Synthesis and Reactivity of Mono-, Tri-, and Poly-nuclear Ruthenium Carbonyl Complexes containing the Pyridine-2-thiolate Ligand (pyS). Stepwise Preparation of $[Ru(pyS)_2(CO)_2]$ by Reaction of $[Ru_3(CO)_{12}]$ with Pyridine-2-thiol

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The thermal reaction of $[Ru_3(CO)_{12}]$ with pyridine-2-thiol (pySH) gives the trinuclear complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}pyS)(CO)_9]$ (**1**), which is subsequently converted into the polymer $[\{Ru(\mu_3\text{-}pyS)(CO)_2\}_n]$ (**2**). Further reaction of polymer (**2**) with pyridine-2-thiol gives the monomeric compound $[Ru(pyS)_2(CO)_2]$ (**3**). Complexes (**1**) and (**2**) contain triply bridging pyS ligands while in complex (**3**) both pyS ligands are chelating. These results indicate that the reactivity of $[Ru_3(CO)_{12}]$ with pyridine-2-thiol is different to that found for $[Os_3(CO)_{12}]$ and for $[Ru_3(CO)_{12}]$ with 2-aminopyridine and 2-hydroxypyridine. The reactions of complexes (**1**)—(**3**) with several *P*-donor ligands are also described. Infrared and ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectral data for all the compounds are presented and discussed in relation to their structures.

It is well known that the deprotonated derivatives of 2-aminopyridine, 2-hydroxypyridine, and pyridine-2-thiol (pySH) are ligands that give related complexes with many different metals.[1-4] The three ligands have been studied in reactions with $[Os_3(CO)_{12}]$ and although their behaviour is not completely alike, it is very similar.[2-4] However, in a recent paper, we have reported the very different reactivity of 2-aminopyridine and 2-hydroxypyridine with $[Ru_3(CO)_{12}]$.[5] In view of these data we decided to investigate the reactions of pyridine-2-thiol with $[Ru_3(CO)_{12}]$. Here we describe that chemistry as well as the reactivity of the products obtained with several *P*-donor ligands.

Results and Discussion

Complexes (1)—(3).—The reaction of $[Ru_3(CO)_{12}]$ with pySH, in a 1:3 mol ratio, in refluxing toluene for 1 h, gave rise to the precipitation of the brick-red polymer $[\{Ru(\mu_3\text{-}pyS)(CO)_2\}_n]$ (2) (Scheme). However, a transient intermediate was detected during the first 10 min by monitoring the reaction with the aid of i.r. spectroscopy and t.l.c. on silica gel. A short reaction (5 min) in refluxing toluene allowed the isolation of that intermediate in very low yield (lower than 10% after t.l.c.). This compound was subsequently characterized as $[Ru_3(\mu\text{-}H)(\mu_3\text{-}pyS)(CO)_9]$ (1). Attempts were made to obtain complex (1) in larger amounts. Thus, a 29% yield of (1) was obtained from a 1:1 mol ratio of $[Ru_3(CO)_{12}]$ and pySH in refluxing tetrahydrofuran (thf) for 8 h under an atmosphere of carbon monoxide. The polymeric compound (2) reacted with pySH (1 mol per mol of Ru) in refluxing thf to give the yellow mononuclear complex $[Ru(pyS)_2(CO)_2]$ (3). The direct reaction of $[Ru_3(CO)_{12}]$ with pySH, in a 1:6 mol ratio, in refluxing toluene, also gave (3) quantitatively.

