Preparation, Structure and Reactivity of Dinuclear Aminothiolate-bridged Iridium Complexes *

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Addition of the aminothiolate $HS(CH_2)_3NMe_2$ and potassium *tert*-butoxide to $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ (cod = cycloocta-1,5-diene) afforded the aminothiolate-bridged complex $[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](cod)\}_2]$ **1**. This reacted with carbon monoxide to give the dinuclear tetracarbonyl complex $[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](CO)_2\}_2]$ **2**. The reaction of **1** with CO and phosphines or of **2** with phosphines provided the mixed-ligand complexes *trans*-$[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](CO)(PR_3)\}_2]$ ($R = C_6H_{11}$ **3**, *o*-MeC_6H_4 **4** or *p*-FC_6H_4 **5**). When the bulky phosphite $P(OC_6H_4Bu^t\text{-}o)_3$ was used as phosphorus ligand the orthometallated complex *trans*-$[\{Ir[\mu\text{-}S(CH_2)_3NMe_2]H(CO)[P(OC_6H_3Bu^t\text{-}o)(OC_6H_4Bu^t\text{-}o)_2]\}_2]$ **6** was obtained. The crystal structures of **1** and **6**, have been determined by X-ray diffraction methods.

Different types of polynuclear complexes containing N,S ligands have been recently studied.[1-4] Thus, trinuclear $Ir^{III}Co^{III}Ir^{III}$ complexes with 2-aminoethanethiolate (aet) or L-cysteinate have been described and the crystal structure of $\Delta\Lambda$-$[Co\{Ir(aet)_3\}_2]NO_3$ has been determined and shown to be a S-bridged linear complex.[1c] Nickel and platinum complexes with 3-aminoalkanethiolate bridges such as $[\{Ni[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2][BPh_4]_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$), $Na[(PtMe_3)_2\{\mu\text{-}SCH(CH_2CH_2)_2NMe\}_3]$ and $[(PtMe_3)_2\{\mu\text{-}S(CH_2)_3NHMe_2\}_3][BPh_4]_2$ have been structurally characterized.[2a,b] The synthesis and crystal structure of $[(PtMe_3)_3\{\mu\text{-}S(CH_2)_2NHEt_2\}_2(\mu\text{-}I)_2]I$ consisting of a Pt_3 cluster with an incomplete cubane structure has also been reported.[2c]

Other dinuclear rhodium and iridium complexes containing different types of nitrogen–sulfur ligands such as pyridine-2-thiolate[3] ($SC_5H_4N^-$) and benzothiazole-2-thiolate[4] ($C_7H_4NS_2^-$) possess bridging ligand through the nitrogen and sulfur atoms. These complexes react with compounds of Group 11 metals to give heterotrinuclear complexes, which in some cases have been studied by X-ray diffraction methods.[3,4]

We have recently reported the preparation and characterization of $[\{Rh[\mu\text{-}S(CH_2)_3NMe_2](cod)\}_2]$ (cod = cycloocta-1,5-diene).[5] and its structure has been established by X-ray crystallography.[5b] The reactivity of this complex towards carbon monoxide affords the dinuclear tetracarbonyl $[\{Rh[\mu\text{-}S(CH_2)_3NMe_2](CO)_2\}_2]$ which was isolated and characterized. This complex reacts with PR_3 ligands providing the corresponding mixed-ligand *trans* complexes as evidenced by NMR and IR spectroscopy; however, only that with $P(C_6H_4Me\text{-}o)_3$ was isolated.[5b]

The $[\{Rh[\mu\text{-}S(CH_2)_3NMe_2](cod)\}_2]$ complex in conjunction with PR_3 has been shown to be an efficient catalytic precursor system in the hydroformylation of alkenes.[5-7] A systematic study of the regioselective hydroformylation of dihydrofurans and dihydropyrans has shown the crucial influence of the nature of the phosphorus cocatalyst.[5b] The use of bulky phosphites such as $P(OC_6H_4Bu^t\text{-}o)_3$ gives rise to highly active catalytic systems and the regioselectivity of the reaction can be controlled by the auxiliary ligand [PPh_3 or $P(OC_6H_4Bu^t\text{-}o)_3$] used.

Following our studies of aminothiolate bridging complexes and in order to compare the reactivities and catalytic activities of rhodium and iridium complexes, we have undertaken the preparation and characterization of the dinuclear complex $[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](cod)\}_2]$ **1**. Related thiolate-bridged dinuclear d^8 iridium(I) complexes $[\{Ir(\mu\text{-}SR)(cod)\}_2]$, $[\{Ir(\mu\text{-}SR)(CO)_2\}_2]$ ($R = Bu$[8,9] or Ph[9,10]) and $[\{Ir(\mu\text{-}SBu^t)(CO)(PR'_3)\}_2]$[11] [$R'_3$ = Me_3, Me_2Ph, $(NMe_2)_3$, Ph_3 or $(OMe)_3$] have been described. The molecular structures of $[\{Ir(\mu\text{-}SPh)(cod)\}_2]$,[10] $[\{Ir(\mu\text{-}SPh)(CO)_2\}_2]$[12] and $[\{Ir(\mu\text{-}SBu^t)(CO)[P(OMe)_3]\}_2]$[13] have also been determined.

