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Synthesis of monomercurated N-protected pyrroles and the use of these compounds as pyrrolyl group transfer reagents to ruthenium and osmium. Crystal structures of $(2\text{-}C_4H_3NC[O]CH_3)HgCl$, $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ and $Ru(2\text{-}C_4H_3NSO[O]Ph)(S_2CNMe_2)(CO)(PPh_3)$

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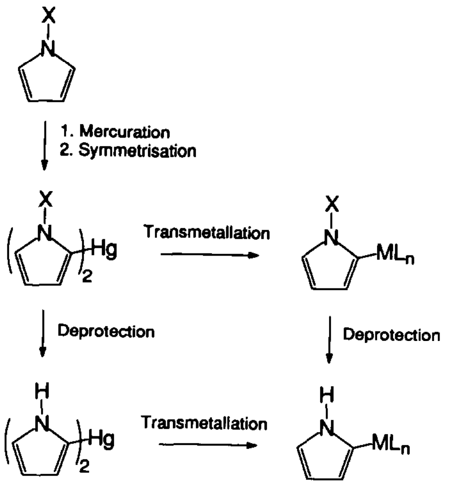
Abstract

N-Acetylpyrrole and *N*-phenylsulfonylpyrrole are each selectively mercurated in the 2-position on treatment with mercuric chloride. The resulting organomercuric chlorides are symmetrized to the corresponding diorganomercury derivatives $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (**2**) and $(2\text{-}C_4H_3NSO[O]Ph)_2Hg$ (**4**) by the action of sodium iodide. The crystal structures of $(2\text{-}C_4H_3NC[O]CH_3)HgCl$ (**1**) and $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (**2**) have been determined. The acetyl oxygen atom interacts weakly with the mercury centre in both cases, but more strongly in **1** than **2**. Treatment of the hydrido complexes $MHCl(CO)(PPh_3)_3$ (M = Ru, Os) with the diorganomercurial **2** or **4** affords in good yield the 2-pyrrolyl complexes $M(2\text{-}C_4H_3NC[O]CH_3)Cl(CO)(PPh_3)_2$ or $M(2\text{-}C_4H_3NSO[O]Ph)Cl(CO)(PPh_3)_2$, respectively. In each case the pyrrolyl group is coordinated in a bidentate fashion through C-2 and an oxygen atom of the *N*-substituent. The chloride ion in $[Ru(2\text{-}C_4H_3NSO[O]Ph)Cl(CO)(PPh_3)_2$ (**7**) is labile, and upon treatment with $AgSbF_6$ and CO, the cationic complex $Ru(2\text{-}C_4H_3NSO[O]Ph)(CO)_2(PPh_3)_2]SbF_6$ is formed. Treatment of **7** with $AgSbF_6$ and sodium dimethyldithiocarbamate gives the neutral monophosphine complex $Ru(2\text{-}C_4H_3NSO[O]Ph)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**10**), the crystal structure of which has been determined.

Keywords: Mercury; Ruthenium; Osmium; Pyrrole; Crystal structure

1. Introduction

We have a continuing research interest in the synthesis and study of 2-pyrrolyl derivatives of ruthenium and osmium [1]. One potential route to compounds of this type involves reaction of bis(2-pyrrolyl)mercury with the metal hydrides $MHCl(CO)(PPh_3)_3$ (M = Ru, Os) [2]. However, bis(2-pyrrolyl)mercury is not yet known and the more obvious routes to this compound, such as direct mercuration, are not applicable. Therefore, an alternative approach involving the synthesis of the N-protected dipyrrolylmercury compounds $(C_4H_3NX)_2Hg$ (X = C(O)Me, SO_2Ph) was investigated. Removal of the protecting group X, either before or after



Scheme 1.

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Table 1
IR data [a] for new compounds

Complex	ν(CO) [b]	Pyrrolyl bands	Other bands
$(2\text{-}C_4H_3NC[O]CH_3)HgCl$ (**1**)		1285w, 1210m, 1202w, 1142m, 1105s, 1034m, 941s, 880w, 870w, 826m, 739s, 650s, 635w, 600m, 554m	3136s, 3107w ν(ring CH); 1676s ν(C–O); 1535s ν(CN); 1391s, 1323s $\nu(C[O]CH_3)$
$(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (**2**)		1281w, 1211m, 1138w, 1103s, 1034m, 937, 880m, 872m, 819m, 725s, 710s, 650s, 606m, 548m	3131m, 3110 ν(ring CH); 1701s ν(CO); 1533s ν(CN); 1393s, 1319s $\nu(C[O]CH_3)$
$(2\text{-}C_4H_3NSO[O]Ph)HgCl$ (**3**)		1449s, 1335w, 1202w, 1180m, 1148s, 1080s, 1051m, 826m, 756m, 727s, 683s, 621s, 606m, 590s, 559s	3096w, 3056w ν(ring CH); 1360s $\nu_{as}(SO_2)$; 1169s $\nu_s(SO_2)$; 345m ν(HgCl)
$(2\text{-}C_4H_3NSO[O]Ph)_2Hg$ (**4**)		1479w, 1447s, 1422w, 1314w, 1290w, 1248w, 1206s, 1146s, 1078s, 1047m, 1024w, 999m, 968w, 872w, 808m, 754s, 725s, 663, 625s, 610s 594s, 563s, 505m	3124w, 3094w, 3060 ν(ring C–H); 1352s $\nu_{as}(SO_2)$; 1172s $\nu_s(SO_2)$
$Ru(2\text{-}C_4H_3NC[O]CH_3)Cl(CO)(PPh_3)_2$ (**5**)	1925	1420sh, 1348w, 1123m, 1072m	1533w, 1591s, 1321m, 918m, $(COCH_3)$
$Os(2\text{-}C_4H_3NC[O]CH_3)Cl(CO)(PPh_3)_2$ (**6**)	1904	1414w, 1333w, 1071w, 852w, 789m	1586s, 1530w, 1352w, 917m, $(COCH_3)$
$Ru(2\text{-}C_4H_3NSO[O]Ph)Cl(CO)(PPh_3)_2$ (**7**)	1942	1425sh, 1229w, 1150m, 1072m, 1044m, 858w	1310s $\nu_{as}(SO_2)$; 1128s $\nu_s(SO_2)$; 781w, 731s, δ(CH) of SO_2Ph; 631m, 588m
$Os(2\text{-}C_4H_3NSO[O]Ph)Cl(CO)(PPh_3)_2$ (**8**)	1921	1451sh, 1231w, 1148m, 1069m, 1044m, 856w	1308s $\nu_{as}(SO_2)$; 1123s $\nu_s(SO_2)$; 778w, 731s δ(CH) of SO_2Ph; 635m, 588m
$[Ru(2\text{-}C_4H_3NSO[O]Ph)(CO)_2(PPh_3)_2]SbF_6$ (**9**)	2070, 1998	1458s, 1242m, 1159s, 1051s, 1030m	1325s $\nu_{as}(SO_2)$; 1113s $\nu_s(SO_2)$; 784w, 729s δ(CH) of SO_2Ph
$Ru(2\text{-}C_4H_3NSO[O]Ph)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**10**)	1933	1456sh, 1393s, 1231m 1128s, 1078m, 1044m, 864w	1314s $\nu_{as}(SO_2)$; 1152s $\nu_s(SO_2)$; 1258m, 978m (S_2CNMe_2); 783w, 729s δ(CH) of SO_2Ph

[a] In cm^{-1}. Spectra recorded as Nujol mulls between KBr plates. Intensity of IR bands described as s, strong; m, medium; w, weak; sh, shoulder.

[b] All carbonyl bands are strong in intensity.

transfer to Ru or Os, could then give unsubstituted 2-pyrrolyl metal derivatives (Scheme 1).