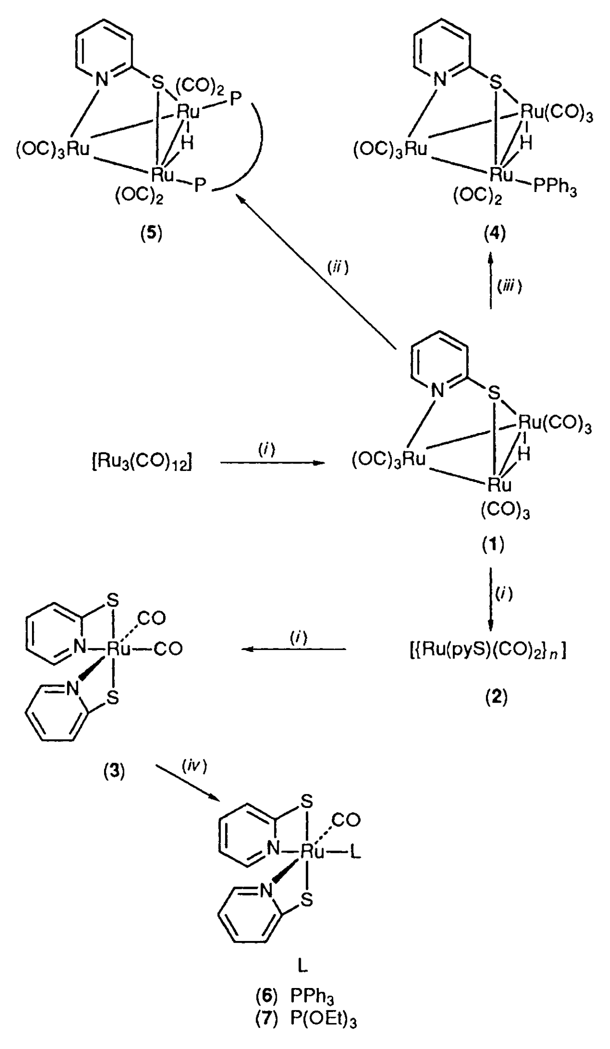
These data suggest that the conversion of $[Ru_3(CO)_{12}]$ into $[\{Ru(\mu_3\text{-}pyS)(CO)_2\}_n]$ or $[Ru(pyS)_2(CO)_2]$ proceeds stepwise through a series of trinuclear intermediates {such as (1), $[Ru_3(\mu\text{-}H)(\mu_3\text{-}pyS)(pySH)(CO)_8]$, or $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}pyS)(\mu\text{-}pyS)(CO)_7]$} and, since only complex (1) was observed, they must readily react with more pySH, releasing CO, before they break down into (2) or (3). However, it is not clear that polymer (2) is an intermediate in the formation of the mononuclear complex (3) from $[Ru_3(CO)_{12}]$, since (2) was never observed when the solution contained enough pySH for (3) to be formed quantitatively, and also because the reaction of (2) with pySH to give (3) is rather slow (see Experimental section).

The above described results are different to those obtained from the reactions of $[Ru_3(CO)_{12}]$ with 2-aminopyridine ($pyNH_2$) and 2-hydroxypyridine (pyOH), which give $[Ru_3(\mu\text{-}H)(\mu_3\text{-}pyNH)(CO)_9]$, $[\{Ru(\mu_3\text{-}pyO)(CO)_2\}_n]$, and $[Ru_2(\mu\text{-}pyO)_2(pyOH)_2(CO)_4]$ as the only observed and isolated products.[5] The reaction of $[Os_3(CO)_{12}]$ with pySH leads to a mixture of $[Os_3(\mu\text{-}H)(\mu\text{-}pyS)(CO)_{10}]$, $[Os_3(\mu\text{-}H)(\mu_3\text{-}pyS)(CO)_9]$, and $[Os(pyS)_2(CO)_2]$, but the reports[3,4] do not mention any polymeric compound. Interestingly, although $[Ru_3(\mu\text{-}H)(\mu\text{-}pyS)(CO)_{10}]$ has to be a precursor of complex (1), it must be very unstable, since it was not detected during the preparation of (1) under carbon monoxide.

The proposed structures for complexes (1)—(3) (Scheme) are based on their analytical and spectroscopic data (Table). The i.r. spectrum of complex (1) shows the same pattern of ν(CO) absorptions as that of the analogous complexes $[Ru_3(\mu\text{-}H)(\mu_3\text{-}pyNH)(CO)_9]$[5] and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ppy)(CO)_9]$[6] (ppy = pyrrolo[2,3-*b*]pyridinate). The presence of the bridging hydride was confirmed by the ^1H n.m.r. spectrum, showing a singlet at δ − 13.14. Its nuclearity was indicated by its fast atom bombardment (f.a.b.) mass spectrum, which gave the parent ion and the successive loss of nine CO ligands.