Catalytic experiments using the $[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](cod)\}_2]$–$PR_3$ as catalyst precursor in the hydroformylation of hex-1-ene and styrene have shown, as expected,[14] much lower activities than in the case of the related rhodium complexes. In contrast to the result obtained with the rhodium complex, when $P(OC_6H_4Bu^t\text{-}o)_3$ was used as auxiliary ligand, no activity at all was observed. In order to obtain more information about this system we have studied the reactivity of **1** towards CO and PR_3.

Results and Discussion

Preparation and Characterization of the $[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](cod)\}_2]$ *Complex*.—The dinuclear complex $[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](cod)\}_2]$ **1** has been prepared by reaction of a solution of $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ in dichloromethane with a stoichiometric amount of 3-dimethylaminopropanethiol $HS(CH_2)_3NMe_2$, and potassium *tert*-butoxide in methanol (Scheme 1). The compound was isolated as a red air-stable crystalline solid.

A view of the molecule with the atom labelling scheme is shown in Fig. 1. Table 1 shows the atomic coordinates and Table 2 the most significant intramolecular distances and bond angles with their standard deviations.

The crystal structure consists of discrete dinuclear units separated by van der Waals contacts. The co-ordination about

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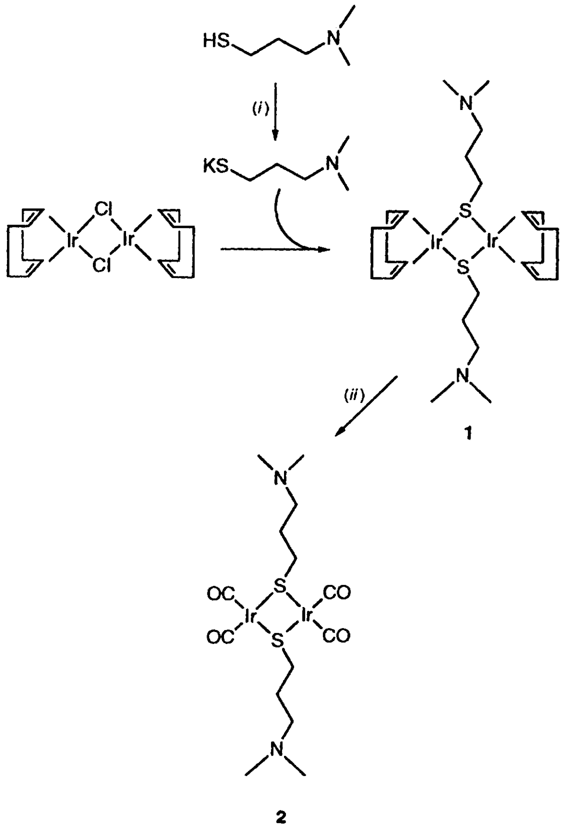
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Atomic coordinates (× 10^4) for $[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](cod)\}_2]$ **1**

Atom	*x*	*y*	*z*
Ir(1)	1 303(0)	5 381(0)	1 353(0)
Ir(2)	1 168(0)	7 750(0)	1 030(0)
S(1)	584(1)	6 232(2)	605(1)
S(2)	1 875(1)	6 471(3)	776(2)
C(17)	− 197(5)	6 114(12)	702(6)
C(18)	− 591(6)	6 780(16)	200(7)
C(22)	2 661(6)	6 701(15)	1 103(10)
C(23)	3 064(7)	6 149(20)	727(13)
C(1)	1 744(8)	8 597(14)	1 717(8)
C(2)	1 743(7)	9 164(13)	1 115(11)
C(3)	1 404(12)	10 241(17)	905(14)
C(4)	752(9)	10 130(14)	802(16)
C(5)	491(7)	8 998(13)	915(11)
C(6)	519(7)	8 520(16)	1 485(9)
C(7)	785(7)	8 984(23)	2 127(10)
C(8)	1 421(11)	9 051(22)	2 246(12)
C(9)	1 951(6)	5 188(14)	2 171(7)
C(10)	2 010(8)	4 238(15)	1 765(9)
C(11)	1 761(9)	3 117(12)	1 824(11)
C(12)	1 130(9)	3 029(15)	1 826(14)
C(13)	763(7)	4 072(13)	1 617(8)
C(14)	691(6)	5 016(14)	1 988(7)
C(15)	990(10)	5 091(22)	2 663(9)
C(16)	1 707(10)	5 077(27)	2 770(10)
N(1)	− 1 480(6)	6 674(14)	759(7)
N(2)	3 968(7)	6 988(15)	1 361(8)
C(24)	3 761(12)	6 179(31)	1 099(22)
C(25)	4 511(13)	6 833(28)	1 818(16)
C(26)	4 139(23)	7 573(40)	924(20)
C(19)	− 1 234(8)	6 539(22)	185(11)
C(20)	− 2 060(10)	6 266(32)	697(16)
C(21)	− 1 491(20)	7 811(37)	943(19)



Scheme 1 (*i*) $KOBu^t$; (*ii*) CO

Table 2 Selected distances (Å) and angles (°) for $[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](cod)\}_2]$ **1**

