J. CHEM. SOC. DALTON TRANS. 1990

Complexes of the Platinum Metals. Part 39.[1] Salicylaldehydato(2−) Derivatives of Ruthenium, Osmium, and Iridium. *X*-Ray Crystal Structures of $[Ru(OC_6H_4CO)(HOC_6H_4CH_2OH)(CO)(PPh_3)_2]\cdot CH_2Cl_2$ and $[Ru(OC_6H_4CO)(MeOH)(CO)(PPh_3)_2]\cdot MeOH$ *

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Salicylaldehyde reacts with $[RuH_2(CO)(PPh_3)_3]$ in refluxing toluene to afford a ruthenium(II) salicylaldehydato(2−) complex which crystallised from CH_2Cl_2–light petroleum as a dichloromethane-solvated *o*-hydroxybenzyl alcohol adduct $[Ru(OC_6H_4CO)(HOC_6H_4CH_2OH)(CO)(PPh_3)_2]\cdot CH_2Cl_2$, and from CH_2Cl_2–MeOH as the methanol- solvated methanol adduct $[Ru(OC_6H_4CO)(MeOH)(CO)(PPh_3)_2]\cdot MeOH$. Formation of the *o*-hydroxybenzyl alcohol adduct clearly implies the ruthenium-mediated reduction of the CHO group in salicylaldehyde. Carbon monoxide and pyridine react with $[Ru(OC_6H_4CO)(MeOH)(CO)(PPh_3)_2]\cdot MeOH$ to form $[Ru(OC_6H_4CO)L(CO)(PPh_3)_2]$ (L = CO or py respectively). The reaction of salicylaldehyde with $[OsH_2(CO)(PPh_3)_3]$ includes a carbonylation step and affords $[Os(OC_6H_4CO)(CO)_2(PPh_3)_2]$. Reactions of $[RhH(PPh_3)_4]$ and *mer*-$[IrH_3(PPh_3)_3]$ with salicylaldehyde in boiling toluene afford $[Rh(OC_6H_4CHO)(CO)(PPh_3)_2]$ and $[Ir(OC_6H_4CO)H(CO)(PPh_3)_2]$ respectively. *X*-Ray diffraction studies on $[Ru(OC_6H_4CO)(HOC_6H_4CH_2OH)(CO)(PPh_3)_2]\cdot CH_2Cl_2$ and $[Ru(OC_6H_4CO)(MeOH)(CO)(PPh_3)_2]\cdot MeOH$ establish the presence of O,C-chelated salicylaldehydate(2−) ligands in both cases and a monodentate *o*-hydroxybenzyl alcohol ligand in the former complex.

Salicylaldehyde (HOC_6H_4CHO, H_2sal) is a dibasic acid and as such can function as a neutral (H_2sal), monobasic ($OC_6H_4CHO^-$, $Hsal^-$), or dibasic ($OC_6H_4CO^{2-}$, sal^{2-}) ligand. Most platinum-metal salicylaldehyde derivatives involve the OO′ chelate $Hsal^-$ anionic ligand, *e.g.* $[Ru(Hsal)_2(diene)]$ {diene = barrelene (bicyclo[2.2.2]octa-2,5,7-triene)[2] or cyclo-octa-1,5-diene[3]}, $[Ru(Hsal)_2(CO)_2(N\text{-}N)]$ (N–N = 2,2′-bipyridyl or 1,10-phenanthroline),[4] $[Ru(Hsal)_2(CO)_2]$,[5] $[RuH(Hsal)(CO)(PPh_3)_2]$,[6] $[Rh(Hsal)(diene)]$ {diene = cyclo-octa-1,5-diene, norbornadiene, or tetrafluorobenzobarrelene (tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene)},[7,8] $[Rh(Hsal)(CO)(PPh_3)_2]$,[9] $[Ir(Hsal)(CO)(PPh_3)_2(O_2)]$,[10] $[Pd(Hsal)(allyl)]$,[11] $[Pd(Hsal)(C_6H_4NMe_2\text{-}o)]$,[12] $[PtMe_2(Hsal)_2]$,[13,14] $[NBu_4][PtBr_2Me_2(Hsal)]$,[15] and $[\{PtMe_3(Hsal)\}_2]$.[16–18] Platinum-metal salicylaldehyde derivatives containing the O,C chelate sal^{2-} dianionic ligand are far less common. The first and, to the best of our knowledge, only published examples are the palladium(II) and platinum(II) species $[M(OC_6H_4CO)L(L')]$ (L,L′ = N-, P-, or As-donor ligands)[19,20] one of which, $[Pt(OC_6H_4CO)\{P(C_6H_4Me\text{-}o)_3\}_2]$, has been characterised by diffraction methods.[20] Whereas most of the above-mentioned complexes were obtained from reactions between metal chlorides and sodium, potassium, or thallium salicylaldehydates, the new complexes reported in the present work are formed by direct reactions between metal hydrides and free salicylaldehyde. Reactions of this type presumably involve insertion of metal into aroyl RC(O)–H bonds, a process similar to that proposed for the decarbonylation of aldehydes by certain platinum-metal complexes, and provide further examples of aroyl intermediates stabilised by chelate-ring formation.[21]

Experimental

Hydride complexes were prepared as previously described. Salicylaldehyde was used as purchased. Reagent-grade organic solvents were dried over molecular sieves. The light petroleum used has a boiling range of 60—80 °C. Reactions were performed under a nitrogen atmosphere but products were worked up in open flasks. Elemental analyses were performed by the microanalytical service at University College, London. Melting points were taken in sealed tubes under nitrogen. Spectroscopic data are given in Table 1.

