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Rhodium-103 NMR of Carboxylate and Thiolate Complexes by Indirect Detection using Phosphorus

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Fifty four carboxylate and thiolate complexes of rhodium including $[Rh(O_2CR)(PPh_3)_3]$ ($R = CH_3$, CF_3), $[Rh_2(SC_6F_5)_2(PPh_3)_4]$ and derivatives obtained by reaction with hydrogen, pyridine and methyldiphenylphosphine, $[Rh(O_2CArN)(H)_2(PPh_3)_2]$ (O_2CArN = pyridine-2-carboxylate and related chelating ligands) and complexes prepared *in situ* (many as mixtures) by the reaction of $[Rh(H)(PPh_3)_4]$ with various thiols were studied by two-dimensional inverse ^{103}Rh–^{31}P correlated NMR (HMQC). Rhodium chemical shifts were found to fall within the range 840 to −422 ppm. Trends in $\delta^{103}Rh$ for thiolate and carboxylate complexes are similar but not identical, with somewhat lower δ for most of the thiolates, increasing in the approximate order $[Rh(SR)(H)_2(PPh_3)_3] < [Rh(SR)(PPh_3)_3]$, *cis*-$[Rh(SR)(PPh_3)_2(py)] < [Rh_2(SR)_2(PPh_3)_4] < [Rh(SR)(H)_2(PPh_3)_2(py)] < [Rh(SR)_2(H)(PPh_3)_2(py)]$.

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INTRODUCTION

Rhodium-103 NMR is potentially of considerable value in the study of catalytic and other systems involving transformations promoted by rhodium. The low magnetic moment of ^{103}Rh and long relaxation times have led to the use of polarization transfer methods, principally INEPT[1] and HMQC[2] (indirect detection), which require that a suitable nucleus of high sensitivity is present in the compound of interest. The majority of studies have made use of ^{1}H for this purpose,[3] which allows enhancement by factors of up to $(\gamma_H/\gamma_{Rh}) = 31.5$ (INEPT) and $(\gamma_H/\gamma_{Rh})^{5/2} = 5635$ (HMQC).[4] When hydrogen is not directly bound to the metal, the magnitude of $J(^{103}Rh,^{1}H)$ is low (rarely exceeding 2 Hz) and optimization of the pulse sequence requires delay times during which appreciable loss of magnetization occurs. Many complexes lack any such hydrogen but are stabilised by P-donor ligands, permitting the use of ^{31}P for indirect detection.[5] The magnitude of $^{1}J(^{103}Rh,^{31}P)$ is rarely less than *ca.* 80 Hz and loss of magnetization during the application of the pulse sequence is relatively low, compensating, to some extent, for the intrinsically lower sensitivity of the ^{103}Rh–^{31}P method [enhancement by factors of up to $(\gamma_H/\gamma_{Rh})^{5/2} = 590$] as compared with ^{103}Rh–^{1}H. This paper reports ^{103}Rh data for a variety of Rh(I) and Rh(III) thiolate and carboxylate complexes, obtained using indirect ^{103}Rh–^{31}P NMR.

EXPERIMENTAL

The complexes $[Rh(O_2CR)(PPh_3)_3]$ ($R = CH_3, CF_3, Ph$),[6] $[Rh_2(SC_6F_5)_2(PPh_3)_4]$,[7] $[Rh(O_2CArN)(H)_2(PPh_3)_4]$ [O_2CArN = pyridine-2-carboxylate (O_2CPy), pyrazine-2-carboxylate ($O_2CPyraz$), quinoline-2-carboxylate (O_2CQuin), isoquinoline-1-carboxylate (O_2CIsoq) and quinoxaline-2-carboxylate ($O_2CQuinox$)][8] and $[Rh(H)(PPh_3)_4]$[9] were prepared according to published methods. Toluene and pyridine were dried over calcium hydride. Samples for NMR spectroscopy were prepared under argon in $CDCl_3$ or *ca.* 8:1 toluene–toluene-d_8 at room temperature. Preparation of thiolate derivatives *in situ* from $[Rh(H)(PPh_3)_4]$ involved the addition of the thiol (*ca.* fivefold excess) to a suspension of $[Rh(H)(PPh_3)_4]$ (15–30 mg) in toluene or 10% pyridine–toluene (0.6 ml) with shaking and (where necessary) gentle warming to dissolve. Hydride derivatives of $[Rh(O_2CR)(PPh_3)_3]$ ($R = CH_3$, Ph) were prepared *in situ* by bubbling H_2 at atmospheric pressure through solutions in toluene or pyridine–toluene at room temperature.