Ir(1) • • • Ir(2)	2.946(1)	Ir(2)–C(1)	2.091(12)
Ir(1)–S(1)	2.332(3)	Ir(2)–C(2)	2.172(12)
Ir(1)–S(2)	2.339(4)	Ir(2)–C(5)	2.162(13)
Ir(2)–S(1)	2.346(3)	Ir(2)–C(6)	2.119(12)
Ir(2)–S(2)	2.341(3)	C(5)–C(6)	1.406(12)
Ir(1)–C(9)	2.137(12)	C(1)–C(2)	1.421(12)
Ir(1)–C(10)	2.147(12)	C(9)–C(10)	1.413(11)
Ir(1)–C(13)	2.123(13)	C(13)–C(14)	1.414(11)
Ir(1)–C(14)	2.136(12)		
Ir(1)–S(1)–Ir(2)	78.0(1)	S(2)–Ir(2)–C(1)	99.0(4)
Ir(1)–S(2)–Ir(2)	78.1(1)	S(2)–Ir(2)–C(2)	96.7(4)
S(1)–Ir(1)–S(2)	76.1(1)	S(2)–Ir(2)–C(5)	158.8(4)
S(1)–Ir(2)–S(2)	75.6(1)	S(2)–Ir(2)–C(6)	161.8(4)
Ir(1)–S(1)–C(17)	117.4(4)	S(1)–Ir(2)–C(1)	158.4(5)
Ir(2)–S(1)–C(17)	120.0(4)	S(1)–Ir(2)–C(2)	160.9(4)
Ir(2)–S(2)–C(22)	117.56(6)	S(1)–Ir(2)–C(6)	98.8(4)
S(1)–Ir(1)–C(9)	159.6(3)	S(2)–Ir(1)–C(9)	98.8(4)
S(1)–Ir(1)–C(10)	160.4(4)	S(2)–Ir(1)–C(10)	97.2(4)
S(1)–Ir(1)–C(13)	98.4(3)	S(2)–Ir(1)–C(13)	161.6(4)
S(1)–Ir(1)–C(14)	95.6(3)	S(2)–Ir(1)–C(14)	157.6(3)

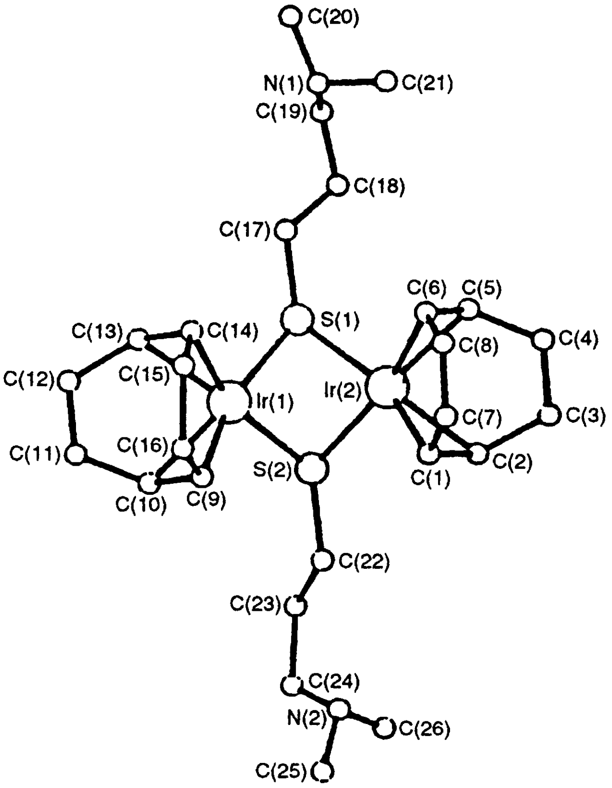


Fig. 1 Molecular structure of the precursor catalyst complex $[\{Ir[\mu\text{-}S(CH_2)_3NMe_2]cod)\}_2]$ **1**

each iridium atom is approximately square planar. Two bridging sulfur atoms and a chelating cyclooctadiene are bonded to each metal atom, and none of the amine groups is involved in the co-ordination. The Ir_2S_2 ring is highly puckered. The dihedral angle between the co-ordination planes is 105.9(1)°. The aminothiolato bridging groups are in a *syn-endo* configuration with respect to the four-membered Ir_2S_2 core.

The intramolecular Ir • • • Ir distance is 2.946(1) Å, slightly shorter than the Rh • • • Rh distance in the case of the dinuclear rhodium complex $[\{Rh[\mu\text{-}S(CH_2)_3NMe_2](cod)\}_2]$, average 2.960(1) Å, despite the fact that the covalent radius of iridium is larger than that of rhodium. This distance is also shorter than in the related $[\{Ir(\mu\text{-}SPh)(cod)\}_2]$ Ir···Ir 3.181(1) Å,[10] $[\{Ir(\mu\text{-}SPh)(CO)_2\}_2]$, Ir···Ir 3.10(1) Å,[12] and $[\{Ir(\mu\text{-}SBu^t)(CO)\{P(OMe)_3\}]_2$,[13] Ir···Ir 3.216(2) Å. However, it is larger than that found in the closely related dinuclear iridium thiolate complex $[Ir_2(\mu\text{-}pz)(\mu\text{-}SBu^t)(\mu\text{-}MeO_2CC{=}CCO_2Me)(CO)_2\{P(OMe)_3\}_2]$, average 2.614(2) Å, where a clear Ir–Ir bond is present.[15] In the same way, the distance of 2.673(1) Å between the two iridium atoms in the dinuclear iridium(II) complex $[\{IrH(\mu\text{-}SBu^t)(CO)[P(OMe)_3]\}_2]$, has been attributed to the presence of a normal two-electron Ir–Ir single bond.[13]

