Organometallics **1990**, *9*, 131–136

Rhodium Complexes of C-Bonded Pyridines: Synthesis and X-ray Structure of $[C_5Me_5Rh(Me)(CO)\{3\text{-}C_5H_4N\text{-}Rh(CO)_2Cl\}]$, a Complex Containing 3-Pyridyl C,N-Bridging Rh(I) and Rh(III)

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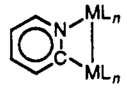
Received May 15, 1989

The reaction of $[C_5Me_5RhMe_2(Me_2SO)]$ with 2-, 3-, and 4-pyridinecarboxaldehyde gave the appropriately substituted $[C_5Me_5Rh(Me)(CO)(x\text{-}C_5H_4N)]$ (**2**, $x = 2$–4) in 80–90% yields; $[C_5Me_5Ir(Me)(CO)(4\text{-}C_5H_4N)]$ was prepared analogously. The 2- and 3-pyridyl complexes were readily quaternized by reaction with MeI to give $[C_5Me_5Rh(Me)(CO)(x\text{-}C_5H_4NMe)]I$, ($x = 2, 3$), but the (4-pyridyl)rhodium complex underwent coupling to give 1,4-dimethylpyridinium iodide and $[C_5Me_5Rh(CO)Me(I)]$. The products from the last reaction with CD_3I were $[C_5Me_5Rh(CO)CD_3(I)]$ and $4\text{-}CH_3C_5H_4NCD_3{}^+I^-$. On reaction of $[C_5Me_5Rh(Me)(CO)(4\text{-}C_5H_4N)]$ with other electrophiles ($H^+BF_4^-$, $Et_3O^+BF_4^-$), evidence for the formation of unstable salts, $[C_5Me_5Rh(Me)(CO)(4\text{-}C_5H_4NH)]^+$ and $[C_5Me_5Rh(Me)(CO)(4\text{-}C_5H_4NEt)]^+$, was obtained. In contrast, the complex $[C_5Me_5Ir(Me)(CO)(4\text{-}C_5H_4N)]$ reacted with methyl iodide to give the stable $[C_5Me_5Ir(Me)(CO)(4\text{-}C_5H_4NMe)]^+I^-$. $[C_5Me_5Rh(Me)(CO)(x\text{-}C_5H_4N)]$ ($x = 3, 4$) reacted with $[Rh_2(CO)_4Cl_2]$ to give the novel dinuclear adducts $[C_5Me_5Rh(Me)(CO)\{x\text{-}C_5H_4NRh(CO)_2Cl\}]$, in which a 3- or a 4-pyridyl bridges Rh(III) and Rh(I). An X-ray determination of $[C_5Me_5Rh(Me)(CO)\{3\text{-}C_5H_4NRh(CO)_2Cl\}]$ confirmed the structure.

Introduction

There is currently considerable interest in molecular species containing two (or more) metal atoms,[1] in particular to elicit what, if any, interactions take place between them. Two situations may be differentiated: one where a group bridges the metals and the other where only a metal–metal bond is present. We are concerned with complexes of the first type, where the metals are joined in C,N fashion by a pyridyl. Numerous complexes containing a carbon-bonded 2-pyridyl ligand have been made,[2] and many of these span a metal–metal bond:[3]



Comparatively few complexes bearing a pyridine substituted in the 3- or 4-position are known,[4] and no complexes appear to have been reported in which a 3- or 4-pyridyl group spans two metal atoms.

To explore such interactions, we have constructed a molecular framework based on the rhodium pyridyl complexes $[C_5Me_5Rh(Me)(CO)(x\text{-}C_5H_4N)]$, which can be used to coordinate further through the pyridyl nitrogen. We report here the preparation of the framework compounds, and some of their reactions, including the formation of two adducts with $Rh(CO)_2Cl$ and the X-ray structure of one of them.

Results and Discussion

Synthesis of the (2-Pyridyl)-, (3-Pyridyl)-, and (4-Pyridyl)rhodium Complexes (2a–c) and of the (4-Pyridyl)iridium Complex (4). The rhodium pyridyl complexes **2** were synthesized by the method of Gomez et al.[5] by reaction of $[C_5Me_5Rh(Me)_2(Me_2SO)]$ (**1**) with the appropriate pyridinecarboxaldehyde. The reactions with

$$\underset{\mathbf{1}}{[C_5Me_5Rh(Me)_2(Me_2SO)]} + x\text{-}CHOC_5H_4N \rightarrow$$
$$[C_5Me_5Rh(Me)(CO)(x\text{-}C_5H_4N)] + CH_4 + Me_2SO$$

2a, $x = 2$
2b, $x = 3$
2c, $x = 4$

$$\underset{\mathbf{3}}{[C_5Me_5Ir(Me)_2(Me_2SO)]} + 4\text{-}CHOC_5H_4N \rightarrow$$
$$\underset{\mathbf{4}}{[C_5Me_5Ir(Me)(CO)(4\text{-}C_5H_4N)]} + CH_4 + Me_2SO$$

the 3- and 4-pyridinecarboxaldehydes were carried out in cyclohexane at 55 °C with a 1.5-fold excess of the aldehyde, to give the products **2b,c** in 80–90% yields. The iridium complex **3** reacted similarly with 4-pyridinecarboxaldehyde to give **4** in 61% yield. In cyclohexane or dichloromethane, complex **1** gave only very low yields of **2a** on reaction with 2-pyridinecarboxaldehyde, and the more polar solvent acetone was needed to give the complex. However, that reaction was then complicated by the formation of the aldol adduct, $NC_5H_4CHOHCH_2C(=O)Me$; to get good yields of **2a**, a very large excess (17×) of the aldehyde was needed.