Spectra were recorded using the pulse sequence of Bax *et al.*[2] $\{\pi/2(^{31}P)$–$1/[2J(^{103}Rh,^{31}P)]$–$\pi/2(^{103}Rh)$–τ–$\pi(^{31}P)$–τ–$\pi/2(^{103}Rh)$–$Aq(^{31}P)\}$ on a Bruker DRX 400 spectrometer equipped with a 5 mm triple resonance inverse probe with dedicated ^{31}P channel, operating at 161.98 (^{31}P) and 12.65 (^{103}Rh) MHz. ^{103}Rh–^{31}P spectra were recorded without decoupling using a spectral

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width in f_2 (^{31}P) of 8 ppm and an acquisition time of 0.396 s giving a digital resolution of 1.26 Hz per point and in f_1 (^{103}Rh) a spectral width of 40 ppm with either 64, 128 or 256 increments (for broadened signals the signal-to-noise ratio declined significantly after *ca.* 64 increments) and 4, 8 or 16 (occasionally more) scans per increment giving, after zero filling, a digital resolution of 0.49 Hz per point. The relaxation delay in each case was 1 s. For experiments using 256 increments and four scans, data collection required 27 min. With the exception of the spectrum shown in Fig. 1, all spectra [including those recorded for the accurate determination of the chemical shifts of the signals shown in Fig. 1 and also the spectrum shown in Fig. 2(d)] were obtained using these parameters. In order to eliminate the possibility of a folded signal in f_1, spectra (*ca.* 20 increments only) were first recorded with a spectral width of 2000 ppm. For the spectrum shown in Fig. 1 the parameters were as follows: spectral width in f_2, 34 ppm; acquisition time, 0.186 s; spectral width in f_1, 1300 ppm; number of increments, 208; scans per increment, 48. The digital resolution in f_2 was 2.69 Hz per point and in f_1 (after zero filling) 16.06 Hz per point; data collection required 3 h 20 min. Chemical shifts were referenced to $\Xi(^{103}\text{Rh}) = 3.16$ MHz, positive values to high frequency.

Spectra were recorded at $-25\,^{\circ}$C in order to stabilize a number of complexes and, in several cases, to improve the resolution of signals broadened at room temperature. Temperature control was accurate to $<0.1\,^{\circ}$C.

RESULTS AND DISCUSSION

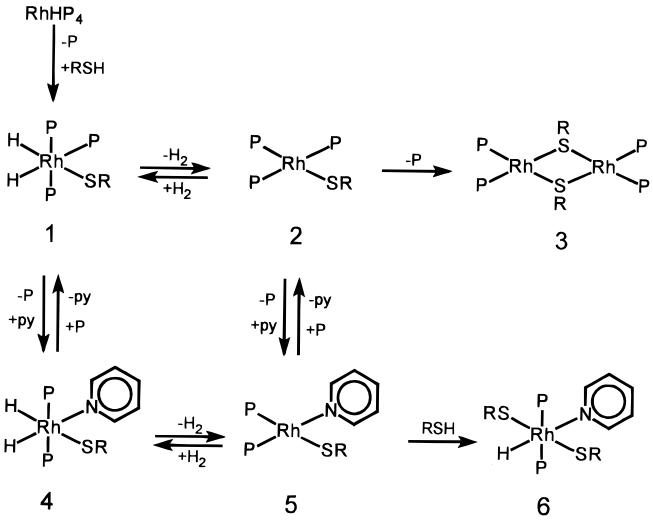
The chemistry of tris(triphenylphosphine)rhodium carboxylate and thiolate complexes shows the two series of compounds to possess a number of features in common. Each is formed by the reaction of $[Rh(H)(PPh_3)_4]$ with YH (Y = carboxylate or thiolate) to give a dihydro complex which then loses H_2 (reversibly):[8]