The average Ir–S bond length of complex **1**, at 2.340 Å, is very similar to that in the related complex $[\{Ir(\mu\text{-}SPh)(cod)\}_2]$[10] of 2.345(7) Å, and slightly shorter than the 2.370(1) Å in $[\{Ir(\mu\text{-}SPh)(CO)_2\}_2]$.[12] These distances are also slightly shorter than those found in the related dinuclear iridium(I) complex $[\{Ir(\mu\text{-}SBu^t)(CO)[P(OMe)_3]\}_2]$[13] [average 2.385(9) Å]. The Ir–C distances (2.09–2.17 Å) are in the range reported for other iridium complexes containing cod ligands *trans* to S-donor atoms.[10]

The ^{1}H NMR spectrum shows one broad signal corresponding to the olefinic protons of the co-ordinated cycloocta-1,5-diene at δ 3.95 (m) and two at 2.20 (m) and 1.80 (m), attributed to its methylenic protons. The presence of only one type of olefinic protons indicates that the complex is not rigid in solution. A plausible mechanism accounting for the simplicity of the spectrum involves inversion of the butterfly-shaped core.[10] The ^{13}C-{^{1}H} NMR spectrum shows one signal for the olefinic carbons (δ 63.8) and one for the methylenic carbons (δ 32.1) of the co-ordinated cycloocta-1,5-diene. The aminothiolate ligand shows signals at δ 58.7 (CH_2N), 45.4 (Me_2N), 30.1 (CH_2) and 20.3 (CH_2S). The ^{1}H NMR resonances corresponding to the aminothiolate ligand appear at δ 2.57 (SCH_2), 2.33 (NCH_2), 2.18 (NMe_2) and 1.77 (CH_2), slightly downfield shifted with regard to the signals of the free thiolate. The assignment of ligand signals in the ^{1}H NMR spectrum has been carried out with the help of an heteronuclear correlation (HETCOR) experiment.

Preparation and Characterization of the $[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](CO)_2\}_2]$ *Complex*.—The $[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](cod)\}_2]$ complex reacts in CH_2Cl_2 solvent with CO at normal pressure to give dinuclear $[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](CO)_2\}_2]$ **2**, which has been isolated and spectroscopically characterized (Scheme 1). The infrared spectrum in dichloroethane solution shows, in the carbonyl region, three ν(CO) frequencies, 2067m, 2044s and 1993s cm^{-1}, corresponding to the pattern for a dinuclear folded tetracarbonyl.[12,13] These are lower than in the case of the corresponding rhodium tetracarbonyl $[\{Rh[\mu\text{-}S(CH_2)_3NMe_2](CO)_2\}_2]$.[5]

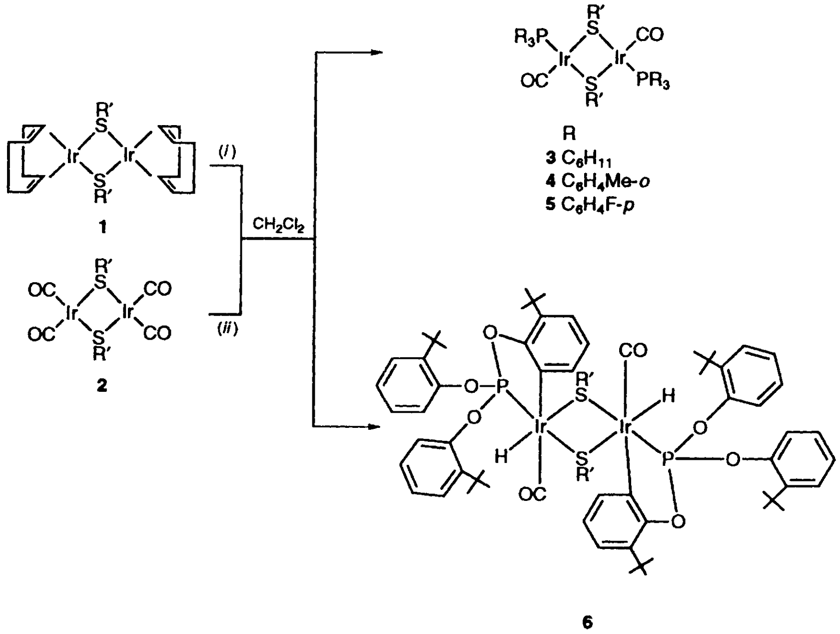
The dark blue colour of the solid is probably due to the existence of solid interactions as has previously been observed for related iridium complexes.[12]

The ^{1}H and ^{13}C NMR spectra of this complex show the presence of the aminothiolate ligand.