The complexes were characterized by elemental analysis and spectroscopy (Tables I–III). The ^1H and $^{13}C\{^1H\}$ NMR spectra showed clearly that in each case only one isomer was formed and that this was the isomer with the metal

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[1] See for example: *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, England, 1982. For recent references to bimetallic complexes bridged by an organic group, see Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167. Mackenzie, P. B.; Coots, R. J.; Grubbs, R. H. *Organometallics* **1989**, *8*, 8. Bruno, G.; Lo Schiavo, S.; Rotondo, E.; Arena, C. G.; Faraone, F. *Organometallics* **1989**, *8*, 886.

[2] Isobe, K.; Nakamura, Y.; Kawaguchi, Y. *Bull. Chem. Soc. Jpn.* **1980**, *63*, 139. Isobe, K.; Nanjo, K.; Nakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1986**, *54*, 2141. Crociani, B.; Di Bianca, F.; Giovenco, A.; Berton, A.; Bertani, R. *J. Organomet. Chem.* **1989**, *361*, 255.

[3] Tomasik, P.; Ratajewicz, Z. Pyridine-Metal Complexes In *Heterocyclic Compounds*; Wiley-Interscience: New York, 1985; Vol. 14, Parts 6a–6c, and references therein. Crociani, B.; Di Bianca, F.; Giovenco, A.; Scrivanti, A. *J. Organomet. Chem.* **1983**, *251*, 393.

[4] Isobe, K.; Nakamura, Y.; Miwa, T.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 149. Isobe, K.; Kai, E.; Nakamura, Y.; Nishimoto, K.; Miwa, T.; Kawaguchi, S.; Kinoshita, K.; Nakatsu, K. *J. Am. Chem. Soc.* **1980**, *102*, 2475. See also: Cooke, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 173. Cordone, R.; Harman, W. D., Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 2896.

[5] Gomez, M.; Kisenyi, J. M.; Sunley, G. J.; Maitlis, P. M. *J. Organomet. Chem.* **1985**, *296*, 197.

0276-7333/90/2309-0131$02.50/0

Table I. Yield, Microanalysis, and Infrared Data

		anal. found (calcd), %				
complex	yield, %	C	H	N	other	ν(CO), cm^{-1}
2a	80	57.8	6.4	3.3		1999^a
		(56.8)	(6.2)	(3.9)		
2b	80	56.7	6.0	3.7		2009^b
		(56.8)	(6.2)	(3.9)		
2c	90	57.1	6.3	4.1		2010^b
		(56.8)	(6.2)	(3.9)		
4	61	45.4	5.2	2.9		1988^b
		(45.5)	(4.9)	(3.1)		
5a	70	43.7	5.0	2.8		2024^a
		(43.1)	(5.0)	(2.8)		
5b	95	43.0	5.3	2.7		2012^a
		(43.1)	(5.0)	(2.8)		
6	96	35.9	4.2	2.1		2004^b
		(36.6)	(4.3)	(2.4)		
7	65	35.9	4.6		30.5 [I]	2036^c
		(35.3)	(4.4)		(31.1)	
8b	76	46.1	5.3	3.2		2025^b
		(45.7)	(5.2)	(3.1)		
8c	60	43.0	5.1	2.8		2027^b
		(45.7)	(5.2)	(3.1)		
9b	63	40.9	4.0	2.4	6.5 [Cl]	2083, 2024, 2019, 2005^c
		(41.2)	(4.0)	(2.5)	(6.4)	
9c	87	41.4	4.0	2.2	6.1 [Cl]	2083, 2025, 2002^c
		(41.2)	(4.0)	(2.2)	(6.4)	
10	44	45.7	5.0	3.0	8.1 [Cl]	2015^b
		(45.6)	(5.0)	(3.1)	(7.9)	

^{a} KBr disk. ^{b} Dichloromethane. ^{c} Pentane.

attached to the pyridyl carbon that originally bore the CHO; no detectable isomerization had taken place. The pyridyl carbons attached to the rhodium in **2a–c** showed coupling (34–37 Hz) to ^{103}Rh but no coupling to H (J(mod)); similarly the pyridyl carbon in 4 attached to iridium was identified since it had no hydrogen attached. The complexes **2a–c** showed shifts of the rhodium-bonded pyridyl carbons of between 25 and 35 ppm to higher frequency compared to those for pyridine itself.[6] Isobe et al.[4] have prepared, though by quite different routes, the C-bonded pyridylpalladium complexes [Pd(PEt$_3$)$_2$(x-pyridyl)Br] and have noted $\Delta\delta$ values of ca 30 ppm for these compounds. The Ir-bonded 4-pyridyl carbon in 4 resonated at δ 145.9, only some 10 ppm higher than in pyridine (δ 135.5).

Quaternization Reactions of 2a–c and 4 with Electrophiles. The 2- and 3-substituted complexes **2a** and **2b** quaternized readily with methyl iodide in dichloromethane (1.5 h/20 °C), and the corresponding adducts **5a** and **5b** were obtained in high yields. The iridium complex 4 reacted similarly to give [C$_5$Me$_5$Ir(Me)(CO)(4-C$_5$H$_4$NMe)]$^+$I$^-$ (**6**). The complexes were again characterized by analysis[7]

$$\begin{array}{l}[\mathrm{C_5Me_5M(Me)(CO)}(x\text{-}\mathrm{C_5H_4N})] + \mathrm{CH_3I} \rightarrow \\ \quad \mathbf{2a},\ x = 2 \\ \quad \mathbf{2b},\ x = 3 \\ \quad 4,\ x = 4 \\ \qquad\qquad [\mathrm{C_5Me_5M(Me)(CO)}(x\text{-}\mathrm{C_5H_4NMe})]^+\mathrm{I}^- \\ \qquad\qquad\quad \mathbf{5a},\ \mathrm{M} = \mathrm{Rh},\ x = 2 \\ \qquad\qquad\quad \mathbf{5b},\ \mathrm{M} = \mathrm{Rh},\ x = 3 \\ \qquad\qquad\quad 6,\ \mathrm{M} = \mathrm{Ir},\ x = 4 \end{array}$$

and spectroscopy. The IR spectra showed an increase of ν(CO), by comparison to ν(CO) bands in **2a**, **2b**, and 4, respectively, consistent with a decrease in back-bonding from the metal in the cationic complex over that in the neutral compound. This suggests that the positive charge is to some extent delocalized over the metal as well as the pyridine ring. The coupling, J(Rh–C), of the pyridyl carbon bonded to Rh also increased from 36–37 Hz in **2a,b** to 46 (**5a**) and 41 Hz (**5b**), respectively.