$$[Rh(H)(PPh_3)_4] \xrightarrow{YH} [Rh(Y)(H)_2(PPh_3)_3] \underset{+H_2}{\overset{-H_2}{\rightleftharpoons}} [Rh(Y)(PPh_3)_3]$$

$$Y = RCO_2—, RS—$$

With $Y = RCO_2$—the product is stable and can be isolated in good yield,[6] whereas with Y = RS— dimerization occurs with loss of a phosphine to give a thiolate-bridged complex (Scheme 1). The dihydrotris(phosphine) acetate complex exists (in solution) in equilibrium with a bis(phosphine) form for which there is no thiolate analogue.

In the presence of pyridine other products are formed by exchange of a phosphine for pyridine (shown in Scheme 1 for thiolate derivatives): $[Rh(O_2CCH_3)(PPh_3)_3]$ is converted into *cis*-$[Rh(O_2CCH_3)(PPh_3)_2(py)]$ [which gives a ^{31}P{^{1}H} spectrum consisting of two doublets of doublets with J(Rh,P) and J(P,P) characteristic of an Rh(I) complex] in 10% pyridine–toluene and into the *trans* isomer in



Scheme 1. P = PPh_3.

10% pyridine–chloroform, while $[Rh(O_2CCF_3)(PPh_3)_3]$ forms only the *trans* isomer (giving a doublet in the ^{31}P{^{1}H} spectrum). With SR in place of O_2CR the product is *cis*-$[Rh(SR)(PPh_3)_2(py)]$.[7,10] This compound is prepared *in situ* from $[Rh(H)(PPh_3)_4]$ and RSH in 10% pyridine–toluene and is a component of a mixture containing two or more of the six products shown in Scheme 1. Also present, in varying concentrations, is an unidentified product with two hydrides per rhodium. This product is also formed from $[Rh(O_2CR)(PPh_3)_3]$ (R = CH_3, Ph) in the presence of H_2 and pyridine and must therefore contain neither of the groups O_2CR and SR. In the case where R is cyclohexyl the mixture of thiol plus $[Rh(H)(PPh_3)_4]$ in 10% pyridine–toluene, after warming to *ca.* 50 °C for 15–20 s, gives ^{31}P and ^{103}Rh spectra (Fig. 1) showing all seven products. At $-25\,^{\circ}$C very little change occurs over a period of several hours, but after 1–2 days the concentration of the dinuclear product has increased significantly.

The spectrum shown in Fig. 1 was obtained without ^{1}H decoupling and so contains data relating to the hydride ligands. ^{31}P–^{1}H coupling is seen clearly in the f_2 projection of signals from complexes **1**, **4** and **6** [Fig. 2(a)–(c)] and ^{103}Rh–^{1}H coupling is visible in the f_1 projection (^{103}Rh) of spectra recorded with higher resolution in this dimension [Fig. 2(d)], providing a useful means of characterizing hydride-containing products. The positions of the cross peaks in Fig. 2(d) indicate that $^1J(^{103}\text{Rh},^{31}\text{P})$ is of opposite sign to $^2J(^{31}\text{P},^1\text{H})$.[11] When ^{31}P–^{31}P coupling is present (e.g. complexes **1**, **2** and **5**), this also appears in both the f_1 and f_2 dimensions leading, in cases where the full coupling pattern is sufficiently complex, to a significantly reduced signal intensity: in Fig. 1 the ^{103}Rh signal associated with the phosphine positioned *trans* to H in complex **1** is not readily detected.