2. Results and discussion

2.1. Mercuration of N-protected pyrroles

Although mercuration of free pyrrole is very difficult to control and only polymercurated products are obtained [3], it is well known that the selectivity for electrophilic attack at the pyrrole 2-position can be increased markedly by substitution at nitrogen with an electron withdrawing group [4]. Therefore pyrroles substituted in this way should react preferentially at the 2-position with the electrophile Hg^{2+}. In addition, if the electron withdrawing group on nitrogen contained a suitably positioned donor atom that could coordinate to the incoming mercuric ion, this could further help to direct the point of mercuration to the 2-position. Substitution at nitrogen would also protect the nitrogen atom from undergoing mercuration.

Indeed it was found that *N*-acetylpyrrole, $C_4H_4NC(O)CH_3$, undergoes mercuration on reaction with mercuric chloride/sodium acetate at 20–25°C and $(2\text{-}C_4H_3NC[O]CH_3)HgCl$ (**1**) is rapidly formed. IR and NMR spectral data for **1** and all other new compounds reported in this paper are collected in Tables 1 and 2. One noteworthy feature of the IR spectrum of **1** is that $\nu(CO)$ appears at 1676 cm^{-1}. This is 50 cm^{-1} lower than for the corresponding band in free *N*-acetyl pyrrole and it is consistent with the presence of a weak Hg–O interaction. This has been confirmed by a single crystal X-ray structure determination. The molecular geometry of **1** is depicted in Fig. 1 (vide infra).

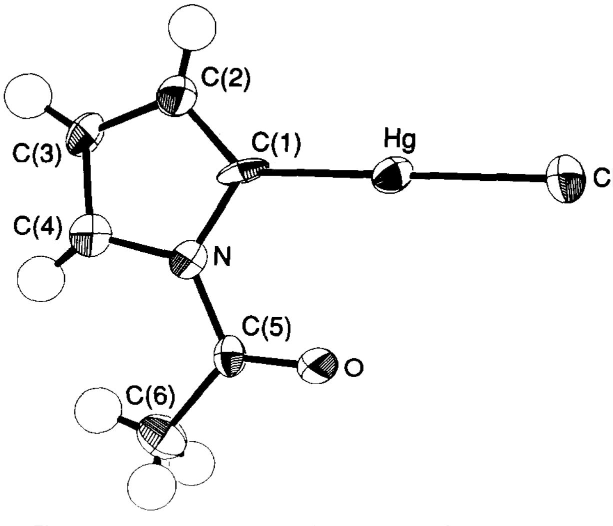

Fig. 1. Molecular structure of $(2\text{-}C_4H_3NC[O]CH_3)HgCl$ (1).

Compound **1** undergoes a symmetrization reaction upon the addition of excess iodide ion and $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (**2**) is formed in high yield. As would be expected, this product is considerably more soluble than **1**. The single crystal X-ray structure determination has also been obtained for this compound (vide infra).

N-Phenylsulfonylpyrrole also undergoes mercuration on reaction with mercuric chloride/sodium acetate, although in contrast to *N*-acetylpyrrole, complete reaction requires heating under reflux for 30 h in methanol/water solution. The product formed is $(2\text{-}C_4H_3NSO[O]Ph)HgCl$ (**3**). The chemical shifts and coupling constants associated with the pyrrolyl group in the ^1H and ^{13}C NMR spectrum of **3** closely resemble those obtained for **1**. This indicates that substitution has also occurred in the 2-position for **3**. Confirmation of this comes from the crystal structure determination of a ruthenium derivative (vide infra) obtained by transfer of the pyrrolyl group from the corresponding symmetrized compound $(2\text{-}C_4H_3NSO[O]Ph)_2Hg$ (**4**).

2.2. Attempts to remove the N-protecting groups in the pyrrolyl mercury compounds 1–4

The *N*-phenylsulfonyl and *N*-acetyl groups have both been widely used as a pyrrole N–H protecting groups [5]. Cleavage of these protecting groups has been achieved through reaction with a diverse range of reagents. However, numerous attempts to selectively remove the *N*-phenylsulfonyl and *N*-acetyl groups in the compounds **1–4** using a range of different bases or acids under a number of conditions were largely unsuccessful. In many cases the Hg–C bond was cleaved in preference to removal of the N-substituent. One exception was the reaction of $(2\text{-}C_4H_3NC[O]CH_3)HgCl$ (**1**) with two equivalents of NaOH in dioxane at 20°C for 40 h. From this reaction 2-pyrrolylmercuric chloride could be isolated in ca. 4% yield. However, since an alternative route to this compound (in ca. 20% yield) [1,6] had already been found using a modified procedure of Katritzky [7], this particular reaction involving **1** was not pursued.

2.3. Synthesis of N-substituted, 2-pyrrolyl complexes of ruthenium and osmium

Treatment of the transition metal hydrides $MHCl(CO)(PPh_3)_3$ (M = Ru, Os) with the bis(2-pyrrolyl)mercury compounds $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (**2**) or $(2\text{-}C_4H_3NSO[O]Ph)_2Hg$ (**4**) affords the corresponding transition metal 2-pyrrolyl derivatives $\overline{M(2\text{-}C_4H_3NC[O]}CH_3)Cl(CO)(PPh_3)_2$ or $\overline{M(2\text{-}C_4H_3NSO}[O]Ph)Cl(CO)(PPh_3)_2$ (M = Ru, Os) respectively in high yield (Scheme 2). As expected for reactions of this type [2], elemental mercury, triphenylphosphine