Carbonyl(2-hydroxybenzyl alcohol)[salicylaldehydato(2−)]bis(triphenylphosphine)ruthenium–Dichloromethane (1/1).—Carbonyldihydridotris(triphenylphosphine)ruthenium (0.7 g, 0.76 mmol) and salicylaldehyde (0.29 g, 2.4 mmol) were heated together under reflux in toluene (30 cm^3) for 13 h. The yellow-brown solution was cooled to ambient temperature, filtered, and then concentrated under reduced pressure to leave an oil which was solidified by dissolving in dichloromethane and reprecipitating by slow addition of light petroleum. Crystallisation using the same solvent combination gave yellow crystals (0.55 g, 85%), m.p. 150—154 °C (Found: C, 64.0; H, 4.5. Calc. for $C_{51}H_{42}O_5P_2Ru\cdot CH_2Cl_2$: C, 63.7; H, 4.35%).

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* Carbonyl(2-hydroxybenzyl alcohol-*O*)[salicylaldehydato(2−)-*CO*^{2}]-bis(triphenylphosphine)ruthenium(II)–dichloromethane (1/1) and carbonyl(methanol)[salicylaldehydato(2−)-*CO*^{2}]bis(triphenylphosphine)ruthenium(II)–methanol (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.

Table 1. Spectroscopic data

	Compound	I.r. (cm^{-1})^a	^{1}H N.m.r.^{b} (δ)	^{31}P-{^{1}H} N.m.r.^{c} (δ/p.p.m.)
(**1a**)	$[\overline{\mathrm{Ru(OC_6H_4C}}\mathrm{O)(HOC_6H_4CH_2OH)(CO)(PPh_3)_2]\cdot CH_2Cl_2}$	ν(CO) 1 925, ν(CO)$_{sal}$ 1 590, 1 525	7.5—7.3 (C_6H_5), 6.98 (d), 6.70 (t), 6.18 (t), 6.03 (d) (OC_6H_4CO), 7.12 (t), 6.93 (d), 6.77 (t), 6.75 (d) ($HOC_6\mathit{H}_4CH_2OH$), 5.29 (s) (CH_2Cl_2), 4.60 (s) ($HOC_6H_4C\mathit{H}_2OH$), 3.00 (s) ($HOC_6H_4CH_2OH$)	34.76 (s) (PPh_3)
(**1b**)	$\overline{\mathrm{Ru(OC_6H_4C}}\mathrm{O)(MeOH)(CO)(PPh_3)_2]\cdot MeOH}$	ν(CO) 1 930, ν(CO)$_{sal}$ 1 590, 1 530	7.5—7.3 (C_6H_5), 6.97 (d), 6.69 (t), 6.13 (t), 5.98 (d) (OC_6H_4CO), 3.47 ($C\mathit{H}_3OH$ co-ordinated), 1.73 ($C\mathit{H}_3OH$ solvated)	34.8 (s) (PPh_3)
(**2**)	$[\overline{\mathrm{Ru(OC_6H_4C}}\mathrm{O)(CO)_2(PPh_3)_2]\cdot MeOH}$	ν(CO) 2 040, 1 970 ν(CO)$_{sal}$ 1 600—1 590, 1 560	*ca.* 7.5—7.3 (C_6H_5) 6.49 (t), 6.42 (d), 6.05 (d), 5.82 (t) (OC_6H_4CO), 1.71 (s) ($C\mathit{H}_3OH$ solvated)	28.48 (s)
(**3**)	$[\overline{\mathrm{Ru(OC_6H_4C}}\mathrm{O)(CO)(py)(PPh_3)_2]\cdot MeOH}$	ν(CO) 1 902, ν(CO)$_{sal}$ 1 590, 1 560	*ca.* 7.5—7.1 (C_6H_5), 6.75 (d), 6.50 (t), 5.90 (m) ($OC_6H_4CO + C_5H_5N$)	33.65 (s) (PPh_3)
(**4**)	$[\overline{\mathrm{Os(OC_6H_4C}}\mathrm{O)(CO)_2(PPh_3)_2]\cdot MeOH}$	ν(CO) 2 020, 1 955, ν(CO)$_{sal}$ 1 595, 1 550	*ca.* 7.6—7.2 (C_6H_5), 6.50 (t), 6.45 (d), 6.02 (d), 5.85 (t), (OC_6H_4CO), 1.6 (s) ($C\mathit{H}_3OH$ solvated)^d	1.97 (s) (PPh_3)^d
(**5**)	$\mathrm{[Rh(OC_6H_4CHO)(CO)(PPh_3)_2]\cdot 0.25CH_2Cl_2}$	ν(CO) 1 980 (vbr), ν(CO)$_{sal}$ obscured	*ca.* 12.15 (s) ($OC_6H_4C\mathit{H}O$), *ca.* 7.70 and 7.35 (C_6H_5), 7.02 (t), 6.90 (d), 6.45 (d), 6.38 (t) ($OC_6\mathit{H}_4CHO$)	32.48 (d) (PPh_3), $J(^{103}\mathrm{Rh}-^{31}\mathrm{P})$ 135
(**6**)	$[\overline{\mathrm{Ir(OC_6H_4C}}\mathrm{O)H(CO)(PPh_3)_2]\cdot MeOH}$	ν(IrH) 2 100, ν(CO) 2 030, ν(CO)$_{sal}$ obscured	*ca.* 7.6—7.0 (m) (C_6H_5), 6.9 (t), 6.6 (d), 6.25 (t) (OC_6H_4CO), *ca.* 1.6 ($C\mathit{H}_3OH$ solvated), −8.64 (d of d), $J(\mathrm{PH})_{cis}$ 19.5, $J(\mathrm{PH})_{trans}$ 148.5	−4.77 (d), −7.24 (d), $^2J(\mathrm{PP'})$ 20

[a] Nujol mulls. [b] In $CDCl_3$ (unless otherwise specified) at 360 MHz and referenced against internal $SiMe_4$; *J* in Hz. [c] In $CDCl_3$ (unless otherwise specified) at 101.25 MHz and referenced against external 85% H_3PO_4; *J* in Hz. [d] In CD_2Cl_2.