Reactivity of $[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](CO)_2\}_2]$ *towards Phosphorus Ligands. Preparation and Characterization of trans*-$[\{\overline{Ir[\mu\text{-}S(CH_2)_3NMe_2]H(CO)[P(OC}_6H_3Bu^t\text{-}o)(OC_6H_4Bu^t\text{-}o)_2]\}_2]$.—The reaction of complex **1** with CO and phosphines and the reaction of the tetracarbonyl **2** with phosphine ligands has been studied. In the case of PR_3 the infrared spectra of the dichloromethane solutions show the presence of a unique ν(CO) frequency (in CH_2Cl_2) according to the formation of the complexes *trans*-$[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](CO)(PR_3)\}_2]$[12] (R = C_6H_{11} **3**, 1942, *o*-MeC_6H_4 **4**, 2025; *p*-FC_6H_4 **5** 7035.5 cm^{-1}) (Scheme 2).

As in the case of the related rhodium complexes, mixed carbonyl–phosphorus complexes are very soluble in most common solvents and difficult to isolate. Thus, they have only been generated in solution, and investigated by infrared and NMR spectroscopy. The ^{31}P-{^{1}H} NMR spectra in $CDCl_3$ show signals at δ 30.7, 37.45 and 27.3, for **3**–**5** respectively, together with minor amounts of free phosphine.

Significantly, when the bulky phosphite $P(OC_6H_4Bu^t\text{-}o)_3$ was used as phosphorus ligand a white air-stable crystalline solid was precipitated. The crystal structure (Fig. 2) shows that the orthometallated iridium(III) complex *trans*-$[\{\overline{Ir[\mu\text{-}S(CH_2)_3NMe_2]H(CO)[P(OC}_6H_3Bu^t\text{-}o)(O\text{-}C_6H_4Bu^t\text{-}o)_2]\}_2]$ **6**, has been obtained (Scheme 2). Orthometallated iridium(III) complexes with phosphite ligands are common[16–18] although diorthometallated dinuclear iridium(III) complexes have not been described. The rapid formation of an intramolecular metal–carbon bond must be due to the bulky phosphite ligand used[19] and to the high electron density of the



Scheme 2 R' = $(CH_2)_3NMe_2$. (*i*) CO, PR_3; (*ii*) PR_3

Table 3 Atomic coordinates (× 10^4) for *trans*-$[\{\overline{\mathrm{Ir}[\mu\text{-}\mathrm{S(CH_2)_3NMe_2]H(CO)[P(OC}}\mathrm{_6H_3Bu^t}\text{-}o)(\mathrm{OC_6H_4Bu^t}\text{-}o)_2]\}_2]$ **6**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ir(1)	991(0)	886(0)	41(0)	O(40)	2637(3)	−919(5)	455(2)
S(1)	−495(1)	1380(2)	−158(1)	C(40)	3456(5)	−1368(8)	648(3)
C(1)	1135(5)	1349(10)	873(4)	C(41)	3666(5)	−1931(8)	1224(4)
O(1)	1258(4)	1700(8)	200(7)	C(42)	4501(6)	−2325(9)	1402(4)
C(17)	−744(6)	2382(8)	445(4)	C(43)	5073(6)	−2220(10)	1023(5)
C(18)	−504(7)	3818(9)	361(5)	C(44)	5817(6)	−1712(10)	447(5)
C(19)	−761(7)	4717(11)	834(6)	C(45)	4017(5)	−1290(9)	259(4)
N(1)	−241(7)	4476(18)	1443(5)	C(46)	3030(6)	−2128(11)	1627(4)
C(20)	579(10)	5061(18)	1486(8)	C(47)	2324(8)	−3060(15)	1285(6)
C(21)	−633(13)	5066(23)	1905(9)	C(48)	2691(10)	−764(15)	1791(6)
P(1)	2295(1)	325(2)	54(0)	C(49)	3433(8)	−2826(15)	2219(5)
O(30)	2352(3)	−97(5)	−615(2)	O(50)	3170(5)	2560(7)	64(3)
C(30)	1615(4)	71(7)	−1061(3)	C(51)	3730(5)	3379(9)	477(4)
C(31)	1663(5)	−298(9)	−165(3)	C(52)	3880(7)	4613(10)	250(5)
C(32)	913(6)	−115(11)	−2072(4)	C(53)	3523(8)	−5024(10)	−318(5)
C(33)	207(6)	409(13)	−1921(4)	C(54)	2992(6)	4186(10)	−710(5)
C(34)	202(5)	749(9)	−1328(3)	C(55)	2824(5)	2920(9)	−513(4)
C(35)	914(4)	570(8)	−877(3)	C(56)	4140(6)	2962(10)	1117(4)
C(36)	2453(6)	−887(9)	−1813(4)	C(57)	3421(7)	2779(14)	1481(5)
C(37)	2682(7)	−2182(10)	−1571(5)	C(58)	4740(9)	4058(13)	1436(5)
C(38)	3193(6)	91(10)	−1663(5)	C(59)	4659(7)	1706(11)	1139(5)
C(39)	2299(8)	−1187(14)	−2496(4)				

aromatic ring.[20] The structure can be described as two distorted octahedra sharing an edge and containing an inversion centre. Each iridium atom is surrounded by six atoms, four of them being in a plane, S(1), S(2), H(1), P(1) around Ir(1) and S(1), S(2), H(2), P(2) around Ir(2). The carbonyl groups and the orthometalated phenyl ring occupy the axial positions. The sulfur atoms of the thiolate bridging groups and the two iridium atoms lie in the same plane. Table 3 shows the atomic coordinates and Table 4 the most significant intramolecular distances and bond angles. The Ir(1)···Ir(2) distance is 3.673(4) Å. This is larger than in the starting iridium(I) dinuclear $[\{\mathrm{Ir}[\mu\text{-}\mathrm{S(CH_2)_3NMe_2](cod)}\}_2]$ and related dinuclear iridium complexes.[21–24]