Table 2
NMR data [a] for new compounds

Compound	^{1}H NMR	^{13}C NMR	^{31}P NMR
(2-C_4H_3NC[O]CH_3)HgCl (**1**)	7.35dd(3.3, 0.8), 1H, pyr C*H*; 6.47dd(3.0, 3.0), 1H, pyr C*H*; 6.34dd (3.0, 1.0), 1H, pyr C*H*; 2.60s, 3H, COC*H*$_3$	123.3, pyr *C*H; 123.2 pyr *C*H; 114.9, pyr *C*H; 22.92, CO*C*H$_3$	
(2-C_4H_3NC[O]CH_3)$_2$Hg (**2**)	7.36dd(3.1, 0.8), 1H, pyr C*H*; 6.45dd(3.0, 3.0) 1H, pyr C*H*; 6.35dd(2.8, 0.7), 1H, pyr C*H*; 2.58s, 3H, COC*H*$_3$	124.0, pyr *C*H; 123.0, pyr *C*H; 114.4, pyr *C*H; 23.2, pyr *C*H; 169.9, *C*OCH$_3$ [b]; 157.5, pyr *C* [b]	
(2-C_4H_3NSO[O]Ph)HgCl (**3**)	7.49dd(3.2, 1.2), 1H, pyr C*H*; 6.47dd(3.2, 3.2), 1H, pyr C*H*; 6.35dd(3.2, 1.2), 1H, pyr C*H*; 7.80m, 2H, Ph$_o$ [d]; 7.66m, 1H, Ph$_p$; 7.54m, 2H, Ph$_m$	124.7, pyr *C*H; 123.6, pyr *C*H; 114.4, pyr *C*H; 134.3, Ph$_p$; 129.7, Ph$_{o/m}$; 126.7, Ph$_{o/m}$; 138.9, pyr C [c]; 130.1, Ph$_i$ [c]	
(2-C_4H_3NSO[O]Ph)$_2$Hg (**4**)	7.52m, 1H, pyr C*H*; 6.49dd(3.1, 3.1), 1H, pyr C*H*; 6.40dd(3.0, 1.2), 1H, pyr C*H*; 7.92m, 2H, Ph$_o$; 7.58m, 1H, Ph$_p$; 7.48m, 2H, Ph$_m$	124.6, pyr *C*H; 124.4, pyr *C*H; 114.2 pyr *C*H; 133.7, Ph$_p$; 129.4, Ph$_{o/m}$; 126.7, Ph$_{o/m}$; 159.8 pyr *C* [c]; 139.4, Ph$_i$ [c]	
$\overline{\mathrm{Ru(2\text{-}C_4H_3NC[O}}\mathrm{]CH_3)Cl(CO)(PPh_3)_2}$ (**5**)	1.54s, 3H, C[O]C*H*$_3$; 5.06m, 1H, pyr C*H*; 5.92dd(3.09, 3.09), pyr C*H*; 6.55m, pyr C*H*; 7.24–7.33m, 7.44–7.49m PPh$_3$	18.31s, 18.40s, C[O]*C*H$_3$; 116.56s, pyr *C*H; 119.25s, pyr *C*H; 121.33s, pyr *C*H; 161.99t(12.5), pyr *C*; 127.57t(4.7), Ph$_{o/m}$; 129.43s, Ph$_p$; 131.42t(22.1), Ph$_i$; 134.42t(5.4), Ph$_{o/m}$; 174.48s, *C*[O]CH$_3$; 205.93t(15.26), *C*O	34.45s
$\overline{\mathrm{Os(2\text{-}C_4H_3NC[O}}\mathrm{]CH_3)Cl(CO)(PPh_3)_2}$ (**6**)	1.40s, 3H, C[O]C*H*$_3$; 4.95dd(1.20, 2.72), 1H, pyr C*H*; 5.60dd(3.13), 1H, pyr C*H*; 6.44dd(0.89, 3.35), 1H, pyr C*H*; 7.27–7.33m, 7.44–7.49m, PPh$_3$	17.4s, C[O]*C*H$_3$; 115.58s, pyr *C*H; 119.94s, pyr *C*H; 120.19s, pyr *C*H; 144.91 [e], pyr *C*; 127.61t(4.9), Ph$_{o/m}$; 129.52s, Ph$_p$; 130.79t(25.0), Ph$_i$; 134.45t(5.1), Ph$_{o/m}$; 176.02s, *C*[O]CH$_3$; 184.75s [e], *C*O	11.13s
$\overline{\mathrm{Ru(2\text{-}C_4H_3NSO}}\mathrm{[O]Ph)Cl(CO)(PPh_3)_2}$ (**7**)	4.54m, 1H, pyr C*H*; 5.75dd(2.9, 2.9), 1H, pyr C*H*; 6.34d(2.9), 1H, pyr C*H*; 7.01d(8.2), 2H, SO$_2$(C$_6$*H*$_5$)$_{o/m}$; 7.13dt(7.7), 2H, SO$_2$(C$_6$*H*$_5$)$_{o/m}$; 7.45t(7.1), 1H, SO$_2$(C$_6$*H*$_5$)$_p$; 7.23–734m, 7.56, 7.71, PPh$_3$	116.72s, pyr *C*H; 117.71s, pyr *C*H; 118.95s, pyr *C*H; 153.70s, pyr *C* [e]; 127.56s, SO$_2$(*C*$_6$H$_5$)$_{o/m}$; 129.13s, SO$_2$(*C*$_6$H$_5$)$_{o/m}$; 133.81s, SO$_2$(*C*$_6$H$_5$)$_p$; 135.99s, SO$_2$(*C*$_6$H$_5$)$_i$; 127.67dd(3.9, 5.3),	30.79 28.71 28.65 26.56 [i]

		127.89dd(3.9, 5.0); 129.44s, 129.78s, 132.43dt(17.5, 26.6); 134.66t(5.4), P(C_6H_5)$_3$ [f]; 205.13m, CO	
$\overline{\mathrm{Os(2\text{-}C_4H_3NSO}}\mathrm{[O]Ph)Cl(CO)(PPh_3)_2}$ **(8)**	4.32m, 1H, pyr CH; 5.78dd(3.12), pyr CH; 6.25d(2.92), 1H, pyr CH; 7.00d(7.85, 2H, $SO_2(C_6H_5)_{o/m}$; 7.10dd(7.52), 2H, $SO_2(C_6H_5)_{o/m}$; 7.45dd(7.51), 1H, $SO_2(C_6H_5)_p$; 7.23–7.32, 7.52–7.68m, PPh_3	115.68s, pyr CH; 116.12s, pyr CH; 119.53s, pyr CH; 137.75t(7.2), pyr C; 127.55s, $SO_2(C_6H_5)_{o/m}$; 129.15s, $SO_2(C_6H_5)_{o/m}$; 133.90s, $SO_2(C_6H_5)_p$; 135.33s, $SO_2(C_6H_5)_i$; 127.57dd(2.8, 6.9), 127.87dd(2.7, 6.4); 129.48s, 129.82s, 131.93dt(16.4, 34.5); 134.72dd(3.6, 6.2), P(C_6H_5)$_3$ [f]; 179.64t(11.1), CO	10.40 8.47 8.31 6.38 [i]
$[\overline{\mathrm{Ru(2\text{-}C_4H_3NSO}}\mathrm{[O]Ph)(CO)_2(PPh_3)_2]SbF_6}$ **(9)**	5.88dd, 1H, pyr CH; 6.48, 1H, pyr CH [g]; 6.72–7.89m [f], SO_2Ph, PPh_3	119.52s, pyr CH; 120.32s, pyr CH; 121.81s, pyr CH; 136.23s [e], pyr C; 125.72s, $SO_2(C_6H_5)$; 126.94s, $SO_2(C_6H_5)$ [h]; 128.64d(10.1), 129.03d(8.85), 129.45m; 132.97d(10.9), 133.58m; 134.11d(9.1), P(C_6H_5)$_3$ [f]	23.29 23.13 13.60 13.43 [i]
$\overline{\mathrm{Ru(2\text{-}C_4H_3NSO}}\mathrm{[O]Ph)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)}$ **(10)**	3.23s, 3H, N(CH_3)$_2$; 3.31s, 3H, N(CH_3)$_2$; 5.70d(2.74), 1H, pyr CH; 6.22dd(3.04), 1H, pyr CH; 6.68m 1H, pyr CH; 7.55dd(7.54, 7.54), 2H, C_6H_5; 7.81m 1H, C_6H_5 [h]; 7.28–7.43m PPh_3	38.97s, N(CH$_3$)$_2$; 39.09s, N(CH$_3$)$_2$; 117.78s, pyr CH; 118.09s, pyr CH; 118.35s, pyr CH; 157.46d(9.8), pyr C; 128.09, $SO_2(C_6H_5)_{o/m}$; 128.84, $SO_2(C_6H_5)_{o/m}$; 133.80, $SO_2(C_6H_5)_p$; 137.84, $SO_2(C_6H_5)_i$; 127.87d(10.0), P(C_6H_5)$_{o/m}$; 129.68d(1.7), P(C_6H_5)$_p$; 133.11d(44.6), P(C_6H_5)$_i$; 133.62d(10.6), P(C_6H_5)$_{o/m}$; 202.97d(16.5), CO	47.43s

