Polyhedron Vol. 11, No. 12, pp. 1501–1506, 1992
Printed in Great Britain

0277–5387/92 $5.00+.00

DIHYDROBIS- AND TRIS(TRIPHENYLPHOSPHINE)RHODIUM(III) CARBOXYLATE COMPLEXES

LAURENCE CARLTON,* MARIE-PAULA BELCIUG and GARY PATTRICK

Centre for Molecular Design, Department of Chemistry, University of the Witwatersrand, Johannesburg, Republic of South Africa

(*Received* 18 *December* 1991; *accepted* 27 *January* 1992)

Abstract—The complexes $[Rh(H)_2(O_2CArN)(PPh_3)_2]$ (O_2CArN = pyridine-2-carboxylate, 6-methylpyridine-2-carboxylate, pyrazine-2-carboxylate, quinoline-2-carboxylate, isoquinoline-1-carboxylate and quinoxaline-2-carboxylate) were formed in high yield by the reaction of $[RhH(PPh_3)_4]$ with the carboxylic acids $NArCO_2H$; their properties are compared with those of $[Rh(H)_2(O_2CR)(PPh_3)_3]$ and $[Rh(H)_2(O_2CR)(PPh_3)_2(py)]$ (O_2CR = acetate, thiophene-2-carboxylate; py = pyridine).

Tris(triphenylphosphine)rhodium(I) carboxylate complexes are readily prepared in good yield from $[RhH(PPh_3)_4]$ and RCO_2H (R = Me, Et etc.) by the method of Robinson and Uttley[1] in a reaction which might be expected to proceed by oxidative addition of the acid to $[RhH(PPh_3)_3]$, the form in which $[RhH(PPh_3)_4]$ largely exists in solution, to give a dihydrorhodium(III) carboxylate complex which subsequently decomposes to give $[Rh(O_2CR)(PPh_3)_3]$. In the present study the reaction of $[RhH(PPh_3)_4]$ with a number of carboxylic acids, several capable of forming chelating ligands binding via carboxylate oxygen and an aromatic nitrogen, was investigated by ^1H and ^{31}P NMR spectroscopy. A ^{15}N NMR study of some of the products was reported elsewhere.[2]

EXPERIMENTAL

Reagents were obtained from various sources and used without further purification; THF was distilled from sodium, and toluene and pyridine were distilled from calcium hydride. $[RhH(PPh_3)_4]$ was prepared by the method of Robinson and co-workers.[3] NMR spectra were recorded on a Bruker AC 200 FT spectrometer at 200.13 MHz (^1H) and 81.01 MHz (^{31}P); IR spectra were recorded on a Perkin–Elmer 580 spectrometer. All operations (other than those involving H_2) were performed under a nitrogen atmosphere.

Low temperature studies

Reactions were carried out *in situ* and monitored by ^1H and ^{31}P NMR spectroscopy. $[RhH(PPh_3)_4]$ (~ 10 mg for ^1H, ~ 25 mg for ^{31}P studies) was dissolved in the appropriate solvent (toluene, ~ 10:1 toluene/pyridine, ~ 4:1 toluene/pyridine) in an NMR tube (5 mm for ^1H, 10 mm for ^{31}P studies) and treated with an excess of RCO_2H (10 mg of thiophene-2-carboxylic acid, 1 drop of acetic acid). The tube was then shaken and quickly transferred to the spectrometer at −40°C (for $^{31}P\{^1H\}$ measurements) or −25°C (for ^1H measurements). After recording a spectrum the sample was taken out in order to flush the solution with nitrogen or hydrogen and/or warm it to 60–70°C for 2–3 min.

Preparation of $[Rh(H)_2(O_2Cpy)(PPh_3)_2]$

A mixture of $[RhH(PPh_3)_4]$ (1.225 g, 1.06 mmol) and pyridine-2-carboxylic acid (0.135 g, 1.10 mmol) in THF (12 cm^3) was warmed to 50–60°C for 2–3 min with stirring to give a dark red solution. On standing at room temperature a yellow crystalline solid quickly began to form. After 15 h the solid

* Author to whom correspondence should be addressed.

