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^{1}H, ^{13}C AND ^{103}Rh NMR SPECTROSCOPY OF RHODIUM(I) COMPLEXES OF 2,2,*N*,*N*-TETRAMETHYL-3-BUTEN-1-AMINE

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Summary

Reaction of μ-dichlorotetraethylenedirhodium(I) with 2,2,*N*,*N*-tetramethyl-3-buten-1-amine (**1**) proceeds with displacement of only one ethylene per rhodium, and with cleavage of the chloride bridges to yield $Cl(C_2H_4)Rh \cdot \mathbf{1}$ (**2**). The remaining ethylene in **2** can be replaced by acetonitrile, which in turn, has been replaced by pyridine, 4-cyanopyridine or 4-dimethylaminopyridine. High-resolution FT ^{1}H and ^{13}C NMR data are consistent with square planar structures for the products, with **1** acting as a bidentate chelate, the chloro ligand being *cis* to the dimethylamino moiety of **1**. High-resolution FT ^{103}Rh NMR data are also reported.

Introduction

There has been considerable interest in rhodium(I) complexes containing chelating olefinic phosphines and arsines (see for example refs. 1 and 2), although apparently there are no reports dealing with amine analogues. In the course of studying the preparation and properties of complexes of chelating ligands containing a quaternary carbon atom in the backbone we have now prepared some rhodium(I) complexes of 2,2,*N*,*N*-tetramethyl-3-buten-1-amine (**1**) [3]. One of the interesting features of rhodium complexes is that the nuclear magnetic resonance (NMR) spectrum of the metal can be obtained in addition to the ^{1}H and ^{13}C NMR spectra [4].

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Results and discussion

Preparation of complexes

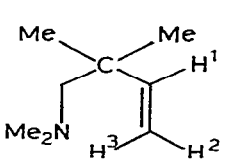
The complex chloro(ethylene)(2,2,*N*,*N*-tetramethyl-3-buten-1-amine)-rhodium(I) (**2**), which appears to be reasonably air-stable as the solid, has been prepared by displacement of ethylene from $Rh_2Cl_2(C_2H_4)_4$. The second ethylene did not suffer displacement in the presence of excess **1** at elevated (40°C) temperature. This contrasts with the observation [2] that 3-buten-1-yldiphenyl-phosphine (mbp) displaces both ethylene ligands to produce $Rh_2Cl_2(mbp)_2$ which reacts with a further mole of mbp giving $RhCl(mbp)_2$. Presumably, the ethylene in **2** is less labilised than it would be in a phosphorus-containing analogue where one would anticipate competition between ethylene and phosphine for back-donation from the metal. However, preparative thin layer chromatography of **2** in air gave small amounts of a yellow crystalline product which appears (^{1}H NMR spectroscopy) to be $Rh_2Cl_2(\mathbf{1})_2$. When **2** is dissolved in deuterioacetonitrile, free ethylene is not observed (^{1}H NMR). However the complex chloro(acetonitrile)-(2,2,*N*,*N*-tetramethyl-3-buten-1-amine)rhodium(I) (**3**), which is again reasonably air-stable as the solid, is obtained by heating an acetonitrile solution of **2** over a period of a few hours. When **3** is dissolved in deuterioacetonitrile, ^{1}H NMR shows that complexed acetonitrile exchanges relatively slowly with solvent. The pyridine and substituted-pyridine adducts RhCl(**1**)(L) (L = 4-cyanopyridine (**4**); pyridine (**5**); 4-dimethylaminopyridine (**6**)) were generated in solution by addition of 1 molar equivalent of the appropriate ligand to **3** in chloroform or dichloromethane under nitrogen. Analogous reaction of stoichiometric amounts of pyridine and **2** in solution resulted in only partial displacement of ethylene while, in contrast, the displacement of acetonitrile from **3** is almost complete.

