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Ruthenium carbonyl complexes with polyfunctional phosphine ligands [☆]

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Abstract

Reactions of $Ru_3(CO)_{12}$ with the polyfunctional phosphines tris(2-thienyl)phosphine and tris(diethylamino)phosphine have been investigated. The reaction of the former phosphine with $Ru_3(CO)_{12}$ yields, inter alia, the complexes $Ru_3(CO)_{10}[P(C_4H_3S)_3]_2$ (**1**) and $Ru(CO)_3[P(C_4H_3S)_3]_2$ (**2**), both of which have been characterized by X-ray diffraction studies. In **1** the two polyfunctional phosphine ligands are coordinated equatorially via their phosphorus atoms to two adjacent metal atoms of the Ru_3 triangle. In **2** the phosphorus atoms of two $P(C_4H_3S)_3$ ligands occupy the axial positions of the trigonal bipyramidal coordination sphere around the ruthenium atom. The six thienyl substituents are arranged in an eclipsed conformation, with all sulphur atoms pointing preferentially towards the center of the molecule. The reaction of $Ru_3(CO)_{12}$ with an excess of $P(NEt_2)_3$ yields the disubstituted cluster $Ru_3(CO)_{10}[P(NEt_2)_3]_2$ (**3**). The IR spectrum of **3** reveals the presence of bridging carbonyl ligands, distinguishing **3** from all previously known clusters of this type.

Keywords: Ruthenium; Carbonyl; Polyfunctional phosphines; Crystal structure

1. Introduction

Substitution reactions of triruthenium dodecacarbonyl brought about by alkyl-, aryl- and alkoxy-substituted phosphines L have been well studied [1–3]. They can be carried out under mild conditions in the presence of catalysts such as sodium diphenyl ketyl [2,3]. Extensive X-ray structural investigations [4–6] of a large number of the resulting complexes $Ru_3(CO)_{12-n}L_n$ ($n = 1$–4) have given exclusive knowledge of their structural features.

In contrast, the reactions of phosphine ligands with additional donor atoms towards $Ru_3(CO)_{12}$ has been investigated in only a few cases, although these donor atoms may offer a variety of further intra- and intermolecular connectivities. For instance, from the reaction of 2-(diphenylphosphino)pyridine with $Ru_3(CO)_{12}$ the normal substitution products $Ru_3(CO)_9L_3$ [7] and $Ru_3(CO)_{11}L$ [8,9] have been obtained. The latter cluster is only metastable, and yields $Ru_3(CO)_9(\mu_2\text{-}OCPh)[\mu_3\text{-}\eta^2\text{-}PPh(C_5H_4N)]$ [8,9] which contains fragments of the ligand. A similar breaking of P–C bonds was found to dominate the reactions of trinuclear ruthenium clusters containing functional phosphine ligands like $PPh_2(CH_2COPh)$ [10] or $PPh_2(C_6H_4X\text{-}2)$ ($X = NH_2$, NCHPh, CHO) [11]. Similar P–C cleavage reactions were recently observed for trinuclear osmium clusters [12,13].

In order to gain more information on the possibilities of activating polyfunctional phosphine ligands on clusters and of linking organometallic units through these phosphines we have now started similar investigations with phosphine ligands containing nitrogen and sulphur donor substituents. We report below our initial observations on the reactions of $Ru_3(CO)_{12}$ with tris(2-thienyl)phosphine and tris(diethylamino)phosphine.

2. Results and discussion

2.1. Reaction between $Ru_3(CO)_{12}$ and $P(C_4H_3S)_3$

Use of sodium diphenyl ketyl to activate $Ru_3(CO)_{12}$ [2] allowed its reaction with a two-fold excess of

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[☆] Dedicated to Prof. F. Calderazzo on the occasion of his 65th birthday.