Abbreviations: O_2Cpy, pyridine-2-carboxylate; O_2CMepy, 6-methylpyridine-2-carboxylate; $O_2Cpyraz$, pyrazine-2-carboxylate; O_2Cquin, quinoline-2-carboxylate; O_2Cisoq, isoquinoline-2-carboxylate; $O_2Cquinox$, quinoxaline-2-carboxylate; O_2Cth, thiophene-2-carboxylate.

Table 1. ^{1}H NMR spectral data for the dihydrocarboxylate complexes[a]

Complex	Signal	δH[b]	J(P–H *trans*)[c]	J(Rh–H)	J(P–H *cis*)	J(H–H)
$[Rh(H)_2(O_2Cpy)(PPh_3)_2]$	ddt	−15.38		14.4	14.4	12.2
	ddt	−20.25		20.7	16.5	12.2
$[Rh(H)_2(O_2CMepy)(PPh_3)_2]$	ddt	−15.69		15.4	15.2	11.8
	ddt	−19.42		18.6	15.7	11.8
$[Rh(H)_2(O_2Cpyraz)(PPh_3)_2]$	ddt	−15.13		14.5	13.7	12.3
	ddt	−20.37		21.1	16.3	12.3
$[Rh(H)_2(O_2Cquin)(PPh_3)_2]$	ddt	−15.29		16.2	14.0	11.5
	ddt	−19.18		19.1	16.2	11.5
$[Rh(H)_2(O_2Cisoq)(PPh_3)_2]$	ddt	−15.36		14.4	14.2	12.5
	ddt	−19.85		20.3	16.5	12.5
$[Rh(H)_2(O_2Cquinox)(PPh_3)_2]$	ddt	−14.96		16.4	13.4	11.4
	ddt	−19.41		19.9	15.7	11.4
$[Rh(H)_2(O_2CCH_3)(PPh_3)_3]$[d,e]	dddt	−9.12	161.2	10.2	10.7	7.5
	mult	−19.26				
$[Rh(H)_2(O_2Cth)(PPh_3)_3]$[d,f]	dddt	−8.68	160.9	10.6	10.7	6.1
	mult	−19.22				
$[Rh(H)_2(O_2CCH_3)(PPh_3)_2(py)]$[e,g]	mult	−15.94		~13	~13	12.2
	ddt	−19.50		19.6	16.7	12.2
$[Rh(H)_2(O_2Cth)(PPh_3)_2(py)]$[g,h]	mult	−15.88		19.4	18.2	11.8
	ddt	−19.63				

[a] Solution in $CDCl_3$ at 22°C unless otherwise stated.
[b] Chemical shifts in ppm from TMS.
[c] Coupling constants (absolute magnitude) in Hz.
[d] Solution in toluene-d_8.
[e] −25°C.
[f] 0°C.
[g] Solution in ~10:1 toluene-d_8/pyridine.
[h] −40°C.

was collected, washed with ether and dried *in vacuo* to give the product as a pale yellow microcrystalline powder (0.695 g, 0.92 mmol, 87%). Found: C, 67.8; H, 5.0; N, 1.7. $C_{42}H_{36}NO_2P_2Rh$ requires: C, 68.9; H, 4.8; N, 1.7%. IR (Nujol mull): ν(Rh—H) 2107, 2026 cm^{-1}. ^{1}H and ^{31}P NMR data are given in Tables 1 and 2.

Preparation of $[Rh(H)_2(O_2CMepy)(PPh_3)_2]$

A mixture of $[RhH(PPh_3)_4]$ (1.57 g, 1.36 mmol) and 6-methylpyridine-2-carboxylic acid (0.194 g, 1.42 mmol) in THF (12 cm^3) was warmed to 50–60°C for 2–3 min to dissolve the reagents and allowed to stand at room temperature for 15 h. The product, a pale yellow microcrystalline powder, was washed with ether and dried *in vacuo* (yield: 0.790 g, 1.03 mmol, 76%). Found: C, 66.4; H, 5.0; N, 1.9. $C_{43}H_{38}NO_2P_2Rh$ requires: C, 67.5; H, 5.0; N, 1.8%. IR (Nujol mull): ν(Rh—H) 2136, 2066 cm^{-1}.