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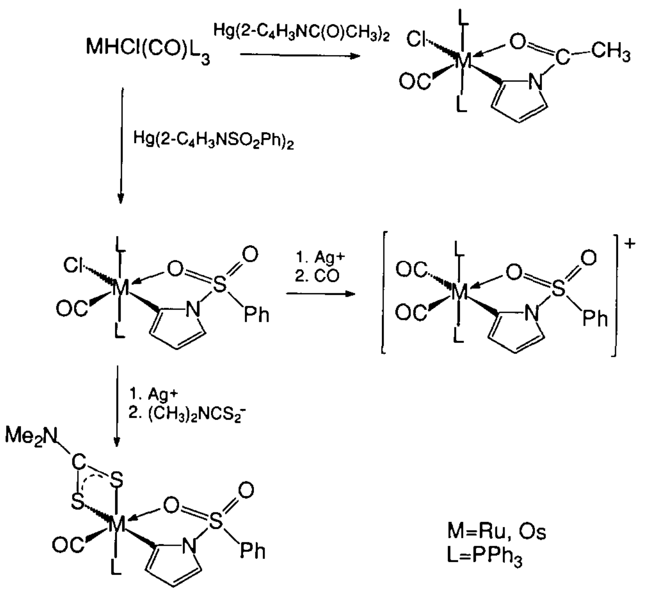
[a] Spectra recorded in $CDCl_3$ at 25°C. Chemical shifts (δ) are given in ppm and are referenced to $(CH_3)_4Si$ (internal standard, $\delta = 0.00$) for ^1H and ^{13}C spectra or 85% H_3PO_4 (external standard, $\delta = 0.00$) for ^{31}P spectra. Splitting patterns are indicated thus: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets; m, multiplet. [b] Tentative assignment: resonance of either pyrrolic quaternary carbon or acetyl carbon. [c] Tentative assignment: resonance of either pyrrolic quaternary carbon or *ipso* carbon of phenyl group. [d] Subscripts *o*, *m*, *p* and *i* refer to *ortho*, *meta*, *para* and *ipso* positions of the benzene ring. [e] Apparent singlet. [f] Complex splitting of patterns, assignments not made. [g] Third pyrrolic proton resonance presumably obscured by other resonances. [h] Other resonances presumably obscured by PPh_3 resonances. [i] Two doublet signals, chemical shift positions of all four signals given.



Scheme 2.

and the corresponding N-substituted pyrrole are also formed as products.

In the IR spectra of both of the *N*-acetylpyrrole derivatives $M(2\text{-}C_4H_3NC[O]CH_3)Cl(CO)(PPh_3)_2$ (M = Ru (**5**), Os (**6**)), the acetyl ν(CO) occurs at very low values (Table 1). This indicates that the acetyl oxygen interacts strongly with the metal centres in these complexes, thereby forming part of a chelate ring. In both **5** and **6** this chelate ring is probably planar since only a single resonance is observed in the ^{31}P NMR spectra of each compound (Table 2).

The low position of the ν(SO) bands in the IR spectra of the compounds $M(2\text{-}C_4H_3NSO[O]Ph)Cl(CO)(PPh_3)_2$ (M = Ru (**7**), Os (**8**)) indicates that an oxygen atom of the phenyl sulfonate group is coordinated to the metal centre in both cases. The observation of two doublet resonances in the ^{31}P NMR of both **7** and **8** (Table 2) indicates that the two PPh_3 ligands are inequivalent and the large coupling constant indicates a mutually *trans* arrangement. This is consistent with the *N*-phenylsulfonylpyrrolyl group forming a five-membered chelate ring in which the sulfur bound phenyl group is directed towards one PPh_3 ligand while the terminal oxo group is directed towards the other. A chelate ligand of this type has been found in the structure of $Ru(2\text{-}C_4H_3NSO[O]Ph)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**10**) (vide infra) which has been prepared by treatment of **7** with Ag^+ followed by the addition of $Me_2NCS_2^-$.

2.4. Reactions of N-acetyl and N-phenylsulfonylpyrrolyl complexes of ruthenium and osmium

The metal bound chloride in **7** is labile and on treatment with $AgSbF_6$, AgCl is precipitated. Treatment of the resulting cationic complex (which was not isolated) with CO yields the dicarbonyl cationic complex $[Ru(2\text{-}C_4H_3NSO[O]Ph)(CO)_2(PPh_3)_2]SbF_6$ (**9**). Treatment of **7** with $AgSbF_6$ and then sodium dimethyldithiocarbamate yields the neutral, monophosphine complex $Ru(2\text{-}C_4H_3NSO[O]Ph)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**10**) (Scheme 2). In this latter reaction one of the PPh_3 ligands is lost and both the dimethyldithiocarbamate and the *N*-phenylsulfonylpyrrolyl ligands adopt bidentate bonding modes.

Spectral data for **9** and **10** are collected in Tables 1 and 2. As for compounds **7** and **8**, the chelate *N*-phenylsulfonylpyrrolyl ligand is responsible for the inequivalence of the two PPh_3 ligands in **9**. This effect is clearly evident in both the ^{31}P and ^{13}C NMR spectra of **9**. IR absorption bands for **9** and **10** which are associated with the chelate *N*-phenylsulfonylpyrrolyl ligand appear in similar positions to those observed for **7** and **8**.

Preliminary attempts to selectively remove the *N*-phenylsulfonyl substituents from the pyrrolyl ligands in **7**, **8** and **9** were not successful.

2.5. Structures of $(C_4H_3NC[O]CH_3)HgCl$ (1), $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (2) and $Ru(2\text{-}C_4H_3NSO[O]Ph)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (10)

Single crystal X-ray structure determinations have been carried out for $(C_4H_3NC[O]CH_3)HgCl$ (**1**), $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (**2**) and $Ru(2\text{-}C_4H_3NSO[O]Ph)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**10**). The molecular geometries are depicted in Figs. 1, 2 and 3, respectively. Bond lengths and bond angles are listed in Tables 3–8.

In both the pyrrolylmercury derivatives **1** and **2**, the geometry about mercury is linear. In **2** the centrosymmetrically-related pyrrolyl rings are essentially copla-

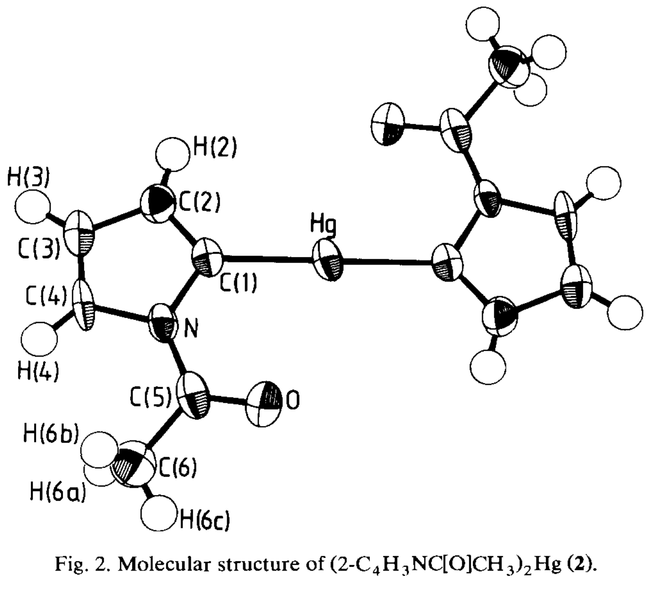


Fig. 2. Molecular structure of $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (**2**).

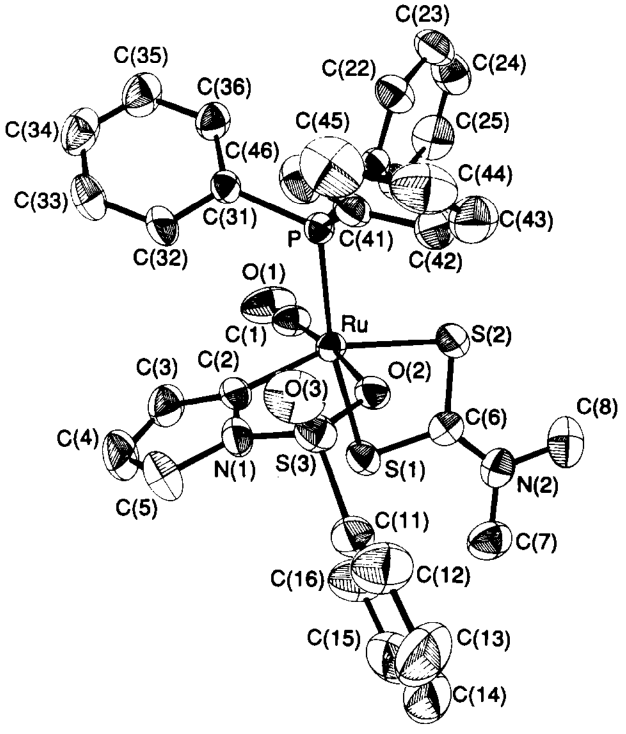


Fig. 3. Molecular structure of $\overline{\mathrm{Ru(2\text{-}C_4H_3NSO}}\mathrm{[O]Ph)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)}$ (**10**).

nar with the two acetyl oxygen atoms directed towards the mercury atom. The long Hg–O distance of 2.87(1) Å in this compound is slightly shorter than the Van der Waals distance of 2.90–3.13 Å and much longer than the sum of the covalent radii of oxygen and mercury (2.01–2.16 Å) [8], suggesting that any mercury–oxygen interaction here is weak. The corresponding Hg–O distance in **1** is shorter at 2.78(2) Å implying a slightly stronger Hg–O interaction in this compound. This is consistent with the observation that ν(CO) is observed in the IR spectrum at a lower value for **1** than it is for **2** (Table 1). Other bond distances and angles in **1** and **2** are normal.