However, when the quaternization reaction was attempted with the (4-pyridyl)rhodium complex **2c**, no adduct corresponding to **5** or **6** could be isolated; instead, a complex decomposition occurred. On addition of diethyl ether to the dichloromethane solution, the solid that precipitated was shown to be 1,4-dimethylpyridinium iodide, and [C$_5$Me$_5$Rh(Me)(CO)I] (**7**; 65%) was obtained from the solution. The same reaction was repeated with CD$_3$I, and the two products were again isolated. The ^{1}H NMR spectrum showed no significant protons either on the rhodium methyl (δ 1.05) or at the 1-methyl of the 1-4-dimethylpyridinium salt (δ 4.59). In contrast, the ^{2}H NMR spectrum showed resonances in these two positions, indicating that reaction according to

$$\begin{array}{l}[\mathrm{C_5Me_5Rh(CH_3)(CO)(4\text{-}C_5H_4N)}] + \mathrm{CD_3I} \rightarrow \\ \qquad\qquad \mathbf{2c} \\ \qquad [\mathrm{C_5Me_5Rh(CD_3)(CO)I}] + [(\mathrm{4\text{-}CH_3C_5H_4NCD_3})]^+\mathrm{I}^- \\ \qquad\qquad\quad \mathbf{7}\text{-}d_3 \end{array}$$

had taken place.

It is probable that quaternization of the pyridine nitrogen occurs in this reaction but that the product [C$_5$Me$_5$Rh(Me)(CO)(4-C$_5$H$_4$NMe)]$^+$I$^-$ rapidly reductively eliminates, giving the dimethylpyridinium salt, and perhaps the transient "C$_5$Me$_5$RhCO", which then reacts readily with methyl iodide to give **7**.

We have investigated this process, by reacting **2c** with a variety of other Lewis acid reagents. Thus, **2c** reacted rapidly with triethyloxonium tetrafluoroborate, as indicated by the IR spectrum, giving a species with ν(CO) at 2025 cm^{-1}, in the same region as for [C$_5$Me$_5$Rh(Me)(CO)(2-C$_5$H$_4$NMe)]$^+$I$^-$ (ν(CO) 2024 cm^{-1}). Although this material decomposed very quickly, we presume that ν(CO) at 2025 cm^{-1} arises from [C$_5$Me$_5$Rh(Me)(CO)(4-C$_5$H$_4$NEt)]$^+$BF$_4^-$. In fact a deep blue color, associated with ν(CO) at 1724 cm^{-1}, accompanies the decomposition of this complex; these features are due to the formation of the well-known [{C$_5$Me$_5$Rh(μ-CO)}$_2$].[8] This indicates that, in the presence of a poor nucleophile, the reaction can proceed according to

$$\begin{array}{l}[\mathrm{C_5Me_5Rh(Me)(CO)(4\text{-}C_5H_4NEt)}]^+ \rightarrow \\ \qquad \tfrac{1}{2}[\{\mathrm{C_5Me_5Rh}(\mu\text{-}\mathrm{CO})\}_2] + \mathrm{4\text{-}MeC_5H_4NEt^+}\end{array}$$

The reaction of **2c** with HBF$_4$ gave an immediate precipitate, which was shown to be [C$_5$Me$_5$Rh(Me)(CO)(4-C$_5$H$_4$NH)]$^+$BF$_4^-$ (**8c**) by spectroscopy. The microanalysis was low in carbon, probably again due to a slow decomposition, since the characteristic blue color of [{C$_5$Me$_5$Rh(μ-CO)}$_2$] was also observed there. The same reaction with the 3-pyridyl isomer **2b** gave the relatively stable [C$_5$Me$_5$Rh(Me)(CO)(3-C$_5$H$_4$NH)]$^+$BF$_4^-$ (**8b**), which was completely characterized, including microanalysis.

Again, these cations showed ν(CO) values significantly higher than those of the parent neutral compounds. Since in none of the cations of **5**, **6**, or **8** is the formal oxidation state of the metal altered with respect to that in **2** or **3**, we must conclude that the *positive charge* actually has the effect of withdrawing electron density from the metal.

Reactions of the (3-Pyridyl)- and (4-Pyridyl)rhodium Compounds 2b and 2c with [Rh$_2$(CO)$_4$Cl$_2$] and

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[6] Maciel, G. E.; McIver, J. W.; Ostlund, N. S.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 1.

[7] C, H, and N analyses were all good (Table I), but I$^-$ values were uniformly low.

[8] Nutton, A.; Maitlis, P. M. *J. Organomet. Chem.* **1979**, *166*, C21.