The ^{103}Rh chemical shifts fall within a range of 1300 ppm and show no correlation with the oxidation state of the metal. The complexes $[Rh(Y)(PPh_3)_3]$ (Y = O_2CR, SR) display a greater change in δ^{103}Rh on replacement of a phosphine by pyridine than on loss of H_2 to give $[Rh(Y)(H)_2(PPh_3)_3]$, which has chemical shifts intermediate between those of the two hydride-containing complexes. With the exception of the $SCPh_3$ and SPh derivatives (where shielding by local fields

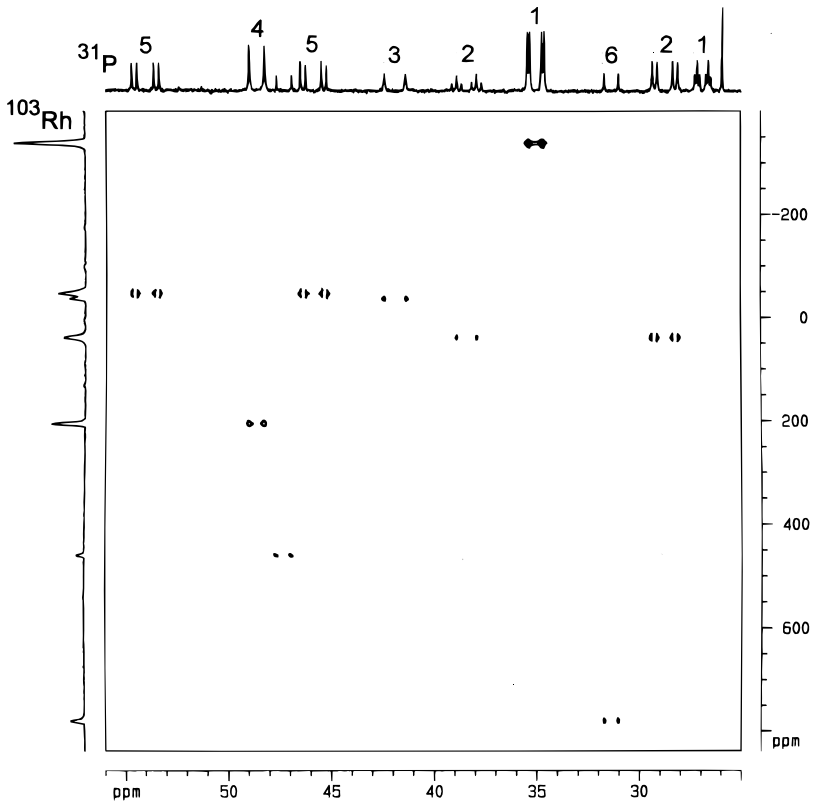


Figure 1. ^{103}Rh–^{31}P spectrum obtained from a mixture of [Rh(H)(PPh_3)$_4$] (0.02 M), CySH (0.2 M) and Ph_3P (0.2 M) in 10% pyridine–toluene at −25 °C. Products are identified in Scheme 1. The ^{31}P signal at δ 26 ppm is from Ph_3PO.