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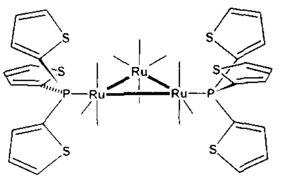
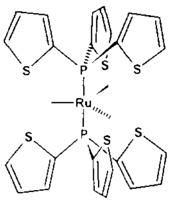
$P(C_4H_3S)_3$ under mild conditions, leading to a reaction mixture containing two main products. Both products were found to decompose slowly in solution, and during attempted chromatography. Crystallization allowed isolation of $Ru_3(CO)_{10}[P(C_4H_3S)_3]_2$ (**1**) and $Ru(CO)_3[P(C_4H_3S)_3]_2$ (**2**) in low yields. By ^{31}P NMR spectroscopy it was shown that **1** (but not **2**) is one of the initially formed products. The NMR spectra of both compounds indicated that they contain intact thienylphosphine ligands.



1



2

In contrast to other phosphines containing heteroatoms, the sulphur atoms in **1** and **2** do not seem to be involved in the coordination of the phosphine ligands. They seem to be responsible, however, for the decomposition of the initially formed complexes. In particular, **2** is a typical product of a donor-induced cluster degradation.

2.2. X-ray structure determination of 1

The identities of **1** and **2** were established by X-ray structure determinations. The molecular structure of **1** is illustrated in Fig. 1. Fractional atomic coordinates are given in Table 1, and important bond lengths and angles in Table 2. The molecular structure of **1** is based on a triangular arrangement of the three ruthenium atoms. Two phosphine ligands are coordinated via their phosphorus atoms to Ru(1) and Ru(3) which occupy equatorial positions approximately *trans* to each other. The distances of these atoms to Ru(2) [(Ru(1)–Ru(2) 300.3(1) pm, Ru(2)–Ru(3) 294.5(1) pm)] are significantly longer than the metal–metal distances in

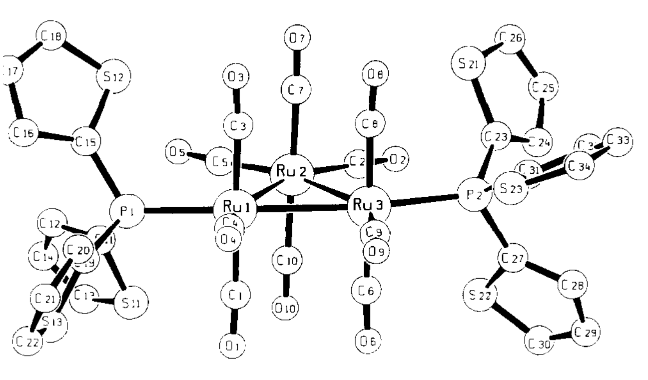


Fig. 1. Molecular structure of **1** (preferred thienyl orientations only).

Table 1
Fractional atomic coordinates (×10⁴) and equivalent isotropic thermal coefficients (pm² × 10⁻¹) for **1**