Carbonyl(methanol)[salicylaldehydato(2 −)]bis(triphenylphosphine)ruthenium(II)*-Methanol* (1/1).—Carbonyldihydridotris(triphenylphosphine)ruthenium (0.6 g, 0.65 mmol) and salicylaldehyde (0.09 g, 0.74 mmol) were heated under reflux in toluene (30 cm^3) for 2 h. The yellow-brown solution was filtered and then concentrated under reduced pressure to leave an oil. Crystallisation from dichloromethane–methanol afforded yellow crystals (0.44 g, 74%), m.p. 194–196 °C (Found: C, 65.6; H, 4.75. Calc. for $C_{45}H_{38}O_4P_2Ru\cdot CH_3OH$: C, 65.9; H, 5.0%).

Dicarbonyl[salicylaldehydato(2 −)]bis(triphenylphosphine)ruthenium(II)*-Methanol* (1/1).—Carbonyl(methanol)[salicylaldehydato(2 −)]bis(triphenylphosphine)ruthenium (0.5 g, 0.62 mmol) was dissolved in toluene (30 cm^3) and heated under reflux with slow passage of carbon monoxide for 3 h. The solution was then cooled to ambient temperature and concentrated under reduced pressure to leave an oil. Crystallisation from dichloromethane–methanol afforded yellow crystals (0.38 g, 94%), m.p. 246—250 °C (Found: C, 67.4; H, 4.25. Calc. for $C_{45}H_{34}O_4P_2Ru\cdot CH_3OH$: C, 67.4; H, 4.25%).

Carbonyl(pyridine)[salicylaldehydato(2 −)]bis(triphenylphosphine)ruthenium(II)*-Methanol*(1/1).—Carbonyl(methanol)-[salicylaldehydato(2 −)]bis(triphenylphosphine)ruthenium (0.5 g, 0.62 mmol) and pyridine (0.4 g, 6.3 mmol) were heated together under reflux in toluene (30 cm^3) for 3 h. The yellow solution was cooled to ambient temperature and then concentrated under reduced pressure to leave an oil which was solidified by dissolving in dichloromethane and reprecipitating by slow addition of light petroleum. Crystallisation from the same solvent pair gave a pale yellow microcrystalline powder (0.3 g, 74%), m.p. 165—168 °C (Found: C, 68.45; H, 4.45; N, 1.65. Calc. for $C_{49}H_{39}NO_3P_2Ru\cdot CH_3OH$: C, 69.0; H, 4.55; N, 1.65%).

Dicarbonyl[salicylaldehydato(2 −)]bis(triphenylphosphine)osmium(II)*-Methanol*(1/1).—Carbonyldihydridotris(triphenylphosphine)osmium (0.42 g, 0.42 mmol) and salicylaldehyde (0.23 g, 1.8 mmol) were heated together under reflux in toluene (30 cm^3) for 13 h. The yellow-brown solution was cooled to ambient temperature, filtered, and then concentrated under reduced pressure to leave an oil. Crystallisation from dichloromethane–methanol afforded yellow crystals (0.3 g, 80%), m.p. 232—235 °C (Found: C, 59.85; H, 3.75. Calc. for $C_{45}H_{34}O_4OsP_2\cdot CH_3OH$: C, 60.65; H, 3.85%).

Carbonyl[salicylaldehydato(1 −)]bis(triphenylphosphine)rhodium(I)*-Dichloromethane* (4/1).—Hydrotetrakis(triphenylphosphine)rhodium (0.35 g, 0.33 mmol) and salicylaldehyde (0.17 g, 1.4 mmol) were heated under reflux in toluene (30 cm^3) for 3 h. The yellow-brown solution was cooled to ambient temperature, filtered, and then concentrated under reduced pressure to leave an oil. Crystallisation from dichloromethane–methanol afforded yellow microcrystals (0.23 g, 63%), m.p. 123—125 °C (Found: C, 66.15; H, 4.5. Calc. for $C_{44}H_{35}O_3P_2Rh\cdot 0.25CH_2Cl_2$: C, 66.55; H, 4.6%).

Carbonylhydrido[salicylaldehydato(2 −)]bis(triphenylphosphine)iridium(III).—*mer*-Trihydrotris(triphenylphosphine)iridium (0.23 g, 0.3 mmol) and salicylaldehyde (0.17 g, 1.4 mmol) were heated together under reflux in toluene (30 cm^3) for 4 h. The yellow-brown solution was cooled to ambient temperature, filtered, and then concentrated under reduced pressure to leave an oil. Crystallisation from dichloromethane–methanol afforded yellow microcrystals (0.12 g, 66%), 165—169 °C (Found: C, 61.2; H, 4.05. Calc. for $C_{44}H_{35}IrO_3P_2$: C, 61.05; H, 4.05%).

A similar reaction using carbonylhydridotris(triphenylphosphine)iridium(I) as the iridium precursor gave an identical product (50%).

Crystallography.—Crystal data for $[\overline{\mathrm{Ru(OC_6H_4C}}\mathrm{O)(\mathit{o}\text{-}HOC_6H_4CH_2OH)(CO)(PPh_3)_2]\cdot CH_2Cl_2}$, (**1a**), $C_{51}H_{42}O_5P_2Ru\cdot CH_2Cl_2$, $M = 881.766$, monoclinic, $a = 12.029(3)$, $b =$

Table 2. Fractional atomic-co-ordinates (× 10^4) for $[\overline{\text{Ru}(\text{OC}_6\text{H}_4\text{C}}\text{O})(\text{HOC}_6\text{H}_4\text{CH}_2\text{OH})(\text{CO})(\text{PPh}_3)_2]\cdot\text{CH}_2\text{Cl}_2$