The structure of $\overline{\mathrm{Ru(2\text{-}C_4H_3NSO}}\mathrm{[O]Ph)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)}$ (**10**) can be described in terms of a distorted octahedron. The *N*-phenylsulfonylpyrro-

Table 3
Interatomic distances (Å) for $(2\text{-}C_4H_3NC[O]CH_3)HgCl$ (**1**)

Hg–Cl	2.292(4)
Hg–C(1)	2.042(16)
O–C(5)	1.201(16)
N–C(1)	1.41(2)
N–C(4)	1.42(2)
N–C(5)	1.42(2)
C(1)–C(2)	1.36(2)
C(2)–C(3)	1.38(2)
C(3)–C(4)	1.38(2)
C(5)–C(6)	1.48(2)

Table 4
Bond angles (°) for $(2\text{-}C_4H_3NC[O]CH_3)HgCl$ (**1**)

Cl–Hg–C(1)	178.6(4)
C(1)–N–C(4)	109.1(11)
C(1)–N–C(5)	125.0(11)
C(4)–N–C(5)	125.8(12)
Hg–C(1)–N	121.1(9)
Hg–C(1)–C(2)	132.5(12)
N–C(1)–C(2)	106.3(14)
C(1)–C(2)–C(3)	109.7(14)
C(2)–C(3)–C(4)	109.7(13)
N–C(4)–C(3)	105.2(14)
O–C(5)–N	118.3(13)
O–C(5)–C(6)	124.6(15)
N–C(5)–C(6)	117.1(13)

Table 5
Interatomic distances (Å) for $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (**2**)

Hg–C(1)	2.068(9)	C(1)–C(2)	1.319(14)
O–C(5)	1.217(13)	C(2)–C(3)	1.459(17)
N–C(1)	1.412(12)	C(3)–C(4)	1.306(17)
N–C(4)	1.395(13)	C(5)–C(6)	1.525(18)
N–C(5)	1.386(14)		

Table 6
Bond angles (°) for $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (**2**)

C(1)–Hg–C(1)′	180.0	C(1)–C(2)–C(3)	108.8(10)
C(1)–N–C(4)	107.8(9)	C(2)–C(3)–C(4)	107.1(10)
C(1)–N–C(5)	125.6(9)	N–C(4)–C(3)	109.3(10)
C(4)–N–C(5)	126.6(10)	O–C(5)–N	121.6(11)
Hg–C(1)–N	120.8(7)	O–C(5)–C(6)	121.6(12)
Hg–C(1)–C(2)	132.1(7)	N–C(5)–C(6)	116.8(11)
N–C(1)–C(2)	107.1(8)		

Table 7
Interatomic distances (Å) for $\overline{\mathrm{Ru(2\text{-}C_4H_3NSO}}\mathrm{[O]Ph)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)}$ (**10**)

P–Ru	2.334(2)	C(12)–C(11)	1.363(10)
S(1)–Ru	2.451(2)	C(16)–C(11)	1.357(10)
S(2)–Ru	2.419(2)	C(13)–C(12)	1.378(12)
O(2)–Ru	2.240(4)	C(14)–C(13)	1.343(15)
C(1)–Ru	1.791(8)	C(15)–C(14)	1.344(14)
C(2)–Ru	2.051(7)	C(16)–C(15)	1.393(11)
C(21)–P	1.827(7)	C(22)–C(21)	1.387(9)
C(31)–P	1.834(6)	C(26)–C(21)	1.389(9)
C(41)–P	1.825(7)	C(23)–C(22)	1.374(10)
C(6)–S(1)	1.736(7)	C(24)–C(23)	1.357(11)
C(6)–S(2)	1.717(7)	C(25)–C(24)	1.367(11)
O(2)–S(3)	1.450(5)	C(26)–C(25)	1.389(10)
O(3)–S(3)	1.412(5)	C(32)–C(31)	1.387(9)
N(1)–S(3)	1.622(6)	C(36)–C(31)	1.383(9)
C(11)–S(3)	1.769(7)	C(33)–C(32)	1.374(9)
C(1)–O(1)	1.153(8)	C(34)–C(33)	1.365(11)
C(2)–N(1)	1.432(8)	C(35)–C(34)	1.353(11)
C(5)–N(1)	1.402(9)	C(36)–C(35)	1.380(9)
C(6)–N(2)	1.311(8)	C(42)–C(41)	1.400(9)
C(7)–N(2)	1.460(9)	C(46)–C(41)	1.378(9)
C(8)–N(2)	1.447(9)	C(43)–C(42)	1.369(10)
C(3)–C(2)	1.363(9)	C(44)–C(43)	1.376(11)
C(4)–C(3)	1.422(11)	C(45)–C(44)	1.362(11)
C(5)–C(4)	1.335(11)	C(46)–C(45)	1.382(10)

Table 8
Bond angles (°) for $\overline{\mathrm{Ru(2\text{-}C_4H_3NSO}}\mathrm{[O]Ph)\,(\eta^2\text{-}S_2CNMe_2)(CO)PPh_3}$ (**10**)