Preparation of $[Rh(H)_2(O_2Cpyraz)(PPh_3)_2]$

A mixture of $[RhH(PPh_3)_4]$ (0.716 g, 0.62 mmol) and pyrazine-2-carboxylic acid (0.081 g, 0.65 mmol) in THF (12 cm^3) was warmed to 50–60°C for 2–3 min to dissolve the reagents and allowed to stand at room temperature for 15 h. The product, a pale yellow crystalline powder, was washed with ether and dried *in vacuo* (yield 0.42 g, 0.56 mmol, 90%). Found: C, 65.6; H, 5.3; N, 3.3. $C_{41}H_{35}N_2O_2P_2Rh$ requires: C, 65.4; H, 4.7; N, 3.7%. IR (Nujol mull): ν(Rh—H) 2110, 2035 cm^{-1}

Preparation of $[Rh(H)_2(O_2Cquin(PPh_3)_2]$

A mixture of $[RhH(PPh_3)_4]$ (0.946 g, 0.82 mmol) and quinoline-2-carboxylic acid (0.145 g, 0.84 mmol) in THF (7 cm^3) was warmed to 50–60°C for 2–3 min to dissolve the reagents and allowed to stand at room temperature for 15 h. The product,

Table 2. ^{31}P NMR spectral data for the carboxylate complexes[a]

Complex	Signal	δP^b	J(Rh–P)[c]	J(P—P)
$[Rh(H)_2(O_2Cpy)(PPh_3)_2]$	d	43.83	118.5	
$[Rh(H)_2(O_2CMepy)(PPh_3)_2]$	d	43.29	119.6	
$[Rh(H)_2(O_2Cpyraz)(PPh_3)_2]$	d	43.50	117.7	
$[Rh(H)_2(O_2Cquin)(PPh_3)_2]$	d	43.77	118.7	
$[Rh(H)_2(O_2Cisoq)(PPh_3)_2]$	d	44.19	118.9	
$[Rh(H)_2(O_2Cquinox)(PPh_3)_2]$	d	43.58	118.0	
$[Rh(H)_2(O_2CCH_3)(PPh_3)_3]$[d]	dd	41.35	117.1	18.4
	dt	23.30	89.4	18.4
$[Rh(H)_2(O_2Cth)(PPh_3)_3]$[d]	dd	41.36	117.8	18.2
	dt	24.43	89.7	18.2
$[Rh(H)_2(O_2CCH_3)(PPh_3)_2(py)]$[e]	d	46.34	121.1	
$[Rh(H)_2(O_2Cth)(PPh_3)_2(py)]$[e]	d	46.59	120.5	
$[Rh(O_2CCH_3)(PPh_3)_3]$[d]	dt	54.48	176.4	40.6
	dd	37.40	150.8	40.6
$[Rh(O_2Cth)(PPh_3)_3]$[d,f]	dt	54.06	176.7	40.3
	dd	37.15	150.3	40.3
[*trans*-$Rh(O_2CCH_3)(PPh_3)_2(py)$][g]	d	51.47	170.8	
[*trans*-$Rh(O_2Cth)(PPh_3)_2(py)$][g]	d	51.57	170.5	
[*cis*-$Rh(O_2CCH_3)(PPh_3)_2(py)$][g]	dd	60.58	190.4	50.8
	dd	51.81	174.3	50.8
[*cis*-$Rh(O_2Cth)(PPh_3)_2(py)$][g]	dd	61.30	194.2	51.0
	dd	51.51	170.6	51.0