The polymeric structure of complex (2) is proposed on the basis of its high insolubility. The presence of Ru, CO, and pyS in a ratio of 1:2:1 was deduced from the microanalysis, i.r. spectrum, and reactivity with pySH. Most probably, the $Ru(CO)_2$ units are linked in the polymer through μ_3-pyS ligands, as occurs in the related complexes $[\{Ru(\mu_3\text{-}MeCO_2)(CO)_2\}_n]$[7] and $[\{Ru(\mu_3\text{-}pyO)(CO)_2\}_n]$.[5]

The monomeric nature of complex (3) was indicated by its



Scheme. (*i*) pySH; (*ii*) dppm; (*iii*) PPh_3; (*iv*) L

f.a.b. mass spectrum. The ^1H n.m.r. spectrum shows equivalent pyS ligands and the i.r. spectrum is consistent with a *cis*-dicarbonyl structure. Although there could be two isomers which fit these data (CO ligands *trans* to both nitrogens or *trans* to both sulphurs) we propose the structure shown in the Scheme because complex (**3**) can be related to the *X*-ray structurally characterized compounds $[Os(pyS)_2(CO)_2]$,[4] $[Ru(pyS)_2(PPh_3)_2]$,[8] and $[Ru(pyS)_2(CO)(PPh_3)]$,[9] having the sulphur atoms mutually *trans* and a *cis*-dicarbonyl arrangement.

Reactions of Complexes (**1**)—(**3**) *with* P-*Donor Ligands*.—The pyS ligand has been found to be very versatile. It is able to co-ordinate in a monodentate manner through the sulphur atom,[9] as a bridging ligand through both nitrogen and sulphur and also through sulphur alone,[10,11] as a triply bridging ligand,[3,12] and as a chelate.[9] Since in complexes (**1**)—(**3**) the pyS ligands co-ordinate to ruthenium through both nitrogen and sulphur atoms, we thought it worthwhile to determine whether or not the Ru–S or Ru–N bonds could be broken by reaction with *P*-donor ligands.

Complex (**1**) reacted with PPh_3 and bis(diphenylphosphino)methane (dppm) to give the trinuclear compounds $[Ru_3(\mu\text{-}H)(\mu_3\text{-}pyS)(CO)_8(PPh_3)]$ (**4**) and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}pyS)(CO)_7(dppm)]$ (**5**) (Scheme). In both complexes the displaced CO ligands were those *cis* to the sulphur atom and *cis* to the hydride, as deduced from their *J*(P–H) coupling constants (Table) and by comparison of their i.r. and n.m.r. spectra to those of the related complexes $[Ru_3(\mu\text{-}H)(\mu_3\text{-}pyNH)(CO)_8(PPh_3)]$ and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}pyNH)(CO)_7(dppm)]$.[13] It is evident from these data that the bonds between the μ_3-pyS ligand and the ruthenium atoms of (**1**) cannot be broken, at least as easily as some Ru–CO bonds.

A suspension of polymer (**2**) in thf reacted very slowly (*ca.* 24 h) at room temperature with different *P*-donor ligands [PPh_3, $P(OPh)_3$, and $P(OEt)_3$], in a 1:1 P:Ru ratio, giving brown solutions. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of these solutions indicated that they contained a mixture of several complexes (*e.g.* up to nine singlet resonances were observed in the spectrum upon reaction with PPh_3). No attempts were made to separate the mixtures. However, we have reported previously that the polymer $[\{Ru(\mu_3\text{-}pyO)(CO)_2\}_n]$, which contains 2-pyridonate bridges, reacts with *P*-donor ligands (L) to give the binuclear complexes $[Ru_2(\mu\text{-}pyO)_2(CO)_4L_2]$ quantitatively.[5] This different reactivity of the pyS-and pyO-bridged polymers has to be related to the difference in the hard–soft character of the mercapto, hydroxy, and pyridinic parts of the bridging ligands and also of the metal. Ruthenium(I) is a soft metal and hardness decreases in the series *O*-, *N*-, and *S*-donor ligands. Thus, the splitting of the polymer $[\{Ru(\mu_3\text{-}pyO)(CO)_2\}_n]$ takes place selectively through the breaking of Ru–O bonds (a soft metal prefers a soft ligand), while Ru–N and probably Ru–S bonds are broken during the reaction of (**2**) with *P*-donor ligands. This behaviour is in accord with the fact that, when co-ordinated to a soft metal as a monodentate ligand, pySH binds through the sulphur atom,[4,9] whereas pyOH binds through the nitrogen.[5]