Atom	x	y	z	U_{eq}
Ru(1)	380(1)	1293(1)	3486(1)	38(1)
Ru(2)	1768(1)	1359(1)	3718(1)	45(1)
Ru(3)	839(1)	2859(1)	4077(1)	38(1)
C(1)	158(5)	382(9)	3950(3)	45(3)
O(1)	−23(4)	−175(6)	4210(3)	60(2)
C(2)	2536(5)	1790(9)	4039(4)	58(3)
O(2)	2991(4)	1984(7)	4228(3)	86(3)
C(3)	593(6)	2260(9)	3031(4)	54(3)
O(3)	655(5)	2822(7)	2746(3)	83(3)
C(4)	−518(6)	1754(8)	3435(4)	50(3)
O(4)	−1048(4)	2053(7)	3412(3)	74(3)
C(5)	2097(6)	218(11)	3397(4)	62(3)
O(5)	2339(4)	−470(8)	3209(3)	95(3)
C(6)	657(6)	1883(9)	4527(4)	56(3)
O(6)	516(5)	1370(7)	4812(3)	82(3)
C(7)	1956(6)	2374(11)	3263(4)	65(4)
O(7)	2137(5)	2892(9)	2997(3)	89(3)
C(8)	1028(5)	3802(9)	3618(3)	48(3)
O(8)	1120(4)	4444(7)	3367(3)	69(2)
C(9)	−46(5)	3348(9)	4130(3)	48(3)
O(9)	−580(4)	3610(7)	4154(3)	74(3)
C(10)	1517(5)	381(10)	4162(4)	59(3)
O(10)	1444(4)	−205(8)	4424(3)	81(3)
P(1)	296(1)	−189(2)	3046(1)	41(1)
C(11)	767(5)	−1372(9)	3176(3)	51(3)
S(11)	1135(4)	−2100(7)	2795(4)	58(2)
C(12)	912(20)	−1889(26)	3562(9)	66(14)
S(11′)	825(13)	−1800(16)	3678(6)	80(6)
C(12′)	1110(23)	−2131(30)	2937(12)	80(30)
C(13)	1286(6)	−2827(9)	3537(5)	78(4)
C(14)	1427(6)	−2977(10)	3143(5)	70(4)
S(12)	1205(2)	595(4)	2339(1)	91(1)
C(15)	494(5)	−44(8)	2497(3)	46(3)
C(16)	112(5)	−482(8)	2139(3)	41(3)
C(17)	496(7)	−214(11)	1774(4)	70(4)
C(18)	1053(7)	352(11)	1830(4)	70(4)
S(13)	−766(2)	−1878(3)	3249(1)	77(1)
C(19)	−554(5)	−696(9)	3022(3)	51(3)
C(20)	−1119(5)	−168(10)	2857(3)	55(3)
C(21)	−1695(6)	−780(12)	2926(4)	69(4)
C(22)	−1587(6)	−1692(13)	3126(4)	81(5)
P(2)	1437(1)	4012(2)	4519(1)	38(1)
S(21)	2539(1)	4675(3)	3893(1)	60(1)
C(23)	2293(5)	4334(8)	4394(3)	45(3)
C(24)	2822(5)	4384(9)	4677(3)	46(3)
C(25)	3412(5)	4685(9)	4466(4)	60(3)
C(26)	3340(5)	4867(10)	4048(4)	56(3)
C(27)	1545(5)	3631(10)	5065(3)	48(3)
S(22)	1836(5)	2430(8)	5190(3)	71(3)
C(28)	1467(16)	4211(22)	5448(7)	46(10)
S(22′)	1453(9)	4468(14)	5470(4)	64(5)
C(28′)	1779(26)	2679(30)	5257(10)	88(35)
C(29)	1663(7)	3611(13)	5811(4)	89(5)
C(30)	1854(7)	2668(12)	5702(4)	84(5)
C(31)	1091(5)	5343(8)	4567(3)	41(2)
S(23)	295(5)	5609(6)	4459(3)	59(2)
C(32)	1386(12)	6301(18)	4702(9)	54(10)
S(23′)	1565(7)	6373(9)	4695(5)	72(5)
C(32′)	465(15)	5752(26)	4531(16)	83(30)
C(33)	946(7)	7172(9)	4720(4)	72(4)
C(34)	350(7)	6844(11)	4609(4)	76(4)

$Ru_3(CO)_{12}$ (285.4 pm) [14]. They are also longer than corresponding ones found in other clusters of the type $Ru_3(CO)_{10}L_2$ reported earlier [5]. The distances Ru–P lie in the normal range. In comparable clusters $Ru_3(CO)_{10}L_2$, the two $Ru(CO)_3L$ moieties are found to be related to each other by a twisting about the M–M bonds that changes the molecular symmetry from C_{2v} to C_2 [5]. Such a distortion is not found in the case of **1**, although the bulky phosphines would be expected to favour it because it would reduce the steric strain.

Three thienyl substituents (Rings with S(11), S(22) and S(23)) were found to be disordered in such a way that their orientations are related by a 180° rotation about the P–C axis. Refinement of the occupancy factors of the disordered fragments (occupancy factors: S(11) 0.615, S(22) 0.645, S(23) 0.624) showed that the sulphur atoms of the thienyl rings, like those of the thienyl rings where disorder could not be refined (occupancy factors greater than 0.9), are directed preferentially towards the ruthenium atoms. The ruthenium–sulphur distances (all greater than 380 pm) however, exclude the possibility of an interaction between them and the metal atoms.

