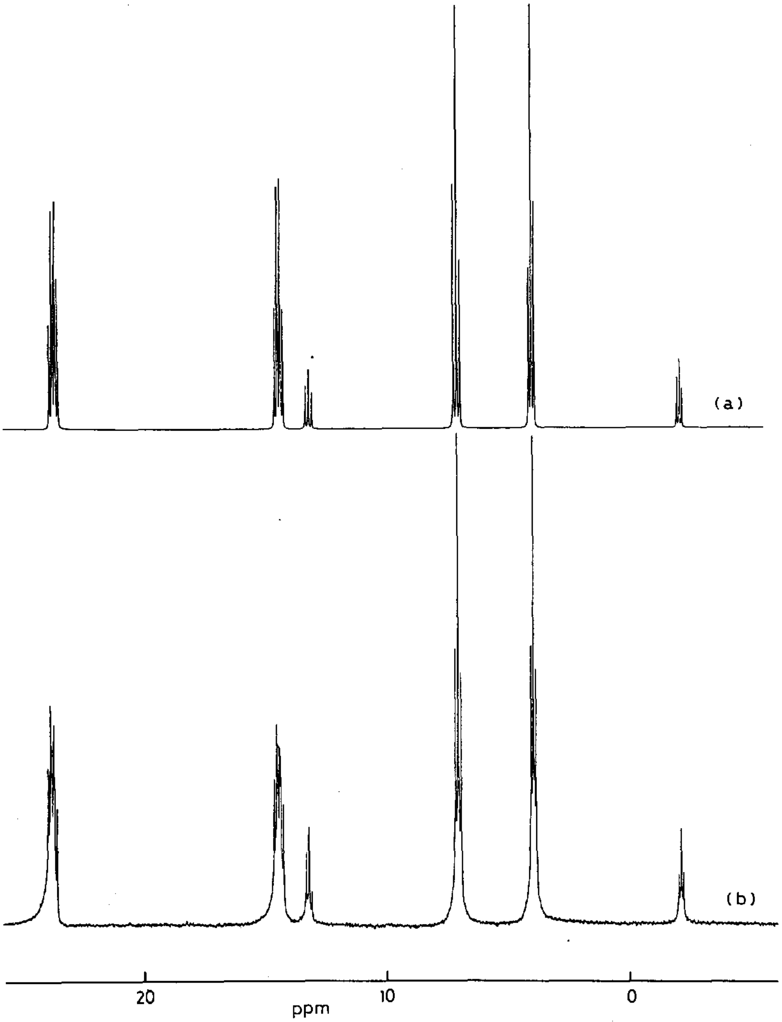

Fig. 3. 81.01 MHz $^{31}P\{^1H\}$ NMR spectra of complex **1** in CD_2Cl_2 at room temperature. (a) Simulated spectrum (PANIC Program). (b) Experimental spectrum.

The values of both *cis* and *trans* bond lengths agree well with those for W–C linkages reported previously [20].

The $^{31}P\{^1H\}$ NMR spectra of **1** and **3** have been recorded at room temperature in CD_2Cl_2 solution. The two spectra show a similar pattern and have been analyzed by computer simulation (program PANIC) (Fig. 3), to give the parameters listed in Table 6. The four phosphorus atoms act as an ABXR system, with strong coupling between A/B (*trans*-atoms) and weak couplings between X/R, A/X, A/R, B/X and B/R (*cis*-atoms). This finding is consistent with the results of the X-ray studies, showing that the complexes have a static structure in solution at room temperature.

It is of interest to make a comparison with the ^{31}P NMR spectra of the related complexes $[(diphos)_2IrHCl]^+$ [9] (diphos = dppm, bis(diphenylphosphino)methane;

TABLE 6

$^{31}P\{^1H\}$ NMR PARAMETERS OF THE COMPLEXES IN CD_2Cl_2 AT ROOM TEMPERATURE [a].

Complexes	δ_A	δ_B	δ_R	δ_X	$^2J(P_A-P_B)$	$^2J(P_A-P_R)$	$^2J(P_A-P_X)$	$^2J(P_B-P_R)$	$^2J(P_B-P_X)$	$^2J(P_R-P_X)$
$[(dppen)_2Ir(S_2N_2)]BPh_4$	2.0	8.9	14.4	23.7	496.9	8.0	7.7	11.1	11.7	9.0
$\{(dppen)_2Ir(S_2N_2)[W(CO)_5]\}BPh_4$	4.3	13.4	13.2	21.9	496.9	6.1	8.5	6.5	5.2	14.6

[a] Chemical shifts in ppm.

dppe, bis(diphenylphosphino)ethane; dppp, bis(diphenylphosphino)propane), which have been shown to have a non-rigid structure even at liquid nitrogen temperature. The presence of the metal-sulfur-nitrogen heterocyclic ring in compounds **1** and **3** probably prevents axial-equatorial phosphorus permutation.

The linkage of the $W(CO)_5$ group to the nitrogen atom (b) of the N(a)–S–N(b)–S–Ir ring does not much affect the two bond phosphorus-phosphorus coupling constants, since the geometric arrangement of the two diphosphine ligands remains practically unchanged. However the withdrawal of electronic density from the N–S–N–S–Ir ring to the $W(CO)_5$ fragment results in some changes in the ^{31}P chemical shifts, the $\delta(P)$ of the apical and equatorial phosphorus atoms being significantly shifted to lower and higher fields, respectively.

On the basis of the available data we cannot assign individual phosphorus resonances. In the case of the equatorial phosphorus atoms it may be possible to attribute the resonance at higher fields to the phosporus atom *trans* to nitrogen as for the ^{31}P NMR spectrum of the $Pt(S_2N_2)(PPh_3)_2$ complex [19].

These results, together with those previously reported, show that the S_4N_4 reactions with low-oxidation state platinum metal complexes give rise to a metal-dinitrogen-disulfur heterocycle. The formation mechanism is not clear, but the stoichiometry suggested in Scheme 1 seems reasonable when account is taken of the fact that use of larger quantities of S_2N_2 does not improve the yield. Since the obtained complexes appear to result from an oxidative addition ($Ir^I \rightarrow Ir^{III}$); $S_2N_2 \rightarrow S_2N_2^{2-}$), the following route can be suggested: a) attack of S_4N_4 on the unsaturated metal center; b) cleavage of S_4N_4; and c) oxidative addition of S_2N_2 to the metal.

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