The mononuclear complex (**3**) is extremely stable. No reaction was observed between it and a large excess of pySH, PPh_3, or $P(OEt)_3$ in refluxing thf for 24 h. Nevertheless, moderate yields of the compounds $[Ru(pyS)_2(CO)L]$ [L = PPh_3, (**6**); or $P(OEt)_3$, (**7**)] could be achieved by reaction of (**3**) with an excess of the appropriate ligand L in refluxing toluene for longer than 24 h. The nature of the products of these reactions suggests that the Ru–S and Ru–N bonds of (**3**) are extremely stable, in spite of the short bite of the chelating ligand, *ca.* 68°.[4,9] Complex (**6**) can be alternatively prepared by reaction of $[Ru(CO)_3(PPh_3)_2]$ with pySH or pySSpy.[9]

Experimental

All reagents were commercially available analytical grade chemicals and were used without further purification. Solvents were dried and distilled under nitrogen over sodium (hexane, toluene), sodium diphenylketyl (tetrahydrofuran, diethyl ether), or calcium hydride (dichloromethane). Unless otherwise noted, the reactions were carried out at room temperature, under nitrogen, using standard Schlenk techniques. Instrumentation was as reported previously.[5]

Preparations.—$[Ru_3(\mu\text{-}H)(\mu_3\text{-}pyS)(CO)_9]$ (**1**). The complex $[Ru_3(CO)_{12}]$ (100 mg, 0.156 mmol) and pyridine-2-thiol (20 mg, 0.18 mmol) were stirred in refluxing tetrahydrofuran (15 cm^3), under an atmosphere of CO, for 8 h. The solvent was removed under reduced pressure and the residue chromatographed on a neutral alumina column (activity IV). Hexane eluted two bands, the first being unreacted $[Ru_3(CO)_{12}]$. The second band yielded complex (**1**) as red crystals on evaporating the solution to dryness (30 mg, 29%) (Found C, 25.5; H, 1.0; N, 1.8. $C_{14}H_5NO_9Ru_3S$ requires C, 25.25; H, 0.75; N, 2.1%). F.a.b. mass spectrum: *m*/*z* 666 (M^+) and the successive loss of nine CO ligands.

$[\{Ru(\mu_3\text{-}pyS)(CO)_2\}_n]$ (**2**). The complex $[Ru_3(CO)_{12}]$ (400 mg, 0.625 mmol) and pyridine-2-thiol (209 mg, 1.88 mmol) were refluxed in toluene (30 cm^3) for 2 h, giving a brick-red solid. The solvent was decanted off and the solid washed with diethyl ether

Table. I.r. and n.m.r. data for complexes (**1**)—(**7**)

Complex	ν(CO)/cm^{-1}	δ^a	
		^{1}H	^{31}P
(**1**)	2 085m, 2 055vs, 2 034vs, 2 007s, 1 997s, 1 974w, 1 968w^b	8.54 (d, 1 H), 7.44 (m, 2 H), 7.09 (dd, 1 H), −13.14 (s, 1 H)	
(**2**)	2 015vs, 1 975s, 1 948s, 1 917s^c		
(**3**)	2 047vs, 1 984vs^d	8.14 (d, 1 H), 7.38 (t, 1 H), 6.86 (d, 1 H), 6.75 (t, 1 H)	
(**4**)	2 065m, 2 038vs, 2 000s, 1 993s, 1 973m, 1 958w, 1 950w^b	8.59 (d, 1 H), 7.31 (m, 17 H), 7.00 (t, 1 H), −12.66 (d, 1 H)^e	31.4 (s)
(**5**)	2 038s, 1 992vs, 1 961s, 1 932w^f	8.71 (d, 1 H), 7.20 (m, 23 H), 3.31 (m, 1 H), 2.92 (m, 1 H), −12.12 (t, 1 H)^g	2.3 (s)
(**6**)	1 948vs^d	8.18 (d, 1 H), 7.50 (m, 7 H), 7.26 (m, 10 H), 6.98 (t, 1 H), 6.76 (d, 1 H), 6.65 (t, 1 H), 6.44 (d, 1 H), 6.26 (t, 1 H)	57.5 (s)
(**7**)	1 964vs^b	8.15 (m, 2 H), 7.28 (m, 2 H), 6.78 (m, 2 H), 6.66 (m, 2 H), 3.97 (m, 6 H), 1.19 (t, 9 H)	145.6 (s)

[a] In $CDCl_3$. [b] In hexane. [c] Nujol mull. [d] In toluene. [e] J(P–H) = 9 Hz. [f] In CH_2Cl_2. [g] J(P–H) = 13.7 Hz.