The average Ir–S bond length is 2.448 Å. The Ir–P distance, 2.197(2) Å is slightly shorter than in related iridium complexes (2.20–2.30 Å).[22–24] The Ir–S–Ir angle, 97.04(6)°, and the S–Ir–S angle, 82.95(6)°, are significantly larger than in related complexes.[11–13] This fact could be due to the $\mathrm{Ir_2S_2}$ planar arrangement in this orthometallated complex.

The ^{1}H NMR spectrum shows several signals for *tert*-butyl groups (δ 1.64, 1.44 and 1.07) and an ensemble of complex signals between δ 6.5 and 8.5 for aromatic protons, consistent with the presence of different *tert*-butylphenyl groups (metallated and non-metallated) in the molecule. At δ −14.3 there is a complex hydride signal [Fig. 3 (*a*)] corresponding to a second-order spectrum, which indicates that other coupling constants, apart from $^2J_{\mathrm{HP}}$ are present. The ^{31}P NMR spectrum shows a multiplet at δ 109.1 which becomes similar to the hydride signal in the ^{1}H NMR spectrum when the aromatic protons are irradiated [Fig. 3(*b*), 3(*c*)]. This suggests that these signals correspond to an AA′XX′ spin system formed by the two hydride protons and the two phosphorus.

In conclusion, the $[\{\mathrm{Ir}(\mu\text{-}\mathrm{Cl})(\mathrm{cod})\}_2]$ complex gives rise to the dinuclear sulfur-bridged complex **1** when treated with a stoichiometric amount of $\mathrm{HS(CH_2)_3NMe_2}$. Complex **1** affords the dinuclear tetracarbonyl complex **2** when treated with CO, and mixed carbonyl-phosphorus complexes were obtained when $\mathrm{PR_3}$ (R = *o*-$\mathrm{MeC_6H_4}$ **3**, $\mathrm{C_6H_{11}}$ **4** or *p*-$\mathrm{FC_6H_4}$ **5**) was added to a solution of **2** in dichloromethane. However, in the presence of $\mathrm{P(OC_6H_4Bu^t}\text{-}o)_3$ the dinuclear iridium(III) complex **6** was obtained from **2**, as result of an orthometallation process involving one aromatic ring of the phosphorus ligand. This fact explains the inactivity of the catalytic system formed by the addition of $\mathrm{P(OC_6H_4Bu^t}\text{-}o)_3$ to **1** since no oxidative addition can take place, once **6** is formed.

Table 4 Selected distances (Å) and angles (°) for complex **6**

Ir(1)···Ir(2)	3.673(2)	S(1)–C(17)	1.813(7)
Ir(1)–S(1)	2.423(2)	C(1)–O(1)	1.129(9)
Ir(1)–S(2)	2.474(2)	N(1)–C(19)	1.485(16)
Ir(1)–C(1)	1.910(8)	N(1)–C(20)	1.448(19)
Ir(1)–P(1)	2.197(2)	N(1)–C(21)	1.465(30)
Ir(1)–C(35)	2.099(6)	C(18)–C(17)	1.534(29)
P(1)–O(30)	1.600(5)	C(18)–C(19)	1.535(26)
P(1)–O(40)	1.589(5)	O(30)–C(30)	1.420(8)
P(1)–O(50)	1.585(5)		
Ir(1)–S(1)–Ir(2)	97.04(6)	Ir(1)–C(1)–C(35)	173.56(4)
Ir(1)–S(2)–Ir(2)	97.07(1)	Ir(1)–P(1)–O(30)	107.8(2)
S(1)–Ir(1)–S(2)	82.95(6)	Ir(1)–P(1)–O(40)	115.7(2)
S(1)–Ir(2)–S(2)	82.93(1)	Ir(1)–P(1)–O(50)	123.4(2)
Ir(1)–S(1)–P(1)	169.81(4)	O(30)–P(1)–O(40)	104.45(3)
Ir(1)–S(1)–C(1)	92.75(4)	O(30)–P(1)–O(50)	105.2(3)
Ir(1)–P(1)–C(1)	97.52(3)	O(40)–P(1)–O(50)	98.3(3)
Ir(1)–S(1)–C(35)	89.73(4)	Ir(1)–S(1)–C(17)	110.2(3)
Ir(1)–P(1)–C(35)	80.25(5)		