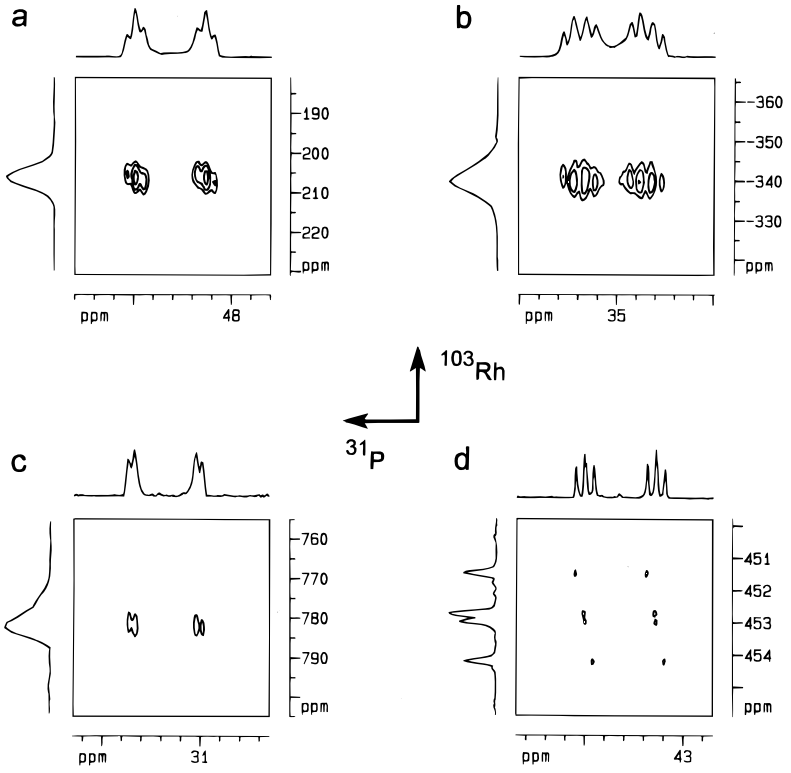


Figure 2. (a)–(c) Expanded regions from Fig. 1. Signals from hydride-containing complexes with f_2 internal projection showing ^{31}P–^{1}H coupling. (d) High-resolution ^{103}Rh–^{31}P spectrum of [Rh(O_2CQuin)(H)$_2$(PPh_3)$_2$] showing ^{31}P–^{1}H and ^{103}Rh–^{1}H coupling.

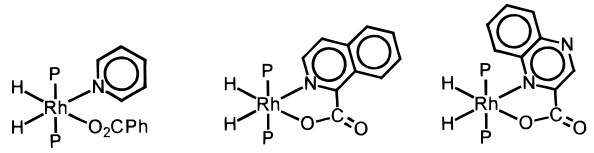


Figure 3. Coordination geometries of dihydrobis-(triphenylphosphine) complexes with non-chelating (benzoate, pyridine) and chelating (isoquinoline-1-carboxylate, quinoxaline-2-carboxylate) ligands.

from the phenyl groups is likely to influence δ^{103}Rh), there is remarkably little difference (less than 100 ppm) in the chemical shifts of the $[Rh(Y)(PPh_3)_3]$ complexes, consistent with a low value for the paramagnetic shielding term in the Ramsey equation:[4]

$$\delta = -A + B\langle r^{-3}\rangle \Delta E^{-1}$$

where A is the diamagnetic shielding, $B\langle r^{-3}\rangle \Delta E^{-1}$ is the paramagnetic shielding (generally considered to make the greater contribution to δ for heavy nuclei), B is a constant, r is the effective radius of the metal d orbitals and ΔE is an average excitation energy between filled and empty d orbitals. In the case of $[Rh(O_2CCH_3)(PPh_3)_3]$ and $[Rh(SCH_2Ph)(PPh_3)_3]$ δ^{103}Rh differs by only 1 ppm, suggesting that for these complexes the differences in ΔE and $\langle r^{-3}\rangle$, reflected by the relative positions of the ligands O_2CCH_3 and SCH_2Ph in the spectrochemical and nephelauxetic series, respectively, almost exactly cancel each other.

On treating $[Rh(Y)(PPh_3)_3]$ with pyridine to give *cis*-$[Rh(Y)(PPh_3)_2(py)]$, the chemical shift of the carboxylate complexes increases by 246–368 ppm and for the thiolate complexes decreases by 10–86 ppm, the smallest decrease being observed for the complex of the most weakly nucleophilic thiolate, $—SC_6F_5$. This pattern of change in δ^{103}Rh on replacing PPh_3 by the more nucleophilic pyridine can be rationalized in terms of a greater increase in electron density on the metal (and hence an increase in the d orbital radius) in complexes of the electron-rich thiolates than for the carboxylate complexes in which electron density is attracted by the O_2CR ligand. In this interpretation the effect of replacing PPh_3 by pyridine (a weaker ligand in terms of its effect on ΔE) is to reduce ΔE for both carboxylate and thiolate complexes, but to have a much greater effect on the thiolate complexes in terms of a decrease in $\langle r^{-3}\rangle$, the influence of the two opposing effects being approximately equal in the case where $Y = —SC_6F_5$.