Atom	*x*	*y*	*z*
Ru	1 174.4(4)	2 470.4(3)	9 064.0(2)
Cl(1)	5 455(2)	−136(1)	12 527(1)
Cl(2)	6 999(3)	483(2)	11 853(2)
P(1)	2 876.5(11)	2 509.7(9)	8 673.5(6)
P(2)	−575.2(11)	2 492.4(9)	9 401.5(6)
O(1)	687(4)	3 933(2)	8 699(3)
O(2)	2 441(3)	3 211(2)	10 337(2)
O(3)	1 544(3)	1 454(2)	9 365(2)
O(4)	102(3)	1 896(2)	8 036(2)
O(5)	−977(4)	1 415(3)	6 501(3)
C(1)	869(5)	3 366(3)	8 825(3)
C(2)	2 146(4)	2 655(3)	10 039(3)
C(3)	2 547(5)	2 012(3)	10 404(3)
C(4)	2 198(5)	1 414(3)	10 013(3)
C(5)	3 249(6)	1 954(4)	11 095(3)
C(6)	3 580(6)	1 326(4)	11 386(4)
C(7)	3 265(6)	740(4)	10 994(4)
C(8)	2 579(6)	774(3)	10 318(4)
C(9)	337(6)	1 212(4)	7 848(4)
C(10)	−750(5)	808(3)	7 524(3)
C(11)	−1 164(8)	299(4)	7 894(4)
C(12)	−2 128(8)	−78(4)	7 565(5)
C(13)	−2 707(7)	44(4)	6 892(5)
C(14)	−2 352(6)	531(3)	6 527(4)
C(15)	−1 397(5)	920(3)	6 837(3)
C(16)	6 861(8)	141(6)	12 620(5)
C(111)	3 617(3)	3 336(2)	8 720(2)
C(112)	3 502(3)	3 831(2)	9 196(2)
C(113)	4 059(3)	4 458(2)	9 223(2)
C(114)	4 731(3)	4 591(2)	8 775(2)
C(115)	4 846(3)	4 096(2)	8 299(2)
C(116)	4 288(3)	3 468(2)	8 272(2)
C(121)	4 046(3)	1 935(2)	9 115(2)
C(122)	5 095(3)	2 189(2)	9 540(2)
C(123)	5 969(3)	1 741(2)	9 890(2)
C(124)	5 796(3)	1 039(2)	9 815(2)
C(125)	4 747(3)	785(2)	9 390(2)
C(126)	3 872(3)	1 233(2)	9 040(2)
C(131)	2 556(3)	2 310(2)	7 745(2)
C(132)	3 168(3)	1 824(2)	7 483(2)
C(133)	2 848(3)	1 684(2)	6 771(2)
C(134)	1 916(3)	2 029(2)	6 320(2)
C(135)	1 305(3)	2 514(2)	6 582(2)
C(136)	1 625(3)	2 655(2)	7 294(2)
C(211)	−658(4)	1 896(2)	10 085(2)
C(212)	−483(4)	1 203(2)	9 992(2)
C(213)	−537(4)	735(2)	10 506(2)
C(214)	−766(4)	960(2)	11 113(2)
C(215)	−942(4)	1 652(2)	11 206(2)
C(216)	−888(4)	2 120(2)	10 692(2)
C(221)	−1 001(3)	3 301(2)	9 722(2)
C(222)	−2 172(3)	3 470(2)	9 582(2)
C(223)	−2 496(3)	4 059(2)	9 869(2)
C(224)	−1 649(3)	4 478(2)	10 297(2)
C(225)	−478(3)	4 309(2)	10 437(2)
C(226)	−154(3)	3 720(2)	10 149(2)
C(231)	−1 828(4)	2 317(2)	8 652(2)
C(232)	−2 513(4)	1 735(2)	8 605(2)
C(233)	−3 428(4)	1 616(2)	8 007(2)
C(234)	−3 659(4)	2 078(2)	7 455(2)
C(235)	−2 974(4)	2 660(2)	7 502(2)
C(236)	−2 059(4)	2 780(2)	8 101(2)

19.613(3), $c = 20.049(2)$ Å, $U = 4\,529.37$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.29$ g cm^{-3}, $F(000)$ 1 840, $\mu(\text{Mo-}K_\alpha) = 2\,574$ cm^{-1}.

Data collection. Intensity data were recorded on a Nonius CAD4 diffractometer in a standard manner[22] using Mo-K_α radiation [graphite monochromatised $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å] and a ω—2θ scan mode with $1.5 < \theta < 25.0°$. A total of 8 786 reflections were measured, of which 7 956 were unique and 4 212 satisfied the condition $F_o > 3\sigma(F_o)$.

Structure solution. The structure was solved *via* the heavy-atom method and refined by least squares. In the refinement the C_6H_5 groups were treated as rigid bodies with hexagonal C_6 units and C–C and C–H distances of 1.395 and 0.96 Å respectively. All other hydrogens, including those on the hydroxy groups of *o*-hydroxybenzyl alcohol, were experimentally located, but those on methylene carbon atoms were included in idealised positions. Hydroxy hydrogens were refined with individual isotropic thermal parameters. An ordered dichloromethane molecule of solvation was also identified and the atoms refined normally. The final *R* and *R′* values are 0.050 and 0.0496 respectively. Final atomic fractional co-ordinates are given in Table 2.

Crystal data for $[\overline{\text{Ru}(\text{OC}_6\text{H}_4\text{C}}\text{O})(\text{MeOH})(\text{CO})(\text{PPh}_3)_2]\cdot$MeOH, (**1b**), $C_{45}H_{38}O_4P_2Ru\cdot CH_3OH$, $M = 825.841$, orthorhombic, $a = 9.467(3)$, $b = 12.329(2)$, $c = 33.983(3)$ Å, $U = 3\,966.45$ Å^3, space group $P2_12_12_1$, $Z = 4$, $D_c = 1.39$ g cm^{-3}, $F(000)$ 1 712, $\mu(\text{Mo-}K_\alpha) = 5.09$ cm^{-1}.

Data collection. Intensity data were recorded as for compound (**1a**). A total of 4 089 reflections were measured, of which 3 951 were unique and 3 604 satisfied the condition $F_o > 3\sigma(F_o)$.