S(1) -Ru-P	98.3(1)	C(3)-C(2)-N(1)	103.0(6)
S(2) -Ru-P	170.1(1)	C(4)-C(3)-C(2)	111.6(8)
S(2) -Ru-S(1)	72.4(1)	C(5)-C(4)-C(3)	107.5(8)
O(2) -Ru-P	90.7(1)	C(4)-C(5)-N(1)	107.6(8)
O(2) -Ru-S(1)	87.7(1)	S(2)-C(6)-S(1)	112.9(4)
O(2) -Ru-S(2)	85.6(1)	N(2)-C(6)-S(1)	124.4(6)
C(1) -Ru-P	90.6(2)	N(2)-C(6)-S(2)	122.8(6)
C(1) -Ru-S(1)	100.1(3)	C(12) -C(11) -S(3)	117.5(6)
C(1) -Ru-S(2)	94.4(2)	C(16) -C(11) -S(3)	119.7(6)
C(1) -Ru-O(2)	171.8(3)	C(16) -C(11) -C(12)	122.7(8)
C(2) -Ru-P	99.9(2)	C(13) -C(12) -C(11)	117.4(10)
C(2) -Ru-S(1)	157.6(2)	C(14) -C(13) -C(12)	121.6(11)
C(2) -Ru-S(2)	88.5(2)	C(15) -C(14) -C(13)	120.0(10)
C(2) -Ru-O(2)	79.0(2)	C(16) -C(15) -C(14)	120.9(10)
C(2) -Ru-C(1)	92.8(3)	C(15) -C(16) -C(11)	117.4(9)
C(21)-P-Ru	115.6(2)	C(22) -C(21) -P	121.1(5)
C(31)-P-Ru	117.5(2)	C(26) -C(21) -P	121.6(5)
C(31)-P-C(21)	103.2(3)	C(26) -C(21) -C(22)	117.3(6)
C(41)-P-Ru	113.3(2)	C(23) -C(22) -C(21)	121.9(7)
C(41)-P-C(21)	100.9(3)	C(24) -C(23) -C(22)	119.8(8)
C(41)-P-C(31)	104.3(3)	C(25) -C(24) -C(23)	120.3(8)
C(6) -S(1)-Ru	85.6(2)	C(26) -C(25) -C(24)	120.2(8)
C(6) -S(2)-Ru	87.0(2)	C(25) -C(26) -C(21)	120.5(7)
O(3) -S(3)-O(2)	118.6(3)	C(32) -C(31) -P	118.2(5)
N(1) -S(3)-O(2)	103.5(3)	C(36) -C(31) -P	123.9(5)
N(1) -S(3)-O(3)	110.4(3)	C(36) -C(31) -C(32)	117.9(6)
C(11)-S(3)-O(2)	107.3(3)	C(33) -C(32) -C(31)	120.5(7)
C(11)-S(3)-O(3)	108.5(3)	C(34) -C(33) -C(32)	120.7(8)
C(11)-S(3)-N(1)	108.1(3)	C(35) -C(34) -C(33)	119.6(8)
S(3) -O(2)-Ru	119.2(2)	C(36) -C(35) -C(34)	120.8(8)
C(2) -N(1)-S(3)	121.5(5)	C(35) -C(36) -C(31)	120.6(7)
C(5) -N(1)-S(3)	127.8(6)	C(42) -C(41) -P	117.4(5)
C(5) -N(1)-C(2)	110.2(6)	C(46) -C(41) -P	124.6(6)
C(7) -N(2)-C(6)	121.7(7)	C(46) -C(41) -C(42)	117.9(7)
C(8) -N(2)-C(6)	122.0(7)	C(43) -C(42) -C(41)	120.1(7)
C(8) -N(2)-C(7)	116.3(6)	C(44) -C(43) -C(42)	121.8(8)
O(1) -C(1)-Ru	179.6(4)	C(45) -C(44) -C(43)	119.3(8)
N(1) -C(2)-Ru	115.3(4)	C(46) -C(45) -C(44)	120.3(8)
C(3) -C(2)-Ru	141.4(6)	C(45) -C(46) -C(41)	121.2(8)

lyl group is coordinated to ruthenium via C(2) and one of the sulfonate oxygen atoms. The other sulfonate oxygen atom projects above the resulting chelate ring, towards the PPh_3 ligand. The sulfonyl phenyl group is oriented below the chelate ring. The pyrrolyl ring and the sulfonate chelate ring are tilted slightly (4.8°) with respect to each other. The Ru-O(2) distance is 2.240(4) Å and this is similar to the Ru-O distances found in the dihapto-carboxylate complexes $Ru(\eta^2\text{-}O_2CCH_3)H(PPh_3)_3$ (2.198 and 2.210 Å) [9] and $Ru(\eta^2\text{-}O_2CCH_3)[\eta^1\text{-}CHN\text{-}p\text{-}tolyl](CO)(PPh_3)_2$ (2.173 and 2.279 Å) [10]. The Ru-C(2) distance of 2.051(7) Å is very close to the Ru-C(aryl) distances found in the σ-aryl complexes Ru(*p*-tolyl)Cl(CO)$(PPh_3)_2$ (2.056(3) Å) and Ru(*o*-tolyl)Cl(CO)$(PPh_3)_2$ (2.04(3) Å) [2].

3. Experimental details

The general experimental conditions were as described previously [11].

3.1. $(2\text{-}C_4H_3NC[O]CH_3)HgCl$ (1)

A solution of sodium acetate (7.14 g, 0.95 equiv.) in water (85 ml) was added to one of mercuric chloride (34.83 g, 1.4 equiv.) in methanol (400 ml). This mixture was then added simultaneously with *N*-acetylpyrrole (10 ml) to a rapidly stirred solution of methanol (30 ml) and water (20 ml). A white precipitate formed immediately. After the addition of methanol (200 ml) the mixture was filtered through Celite and the filtrate evaporated to dryness on a rotary evaporator. The resulting crude, white product was extracted with dichloromethane and the dichloromethane solution evaporated to dryness. The resulting white product was recrystallized three times from dichloromethane/ethanol/heptane to give an analytically pure sample of **1** (11.69 g, 37%), m.p. 218-219°C. Anal. (as 0.5 CH_2Cl_2 solvate, as confirmed by ^1H NMR) Found: C, 20.11; H, 1.69; N, 3.78. $C_6H_6ClHgNO\cdot(CH_2Cl_2)_{0.5}$ Calc.: C, 20.19; H, 1.82; N, 3.62%.

3.2. $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (2)

Compound **1** (2.7 g) was dissolved in acetone (500 ml) and sodium iodide (11.8 g, 10 equiv.) in acetone was added. An off-white precipitate formed immediately. The mixture was stirred at 20°C for 5 min and then filtered through Celite. Ethanol was added to the filtrate and the solvent volume reduced under reduced pressure to give an off-white crystalline product. This was collected, washed with water, ethanol and hexane and then recrystallized three times from dichloromethane/ethanol/heptane to give analytically pure **2** as white microcrystals (1.56 g, 95%), m.p. 211-212°C. Anal. (as 0.25 CH_2Cl_2 solvate, as confirmed by ^1H NMR) Found: C, 33.54; H, 2.73; N, 6.35. $C_{12}H_{12}HgN_2O_2\cdot(CH_2Cl_2)_{0.25}$ Calc.: C, 33.59; H, 2.88; N, 6.39%.

3.3. $(2\text{-}C_4H_3NSO[O]Ph)HgCl$ (3)

Solutions of mercuric chloride (3.15 g, 1.2 equiv.) in methanol (50 ml) and sodium acetate (1.58 g, 2 equiv.) in water (50 ml) were added to a solution of *N*-phenylsulfonylpyrrole (2.00 g) in methanol (200 ml). The resulting solution was heated under reflux for 30 h. A white precipitate slowly formed during this time. The precipitate was filtered and washed with methanol. The filtrate and washings were combined, ethanol added and the solvent volume lowered under reduced pressure to give a white solid. This was removed by filtration, washed with water ethanol and hexane and extracted with dichloromethane. The dichloromethane solution was evaporated to dryness and the resulting crude product recrystallized three times from dichloromethane/ethanol/hexane to give an analytically pure sample of **3** (1.45 g, 34%), m.p. 186–187°C. Anal. (as 1.00 CH_2Cl_2 solvate, as confirmed by ^1H NMR) Found: C, 37.49; H, 2.53; N, 4.16. $C_{10}H_8HgClNO_2S \cdot (CH_2Cl_2)$ Calc.: C, 37.56; H, 2.61; N, 4.27%.

3.4. $(2\text{-}C_4H_3NSO[O]Ph)_2Hg$ (4)

Compound **3** (2.4 g) was dissolved in acetone (650 ml) and sodium iodide (8.14 g, 10 equiv.) in acetone was added. An off-white precipitate formed immediately. The mixture was stirred at 20°C for 5 min and then filtered through Celite. The solid on the Celite pad was washed well with acetone and the filtrate and washings combined. Ethanol and heptane were added to the solution and the volume lowered under reduced pressure. The resulting white solid was removed by filtration and washed with water, ethanol and heptane. An analytically pure sample of **4** was obtained by recrystallization three times from dichloromethane/ethanol/heptane (1.20 g, 72%), m.p. 185–186°C. Anal. (as 0.75 C_2H_5OH solvate, as confirmed by ^1H NMR) Found: C, 36.45; H, 2.15; N, 4.16. $C_{20}H_{16}HgN_2O_4S_2 \cdot (C_2H_5OH)_{0.75}$ Calc.: C, 36.82; H, 2.61; N, 4.14%.