A general trend observed in the ^{103}Rh chemical shifts is an increase in δ in the order of decreasing nucleophilicity, $Y = —SR < —SC_6F_5 < —O_2CR$, for complexes differing only in Y. A similar trend is indicated for the three complexes differing in phosphine (PPh_3 replaced by $PMePh_2$). The presence of two thiolate ligands and one hydride in the complex $[Rh(SR)_2(H)(PPh_3)_2(py)]$ (which has no carboxylate analogue) results in an increase in δ^{103}Rh of 576–617 ppm relative to $[Rh(SR)(H)_2(PPh_3)_2(py)]$. This compares with an increase of 253–360 ppm on hydrogenating *cis*-$[Rh(Y)(PPh_3)_2(py)]$ and would appear to be related to the greater opportunities for the creation of low-lying vacant orbitals in the bis(thiolate) complexes.

The exchange of ligands $—O_2CPh$ and pyridine in the complex $[Rh(O_2CPh)(H)_2(PPh_3)_2(py)]$ for the chelating O_2CPy causes the value of δ^{103}Rh to fall by 198 ppm. This change is likely to be a result of the differing shielding effects of the carbonyl groups in the two complexes. In the benzoate complex free rotation about the O—C bond allows the C=O group to take up a wide range of orientations with respect to rhodium while in the pyridine-2-carboxylate complex such changes in geometry are prevented by the ring structure. The pyrazine-2- and isoquinoline-1-carboxylate complexes have ^{103}Rh chemical shifts that are lower than that of $[Rh(O_2CPy)(H)_2(PPh_3)_2]$ by 14 and 33 ppm respectively, a much smaller change than that found for the quinoline-2- and quinoxaline-2-carboxylate analogues.

The only significant difference between the two groups of ligands is that the latter has a second aromatic ring positioned so as to approach closely to the metal on complexation, while the former either has no such ring or has a second ring positioned so as to face away from the metal (Fig. 3). Magnetic fields generated by electrons circulating within the quinoline- and quinoxalinecarboxylate ligands would be expected to have a deshielding influence on the metal, if, as would be expected, the metal lies in the plane of the ligand. The low values of δ for the quinoline-2- and quinoxaline-2-carboxylate complexes may be caused by changes in the coordination geometry arising from repulsion between the 8-hydrogen of the ligand and the adjacent hydride. If so, these changes are reflected in ^1J(Rh, H) (H *trans* to N)[8] and to a barely significant extent in other spectral parameters (^{1}H, ^{15}N, ^{31}P).[8,12]

The effects of change of solvent, concentration and temperature were measured for selected complexes. Values of δ^{103}Rh recorded from $[Rh(O_2CCH_3)(PPh_3)_3]$ and $[Rh_2(SC_6F_5)_2(PPh_3)_4]$ (0.025 M, 248 K) in chloroform are -14 and 300 and in toluene -26 and 311, respectively. Variations in concentration cause much smaller changes, amounting to less than 1 ppm for $[Rh_2(SC_6F_5)_2(PPh_3)_4]$ and $[Rh(O_2CQuin)(H)_2(PPh_3)_2]$ at concentrations in the range 0.01–0.1 M (solution in chloroform at 300 K). On increasing the concentration of pyridine from 10% to 30%, δ for *cis*-$[Rh(SC_6F_5)(PPh_3)_2(py)]$ decreases by 1.5 ppm and for $[Rh(SC_6F_5)(H)_2(PPh_3)_2(py)]$ increases by 1.0 ppm. The largest changes in δ are found to occur on varying the temperature and are shown in Table 1 for $[Rh_2(SC_6F_5)_2(PPh_3)_4]$ (in $CDCl_3$ at 300 K $\delta = 357$) and for $[Rh(O_2CArN)(H)_2(PPh_3)_2]$ and fall in the range 30–52 ppm on increasing the temperature from 248 to 300 K.