2.3. X-ray structure determination of 2

The molecular structure of **2** is illustrated in Fig. 2. Fractional atomic coordinates are given in Table 3, important bond lengths and angles in Table 4. The molecules of **2** are located on a C_2 axis containing Ru, C(2), and O(2). The molecular geometry of **2** is trigonal bipyramidal, with the three carbonyl ligands occupying the equatorial positions and the two $P(C_4H_3S)_3$ ligands occupying the axial sites. All thienyl substituents of these ligands show disorder. As in **1**, in the preferred orientations the sulphur atoms (occupancy factors: S(1) 0.554, S(2) 0.738, S(3) 0.746) point towards the ruthenium atoms. All the distances from these sulphur atoms to the metal atom exceed 370 pm. The thienyl substituents and the carbonyl ligands in **2** have a staggered conformation.

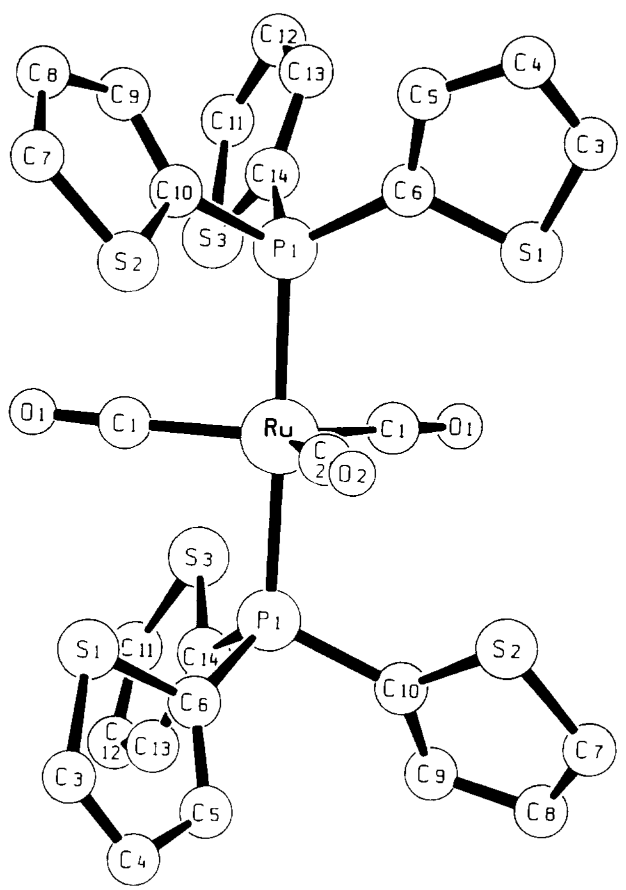


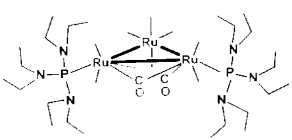
Fig. 2. Molecular structure of **2** (preferred thienyl orientations only).

Table 2
Selected bond legths [pm] and angles [°] of **1** with e.s.d.s in parentheses