Table II. ^1H NMR Spectroscopic Data (δ, ppm)[a]

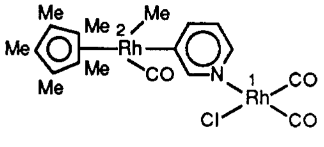
complex	C_5Me_5	M–Me		other
2a	1.70	0.54 [3.0]	H(3) 7.03 dddd (7, 1.5, 1, 1) H(4) 7.12 ddd (7, 6, 2) H(5) 6.77 ddd (6, 5, 1.5) H(6) 8.38 ddd (5, 2, 1)	
2b	1.78	0.51 [2.5]	H(2) 8.29 m H(4) 7.39 dddd (8, 2, 2, 2) H(5) 6.92 ddd (8, 4, 1) H(6) 8.16 dd (4, 2)	
2c	1.69	0.49 [2.0]	H(2/6) 8.00 dd (4.5, 1.5) H(3/5) 7.17 ddd (4.5, 1.5, 1.5)	
4	1.78	0.59	H(2/6) 7.97 dd (4.5, 1.5) H(3/5) 7.12 dd (4.5, 1.5)	
5a	1.79	0.69 [2]	H(3) 7.51 d, br (7.5) H(4) 7.73 ddd (7.5, 1.5, 1.5) H(5) 7.57 ddd (7.5, 1.5, 1.5) H(6) 9.53 dd (7.5, 1.5)	N–Me 4.62
5b	1.79	0.58 [2]	H(2) 8.35 H(4) 8.14 dd (8, 1) H(5) 7.61 dd (8, 6) H(6) 8.90 dd (6, 1)	N–Me 4.59
6	1.85	0.52	H(2/6) 8.33 m H(3/5) 7.75 m	N–Me 4.37
7	1.93	1.05 [2]		
8b	1.71	0.57 [2]	H(1) 8.33 br H(4) 8.26 m H(5) 7.52 dd (8, 6) H(6) 8.40 m	
8c	1.74	0.55 [2.5]	H(2/6) 8.05 br H(3/5) 7.85 m	
9b	1.72	0.52 [2.5]	H(2) 8.30 m, br H(4) 7.61 ddd (7.5, 3, 1.5) H(5) 7.03 ddd (7.5, 5.5, 1.0) H(6), 8.22 m	
9c	1.71	0.50 [2.5]	H(2/6) 8.01 m H(3/5) 7.31 m	
10	1.68	0.45 [2.5]	H(2/6) 8.08 m H(3/5) 7.04 m	

[a] Coupling (in Hz) to ^1H, $J(H-H)$, is given in parentheses; coupling to ^{103}Rh, $J(Rh-H)$, is given in brackets. All spectra were measured in $CDCl_3$, with the solvent as internal reference.

with $[PdCl_2(PhCN)_2]$. Both the 3- and the 4-isomers **2b** and **2c** reacted readily with a variety of metal complexes. Of these, the reactions with $[Rh_2(CO)_4Cl_2]$ were the most closely investigated. The complex **9c** from reaction of the 4-pyridyl isomer was formulated as $[C_5Me_5Rh(Me)(CO)\{4-C_5H_4N-Rh(CO)_2Cl\}]$. By comparison with a sample of authentic $[4-MeC_5H_4NRh(CO)_2Cl]$, it was shown that ν(CO) at 2002 and 2083 cm^{-1} corresponded to the $LRh(CO)_2Cl$ moiety, while that at 2025 cm^{-1} arose from $C_5Me_5RhCOMe(4-C_5H_4N)$. A similar analysis of the 3-isomer assigned ν(CO) at 2005 and 2083 cm^{-1} to $LRh(CO)_2Cl$. The pattern due to $C_5Me_5RhCOMe(3-C_5H_4N)$ consisted of *two* bands, at 2024 and 2019 cm^{-1}.

Solution molecular weight measurements for both **9b** and **9c** were consistent with the structures proposed; neither showed any evidence for dissociation (found, 563 and 567, respectively; calculated, 554). None of the other data gave any indication of the presence of impurities, and therefore we conclude that the extra ν(CO) band in **9b** is a solution property. Models show that the least hindered arrangement is with the 3-pyridyl ring very approximately parallel to the C_5Me_5 ring; this allows two orientations of the $N-Rh(CO)_2Cl$ moiety, which can be on the "same side" as either the Me or the CO attached to Rh(2). The two ν(CO) bands are therefore probably due to the conformational isomers arising from restricted rotation about Rh(2)–C(pyridine).

$[C_5Me_5Rh(Me)(CO)(3-C_5H_4N)] + {}^1/_2[Rh_2(CO)_4Cl_2] \longrightarrow$

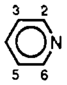


9b

To check on the identity of **9b**, we also determined its crystal structure by X-ray diffraction. The crystal structure reveals the presence of four molecules in the unit cell. Two of these are *two inequivalent but visually similar* molecules (Figure 1); the other two are the enantiomers of each of these molecules. In each molecule in the crystal $N-Rh(CO)_2Cl$ is on the same side as the CO.

The molecule showed the expected structure, in that it contained two distinct rhodium atoms bridged by a pyridine. The distance between them, 5.89 Å, is well outside bonding range. One metal atom, Rh(1), is formally in the +1 state and has a square-planar coordination to two cis carbonyls, the pyridine nitrogen, and a chlorine. The other rhodium (Rh(2), formally in the +3 state) carries a fairly

Table III. $^{13}C\{^1H\}$ **NMR Spectroscopic Data**[a]

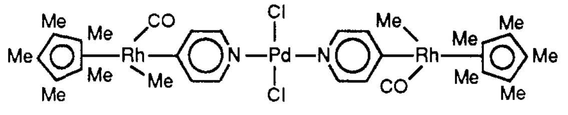
complex	C_5Me_5	CO	M–Me		other
2a	9.0 101.9 d [3]	192.6 d [80]	−2.8 d [24]	C(2) 181.2 d [37] C(3–6) 149.1, 134.6, 133.1, 117.6	
2b	9.0 101.8 d [3]	192.1 d [77]	−3.1 d [25]	C(3) 148.4 d [36] C(2,4–6) 158.5, 146.1, 144.4, 123.6	
2c	9.0 101.9 d [3]	192.0 d [77]	−2.5 d [24]	C(4) 169.0 d [34] C(3/5) 136.0 C(2/6) 146.6	
4	8.7 98.5	171.9	−21.9	C(4) 145.9 C(3/5) 136.5 C(2/6) 147.2	
5a	9.2 103.7 d [4]	190.1 d [73]	1.0 d [22]	C(2) 189.2 d [46] C(3–5) 147.5, 139.6, 137.5, 122.6	N–Me 54.9
5b	9.3 102.6 d [4]	190.5 d [75]	−2.0 d [23]	C(3) 157.9 d [41] C(2,4–6) 155, 149.8, 140.0, 125.3	N–Me 48.6
6	8.8 99.5	169.8[b]	−3.9	C(4) 170.4[b] C(2–3,5–6) 140.0, 138.6	N–Me 47.0
7	9.9 103.3 d [4]	189.5 d [78]	−5.9 d [19]		