(2 × 5 cm^3) and dried (436 mg, 87%) (Found: C, 31.4; H, 1.55; N, 4.85. $C_7H_4NO_2RuS$ requires C, 31.45; H, 1.5; N, 5.25%). This compound is insoluble in all common solvents.

[Ru(pyS)$_2$(CO)$_2$] (**3**). The complex [$Ru_3(CO)_{12}$] (200 mg, 0.313 mmol) and pyridine-2-thiol (226 mg, 2.033 mmol) were stirred in refluxing toluene (20 cm^3) for 1 h. The solvent was removed under reduced pressure and the residue washed with diethyl ether (2 × 5 cm^3) and dried to give complex (**3**) as a yellow solid (234 mg, 67%) (Found: C, 38.4; H, 2.25; N, 7.45. $C_{12}H_8N_2O_2RuS_2$ requires C, 38.2; H, 2.15; N, 7.4%). F.a.b. mass spectrum: m/z 378 (M^+), 350 (M^+ − CO), and 322 (M^+ − 2CO). This compound can also be prepared by reaction of polymer (**2**) with pyridine-2-thiol (one mol per mol of Ru) in refluxing tetrahydrofuran for 2 h.

[Ru_3(μ-H)(μ$_3$-pyS)(CO)$_8$(PPh$_3$)] (**4**). Triphenylphosphine (6 mg, 0.023 mmol) was added to a solution of complex (**1**) (15 mg, 0.023 mmol) in dichloromethane (5 cm^3). The solution was stirred for 15 min and evaporated to dryness under reduced pressure. The residue was washed with hexane (3 cm^3) to give complex (**4**) as an orange solid (15 mg, 72%) (Found: C, 41.6; H, 2.4; N, 1.7. $C_{31}H_{20}NO_8PRu_3S$ requires C, 41.35; H, 2.25; N, 1.55%).

[Ru_3(μ-H)(μ$_3$-pyS)(CO)$_7$(μ-dppm)] (**5**). Complex (**1**) (22 mg, 0.033 mmol) and bis(diphenylphosphino)methane (13 mg, 0.034 mmol) were stirred in dichloromethane (5 cm^3) for 5 min. The solution was worked up as for complex (**4**) to give complex (**5**) as a red-orange solid (26 mg, 79%) (Found: C, 44.9; H, 3.0; N, 1.5. $C_{37}H_{27}NO_7P_2Ru_3S$ requires C, 44.7; H, 2.75; N, 1.4%).

[Ru(pyS)$_2$(CO)(PPh$_3$)] (**6**). Complex (**3**) (81 mg, 0.214 mmol) and triphenylphosphine (224 mg, 0.856 mmol) were refluxed in toluene (20 cm^3) for 26 h. The solvent was removed under reduced pressure and the residue chromatographed on a column of neutral alumina (activity IV). Hexane eluted a small amount of complex (**3**) and the excess of triphenylphosphine. Hexane–dichloromethane (3:1, v/v) eluted a yellow band, which on evaporation to dryness and after washing the residue with diethyl ether (2 × 5 cm^3) gave complex (**6**) as yellow crystals (57 mg, 43%) (Found: C, 57.2; H, 3.9; N, 2.2. $C_{29}H_{23}N_2OPRuS_2$ requires C, 56.95; H, 3.8; N, 2.3%).

[Ru(pyS)$_2$(CO){P(OEt)$_3$}] (**7**). Complex (**3**) (177 mg, 0.468 mmol) and triethyl phosphite (100 mg, 0.583 mmol) were refluxed in toluene (20 cm^3) for 32 h. During this time the solution changed from yellow to dark green. The solvent was removed under reduced pressure and the residue chromatographed on a column of neutral alumina (activity IV). Hexane eluted the excess of phosphite and two yellow bands. The second band contained a small amount of unreacted complex (**3**). The first yellow band was worked up as for complex (**6**) to give complex (**7**) as yellow crystals (114 mg, 47%) (Found: C, 39.8; H, 4.8; N, 5.5. $C_{17}H_{23}N_2O_4PRuS_2$ requires C, 39.6; H, 4.5; N, 5.45%).

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