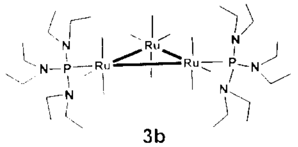
Ru(1)–P(1)	233.3(3)	P(1)–C(15)	180.0(11)
Ru(1)–Ru(3)	288.04(12)	P(1)–C(11)	183.1(11)
Ru(1)–Ru(2)	300.27(12)	P(1)–C(19)	189.5(11)
Ru(2)–Ru(3)	294.54(13)	P(2)–C(27)	180.7(10)
Ru(3)–P(2)	237.0(3)	P(2)–C(31)	183.1(10)
		P(2)–C(23)	188.5(10)
P(1)–Ru(1)–Ru(3)	163.41(8)	C(15)–P(1)–Ru(1)	118.6(4)
P(1)–Ru(1)–Ru(2)	103.79(8)	C(11)–P(1)–Ru(1)	118.5(3)
Ru(3)–Ru(1)–Ru(2)	60.04(3)	C(19)–P(1)–Ru(1)	111.1(4)
Ru(3)–Ru(2)–Ru(1)	57.92(3)	C(27)–P(2)–C(31)	102.2(5)
P(2)–Ru(3)–Ru(1)	167.54(8)	C(27)–P(2)–C(23)	98.2(5)
P(2)–Ru(3)–Ru(2)	105.64(7)	C(31)–P(2)–C(23)	101.5(5)
Ru(1)–Ru(3)–Ru(2)	62.04(3)	C(27)–P(2)–Ru(3)	117.8(4)
C(15)–P(1)–C(11)	99.9(5)	C(31)–P(2)–Ru(3)	113.5(3)
C(15)–P(1)–C(19)	102.5(5)	C(23)–P(2)–Ru(3)	120.7(3)
C(11)–P(1)–C(19)	104.0(5)		

2.4. Synthesis of $Ru_3(CO)_{10}[P(NEt_2)_3]_2$ (3)

Reactions of $Ru_3(CO)_{12}$ with $P(NMe_2)_3$ were described some time ago [1], the studies being hampered by the low stability of the products and by difficulties in separating them. We have now observed that $Ru_3(CO)_{12}$ derivatives containing $P(NEt_2)_3$ ligands are somewhat more stable, but again cannot be separated by chromatography. In order to avoid chromatography an excess of the polyfunctional phosphine was employed, leading to a complete conversion of $Ru_3(CO)_{12}$. Reaction of $Ru_3(CO)_{12}$ with sodium diphenyl ketyl and a two-fold excess of $P(NEt_2)_3$, produced a reaction mixture which, according to ^{31}P NMR spectroscopy, contains **3** in 95% spectroscopic yield. Owing to the very high solubility of **3** in non-polar solvents, only a little of it could be obtained in a crystalline form.



3a



3b

Table 3
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal coefficients ($pm^2 \times 10^{-1}$) for **2**

Atom	x	y	z	U_{eq}
Ru	2500	6401(1)	2500	30(1)
C(1)	2202(1)	5392(2)	1237(1)	45(1)
O(1)	2055(1)	4804(2)	491(1)	73(1)
C(2)	2500	8521(3)	2500	44(1)
O(2)	2500	9787(2)	2500	73(1)
P(1)	619(1)	6278(1)	2451(1)	31(1)
S(1)	−26(2)	7787(3)	444(2)	56(1)
C(3)	−1286(10)	8706(16)	95(9)	55(3)
C(4)	−1947(11)	8767(16)	704(10)	53(2)
C(5)	−1339(7)	8030(12)	1534(8)	55(2)
S(1′)	−1563(3)	8013(4)	1669(3)	58(1)
C(3′)	−1782(12)	8845(20)	509(11)	51(3)
C(4′)	−1064(14)	8712(19)	−45(12)	48(2)
C(5′)	−232(10)	7887(14)	602(8)	58(3)
C(6)	−317(1)	7403(2)	1536(1)	37(1)
S(2)	1020(2)	8160(2)	4312(1)	83(1)
C(7)	207(9)	7970(13)	5141(8)	77(3)
C(8)	−574(9)	6979(13)	4898(8)	62(2)
C(9)	−512(4)	6269(10)	4001(5)	57(1)
S(2′)	−857(3)	6183(8)	3945(4)	57(1)
C(7′)	−447(27)	7205(36)	5000(23)	68(7)
C(8′)	471(23)	8053(31)	5170(21)	56(4)
C(9′)	1048(10)	7731(18)	4427(11)	52(4)
C(10)	288(1)	6802(2)	3596(1)	39(1)
S(3)	884(1)	2930(1)	2458(1)	47(1)
C(11)	−242(7)	1782(8)	2105(7)	61(2)
C(12)	−1199(6)	2470(9)	1774(8)	62(2)
C(13)	−1049(3)	4018(7)	1828(4)	55(1)
S(3′)	−1417(3)	4155(5)	1876(4)	61(1)
C(11′)	−1196(23)	2274(26)	1951(23)	64(6)
C(12′)	−90(19)	1832(19)	2164(21)	58(6)
C(13′)	511(11)	3131(17)	2393(12)	61(5)
C(14)	26(1)	4446(2)	2214(1)	38(1)