Structure solution. The structure was solved *via* the heavy-atom method and refined by least squares. The C_6H_5 groups were treated as for compound (**1a**). In this structure a methanol molecule of solvation was located and the component atoms included with the normal refinement. The final *R* and *R′* values are 0.0663 and 0.0851 respectively. Final atomic fractional co-ordinates are given in Table 3. Details of computers, programs, and atomic scattering factors for both structure solutions are as given in ref. 23.

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

Results and Discussion

Oxidative addition of an aldehydic RC(O)–H bond across a metal centre followed by migratory extrusion of CO from the resultant acyl (or aroyl) ligand have long been accepted as key steps in the catalytic or stoicheiometric decarbonylation of aldehydes by certain transition metals. However, isolation of the acyl or aroyl intermediates proved difficult and was first achieved by use of chelating ligands in which the acyl (or aroyl) group formed part of a metallocycle.[21] More recently salicylaldehyde has been shown[19,20] to undergo a similar cyclometallation reaction to give metallocycles of the form $[\overline{\text{M}(\text{OC}_6\text{H}_4\text{C}}\text{O})\text{L}_2]$ (M = Pd or Pt). However, reactions of this type have not previously been reported for the earlier platinum-group metals. The present paper rectifies this anomaly.

The reaction of $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ with salicylaldehyde in boiling toluene affords a salicylaldehyde derivative which could be crystallised from dichloromethane–light petroleum or from dichloromethane–methanol to give yellow crystalline products (**1a**) and (**1b**) respectively. These both gave spectroscopic data

Table 3. Fractional atomic-co-ordinates (× 10^4) for $[Ru(OC_6H_4CO)(MeOH)(CO)(PPh_3)_2]\cdot MeOH$

Atom	*x*	*y*	*z*
Ru	2 216.0(8)	4 476.1(5)	3 696.8(2)
P(1)	2 730.0(27)	2 591.7(17)	3 649.0(7)
P(2)	1 633.8(28)	6 370.6(18)	3 768.0(7)
O(1)	2 012(9)	4 800(6)	2 829(2)
O(2)	5 124(7)	4 856(5)	3 427(2)
O(3)	2 484(7)	4 338(5)	4 306(2)
O(4)	−148(7)	4 129(6)	3 831(2)
O(5)	2 700(9)	1 000(8)	6 669(3)
C(1)	2 087(10)	4 656(6)	3 167(3)
C(2)	4 284(9)	4 778(6)	3 705(3)
C(3)	4 761(10)	4 851(7)	4 122(3)
C(4)	6 164(11)	5 199(9)	4 224(4)
C(5)	6 501(13)	5 247(9)	4 626(4)
C(6)	5 537(14)	4 958(10)	4 914(4)
C(7)	4 186(12)	4 645(9)	4 818(3)
C(8)	3 796(10)	4 586(7)	4 411(3)
C(9)	−576(11)	3 662(10)	4 201(3)
C(10)	−2 903(14)	−3 951(11)	−2 081(4)
C(11)	3 771(5)	2 115(4)	4 070(2)
C(12)	3 132(5)	2 010(4)	4 438(2)
C(13)	3 940(5)	1 722(4)	4 765(2)
C(14)	5 387(5)	1 539(4)	4 724(2)
C(15)	6 026(5)	1 644(4)	4 356(2)
C(16)	5 217(5)	1 931(4)	4 029(2)
C(21)	3 717(6)	2 046(4)	3 326(2)
C(22)	3 813(6)	920(4)	3 192(2)
C(23)	4 510(6)	460(4)	2 871(2)
C(24)	5 111(6)	1 126(4)	2 584(2)
C(25)	5 015(6)	2 251(4)	2 618(2)
C(26)	4 318(6)	2 711(4)	2 939(2)
C(31)	1 157(6)	1 731(4)	3 618(2)
C(32)	845(7)	876(4)	3 872(2)
C(33)	−371(7)	257(4)	3 814(2)
C(34)	−1 274(7)	493(4)	3 501(2)
C(35)	−962(7)	1 348(4)	3 247(2)
C(36)	253(7)	1 967(4)	3 305(2)
C(41)	508(5)	6 703(4)	4 195(2)
C(42)	952(5)	6 385(4)	4 569(2)
C(43)	219(5)	6 738(4)	4 901(2)
C(44)	−958(5)	7 408(4)	4 859(2)
C(45)	−1 402(5)	7 727(4)	4 485(2)
C(46)	−670(5)	7 374(4)	4 153(2)
C(51)	3 085(6)	7 337(4)	3 820(2)
C(52)	3 033(6)	8 182(4)	4 093(2)
C(53)	4 121(6)	8 944(4)	4 107(2)
C(54)	5 262(6)	8 861(4)	3 849(2)
C(55)	5 314(6)	8 016(4)	3 577(2)
C(56)	4 225(6)	7 254(4)	3 562(2)
C(61)	618(7)	6 938(5)	3 359(2)
C(62)	890(7)	7 964(5)	3 203(2)
C(63)	−4(7)	8 398(5)	2 917(2)
C(64)	−1 170(7)	7 806(5)	2 787(2)
C(65)	−1 441(7)	6 780(5)	2 943(2)
C(66)	−547(7)	6 346(5)	3 299(2)

(Table 1) consistent with the presence of a *trans* pair of triphenylphosphine ligands, a terminal carbonyl group, and a chelating salicylaldehydate(2−) dianion. However, in each case the nature of the group occupying the sixth co-ordination site about the octahedral ruthenium(II) centre was obscure. The possibility of a binuclear structure with bridging tridentate salicylaldehydate(2−) ligands, though considered unlikely, could not be entirely excluded. *X*-Ray diffraction studies (see below), undertaken to resolve this problem, confirmed that the two complexes have similar mononuclear structures differing only in the nature of the ligand occupying the sixth co-ordination site. In complex (**1a**) this site is occupied by a molecule of *o*-hydroxybenzyl alcohol co-ordinated through the oxygen of the CH_2OH functional group. The presence of this alcohol presumably implies that the ruthenium precursor or one of the reaction intermediates catalyses the hydrogenation of the aldehyde function of the salicylaldehyde. This reaction pattern is not entirely unexpected since several ruthenium systems are known to catalyse hydrogenation of the $>C=O$ group.[24,25]