3.5. $\overline{Ru(2\text{-}C_4H_3NC[O}]CH_3)Cl(CO)(PPh_3)_2$ (5)

A mixture of $RuHCl(CO)(PPh_3)_3$ (1.00 g) and $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (**2**) (0.482 g, 1.10 equiv.) in benzene with heated under reflux for 54 h to give a green solution and a precipitate of elemental mercury. The solvent was removed under vacuum, the solid dissolved in dichloromethane and filtered through Celite. The resulting pale green solution was concentrated, placed on an alumina column (ca. 10 cm) and eluted with dichloromethane/hexane (9:1) to first remove unreacted **2** and then eluted with dichloromethane/ethyl acetate (8:2) to remove the pale yellow-green band which contained the product. After the addition of ethanol to this latter fraction the solvent volume was reduced in vacuo and the resulting pale yellow-green crystals collected. Recrystallization from dichloromethane/ethanol gave analytically pure **5** (0.604 g, 73%). Anal. (as 0.5 CH_2Cl_2 solvate, as confirmed by ^1H NMR) Found: C, 62.90; H, 4.56; N, 1.57. $C_{43}H_{36}ClNO_2P_2Ru \cdot (CH_2Cl_2)_{0.5}$ Calc.: C, 62.22; H, 4.44; N, 1.67%.

3.6. $\overline{Os(2\text{-}C_4H_3NC[O}]CH_3)Cl(CO)(PPh_3)_2$ (6)

A mixture of $OsHCl(CO)(PPh_3)_3$ (1.00 g) and $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (**2**) (0.454 g, 1.10 equiv.) in toluene was heated under reflux for 50 h to give a yellow solution and a precipitate of elemental mercury. The solvent volume was reduced in vacuo and ethanol added to precipitate a bright yellow product. This was removed by filtration and then redissolved in dichloromethane and eluted down an alumina column (ca. 10 cm) with dichloromethane/hexane (9:1). The yellow band was collected and pure **6** crystallized after addition of ethanol and reduction of the solvent volume under reduced pressure (0.789 g, 93%). Anal. Found: C, 58.64; H, 4.09; N, 1.69. $C_{43}H_{36}ClNO_2OsP_2$ Calc.: C, 58.27; H, 4.09; N, 1.69%.

3.7. $\overline{Ru(2\text{-}C_4H_3NSO}[O]Ph)Cl(CO)(PPh_3)_2$ (7)

A mixture of $RuHCl(CO)(PPh_3)_3$ (1.95 g) and $(2\text{-}C_4H_3NSO[O]Ph)_2Hg$ (**4**) (1.32 g, 1.05 equiv.) in benzene was heated under reflux for 40 h during which the solution turned yellow and elemental mercury was formed. The solution was cooled to 20°C and filtered through Celite. Ethanol was added to the solution and the solvent volume reduced in vacuo to give a yellow solid. This was removed by filtration and recrystallized three times from dichloromethane/ethanol to give analytically pure **7** (1.74 g, 95%). Anal. (as 1.00 H_2O solvate, as confirmed by ^1H NMR) Found: C, 61.57; H, 3.94; N, 2.00. $C_{47}H_{38}ClNO_3P_2RuS \cdot (H_2O)$ Calc.: C, 61.68; H, 4.19; N, 1.54%.

3.8. $\overline{Os(2\text{-}C_4H_3NSO}[O]Ph)Cl(CO)(PPh_3)_2$ (8)

A mixture of $OsHCl(CO)(PPh_3)_3$ (1.00 g) and $(2\text{-}C_4H_3NSO[O]Ph)_2Hg$ (**4**) (0.65 g, 1.10 equiv.) in toluene was heated under reflux for 5 h, during which the solution turned yellow and elemental mercury was formed. The solution was cooled to 20°C and filtered through Celite. Ethanol was added and the volume of the solution reduced in vacuo to precipitate a yellow solid. This was removed by filtration, redissolved in dichloromethane, loaded onto a silica gel column and eluted with dichloromethane/hexane (8:2). The yellow band was collected and crystallized with ethanol. Recrystallization two times from dichloromethane/ethanol gave analytically pure **8** (0.87 g, 92%). Anal. Found: C, 57.33; H, 4.09; N, 1.41. $C_{47}H_{38}ClNO_3OsP_2S$ Calc.: C, 57.34; H, 3.89; N, 1.42%.

3.9. $[\overline{Ru(2\text{-}C_4H_3NSO}[O]Ph)(CO)_2(PPh_3)_2]SbF_6$ (9)

$\overline{Ru(2\text{-}C_4H_3NSO}[O]Ph)Cl(CO)(PPh_3)_2$ (**7**) (1.00 g) was dissolved in dichloromethane and $AgSbF_6$ (0.403 g, 1.05 equiv.) in ethanol added. Carbon monoxide gas was then bubbled through the solution at 20°C for 5 min. The solution was filtered through Celite, isopropanol was added and the solvent volume reduced in vacuo to give a pale yellow solid. Recrystallization

Table 9
Crystal data for $(2\text{-}C_4H_3NC[O]CH_3)HgCl$ (**1**), $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (**2**) and $\overline{Ru(2\text{-}C_4H_3NSO}[O]Ph)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (**10**)

	1	**2**	**10**
Formula	$C_6H_6ClHgNO$	$C_{12}H_{12}HgN_2O_2$	$C_{32}H_{29}N_2O_3PRuS_3$
Molecular weight	344.16	416.84	717.83
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P2_1/n$	$P\bar{1}$
a (Å)	12.372(2)	9.4165(9)	9.9200(12)
b (Å)	10.289(1)	5.5525(3)	10.1257(11)
c (Å)	13.730(3)	11.4101(15)	16.1944(18)
α (°)	90.0	90.0	84.23(1)
β (°)	115.45(2)	90.88(1)	96.89(1)
γ (°)	90.0	90.0	102.19(1)
V (Å^3)	1578.2(5)	596.5(1)	1573.8(3)
Z	8	2	2
d(calc) (g cm^{-3})	2.90	2.32	1.51
F(000)	1232	388	732
μ (cm^{-1})	201.8	131.5	7.65
Radiation Mo Kα (monochromatic) λ (Å)	0.71069	0.71069	0.71069
Temperature (°C)	18	20	20
Diffractometer	Nonius CAD-4	Nonius CAD-4	Nonius CAD-4
Scan technique	ω–2θ	ω–2θ	ω–2θ
2θ (min–max)	2–60°	2–60°	2–50°
No. of unique reflections	3992	1445	4648
No. of observed reflections $I > 3\sigma(I)$	2992	971	2906
Crystal size (mm)	0.43 × 0.43 × 0.24	0.20 × 0.14 × 0.07	0.23 × 0.14 × 0.16
A (min–max)	0.451, 0.999	0.299, 0.993	0.889, 1.000
Least squares weights	$2.57/[\sigma^2(F) + 0.00164F^2]$	$1.36/[\sigma^2(F) + 0.00245F^2]$	$1.27/[\sigma^2(F) + 0.00035F^2]$
Function minimised	$\Sigma w[\lvert F_o\rvert - \lvert F_c\rvert]^2$	$\Sigma w[\lvert F_o\rvert - \lvert F_c\rvert]^2$	$\Sigma w[\lvert F_o\rvert - \lvert F_c\rvert]^2$
R and R'	0.062, 0.064	0.041, 0.043	0.040, 0.036

three times from dichloromethane/isopropanol/heptane gave analytically pure **9** (0.620 g, 49%). Anal. Found: C, 51.09; H, 3.58; N, 1.42. $C_{48}H_{38}F_6NO_4P_2RuSSb$ Calc.: C, 51.31; H, 3.41; N, 1.25%.