[a] Coupling (in Hz) to ^{103}Rh, J(Rh–C), is given in brackets. All spectra were measured in $CDCl_3$, with solvent as internal reference. [b] Arbitrary assignments.

symmetrically bonded η^5-C_5Me_5 group, the methyls being displaced slightly (up to 0.16 Å) from the mean plane, as well as a linear CO, a methyl, and a C-bound pyridyl substituted at the 3-position to the N, which form the three legs of the piano-stool arrangement. The coordination about Rh(III) is approximately octahedral, with the angles between the bonds to methyl, CO, and pyridine being close to 90°.

The trinuclear complex **10** (the identity of which was established by analysis and spectroscopy) was also obtained, from the reaction of **2c** with $[PdCl_2(PhCN)_2]$ in dichloromethane.

$$2[C_5Me_5Rh(Me)(CO)(4\text{-}C_5H_4N)] + [PdCl_2(PhCN)_2] \longrightarrow$$



10

The formation of **9c** and **10** and their comparative stability indicate that the 4-pyridyl complexes are not inherently unstable toward coordination at the nitrogen. However, when the pyridine is quaternized (and charged) and a suitable nucleophile (e.g. iodide) is available, a coupling reaction readily takes place.

Experimental Section

All reactions were carried out under nitrogen, in Schlenk tubes or 5-mm NMR tubes; typical procedures are described. Yields, microanalyses, ^{1}H and ^{13}C NMR spectra, and IR spectra are collected in Tables I–III. Microanalyses were carried out by the Sheffield University Microanalytical Service. NMR spectra were measured on Perkin-Elmer R-12B (60 MHz) and Bruker AM-250 spectrometers and IR spectra on a Perkin-Elmer 1710 FT spectrometer. The identities of volatile compounds were checked by GC-MS with a Carlo-Erba gas chromatograph linked to a Kratos MS-25S mass spectrometer; this was also used for analyzing deuteriated compounds.

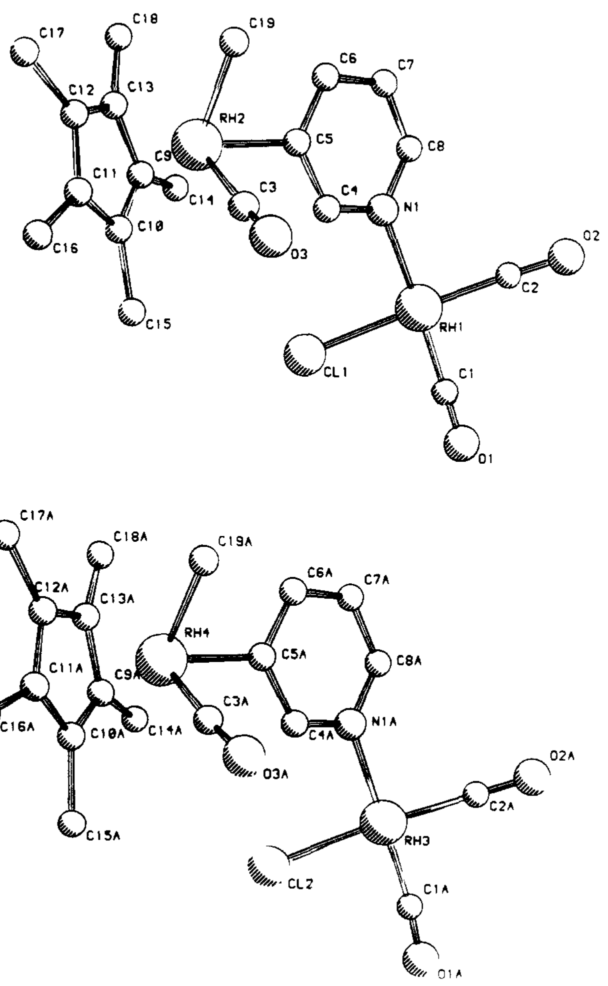


Figure 1. Structure of complex **9b** showing the two inequivalent but chemically identical molecules (H's omitted).

Preparation of $[C_5Me_5Rh(CO)Me(3\text{-}C_5H_4N)]$ (2b). 3-Pyridinecarboxaldehyde (84 mg, 0.75 mmol) was added to a solution of $[C_5Me_5RhMe_2(Me_2SO)]$ (**1**; 173 mg, 0.5 mmol) in cyclohexane (30 cm^3). The solution was heated (24 h, 55 °C); the solvent was then removed in vacuo and the brown residue extracted with pentane (3 × 15 cm^3). The pentane solution was washed with water (3 × 30 cm^3) to remove excess aldehyde and dimethyl sulfoxide, dried (Na_2SO_4), filtered, and allowed to crystallize to give yellow crystals of $[C_5Me_5Rh(CO)Me(3\text{-}C_5H_4N)]$ (145 mg, 80%). The 4-pyridyl complex (**2c**) was made similarly (80%), but the 2-pyridyl complex (**2a**) required acetone as solvent