[a] Solution in $CHCl_3/CDCl_3$ at 22°C unless otherwise stated.
[b] Chemical shifts in ppm from 80% H_3PO_4 (ext. standard) unless otherwise stated.
[c] Coupling constants (absolute magnitude) in Hz.
[d] Solution in toluene at −40°C, chemical shifts relative to PPh_3 at −4.70 ppm.
[e] Solution in ~4:1 toluene/pyridine at 22°C.
[f] Signals not observed at room temperature.
[g] Solution in ~4:1 toluene/pyridine at −40°C, chemical shifts relative to PPh_3 at −4.70 ppm.

a pale yellow crystalline powder, was washed with ether and dried *in vacuo* (yield 0.58 g, 0.72 mmol, 88%). Found: C, 67.8; H, 5.0; N, 1.7. $C_{46}H_{38}NO_2P_2Rh$ requires: C, 68.9; H, 4.8; N, 1.7%. IR (Nujol mull): ν(Rh—H) 2120, 2077 cm^{-1}.

Preparation of $[Rh(H)_2(O_2Cisoq)(PPh_3)_2]$

A mixture of $[RhH(PPh_3)_4]$ (1.295 g, 1.12 mmol) and isoquinoline-1-carboxylic acid (0.200 g, 1.16 mmol) in THF (12 cm^3) was warmed to 50–60°C for 2–3 min to dissolve the reagents and allowed to stand at room temperature for 15 h. The product, a pale yellow crystalline powder, was washed with ether and dried *in vacuo* (yield 0.704 g, 0.878 mmol, 78%). Found: C, 68.7; H, 4.9; N, 1.7. $C_{46}H_{38}NO_2P_2Rh$ requires: C, 68.9; H, 4.8; N, 1.7%. IR (Nujol mull): ν(Rh—H) 2127, 2050 cm^{-1}.

Preparation of $[Rh(H)_2(O_2Cquinox)(PPh_3)_2]$

A mixture of $[RhH(PPh_3)_4]$ (1.110 g, 0.96 mmol) and quinoxaline-2-carboxylic acid (0.170 g, 0.98 mmol) in THF (6 cm^3) was warmed to 50–60°C for 5–10 min to dissolve the reagents and allowed to stand at room temperature for 30 min. The product, a pale yellow crystalline powder, was washed with ether and dried *in vacuo* (yield 0.720 g, 0.90 mmol, 93%). The analytical sample was recrystallized from CH_2Cl_2 to give a product analysing for $[Rh(H)_2(O_2Cquinox)(PPh_3)_2](\{0.5CH_2Cl_2\})$. Found: C, 65.1; H, 4.6; N, 3.3. $C_{45.5}H_{39}ClN_2O_2$

P_2Rh requires: C, 64.7; H, 4.6; N, 3.3%. IR (Nujol mull): ν(Rh—H) 2094, 2080 cm^{-1}.

Preparation of $[Rh(O_2Cth)(PPh_3)_3]$

A solution of $[RhH(PPh_3)_4]$ (0.155 g, 0.134 mmol) in THF (3 cm^3) was treated with a solution of thiophene-2-carboxylic acid (0.020 g, 0.16 mmol) in THF (3 cm^3) and stirred for 5 min to give a dark red solution. Hexane ($\sim$ 5 cm^3) was added and the solution allowed to stand for 3 days at room temperature to give dark brown crystals. The product was washed with ether and dried *in vacuo* (yield 0.113 g, 0.112 mmol, 83%). Found: C, 68.6; H, 5.5; S, 2.9. $C_{59}H_{48}O_2P_3RhS$ requires: C, 69.7; H, 4.8; S, 3.1%.

RESULTS AND DISCUSSION

The reaction of $[RhH(PPh_3)_4]$ with $NArCO_2H$ in THF at room temperature gives the dihydro complexes $[Rh(H)_2(O_2CArN)(PPh_3)_2]$ in good yield as air-stable yellow crystals or crystalline powders. The high field region of the ^1H NMR spectra of these products shows two multiplets, each a ddt (in the case of the three complexes having an $NArCO_2$ ligand with a hydrogen positioned *ortho* to nitrogen and thus four bonds distant from the hydrides, one of the multiplets is not well resolved), indicating two non-equivalent hydride ligands with coupling between the hydrides, rhodium and two phosphines (Table 1). The $^{31}P\{^1H\}$ spectra consist of a single doublet (Table 2), confirming that the phosphines are equivalent, i.e. they are positioned mutually *trans*, giving the complexes the geometry shown in Fig. 1. These compounds are similar to a number of dihydrorhodium(III) complexes in which a common feature is the presence of a chelating ligand occupying the coordination sites *trans* to the hydrides.[4–6]