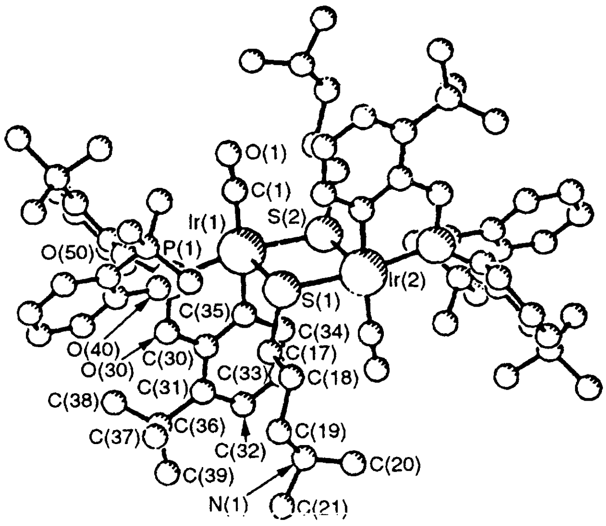


Fig. 2 Molecular structure of the dinuclear mixed complex *trans*-$[\{\overline{\mathrm{Ir}[\mu\text{-}\mathrm{S(CH_2)_3NMe_2]H(CO)[P(OC}}\mathrm{_6H_3Bu^t)(OC_6H_4Bu^t)_2]}\}_2]$ **6**

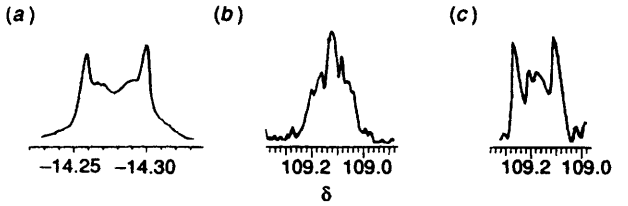


Fig. 3 (*a*) Hydride signal in the H NMR spectrum, (*b*) coupled phosphorus signal in the ^{31}P NMR spectrum and (*c*) decoupled phosphorus signal in the ^{31}P NMR spectrum of complex **6**, in $CDCl_3$

Experimental

All the reactions were carried out under a nitrogen atmosphere at room temperature using standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen immediately prior to use. The starting material $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ was prepared according to reported methods,[25] $IrCl_3 \cdot xH_2O$ and phosphorus reactants were of commercial origin and used without further purification and $P(OC_6H_4\text{-}Bu^t\text{-}o)_3$ was prepared as previously described.[26]

The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Gemini spectrometer with a ^1H resonance frequency of 300 MHz, chemical shifts being reported relative to tetramethylsilane for ^1H and 85% H_3PO_4 for ^{31}P, as external reference. Infrared spectra (range 4000–400 cm^{-1}) were recorded on a Nicolet 5ZDX-FT spectrometer in CH_2Cl_2 solutions or in KBr pellets. Elemental analyses were carried out on a Carlo Erba microanalyser. Fast atom bombardment mass spectra were obtained on a VG Autospect in a 3-nitrobenzyl alcohol matrix.

Preparations.—$[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](cod)\}_2]$ **1**. A solution of potassium *tert*-butoxide (305 mg, 2 mmol) and 3-dimethylaminopropanethiol (0.36 cm^3, 2 mmol) in methanol (6.7 cm^3) was stirred at room temperature for 5 min. This solution was added to a stirred solution of $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ (671 mg, 1 mmol) in dichloromethane (7 cm^3) at room temperature over a period of 30 min. The reaction mixture was then evaporated, and the resulting oil extracted with dichloromethane (10 cm^3) and filtered through Celite to eliminate the potassium chloride formed. The red solution obtained was concentrated to 0.5 cm^3, and acetonitrile was added until a slight cloudiness appeared. The mother-liquor was left overnight in a refrigerator, and the red crystals which had formed were filtered off. Yield (65%) (Found: C, 37.2; H, 5.75; N, 3.40; S, 8.10. Calc. for $C_{26}H_{48}Ir_2N_2S_2$: C, 37.3; H, 5.75; N, 3.35; S, 7.65%). NMR ($CDCl_3$): ^1H, δ 1.77 (q, 2 H, ^3J = 6.7), 1.80 (m, 4 H), 2.18 (s, 6 H), 2.20 (m, 4 H), 2.33 (t, 2 H, ^3J = 6.7), 2.57 (t, 2 H, ^3J = 6.7 Hz) and 3.95 (m, 4 H); ^{13}C, δ 20.3, 30.1, 32.1, 45.4, 58.7 and 63.8.

$[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](CO)\}_2]$ **2**. A stream of CO was bubbled through a solution of complex **1** (40 mg, 0.04 mmol) in methanol (5 cm^3), and a rapid change to blue-black was observed. The solution was concentrated to 0.5 cm^3, and methanol was added until the precipitation of a blue-black microcrystalline solid. Yield (46%). IR ν(CO): in KBr, 2063.4, 2041.8 and 1991.4, in CH_2Cl_2 solution, 2067, 2044, and 1993 cm^{-1} (Found: C, 22.40; H, 3.55; N, 3.80; S, 8.65. Calc. for $C_{14}H_{24}Ir_2N_2O_4S_2$: C, 22.95; H, 3.25; N, 3.80; S, 8.75%). NMR ($CDCl_3$): ^1H, δ 1.98 (q, 2 H, ^3J = 6.9 Hz), 2.20 (s, 6 H), 2.44 (t, 2 H, ^3J = 6.9), and 3.58 (t, 2 H, ^3J = 6.7 Hz); ^{13}C, δ 31.3, 34.8, 45.4, 57.7 and 174.2.