Structure (**1b**) differs from that of (**1a**) in that the co-ordinated *o*-hydroxybenzyl alcohol and the solvating CH_2Cl_2 are both replaced by methanol. Formation of (**1b**) from the ruthenium precursor $[RuH_2(CO)(PPh_3)_3]$ presumably involves co-ordination of a molecule of salicylaldehyde, H_2sal, followed by a series of oxidative-addition and reductive-elimination reactions:

$$[RuH_2(CO)(PPh_3)_3] \xrightarrow{H_2sal} [RuH_2(H_2sal)(CO)(PPh_3)_2] \longrightarrow [RuH_3(Hsal)(CO)(PPh_3)_2] \xrightarrow{-H_2} [RuH(Hsal)(CO)(PPh_3)_2] \longrightarrow [RuH_2(sal)(CO)(PPh_3)_2] \xrightarrow[-H_2]{MeOH} [Ru(sal)(CO)(PPh_3)_2(MeOH)].$$

Formation of compound (**1a**) presumably involves the ruthenium-mediated capture of one of the liberated molecules of dihydrogen by a second molecule of salicylaldehyde.

The methanol adduct (**1b**) reacts with CO to form the dicarbonyl $[Ru(OC_6H_4CO)(CO)_2(PPh_3)_2]$ (**2**) and with pyridine (py) to afford $[Ru(OC_6H_4CO)(CO)(py)(PPh_3)_2]$ (**3**); both products possess *trans*-phosphine stereochemistry.

The reaction of $[OsH_2(CO)(PPh_3)_3]$ with salicylaldehyde is complicated by a carbonylation step not seen in the corresponding ruthenium reaction. Presumably the osmium centre is able to undergo a further oxidative-addition step with the $-C(O)H$ function of a second molecule of salicylaldehyde to afford an aroyl derivative which subsequently undergoes a migratory extrusion reaction then eliminates a molecule of phenol. The product $[Os(OC_6H_4CO)(CO)_2(PPh_3)_2]$ (**4**) has *cis*-carbonyl *trans*-phosphine stereochemistry.

The reaction of $[RhH(PPh_3)_4]$ with salicylaldehyde affords the known[9] species $[Rh(OC_6H_4CHO)(CO)(PPh_3)_2]$ (**5**) as a dichloromethane solvate from dichloromethane–light petroleum. The i.r. [ν(CO) 1 980 cm^{-1}] and ^{31}P n.m.r. spectra [32.48 p.p.m., $^1J(RhP)$ = 135 Hz] are consistent with the proposed rhodium(I) formulation but do not clearly distinguish between four- and five-co-ordination about the rhodium. However, the presence of a broad complex band in the $C=O$ region of the i.r. spectrum largely unshifted with respect to a similar band of free salicylaldehyde, strongly suggests that the CHO group is not co-ordinated. A feasible reaction sequence leading to the required product is: $[RhH(PPh_3)_4] \xrightarrow[-PPh_3]{H_2sal} [RhH(H_2sal)(PPh_3)_3] \longrightarrow [RhH_2(Hsal)(PPh_3)_3] \xrightarrow{-H_2} [Rh(Hsal)(PPh_3)_3] \xrightarrow[-PPh_3]{H_2sal} [Rh(Hsal)(H_2sal)(PPh_3)_2] \longrightarrow [RhH(Hsal')(Hsal)(PPh_3)_2] \longrightarrow [RhH(C_6H_4OH)(CO)(Hsal)(PPh_3)_2] \xrightarrow{-PhOH} [Rh(Hsal)(CO)(PPh_3)_2]$ ($Hsal' = HOC_6H_4CO$).

The corresponding reaction of *mer*-$[IrH_3(PPh_3)_3]$ with salicylaldehyde affords the iridium(III) chelate $[Ir(OC_6H_4CO)H(CO)(PPh_3)_2]$ (**6**). Formation of this product can be rationalised in terms of a reaction sequence parallel to that proposed for the rhodium system (above) followed by an intramolecular oxidative-addition step: $[Ir(Hsal)(CO)(PPh_3)_2] \longrightarrow [IrH(sal)(CO)(PPh_3)_2]$.

Table 4. Selected bond lengths (Å) and angles (°) for $[\overline{\mathrm{Ru(OC_6H_4C}}\mathrm{O)(HOC_6H_4CH_2OH)(CO)(PPh_3)_2]\cdot CH_2Cl_2}$