In the high resolution ^1H spectrum of $[Rh(H)_2(O_2Cpy)(PPh_3)_2]$ (Fig. 2) the multiplet at -15.38 ppm appears as a dddt, the doublet splitting of 1 Hz disappearing on decoupling the pyridyl-6-hydrogen (Fig. 2b). The signal at δ -15.38 therefore

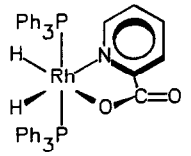
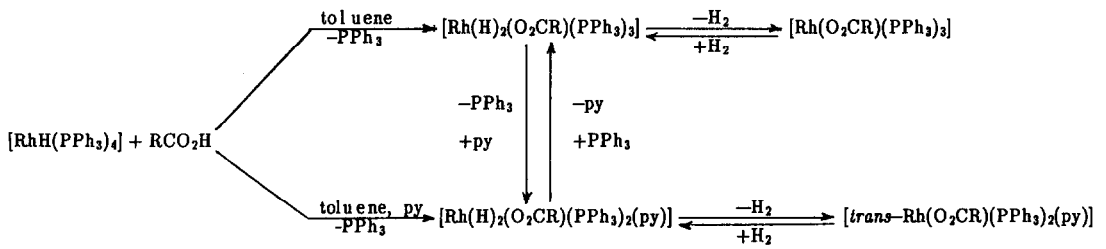


Fig. 1. The coordination geometry of $[Rh(H)_2(O_2Cpy)(PPh_3)_2]$.

arises from the hydride lying *trans* to nitrogen. The magnitude of the coupling of the pyridyl-6-H to the *cis* hydride is expected to be much smaller and such coupling is not seen in the signal at δ -20.25 (Fig. 2c). The multiplet shown in Fig. 2c has fewer overlapping lines (two only, to give the centre line) than that in Fig. 2b and the coupling pattern is more readily distinguished: the first triplet (P–H coupling) of the ddt is formed by lines 1, 3 and 6, the H–H coupling is given by the separation between lines 3 and 5 and the Rh–H coupling by the separation between lines 3 and 7.

The complexes $[Rh(H)_2(O_2CArN)(PPh_3)_2]$ are soluble in chloroform (in which they slowly decompose) and dichloromethane (in which they are more stable). The hydrides are not readily lost and cannot be removed by flushing the solutions with nitrogen or by warming, unlike the hydrides in complexes in which there is no chelating ligand in the *trans* position. Such complexes are formed in the reaction of $[RhH(PPh_3)_4]$ with RCO_2H (acetic acid or thiophene-2-carboxylic acid) in toluene or toluene/pyridine and lose H_2 without difficulty (Scheme 1).

On treatment with a large excess of pyridine $[Rh(H)_2(O_2CR)(PPh_3)_2]$ (in toluene) is converted to $[Rh(H)_2(O_2CR)(PPh_3)_2(py)]$, a process which can be reversed by addition of PPh_3. Displacement of the hydrides from these complexes by flushing the warmed solutions with N_2 for 2–3 min yields $[Rh(O_2CR)(PPh_3)_3]$ and [*trans*-$Rh(O_2CR)(PPh_3)_2(py)$] (together with a little of the *cis* isomer) respectively. This behaviour is consistent with reductive elimination from a five-coordinate intermediate where the ligand lost is the σ-donor (PPh_3 or py) positioned *trans* to hydride, labilized by the large



Scheme 1.