Unlike the situation in the phosphido-bridged cluster $Ru_3(\mu_2\text{-}H)(CO)_9[\mu_3\text{-}\eta^2\text{-}(Et_2N)P\text{-}NEt_2)]$, where there is coordination of one of the nitrogen atoms to a ruthenium atom [15], the ^1H NMR spectrum of **3** rules out such an interaction because all the ethyl protons are equivalent. The IR spectrum of **3** shows two absorptions of bridging carbonyls. Because their intensity is weak, it is assumed that two isomers of **3** are present in solution. The spectroscopic evidence indicates a situation which is very similar to that found for many clusters $Fe_3(CO)_{10}(PR_3)_2$, which also exist as mixtures of bridged and non-bridged isomers in solution [16]. Probably the very bulky phosphine ligands force the adjacent carbonyls away from terminal sites towards the bridging positions in order to reduce the steric strain. The ^{13}C NMR spectrum does not show signals for bridging carbonyls, although the most intense signal in the carbonyl region is attributed to the carbon atoms of $Ru(CO)_3$ fragments. Accordingly the non-bridged isomer **3b** seems to predominate. The occurrence of bridging carbonyl ligands distinguishes **3** from all other known clusters of the type $Ru_3(CO)_{10}L_2$.

Table 4
Selected bond legths [pm] and angles [°] of **2** with e.s.d.s in parentheses

Ru–C(2)	191.7(2)	C(2)–Ru–C(1)	118.28(6)
Ru–C(1)	192.6(2)	C(1)–Ru–C(1)	123.45(11)
Ru–P(1)	232.10(5)	C(2)–Ru–P(1)	92.748(9)
C(1)–O(1)	113.6(2)	C(1)–Ru–P(1)	87.54(5)
C(2)–O(2)	114.5(3)	C(1)′–Ru–P(1)	89.85(5)
P(1)–C(6)	179.7(2)	C(2)–Ru–P(1)	92.748(9)
P(1)–C(10)	180.58(14)	P(1)′–Ru–P(1)	174.50(2)
P(1)–C(14)	180.8(2)	C(6)–P(1)–C(10)	102.73(7)
		C(6)–P(1)–C(14)	103.44(7)
		C(10)–P(1)–C(14)	103.03(7)
		C(6)–P(1)–Ru	116.98(5)
		C(10)–P(1)–Ru	114.82(6)
		C(14)–P(1)–Ru	114.09(5)

3. Conclusion

The derivatives **1** and **2** of $Ru_3(CO)_{12}$ containing tris(thienyl)phosphine ligands, are rather labile compounds that can be obtained only in small yields. In both compounds the phosphine ligands are bonded to the metal atoms exclusively through the phosphorus atom. Although the sulphur atoms are not coordinated to the ruthenium atoms, the X-ray structure analyses reveal that the preferred orientation of the thienyl rings is one in which the sulphur atoms point towards the ruthenium atoms. Because there are structural differences between **1** and known clusters of this type, an interaction between the ligand sulphur atoms and the metal atoms cannot be ruled out.

The reaction of $Ru_3(CO)_{12}$ with an excess of tris(diethylamino)phosphine forms almost exclusively the cluster **3**. The IR spectrum of **3** indicates that it consists of isomers, one of which features bridging carbonyls, distinguishing this compound from all other known clusters of this type.