trans-$[\{Ir[\mu\text{-}S(CH_2)_3NMe_2](CO)(PR_3)\}_2]$ (R = C_6H_{11} **3**, *o*-MeC_6H_4 **4** *or* *p*-FC_6H_4 **5**). Carbon monoxide was bubbled through a solution of complex **1** (40 mg, 0.05 mmol), and PR_3 (0.1 mmol), R = C_6H_{11} (26.5 mg), *o*-MeC_6H_4 (29.1 mg) or *p*-FC_6H_4 (30.2 mg), in CH_2Cl_2. The solution was concentrated, and methanol, ethanol, hexane, diethyl ether or acetonitrile were added, but after cooling to 0° C solid products were not isolated.

trans-$[\{Ir[\mu\text{-}S(CH_2)_3NMe_2]H(CO)[P(OC_6H_3Bu^t\text{-}o)\text{-}(OC_6H_4Bu^t\text{-}o)_2]\}_2]$ **6**. Carbon monoxide was bubbled through a solution of complex **1** (40 mg, 0.047 mmol), and $P(OC_6H_4Bu^t\text{-}o)_3$ (45.5 mg, 0.1 mmol) in CH_2Cl_2. The solution was concentrated, and methanol was added, causing the formation of a yellow crystalline solid which was filtered off, washed with cold methanol, and vacuum-dried to give a white crystalline compound. Yield 76%. IR: in CH_2Cl_2 solution, 2040 [ν(CO)], 2117 cm^{-1} [ν(Ir–H)]. *M* 1633 (calc. 1632.4) (Found: C, 52.60; H, 6.35; N, 1.70; S, 3.70. Calc. for $C_{72}H_{102}Ir_2N_2O_8P_2S_2$: C, 52.95; H, 6.25; N, 1.70; S, 3.95%). NMR ($CDCl_3$): ^1H, δ −14.3 (m, 1 H), 1.07 (s, 9 H), 1.07 (s, 2 H), 1.25 (s, 2 H), 1.44 (s, 9 H), 1.64 (s, 9 H), 1.81 (s, 2 H), 1.81 (s, 6 H), and 6.5–8.5 (aromatics); ^{13}C, δ 26.67, 28.27, 29.9, 30.05, 30.60, 34.4, 34.8, 35.20, 44.90, 58.12, 120.25, 120.55, 123.56, 123.83, 124.19, 124.53, 126.97, 127.56, 127.82 and 133.68.

Crystallography.—Suitable crystals of complexes **1** and **6** were grown from a dichloromethane–acetonitrile and –methanol solution.

Crystal data. $C_{26}H_{48}Ir_2N_2S_2$ **1**, *M* = 837.18, monoclinic, space group *C*2/*c* (no. 15), *a* = 22.459(4), *b* = 12.068(4), *c* = 21.603(3) Å, β = 99.22(1)°, *U* = 5779(2) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections), *Z* = 8, D_c = 1.924 g cm^{-3}. Red, air-stable crystals. Crystal dimensions: 0.4 × 0.4 × 0.15 mm, μ(Mo-Kα) = 93.62 cm^{-1}, *F*(000) = 3232.

$C_{72}H_{102}Ir_2N_2O_8P_2S_2$ **6**, *M* = 1634.02, monoclinic, space group $P2_1n$ (no. 14), *a* = 16.305(2), *b* = 10.1624(7), *c* = 22.740(2) Å, β = 101.959(9)°, *U* = 3686.2(9) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections), *Z* = 2, D_c = 1.472 g cm^{-3}. Colourless, air-stable crystals. Crystal dimensions: 0.5 × 0.36 × 0.32 mm, μ(Mo-Kα) = 37.59 cm^{-1}, *F*(000) = 1656.

Data collection and processing. CAD4 diffractometer, ω–2θ mode with ω scan width = 0.80 + 0.35 tan θ, ω scan speed 1.3–5.5° min^{-1}, graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). For complex **1**, 5364 reflections were measured ($1 < \theta < 25°$, $+h$, $+k$, $+l$), 4965 unique (Lorentz and empirical absorption correction from ψ scans,[27] minimum and maximum transmission = 0.522, 0.998), 3428 with $I > 2\sigma(I)$. For **6**, 7109 reflections were measured, 6440 unique (minimum and maximum transmission = 0.668, 0.999), 5070 with $I > 2\sigma(I)$.

Structure analysis and refinement. Direct methods (SHELXS 86 program).[28] Full-matrix least-squares refinement on F^2 for all reflections (SHELXL 93 program).[29] For complex **1**, methyl carbons were refined isotropically. The remaining non-hydrogen atoms were refined anisotropically. Hydrogens in calculated positions with isotropic thermal parameters fixed at 1.5 times U_{eq} of the corresponding carbon atoms. Weighting scheme $w = 1/\sigma^2[(F_o^2) + (0.0855P)^2]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. Final $R(F)$ and $Rw(F^2)$ values were 0.0497 and 0.1275 for reflections with $I > 2\sigma(I)$. For **6**, all non-hydrogen atoms were refined anisotropically. Hydrogen in calculated positions with an overall refined *U*. Weighting scheme $w = 1/\sigma^2[(F_o^2) + (0.0368P)^2 + 11.3947P]$, *P* as above. Final $R(F)$ and $Rw(F^2)$ values were 0.0391 and 0.0962 for reflections with $I > 2\sigma(I)$.

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

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