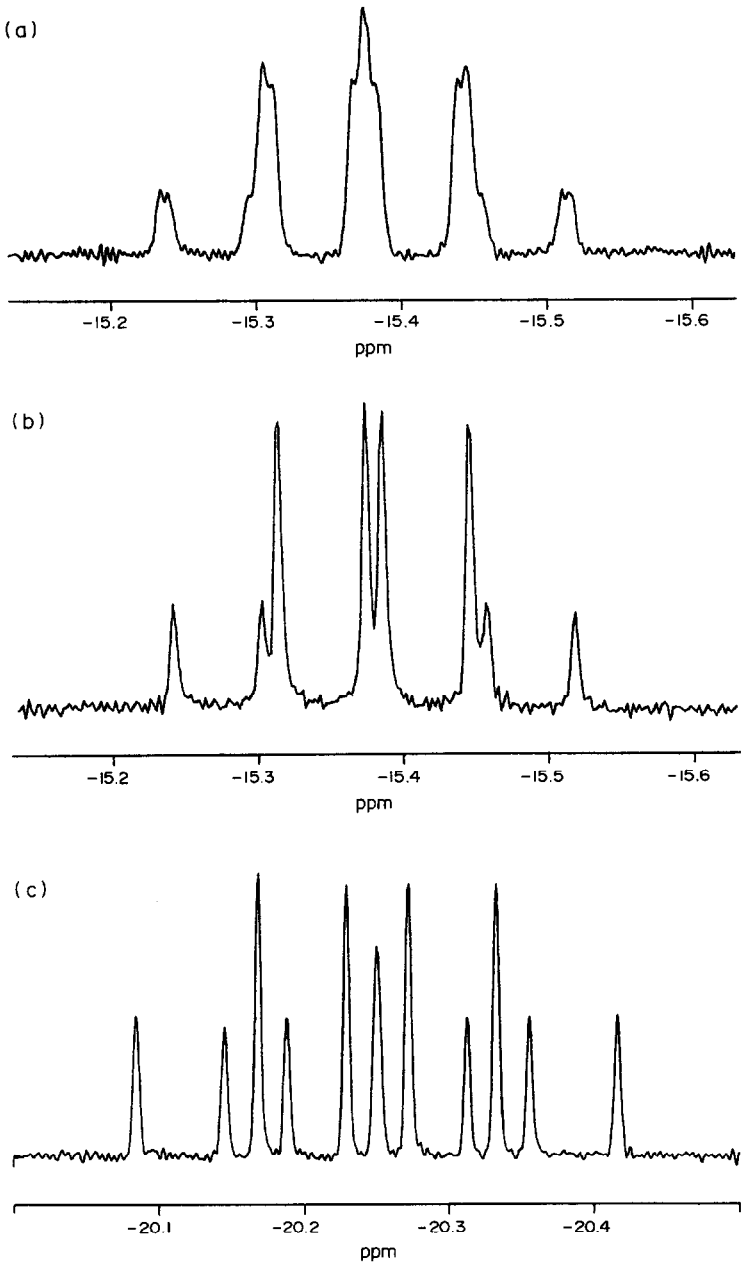


Fig. 2. The high field region of the ^1H NMR spectrum of $[Rh(H)_2(O_2Cpy)(PPh_3)_2]$. (a) Signal from the hydride *trans* to nitrogen. (b) Signal from the same hydride with decoupling of the pyridyl-6-hydrogen. (c) Signal from the hydride *trans* to oxygen.

hydride *trans* effect. The dissociation of a σ-donor ligand has been shown to be a precondition of reductive elimination in numerous cases.[6-9]

The thiophene group of the thiophene-2-carboxylate ligand is clearly not an effective competitor to PPh_3 for the binding site *cis* to carboxylate oxygen and *trans* to hydride. There is no evidence for the formation of a thiophene-2-carboxylate analogue of $[Rh(H)_2(O_2CArN)(PPh_3)_2]$: in toluene $[Rh(O_2Cth)(PPh_3)_3]$ binds H_2 readily and reversibly to give $[Rh(H)_2(O_2Cth)(PPh_3)_3]$.

Acknowledgements—We thank the University of the Witwatersrand for financial support and Johnson Matthey for the loan of rhodium.

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