P(1)–Ru	2.395(4)	P(2)–Ru	2.389(4)
O(3)–Ru	2.093(6)	O(4)–Ru	2.378(6)
C(1)–Ru	1.830(8)	C(2)–Ru	2.000(7)
C(4)–Ru	2.842(9)	C(16)–Cl(1)	1.735(12)
C(16)–Cl(2)	1.728(13)	C(111)–P(1)	1.838(7)
C(121)–P(1)	1.821(6)	C(131)–P(1)	1.832(6)
C(211)–P(2)	1.827(6)	C(221)–P(2)	1.839(6)
C(231)–P(2)	1.828(6)	C(1)–O(1)	1.147(9)
C(2)–O(2)	1.245(8)	C(4)–O(3)	1.314(7)
C(9)–O(4)	1.442(9)	C(15)–O(5)	1.360(10)
C(3)–C(2)	1.468(9)	C(4)–C(3)	1.405(9)
P(2)–Ru–P(1)	176.2(1)	O(3)–Ru–P(1)	89.7(2)
O(3)–Ru–P(2)	93.8(2)	O(4)–Ru–P(1)	91.9(2)
O(4)–Ru–P(2)	87.2(2)	O(4)–Ru–O(3)	79.4(2)
C(1)–Ru–P(1)	90.6(3)	C(1)–Ru–P(2)	86.0(3)
C(1)–Ru–O(3)	178.4(2)	C(1)–Ru–O(4)	102.2(3)
C(2)–Ru–P(1)	90.0(3)	C(2)–Ru–P(2)	92.0(3)
C(2)–Ru–O(3)	82.8(3)	C(2)–Ru–O(4)	162.0(2)
C(2)–Ru–C(1)	95.7(3)	C(4)–Ru–P(1)	89.8(2)
C(4)–Ru–P(2)	94.0(2)	C(4)–Ru–O(3)	25.6(1)
C(4)–Ru–O(4)	104.9(2)	C(4)–Ru–C(1)	152.9(2)
C(4)–Ru–C(2)	57.2(3)	C(4)–O(3)–Ru	111.0(4)
C(9)–O(4)–Ru	124.6(4)	O(1)–C(1)–Ru	177.7(6)
O(2)–C(2)–Ru	129.2(5)	C(3)–C(2)–Ru	110.4(5)
C(3)–C(2)–O(2)	120.4(5)	C(4)–C(3)–C(2)	115.8(6)
C(5)–C(3)–C(2)	125.4(6)	C(5)–C(3)–C(4)	118.8(6)
O(3)–C(4)–Ru	43.4(2)		
C(3)–C(4)–O(3)	120.0(6)		
C(8)–C(4)–O(3)	120.5(6)		
C(10)–C(9)–O(4)	113.0(6)		

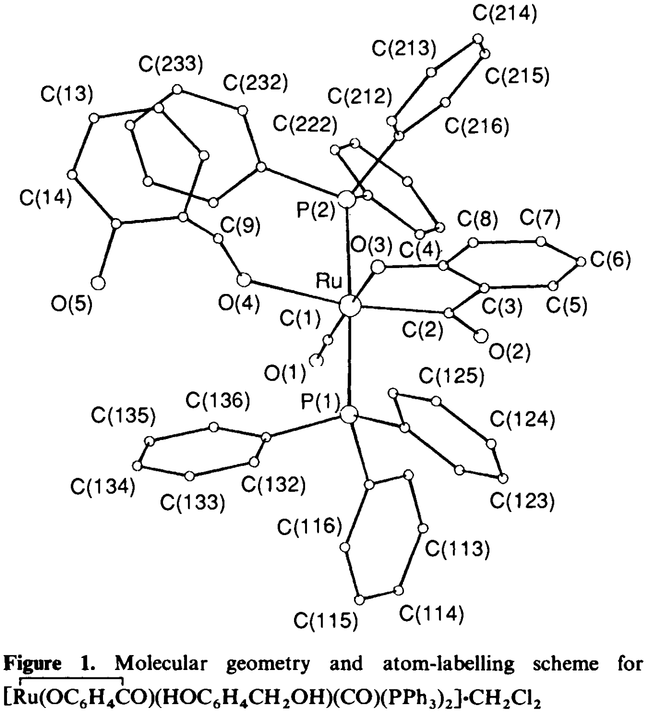

Figure 1. Molecular geometry and atom-labelling scheme for $[\overline{\mathrm{Ru(OC_6H_4C}}\mathrm{O)(HOC_6H_4CH_2OH)(CO)(PPh_3)_2]\cdot CH_2Cl_2}$

Table 5. Selected bond lengths (Å) and angles (°) for $[\overline{\mathrm{Ru(OC_6H_4C}}\mathrm{O)(MeOH)(CO)(PPh_3)_2]\cdot MeOH}$

P(1)–Ru	2.379(4)	P(2)–Ru	2.412(4)
O(3)–Ru	2.092(8)	O(4)–Ru	2.323(9)
C(1)–Ru	1.818(11)	C(2)–Ru	1.993(10)
C(3)–Ru	2.847(13)	C(11)–P(1)	1.834(8)
C(21)–P(1)	1.842(8)	C(31)–P(1)	1.832(9)
C(41)–P(2)	1.846(8)	C(51)–P(2)	1.827(8)
C(61)–P(2)	1.830(9)	C(1)–O(1)	1.166(12)
C(2)–O(2)	1.238(13)	C(8)–O(3)	1.328(12)
C(9)–O(4)	1.443(14)	C(3)–C(2)	1.492(15)
C(4)–C(3)	1.439(15)	C(8)–C(3)	1.381(14)
C(5)–C(4)	1.402(19)	C(6)–C(5)	1.386(19)
C(7)–C(6)	1.375(18)	C(8)–C(7)	1.433(15)
P(2)–Ru–P(1)	177.7(1)	O(3)–Ru–P(1)	87.9(3)
O(3)–Ru–P(2)	90.4(3)	O(4)–Ru–P(1)	91.7(3)
O(4)–Ru–P(2)	86.5(3)	O(4)–Ru–O(3)	84.7(3)
C(1)–Ru–P(1)	93.7(4)	C(1)–Ru–P(2)	88.0(4)
C(1)–Ru–O(3)	176.1(3)	C(1)–Ru–O(4)	98.8(4)
C(2)–Ru–P(1)	89.0(3)	C(2)–Ru–P(2)	92.4(3)
C(2)–Ru–O(3)	83.3(4)	C(2)–Ru–O(4)	167.9(3)
C(2)–Ru–C(1)	93.2(5)	C(3)–Ru–P(1)	91.2(3)
C(3)–Ru–P(2)	89.1(3)	C(3)–Ru–O(3)	53.8(4)
C(3)–Ru–O(4)	138.2(3)	C(3)–Ru–C(1)	122.6(5)
C(3)–Ru–C(2)	29.7(3)	C(8)–O(3)–Ru	111.1(6)
C(9)–O(4)–Ru	121.0(7)	O(1)–C(1)–Ru	178.2(7)
O(2)–C(2)–Ru	129.4(8)	C(3)–C(2)–Ru	108.7(7)
C(3)–C(2)–O(2)	121.7(9)	C(2)–C(3)–Ru	41.5(4)
C(4)–C(3)–Ru	162.3(8)	C(4)–C(3)–C(2)	121.9(10)
C(8)–C(3)–Ru	76.3(6)	C(8)–C(3)–C(2)	117.5(9)
C(8)–C(3)–C(4)	120.6(10)	C(5)–C(4)–C(3)	117.3(11)
C(6)–C(5)–C(4)	121.8(12)	C(7)–C(6)–C(5)	121.0(12)
C(8)–C(7)–C(6)	119.0(11)	C(3)–C(8)–O(3)	118.8(9)
C(7)–C(8)–O(3)	120.8(9)	C(7)–C(8)–C(3)	120.2(10)