Table IV. Selected Bond Lengths (Å) and Angles (deg) for Complex 9b

Rh(1)–Cl(1)	2.341 (8)	Rh(1)–N(1)	2.110 (14)
Rh(1)–C(1)	1.790 (21)	Rh(1)–C(2)	1.825 (20)
Rh(2)–C(3)	1.873 (24)	Rh(2)–C(5)	2.049 (17)
Rh(2)–C(9)	2.273 (17)	Rh(2)–C(10)	2.258 (15)
Rh(2)–C(11)	2.220 (17)	Rh(2)–C(12)	2.219 (19)
Rh(2)–C(13)	2.226 (16)	Rh(2)–C(19)	2.197 (26)
Rh(1)···Rh(2)	5.886		
Rh(3)–Cl(2)	2.339 (9)	Rh(3)–N(1a)	2.104 (15)
Rh(3)–C(1a)	1.837 (23)	Rh(3)–C(2a)	1.839 (19)
Rh(4)–C(3a)	1.800 (18)	Rh(4)–C(5a)	2.048 (18)
Rh(4)–C(9a)	2.259 (21)	Rh(4)–C(10a)	2.252 (17)
Rh(4)–C(11a)	2.223 (18)	Rh(4)–C(12a)	2.246 (19)
Rh(4)–C(13a)	2.188 (20)	Rh(4)–C(19a)	2.142 (22)
Rh(3)···Rh(4)	5.901		
Cl(1)–Rh(1)–N(1)	92.2 (4)	Cl(1)–Rh(1)–C(1)	85.5 (6)
N(1)–Rh(1)–C(1)	175.9 (8)	Cl(1)–Rh(1)–C(2)	177.2 (6)
N(1)–Rh(1)–C(2)	90.1 (7)	C(1)–Rh(1)–C(2)	92.2 (8)
C(3)–Rh(2)–C(5)	88.7 (10)	C(3)–Rh(2)–C(19)	85.4 (9)
C(5)–Rh(2)–C(19)	88.9 (8)	Rh(1)–C(1)–O(1)	179.3 (23)
Rh(1)–C(2)–O(2)	178.2 (16)	Rh(2)–C(3)–O(3)	171.1 (31)
Cl(2)–Rh(3)–N(1a)	92.0 (4)	Cl(2)–Rh(3)–C(1a)	86.3 (7)
N(1a)–Rh(3)–C(1a)	177.4 (8)	Cl(2)–Rh(3)–C(2a)	175.7 (7)
N(1a)–Rh(3)–C(2a)	92.4 (7)	C(1a)–Rh(3)–C(2a)	89.4 (9)
C(3a)–Rh(4)–C(5a)	90.1 (9)	C(3a)–Rh(4)–C(19a)	84.0 (9)
C(5a)–Rh(4)–C(19a)	87.0 (8)	Rh(3)–C(1a)–O(1a)	175.5 (21)
Rh(3)–C(2a)–O(2a)	178.5 (19)	Rh(4)–C(3a)–O(3a)	174.3 (17)

for its preparation; this reaction was then accompanied by the formation of the aldol product, 2-$MeCOCH_2CHOH$-C_5H_4N, which necessitated the use of a 17-fold excess of the original aldehyde.

Reaction of the 2- and 3-Pyridyl Complexes (2a,b) with Methyl Iodide. Methyl iodide (30 μL, 0.48 mmol) was added to a solution of [$C_5Me_5Rh(CO)Me(2$-$C_5H_4N)$] (**2a**; 117 mg, 0.3 mmol) in dichloromethane (5 cm^3) in a Schlenk tube and allowed to stand (1.5 h, 20 °C). The solvent was removed in vacuo, the residue was dissolved in the minimum amount of fresh dichloromethane, and diethyl ether was added to precipitate the iodide salt [$C_5Me_5Rh(CO)Me(2$-$C_5H_4NMe)$]I (**5a**; 115 mg, 78%). The 3-pyridyl complex [$C_5Me_5Rh(CO)Me(3$-$C_5H_4NMe)$]I (**5b**) was made analogously (95%).

The 3-pyridyl salt **5b** was stable in solution (even at 55 °C for 12 h), whereas the 2-pyridyl salt decomposed rapidly in solution and the 4-pyridyl salt could not be isolated at all.

Reaction of the 4-Pyridyl Complex (2c) with Methyl Iodide. When the above procedure was carried out with [$C_5Me_5Rh(CO)Me(4$-$C_5H_4N)$] (0.3 mmol) and methyl iodide (0.6 mmol) in dichloromethane, a quite different reaction took place. Addition of ether precipitated 1,4-dimethylpyridinium iodide (characterization by comparison with a synthetic sample), leaving a solution from which [$C_5Me_5Rh(CO)Me(I)$] (80 mg, 65%) was isolated by extraction with pentane. When the product of an analogous reaction but with CD_3I in place of CH_3I was examined by ^1H NMR spectroscopy, methyl peaks were observed at δ 1.94 (C_5Me_5), due to the presence of [$C_5Me_5Rh(CO)Me(I)$], and at δ 2.70, due to the presence of the 4-methyl of 1,4-dimethylpyridinium iodide. The characteristic peaks due to the rhodium methyl in the first, at δ 1.07, and to the 1-methyl in the second, at δ 4.59, were absent; however, the peaks were seen in the ^2H NMR spectrum, showing that those positions were occupied by CD_3.