3.10. $\overline{Ru(2\text{-}C_4H_3NSO}[O]Ph)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (10)

$\overline{Ru(2\text{-}C_4H_3NSO}[O]Ph)Cl(CO)(PPh_3)_2$ (**7**) (0.200 g) was dissolved in dichloromethane and $AgSbF_6$ (0.077 g, 1.05 equiv.) in ethanol added. The solution was stirred for 1 min and the AgCl precipitated was removed by filtration through Celite. Sodium dimethyldithiocarbamate (0.224 g, 7 equiv.) was added to the yellow filtrate. The solution was stirred at 20°C for 1.5 h, ethanol was added and the solvent volume reduced in vacuo to give a pale yellow solid. Recrystallization two times from dichloromethane/ethanol gave analytically pure **10** (0.155 g, 91%). Anal. (as 1.00 C_2H_5OH solvate, as confirmed by ^1H NMR) Found: C, 53.03; H, 4.49; N, 3.96. $C_{32}H_{29}CN_2O_3PRuS_3 \cdot (C_2H_5OH)$ Calc.: C, 53.46; H, 4.62; N, 3.67%.

3.11. X-Ray diffraction studies of $(C_4H_3NC[O]CH_3)HgCl$ (1) $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (2) and $\overline{Ru(2\text{-}C_4H_3NSO}[O]Ph)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)$ (10)

Crystal data

Details of crystal data and intensity collection parameters are given in Table 9. Unit cell parameters were obtained from least squares fits to the four circle

Table 10
Atomic coordinates for $(2\text{-}C_4H_3NC[O]CH_3)HgCl$ (**1**)

	x	y	z
Hg	0.08256(5)	−0.07904(5)	0.41588(4)
Cl	0.0470(4)	0.1383(4)	0.4245(4)
O	0.1728(11)	−0.1269(11)	0.2654(10)
N	0.1613(9)	−0.3196(11)	0.3376(9)
C(1)	0.1103(11)	−0.2731(14)	0.4050(10)
C(2)	0.0946(13)	−0.3787(17)	0.4573(14)
C(3)	0.1322(15)	−0.4890(13)	0.4237(15)
C(4)	0.1721(15)	−0.4565(17)	0.3473(14)
C(5)	0.1913(12)	−0.2417(12)	0.2679(10)
C(6)	0.2415(19)	−0.3088(20)	0.2013(16)

Table 11
Atomic coordinates for $(2\text{-}C_4H_3NC[O]CH_3)_2Hg$ (**2**)

	x	y	z
Hg	0.0	0.0	0.0
O	−0.0929(9)	0.2137(14)	0.2148(7)
N	0.0935(10)	0.4306(16)	0.1471(8)
C(1)	0.1269(10)	0.2880(17)	0.0489(8)
C(2)	0.2413(12)	0.3822(21)	0.0019(11)
C(3)	0.2854(13)	0.5908(24)	0.0712(11)
C(4)	0.1945(13)	0.6137(20)	0.1558(10)
C(5)	−0.0218(13)	0.3965(22)	0.2193(10)
C(6)	−0.0517(16)	0.5948(28)	0.3080(14)

coordinates of 25 reflections determined on a Nonius CAD-4 diffractometer. Intensity data collections used graphite monochromated Mo Kα radiation (λ = 0.71069 Å) and employed 2θ–ω scans with a peak to background were count time of 2:1. The omega scan angles were 0.80 + 0.347 tan θ. Reflections were counted for 60 s or until $\sigma(I)/I$ was 0.02. Three reflections were monitored throughout data collections as checks on crystal alignment and decomposition. The intensities of the standards for **2** and **10** fell to ~ 90% of their initial values during the course of data collection, and the raw intensities were scaled accordingly. The data sets were corrected for Lorentz, polarization and absorption [12] effects using locally written programs and equivalent reflections were averaged.

Table 12
Atomic coordinates for $\overline{\mathrm{Ru}(2\text{-}\mathrm{C_4H_3NSO}}[\mathrm{O}]\mathrm{Ph})(\eta^2\text{-}\mathrm{S_2CNMe_2})(\mathrm{CO})(\mathrm{PPh_3})$, (**10**)

	x	*y*	*z*
Ru	0.35826(6)	0.22659(6)	0.18870(4)
P	0.42218(18)	0.32828(17)	0.31447(11)
S(1)	0.52643(19)	0.07757(19)	0.20523(12)
S(2)	0.3121(2)	0.09080(19)	0.06998(11)
S(3)	0.06616(19)	0.06341(18)	0.24580(11)
O(1)	0.5162(6)	0.4658(5)	0.0991(3)
O(2)	0.2116(4)	0.0571(4)	0.2507(2)
O(3)	0.0097(5)	0.0770(5)	0.3198(3)
N(1)	0.0530(5)	0.1918(5)	0.1790(3)
N(2)	0.4412(6)	−0.1176(6)	0.0974(3)
C(1)	0.4541(7)	0.3721(7)	0.1340(4)
C(2)	0.1730(7)	0.2859(6)	0.1539(3)
C(3)	0.1179(9)	0.3849(7)	0.1070(4)
C(4)	−0.0293(10)	0.3551(9)	0.1015(5)
C(5)	−0.0678(8)	0.2378(8)	0.1462(5)
C(6)	0.4283(6)	−0.0012(6)	0.1211(4)
C(7)	0.3476(8)	−0.1840(7)	0.0304(4)
C(8)	0.5437(9)	−0.1909(8)	0.1390(5)
C(11)	−0.0297(7)	−0.0848(6)	0.2012(4)
C(12)	−0.1109(8)	−0.1770(8)	0.2510(5)
C(13)	−0.1741(11)	−0.2986(10)	0.2191(8)
C(14)	−0.1592(11)	−0.3244(10)	0.1413(9)
C(15)	−0.0823(9)	−0.2301(10)	0.0924(7)
C(16)	−0.0143(8)	−0.1063(8)	0.1218(5)
C(21)	0.6054(6)	0.3484(6)	0.3535(4)
C(22)	0.6489(7)	0.3622(6)	0.4375(4)
C(23)	0.7864(8)	0.3785(7)	0.4678(4)
C(24)	0.8837(8)	0.3828(8)	0.4149(5)
C(25)	0.8454(8)	0.3684(8)	0.3318(5)
C(26)	0.7067(7)	0.3519(6)	0.3007(4)
C(31)	0.3869(6)	0.4980(6)	0.3188(3)
C(32)	0.2565(7)	0.5206(7)	0.2878(4)
C(33)	0.2256(9)	0.6467(8)	0.2880(4)
C(34)	0.3233(10)	0.7524(8)	0.3173(5)
C(35)	0.4509(9)	0.7320(7)	0.3480(4)
C(36)	0.4838(7)	0.6060(6)	0.3492(4)
C(41)	0.3410(6)	0.2287(6)	0.4023(3)
C(42)	0.3666(7)	0.0978(6)	0.4217(4)
C(43)	0.3029(8)	0.0155(7)	0.4841(4)
C(44)	0.2118(9)	0.0584(9)	0.5279(4)
C(45)	0.1873(8)	0.1861(9)	0.5103(5)
C(46)	0.2518(7)	0.2709(7)	0.4481(4)

The structures were solved by Patterson and difference Fourier techniques and refined by full-matrix least squares [13]. Atomic scattering factors were for neutral atoms [14]. After initial isotropic refinement all atoms were allowed to assume anisotropic motion. Hydrogen atoms were included in calculated positions, assuming a C–H distance of 0.95 Å and allowed to ride on the atom to which they were bonded with a common thermal parameter. Final refinement details are included in Table 9. Atomic coordinates of **1**, **2** and **10** are given in Tables 10, 11 and 12, respectively. Supplementary data available from the authors (G.R.C.) consists of hydrogen atom positions, anisotropic thermal parameters and observed and calculated structure factor listings.

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