^{1}H and ^{13}C NMR spectra and structures of the complexes

Representative ^{1}H and ^{13}C NMR spectra are illustrated in Fig. 1A and 1B respectively, and corresponding data are collected in Tables 1 and 2, respectively. It seems likely that **2**—**6** are square-planar monomers in which **1** acts as a chelating ligand, for the following reasons. First, chelation of **1** is reflected in the observed magnetic non-equivalence within the geminal methyl pairs in the ^{1}H NMR spectra of **2**—**6** and the ^{13}C NMR spectra of **3**—**6**. Surprisingly, both C-methyl and N-methyl pairs are fortuitously equivalent in the ^{13}C NMR spectrum of **2**. Second, the trends in the ^{1}H chemical shifts of H(1), H(2), and H(3) * (as discussed below for complexes **2**—**6**) are consistent with square planar geometry. Finally, the general ^{1}H NMR pattern for coordinated **1** in the five complexes closely resembles that observed [3] for the square-planar palladium(II) complexes of the same ligand except that the olefinic proton resonances undergo upfield shifts in the former and downfield shifts in the latter upon complexation.

The particularly pronounced upfield shift of the H(2) resonance on going from **1** to **2** is consistent [5,6] with long-range shielding from the adjacent

* For numbering scheme, see **1**.



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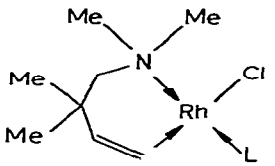


(2 , L = ethylene ;
3 , L = acetonitrile ;
4 , L = 4-cyanopyridine ;
5 , L = pyridine ;
6 , L = 4-dimethylaminopyridine)

ethylene ligand, indicating that the two olefinic moieties are probably *cis* to each other. Certainly, the two olefinic moieties in complex **2** are expected to be mutually *cis* to maximise metal to olefin back-bonding. Since, in contrast to those of H(2), the N—CH_3 resonances suffer only small changes in chemical shift through the series **2**—**6**, it seems likely that the chloro ligand is *cis* to the dimethylamino group in all five complexes. The fact that the resonance position of H(2) is much more sensitive to the nature of the *cis* ligand than are

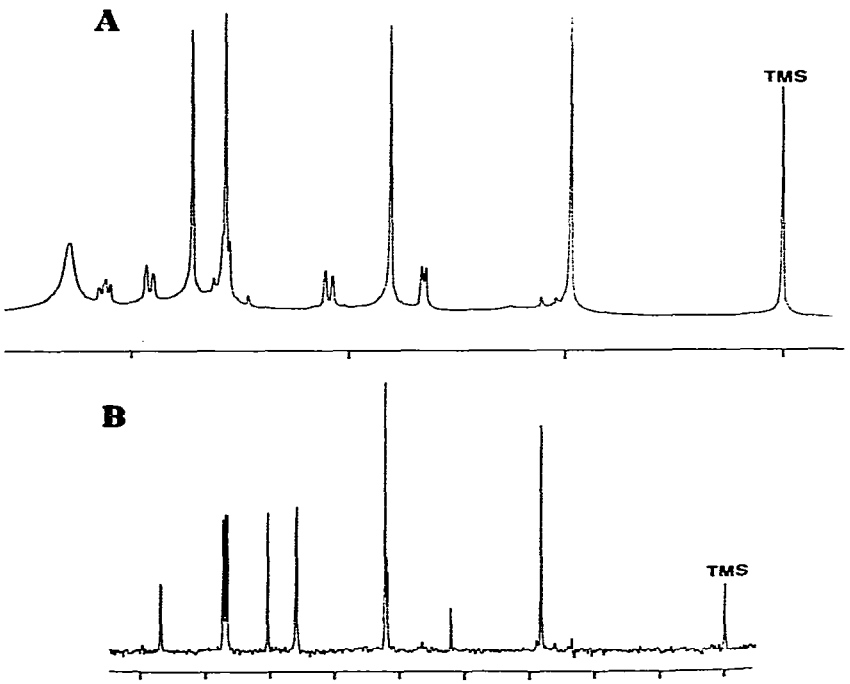


Fig. 1A. FT ^{1}H NMR spectrum of **2** in $CDCl_3$ at 400 MHz and ambient temperature using 5 mm sample. Separation between markers denotes 1 ppm and the field increases from left to right.