Preparation of [$C_5Me_5Rh(Me)(CO)\{3$- and 4-C_5H_4N-$Rh(CO)_2Cl\}$] (9b and 9c). A solution of [$Rh_2(CO)_4Cl_2$] (0.106 g, 0.273 mmol) in pentane (5 cm^3) was added to a solution of [$C_5Me_5Rh(Me)(CO)(4$-$C_5H_4N)$] (**2c**; 0.203 g, 0.565 mmol) in pentane (15 cm^3). The solution was stirred (0.5 h), and a yellow precipitate slowly formed. The solvent was removed by decantation, and the product was washed with cold pentane (3 × 5 cm^3) and dried in vacuo to yield yellow-orange [$C_5Me_5Rh(Me)(CO)\{4$-C_5H_4N-$Rh(CO)_2Cl\}$] (**9c**; 0.271 g, 87%). The 3-isomer **9b** was made similarly in 63% yield; this complex was more soluble and was crystallized from pentane as yellow platelike needles.

Reaction of Complex 2c with [$PdCl_2(PhCN)_2$] To Give 10. A solution of [$PdCl_2(PhCN)_2$] (0.029 g, 0.076 mmol) in dichloromethane (10 cm^3) was stirred (30 min, 20 °C) with a solution of complex **2c** (0.068 g, 0.19 mmol) in dichloromethane (10 cm^3). The solvent was removed in vacuo; the residue was triturated with diethyl ether and crystallized from dichloromethane–diethyl ether to give yellow crystals of **10** (0.03 g, 44%).

Table V. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3)

atom	x	y	z	U_{eq}[a]
Rh(1)	202 (1)	1536 (2)	846 (1)	57 (1)
Rh(2)	1352 (1)	−2436 (2)	3510 (1)	48 (1)
Rh(3)	4994 (1)	3409 (2)	1076 (1)	65 (1)
Rh(4)	6649 (1)	7160 (2)	3209 (1)	56 (1)
Cl(1)	1303 (2)	738 (6)	−45 (4)	79 (2)
Cl(2)	4420 (2)	5063 (6)	2522 (5)	87 (2)
O(1)	510 (8)	4020 (17)	−808 (13)	103 (8)
O(2)	−1169 (7)	2731 (19)	1928 (14)	125 (8)
O(3)	1544 (16)	672 (33)	4319 (26)	221 (20)
O(1a)	3669 (7)	1740 (16)	1538 (14)	105 (8)
O(2a)	5623 (8)	1209 (20)	−764 (15)	133 (9)
O(3a)	6514 (10)	4076 (23)	4224 (17)	155 (11)
N(1)	46 (6)	−199 (15)	2072 (10)	53 (5)
N(1a)	5913 (6)	4611 (15)	876 (10)	57 (6)
C(1)	387 (10)	3056 (23)	−168 (18)	77 (9)
C(2)	−641 (10)	2257 (19)	1525 (15)	77 (9)
C(3)	1473 (12)	−388 (26)	3958 (22)	93 (11)
C(4)	555 (7)	−582 (17)	2450 (11)	43 (6)
C(5)	498 (7)	−1747 (19)	3201 (12)	51 (6)
C(6)	−102 (8)	−2541 (23)	3571 (15)	72 (8)
C(7)	−628 (9)	−2126 (23)	3200 (17)	81 (9)
C(8)	−538 (7)	−995 (19)	2431 (13)	54 (6)
C(9)	1688 (8)	−3676 (20)	1842 (12)	55 (7)
C(10)	2218 (8)	−2642 (18)	1924 (12)	52 (6)
C(11)	2421 (8)	−3109 (21)	2838 (12)	58 (7)
C(12)	2035 (9)	−4432 (19)	3325 (14)	61 (7)
C(13)	1576 (8)	−4777 (17)	2717 (14)	57 (7)
C(14)	1354 (10)	−3679 (22)	948 (15)	76 (9)
C(15)	2541 (10)	−1342 (24)	1100 (15)	84 (9)
C(16)	3005 (8)	−2341 (23)	3187 (16)	76 (8)
C(17)	2160 (12)	−5387 (27)	4247 (16)	105 (11)
C(18)	1095 (12)	−6183 (24)	2850 (20)	109 (12)
C(19)	750 (11)	−2819 (25)	5249 (23)	131 (16)
C(1a)	4185 (11)	2357 (23)	1317 (18)	91 (10)
C(2a)	5384 (9)	2034 (23)	−52 (16)	79 (9)
C(3a)	6539 (10)	5286 (18)	3879 (17)	82 (10)
C(4a)	6039 (7)	5189 (18)	1788 (13)	54 (6)
C(5a)	6605 (8)	6105 (19)	1779 (13)	57 (7)
C(6a)	7066 (8)	6369 (19)	733 (13)	58 (7)
C(7a)	6945 (9)	5754 (20)	−201 (13)	63 (7)
C(8a)	6378 (9)	4885 (18)	−124 (13)	58 (7)
C(9a)	5884 (10)	8931 (19)	3127 (15)	66 (8)
C(10a)	5732 (8)	8430 (19)	4239 (14)	62 (7)
C(11a)	6311 (9)	8821 (21)	4622 (13)	67 (8)
C(12a)	6787 (9)	9624 (20)	3737 (14)	65 (8)
C(13a)	6556 (9)	9612 (22)	2823 (13)	68 (8)
C(14a)	5418 (10)	8851 (26)	2432 (19)	97 (11)
C(15a)	5075 (9)	7608 (25)	4995 (19)	98 (10)
C(16a)	6337 (12)	8573 (25)	5818 (15)	93 (10)
C(17a)	7451 (10)	10378 (26)	3804 (17)	88 (10)
C(18a)	6881 (11)	10479 (27)	1736 (17)	101 (10)
C(19a)	7694 (10)	6612 (25)	2689 (15)	101 (11)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Protonation of Complex 2b with Boron Trifluoride Hydrate To Give 8b. Boron trifluoride hydrate (0.05 cm^3) was added with stirring to a solution of complex **2b** (0.04 g, 0.11 mmol) in diethyl ether (10 cm^3). A precipitate immediately formed, a further 0.05 cm^3 of boron trifluoride hydrate was added to complete the reaction, and the mixture was stirred (0.5 h, 20 °C). The solvent was decanted off, and the residual solid was washed with diethyl ether and pentane and dried in vacuo to give **8b** (0.038 g, 76%).