Spectra obtained by the ^{103}Rh–^{31}P method gave chemical shifts reproducible to *ca.* 0.3 ppm using the ^{103}Rh–^{1}H method for a number of complexes permitting the use of both.

Acknowledgement

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Table 1. ^{103}Rh and ^{31}P NMR data for the carboxylate and thiolate complexes

Complex[a]	δ^{103}Rh[b]	δ^{31}P[c]	^{31}P signal	$J(^{103}Rh, ^{31}P)$[d]
$[Rh(O_2CCH_3)(PPh_3)_3]$	−26	52.08	dt	176.8
		34.68	dd	150.6
$[Rh(O_2CCF_3)(PPh_3)_3]$	−38	51.99	dt	183.3
		33.88	dd	147.3
$[Rh(O_2CPh)(PPh_3)_3]$	−20	51.88	dt	175.0
		35.45	dd	152.2
$[Rh(O_2CCH_3)(PMePh_2)_3]$	−138	33.57	dt	172.5
		17.16	dd	147.1
cis-$[Rh(O_2CCH_3)(PPh_3)_2(py)]$[e]	342	58.99	dd	191.4
		50.16	dd	175.0
cis-$[Rh(O_2CPh)(PPh_3)_2(py)]$[e]	328	59.29	dd	193.1
		50.46	dd	172.3
trans-$[Rh(O_2CCH_3)(PPh_3)_2(py)]$[f]	225	49.07	d	170.5
trans-$[Rh(O_2CCF_3)(PPh_3)_2(py)]$[e]	208	49.78	d	171.4
$[Rh(O_2CCH_3)(H)_2(PPh_3)_2]$	646	41.60	d	120.5
$[Rh(O_2CCH_3)(H)_2(PPh_3)_3]$	207	39.86	dd	117.4
		22.01	dt	89.4
$[Rh(O_2CPh)(H)_2(PPh_3)_3]$	183	38.97	dd	118.5
		23.18	dt	88.3
$[Rh(O_2CCH_3)(H)_2(PPh_3)_2(py)]$[e]	630	47.71	d	121.1
$[Rh(O_2CPh)(H)_2(PPh_3)_2(py)]$[e]	688	47.78	d	121.2
$[Rh(O_2CPy)(H)_2(PPh_3)_2]$[f]	490			
	523[g]	43.83[h]	d	118.5
$[Rh(O_2CPyraz)(H)_2(PPh_3)_2]$[f]	476			
	506[g]	43.50[h]	d	117.7
$[Rh(O_2CQuin)(H)_2(PPh_3)_2]$[f]	419			
	453[g]	43.77[h]	d	118.7
$[Rh(O_2CIsoq)(H)_2(PPh_3)_2]$[f]	457			
	490[g]	44.19[h]	d	118.9
$[Rh(O_2CQuinox)(H)_2(PPh_3)_2]$[f]	405			
	436[g]	43.58[h]	d	118.0
$[Rh(SC_6F_5)(PPh_3)_3]$	17	38.40	dt	169.6
		24.64	dd	148.3
$[Rh(SCPh_3)(PPh_3)_3]$	−338	40.39	dt	164.6
		36.32	dd	150.6
$[Rh(SPh)(PPh_3)_3]$	−164	39.26	dt	168.7
		27.13	dd	149.6
$[Rh(SCH_2Ph)(PPh_3)_3]$	−25	38.13	dt	169.6
		26.89	dd	157.7
$[Rh(S^iPr)(PPh_3)_3]$	33	38.71	dt	158.6
		28.72	dd	161.7
$[Rh(S^nPr)(PPh_3)_3]$	−59	38.36	dt	162.2
		27.52	dd	158.8
$[Rh(SCy)(PPh_3)_3]$	39	38.32	dt	156.3
		28.60	dd	162.5
$[Rh(SC_6F_5)(PMePh_2)_3]$	−414	24.79	dt	167.6
		14.17	dd	142.1
$[Rh_2(SC_6F_5)_2(PPh_3)_4]$	311			
	363[g]	43.85[i]	d	176.4
$[Rh_2(SCPh_3)_2(PPh_3)_4]$	−338	45.36	d	174.6
$[Rh_2(SPh)_2(PPh_3)_4]$	36	43.18	d	169.0
$[Rh_2(S^iPr)_2(PPh_3)_4]$	−41	42.12	d	166.6
$[Rh_2(S^nPr)_2(PPh_3)_4]$	−72	44.69	d	172.5
$[Rh_2(SCy)_2(PPh_3)_4]$	−38	41.94	d	166.5
cis-$[Rh(SC_6F_5)(PPh_3)_2(py)]$[e]	7	50.46	dd	165.2
		47.79	dd	178.9
cis-$[Rh(S^iPr)(PPh_3)_2(py)]$[e]	−49	53.56	dd	173.7
		45.94	dd	165.6
cis-$[Rh(SCy)(PPh_3)_2(py)]$[e]	−47	53.88	dd	174.5
		45.74	dd	166.0
$[Rh(SC_6F_5)(H)_2(PMePh_2)_3]$	−417	25.94	dd	110.0
		3.25	dt	89.7
$[Rh(SC_6F_5)(H)_2(PPh_3)_3]$	−221	36.38	dd	112.7
		22.54	dt	86.4
$[Rh(SCPh_3)(H)_2(PPh_3)_3]$	−422	44.36	dd	113.4
		28.55	dt	93.7