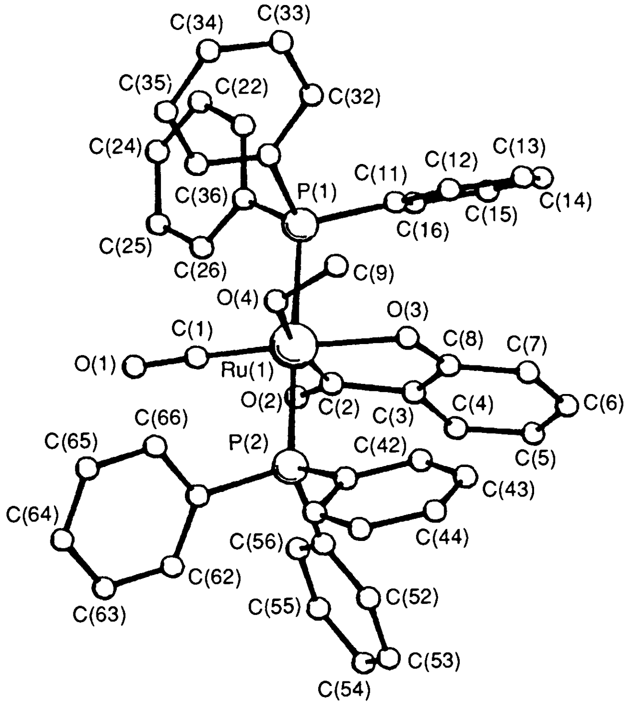

Figure 2. Molecular geometry and atom-labelling scheme for $[\overline{\mathrm{Ru(OC_6H_4C}}\mathrm{O)(MeOH)(CO)(PPh_3)_2]\cdot MeOH}$

Since $[\mathrm{IrH(CO)(PPh_3)_3}]$ also reacts with salicylaldehyde to form the iridium(III) product $[\overline{\mathrm{Ir(OC_6H_4C}}\mathrm{O)H(CO)(PPh_3)_2}]$ it is conceivable that the carbonylation step in the iridium reaction and in the analogous rhodium case precedes incorporation of the chelate (sal) ligand. However, we consider this sequence of reactions to be less probable since oxidative addition across a metal centre is likely to proceed more rapidly for RO–H than for RC(O)–H groups (R = aryl).

X-Ray Crystal Structures of $[\overline{\mathrm{Ru(OC_6H_4C}}\mathrm{O)(HOC_6H_4CH_2OH)(CO)(PPh_3)_2]\cdot CH_2Cl_2}$ (**1a**) *and* $[\overline{\mathrm{Ru(OC_6H_4C}}\mathrm{O)(MeOH)(CO)(PPh_3)_2]\cdot MeOH}$ (**1b**).—The molecular structures of compounds (**1a**) and (**1b**) are given in Figures 1 and 2 respectively. Selected bond lengths and angles are given in Tables 4 and 5. The two complexes have distorted octahedral co-ordination and differ significantly only in the nature of the O-donor ligand occupying the sixth co-ordination site. Angles subtended at the ruthenium centre by adjacent donor atoms range from 79.4(2) [O(4)–Ru–O(3)] to 102.2(3)[C(1)–Ru–O(4)] for (**1a**) and from 83.3(4) [C(2)–Ru–O(3)] to 98.8(4)° [C(1)–Ru–O(4)] for (**1b**). Differences in the steric properties of the alcohol ligands are reflected in the bond angles O(3)–Ru–O(4) and C(1)–Ru–O(4) which are 79.4(2) and 102.2(3)° respectively in (**1a**) but 84.7(3) and 98.8(4)° in (**1b**). The Ru–P and Ru–CO bond lengths for both complexes are typical of octahedral ruthenium(II) and the geometry of the salicylaldehyde(2−) chelate ligand is similar to that previously reported for $[\overline{\mathrm{Pt(OC_6H_4C}}\mathrm{O)\{P(C_6H_4Me\text{-}}o\mathrm{)_3\}_2]}$.[20] The most significant difference is in the aroyl C=O bond length which increases from 1.20 Å in the platinum complex to 1.245(8) and 1.238(13) Å in (**1a**) and (**1b**) respectively. The O-donor ligand occupying the sixth co-ordination site in (**1a**) is identified as *o*-hydroxybenzyl alcohol rather than the parent salicylaldehyde by the length of the CH_2–OH bond [1.442(9) Å] and the detection of electron density at positions corresponding to all three hydrogen atoms of the CH_2OH group. The lengths of the Ru–O (alcohol) linkages in (**1a**) and (**1b**) [2.378(6) and 2.323(9) Å] respectively, reflect the strong *trans* influence of the aroyl ligand in the *trans* co-ordination site. Thus the Ru–O (MeOH) bond in compound (**1b**) is significantly longer than the Ru–O (MeOH) linkage [2.174(7) Å *trans* to PPh_3] in the complex $[\mathrm{Ru(O_2CCF_3)_2(MeOH)(CO)(PPh_3)_2}]$.[26]

Acknowledgements

We thank Johnson-Matthey plc for a generous loan of ruthenium trichloride.

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Received 6*th December* 1989; *Paper* 9/05210K