In all three clusters obtained there are many free donor functions available in the ligand sphere. The low stability of **1** and **2** and the known existence of μ_3 bridging $P\text{-}NEt_2$ units in similar clusters [15] indicate the potential intramolecular utilization of these donor functions. Further experiments are required to show how they can be used for intra- and inter-molecular attachments of further organometallic units.

4. Experimental details

The starting materials $Ru_3(CO)_{12}$ [17], $P(C_4H_3S)_3$ [18], $P(NEt_2)_3$ [19] and the sodium diphenylketyl solution [1] were synthesized by published methods. All reactions and manipulations were carried out under nitrogen by Schlenk techniques. Solvents were purified and dried by standard procedures, and were distilled freshly prior to use. Infrared spectra were measured on a Bruker IFS 25 spectrometer. The NMR spectra were recorded on a Bruker AF200 instrument.

4.1. Preparation of 1 and 2

To a stirred suspension of $Ru_3(CO)_{12}$ (320 mg, 0.5 mmol) and $P(C_4H_3S)_3$ (255 mg, 1 mmol) in THF (25 ml) were added 10 drops of a sodium diphenylketyl solution. The colour of the solution changed immediately from orange to red. The remaining suspended $Ru_3(CO)_{12}$ was dissolved by slight warming. The deep-red solution was stirred overnight. The solvent was removed in vacuo, and the residue dissolved in 5 ml dichloromethane and layered with hexane. After a few days red block-shaped crystals of **1** and yellow plate-like crystals of **2** were obtained, and were seperated mechanically. Yields: **1**: 7 mg (1,2%); **2**: 25 mg (3%). 1: Anal. Found: C, 35.96: H, 1.72. $C_{34}H_{18}O_{10}P_2Ru_3S_6$ (1143.99) Calc.: C, 35.70; H, 1.59%. IR (hexane): ν(CO) 2080w, 2058w, 2045m, 2022s, 1991s, 1968s, 1945m cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ − 0.10 (s); ^1H δ 7.70–7.52 (m, 6H), 7.47–7.38 (m, 6H), 7.19–7.10 (m, 6H). **2**: Anal. Found: C, 43.53; H, 2.41: $C_{27}H_{18}O_3P_2RuS_6$ (745.78) Calc.: C, 43.48; H, 2.43%. IR (THF): ν(CO) 1913 cm^{-1}. NMR ($CDCl_3$): $^{31}P\{^1H\}\delta$ 16.06 (s); ^1H δ 7.70–7.38 (m, 12H), 7.18–7.10 (m, 6H).

4.2. Preparation of 3

To a stirred suspension of $Ru_3(CO)_{12}$ (320 mg, 0.5 mmol) and $P(NEt_2)_3$ (257 μl, 1 mmol) in THF (10 ml) were added 10 drops of a sodium diphenylketyl solution. The colour of the solution changed immediately from orange to red. The remaining suspended

Table 5
Crystal data, details of data collecton and structure refinement for **1** and **2** [a]

	1	**2**
Formula	$C_{34}H_{18}O_{10}P_2Ru_3S_6$	$C_{27}H_{18}O_3P_2RuS_6$
M	1143.99	745.78
Crystal system	monoclinic	monoclinic
Space group	*A*2/*n*	*P*2/*n*
a (Å)	20.978(2)	12.413(2)
b (Å)	12.578(1)	9.043(2)
c (Å)	31.660(4)	13.890(3)
β (°)	90.27(1)	105.10(3)
V (Å^3)	8353.0(2)	1505.3(5)
Z	8	2
D_c (g cm^{-3})	1.819	1.645
μ (Mo-Kα) (mm^{-1})	1.500	1.072
F (000)	4480	748
Diffractometer	Stoe-Siemens AED 2	Enraf-Nonius Turbo-Cad 4
Crystal dimensions (mm^3)	0.53 × 0.30 × 0.19	0.5 × 0.2 × 0.1
Scan mode	$\omega/2\Theta$	$\omega/2\Theta$
$2\theta_{max}$ (°)	50	58
Indices range	$-23 < h < 23, 0 < k < 14, 0 < l < 37$	$-16 < h < 16, -12 < k < 0, -18 < l < 18$
Reflections measured	7035	7961
Independent reflections	7024	3992
Reflections with $I \geq 2\sigma(I)$	4643	3505
Absorption correction	not applied	empirical
Absorption correction factors: max		0.854
min		0.749
Restraints/Parameters refined	36/543	42/289
Experimental *R* values [b] (all data)	$R1 = 0.115$	$R1 = 0.030$
	$wR2 = 0.160$	$wR2 = 0.062$
Experimental *R* values [b], $[I \geq 2\sigma(I)]$	$R1 = 0.067$	$R1 = 0.023$
	$wR2 = 0.130$	$wR2 = 0.058$
Weighting scheme: a, b	0.0513, 71.3080	0.0247, 0.0750
Goodness of Fit (*S*) on F^2 [c]	1.130	1.144
Mean shift/e.s.d.	0.008	0.023
Residual electron density: Max (e Å^3)	+0.80 [d]	+0.35 [d]
Min (e Å^3)	−0.80	−0.60