Table 1. *Continued*

Complex[a]	δ^{103}Rh[b]	δ^{31}P[c]	^{31}P signal	$J(^{103}Rh, ^{31}P)$[d]
$[Rh(SPh)(H)_2(PPh_3)_3]$	−323	35.83	dd	111.9
		26.81	dt	88.9
$[Rh(SCH_2Ph)(H)_2(PPh_3)_3]$	−358	37.16	dd	112.7
		27.97	dt	90.8
$[Rh(S^iPr)(H)_2(PPh_3)_3]$	−328	34.33	dd	113.3
		26.47	dt	89.5
$[Rh(S^nPr)(H)_2(PPh_3)_3]$	−376	37.51	dd	113.3
		27.65	dt	90.9
$[Rh(SCy)(H)_2(PPh_3)_3]$	−340	34.98	dd	113.6
		26.87	dt	89.8
$[Rh(SC_6F_5)(H)_2(PPh_3)_2(py)]$[e]	273	48.30	d	118.2
$[Rh(SCPh_3)(H)_2(PPh_3)_2(py)]$[e]	155	52.73	d	118.1
$[Rh(SPh)(H)_2(PPh_3)_2(py)]$[e]	222	47.15	d	116.6
$[Rh(SCH_2Ph)(H)_2(PPh_3)_2(py)]$[e]	219	49.76	d	117.6
$[Rh(S^iPr)(H)_2(PPh_3)_2(py)]$[e]	215	48.21	d	118.5
$[Rh(S^nPr)(H)_2(PPh_3)_2(py)]$[e]	223	49.46	d	118.3
$[Rh(SCy)(H)_2(PPh_3)_2(py)]$[e]	206	48.62	d	118.8
$[Rh(SPh)_2(H)(PPh_3)_2(py)]$[e]	817	29.87	d	106.0
$[Rh(SCH_2Ph)_2(H)(PPh_3)_2(py)]$[e]	812	29.47	d	109.7
$[Rh(S^nPr)_2(H)(PPh_3)_2(py)]$[e]	840	28.36	d	110.1
$[Rh(SCy)_2(H)(PPh_3)_2(py)]$[e]	782	31.35	d	111.9

[a] Solution in toluene at 248 K unless specified otherwise.
[b] Chemical shifts relative to 3.16 MHz, ±1 ppm.
[c] Chemical shifts relative to 85% H_3PO_4 at 300 K.
[d] Coupling constants in Hz.
[e] Solution in 10% pyridine–toluene.
[f] Solution in chloroform.
[g] Recorded at 300 K.
[h] Data taken from Ref. 8.
[i] Data taken from Ref. 7.

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