X-ray Crystal Structure Determination of [$C_5Me_5Rh(Me)(CO)\{3$-C_5H_4N-$Rh(CO)_2Cl\}$] (9b). A crystal of **9b** (dimensions 0.60 × 0.23 × 0.14 mm) was selected from a batch grown from n-pentane (above). Crystal data: $C_{19}H_{22}ClNO_3Rh_2$, M_r = 553.65, triclinic, a = 20.94 (9) Å, b = 8.560 (16) Å, c = 12.718 (34) Å, α = 90.66 (19)°, β = 71.66 (27)°, γ = 91.47 (26)°, V = 2163 (12) Å^3, D_c = 1.700 g cm^{-3}, Z = 4, space group $P\bar{1}$ (C_i, No. 2), Mo Kα

radiation (λ = 0.71069 Å), μ(Mo Kα) = 16.43 cm^{-1}, $F(000)$ = 1095.89.

Three-dimensional room-temperature X-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 diffractometer by the ω-scan method. The 4215 independent reflections for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarization effects and for absorption, by analysis of six azimuthal scans. The structure was solved by conventional Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Hydrogen atoms were placed in calculated positions with isotropic thermal vibrational parameters related to those of the supporting atom. The refinement converged to a final R value of 0.0728 with allowance for the thermal anisotropy of all non-hydrogen atoms. Complex scattering factors were taken from ref 9 and from the SHELXTL program package, which was used for the refinement. Unit weights were used throughout the refinement. Atom coordinates are given in Table V and selected bond distances and angles in Table IV.

Supplementary Material Available: Complete listings of bond lengths and angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors for complex **9c** (4 pages); a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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Bis(pyridyl)silane and -methanol Ligands. 3. A New Class of Optically Active Ligands Prepared from Readily Available Chiral 2-Bromo-6-alkoxypyridines and Their Application in Rhodium-Catalyzed Hydrosilations and Copper(II)-Catalyzed Cyclopropanations

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Received May 11, 1989

Several chiral 2-bromo-6-alkoxypyridines (**2**) were prepared from the treatment of 2,6-dibromopyridine with the appropriate potassium alkoxide (alkoxides used: methoxide, myrtanoxide, myrtenoxide, isopinocampheoxide, isomenthoxide, fenchoxide, and borneoxide) in dimethylformamide at 80 °C for 30 min. Compound **2** was found to undergo facile halogen-metal exchange with *n*-BuLi in THF at -78 °C to afford the 2-lithio-6-alkoxypyridines (**3**). Treatment of **3** with R_2SiCl_2 resulted in formation of the novel bis(pyridyl)silane compounds [2-(6-alkoxypyridyl)]$_2$SiR$_2$ (**4**, R = Me; **5**, R = Ph) in excellent yield. The latter compounds readily chelated to palladium(II) chloride to form air-stable complexes, {[2-(6-alkoxypyridyl)]$_2$SiR$_2$}PdCl$_2$ (**6**, R = Me; **7**, R = Ph). The palladium complexes were fully characterized by spectroscopic and analytical data. Oxidative coupling of compounds **3** with copper(I) iodide and oxygen at -78 °C afforded the new 6,6′-dialkoxy-2,2′-bipyridines (**8**) in 34-38% isolated yields. Treatment of **3** with dimethylformamide produced a new series of optically pure 6-alkoxy-2-pyridinecarboxaldehydes (**9**) in greater than 90% isolated yield. Subsequent reaction of **9** with **3** afforded the bis[2-(6-alkoxypyridyl)]methanol ligands (**10**) in excellent yield. Compound **10** was O-alkylated (NaH, DMF) with benzyl chloride to afford **11**. The benzylated compound **11** was complexed to palladium(II) chloride and found by NMR spectroscopy to exist as one of the two possible boat conformations. The energy barriers for rotation about the benzyl-oxygen bond in the latter complexes were found to be dependent upon the chiral alkoxy group on the pyridine ring. Ligand **10** was attached to cross-linked polystyrene beads with 56-74% modification of the chloromethyl sites. Further modification of the remaining chloromethyl reaction sites to hydroxymethyl groups was accomplished by treatment of the polymer with methanolic potassium hydroxide. Complete incorporation of the ligand was achieved by utilizing a lower loading of chloromethyl sites (0.75 mequiv/g) in the starting polymer. Treatment of 2-pyridinecarboxaldehyde with **3** resulted in the two diastereoisomeric products, [2-(6-alkoxypyridyl)](2-pyridyl)methanol (**17**): in the case of R*O = (*1S*,*2R*,*4S*)-borneoxy the isomers could not be separated; however, when R*O = (*1R*,*2R*,*4S*)-1,3,3-trimethyl-2-norborneoxy the isomers **17(i)** and **17(ii)** were easily separated by column chromatography. Selected ligands prepared in the study were used in the rhodium-catalyzed hydrosilation (Ph$_2$SiH$_2$) of acetophenone. Chemical yields were ~85%, and optical yields ranged from 0 to 12.7% for the hydrosilations and 0.5 to 10.0% for the asymmetric cyclopropanation of 2,5-dimethyl-2,4-hexadiene.

Introduction

The initial and independent discovery by Horner et al.[1] and Knowles et al.[2] that prochiral alkenes could be catalytically hydrogenated enantioselectively sparked a worldwide effort to develop chiral transition-metal catalysts. The first ligands used in the asymmetric methodology had chiral phosphorus atoms and a later study by Morrison et al.[3] demonstrated that the phosphorus need not be chiral but, rather, the source of chirality could be further removed from the metal center. Two decades of effort by workers in the field of asymmetric catalysis has produced a more rational approach to the design of asymmetric transition-metal catalysts.[4] The very recent

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