[a] E.s.d.s are given in parentheses. [b] $R1 = \Sigma \| F_o | - | F_c | / \Sigma | F_o |$, $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2] / [\Sigma w(F_o^2)^2]\}^{1/2}$, $w = 1/[s^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$ where $P = (F_o^2 - 2F_c^2)/3$, [c] $S = \{\Sigma | w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$, [d] Near the ruthenium atom(s), resp.

$Ru_3(CO)_{12}$ was dissolved by slight warming. The deep-red solution was stirred overnight. The solvent was removed in vacuo and the residue dissolved in 15 ml of hexane. Crystallization at −20°C afforded deep-red crystals of **3**. Yield: 142 mg (26%). Anal. Found: C, 37.42; H, 5.49; N, 7.62, $C_{34}H_{60}N_6O_{10}P_2Ru_3$ (1078.0) Calc.: C, 37.88; H, 5.61; N, 7.80%. IR ($CDCl_3$): ν(CO) 2096vw, 2070w, 2043w, 2016s, 1988vs, 1817w, 1793w cm^{-1}. NMR ($CDCl_3$); $^{31}P\{^1H\}$ δ 134.52 (s); $^{13}C\{^1H\}$ δ 210.42 (s, Ru(CO)$_3$), 210.12 (s, CO), 204.38 (s, CO), 41.27 (s, CH$_2$), 14.35 (CH$_3$); ^1H δ 3.11 (m, 12H, CH_2), 1.09 (t, 18H, CH_3, $J = 7.1$ Hz).

4.3. X-ray structure determinations

Crystals of **1** and **2** suitable for diffraction studies were grown from mixtures of dichloromethane and petroleum ether. Crystal data and data pertaining to data collection and structure refinement of **1** and **2** are given in Table 5. Both datasets were measured at room temperature using Mo Kα radiation ($\lambda = 0.71073$ Å). Analysis of two control reflections each did not indicate any decomposition of the crystals during measurement. The structures were solved by direct methods using SHELXS-86 [20] and refined using SHELXL-93 [21] and XPMA [22] for graphical analysis. Least-squares refinement was performed including all independent reflections using the full matrix on F^2. In both crystals there is disorder of several thienyl rings in involving two orientations related by a 180° rotation. Each fragment thienyl was constrained to be flat, and all the distances S–C and C–C were constrained to 173 pm and 143 pm, respectively. Disordered fragments with an occupancy factor dropping below 0.1 during refinement were cancelled. Hydrogen atoms were placed in calculated positions (C–H = 93 pm) and were constrained to ride on their associated atoms with isotropically thermal parameters of 1.2 times the factor of their associated carbon atom, respectively. Graphical representations of **1** and **2** were produced using SCHAKAL-92 [23]. Further details of the structure determination may be obtained upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, by making reference to the deposition numbers CSD 380072 (for **1**) and CSD 380073 (for **2**) and citing this paper and its authors.

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