Fig. 1B. FT ^{13}C NMR spectrum of **2** in $CDCl_3$ at 100 MHz and ambient temperature using 10 mm sample. Conditions: pulse angle, about 30°; acquisition time, 0.655 s; relaxation delay, zero; and separation between markers, 10 ppm. The triplet 77 ppm downfield from TMS is due to $CDCl_3$.

TABLE 1

HYDROGEN-1 NMR DATA (ppm, J(Hz)) FOR LIGAND [a] AND COMPLEXES [b] AT AMBIENT TEMPERATURE

Compound	Solvent	δ(C—Me)		δ(N—Me)		δ(N—CH_2)	
		(a)	(e)	(a)	(e)	(a)	(e)
1	$CDCl_3$	1.01		2.26		2.17	
2 [c]	$CDCl_3$	1.810	0.978	2.722	2.572	2.579	2.107
3 [d]	$CDCl_3$	1.737	1.011	2.622	2.515	2.274	1.740
4	CH_2Cl_2	1.801	1.006	2.648	2.517	2.302	1.799
5	CH_2Cl_2	1.815	0.993	2.639	2.511	2.258	1.752
6	CH_2Cl_2	1.797	0.982	2.602	2.477	2.206	1.698
$Rh_2Cl_2(1)_2$	CD_2Cl_2	1.632	1.091	2.580	2.422	2.637	2.144 [f]

[a] Values optimised by computer matching, see ref. 3. [b] Data determined directly from spectra. [c] Ethylene signal is observed as broad singlet at 3.283 ppm. [d] Chemical shift of complexed acetonitrile —2.126 ppm.

those of H(1) and H(3) suggests that the olefin is distorted away from an idealised orthogonal orientation with respect to a square coordination plane in such a manner that H(2) makes the closest approach to the *cis* ligand. A similar suggestion has been made [3] for certain palladium(II) complexes of **1**.

Reference to Table 1 shows that the magnitudes of the *cis* and *trans* H—H olefinic couplings are reduced when **1** is complexed to rhodium(I). The effect is larger than that seen for complexation to palladium(II) [3], indicating the formation of a stronger metal olefin bond in the rhodium complexes [7]. In $Rh_2Cl_2(1)_2$, small couplings of all three olefinic protons to rhodium are observed. In addition, H(2) shows long-range coupling to one of the N—CH_2 protons. However, this N—CH proton resonance exhibits more fine structure than can be accounted for by this long-range coupling. Two-dimensional ^{1}H NMR [8] indicates that the additional fine structure is due to spin—spin coupling (J 2.0 Hz) with a spin $\frac{1}{2}$ nucleus, presumably ^{103}Rh. The rhodium—carbon couplings for the olefinic carbon atoms of **1** in **2**—**6** are in the range found for other rhodium complexes [9].

The ^{1}H ethylene resonance for **2** is a reasonably sharp doublet (^2J(Rh—H) 1.6 Hz) at 60 MHz and a broad singlet at 400 MHz, indicating that rotation of the ethylene about the metal—olefin bond [5] is too rapid on the NMR time scale in the former case but not in the latter, for which chemical shift differences are greater.

The large upfield shifts found for the olefinic carbon resonances of the chelating ligand when ethylene is replaced by acetonitrile or a pyridine may reflect an increase in metal-to-olefin back-bonding. The smaller increases in shielding of the same carbon atoms in the sequence **4** to **6**, may be rationalised on the same basis. However, there is considerable dispute concerning the relative importance of the various factors believed to influence the chemical shifts of the olefinic carbon atoms in metal—olefin complexes (for leading references, see ref. 6).

$J(NCH_2)$	δ Olefinic			J Olefinic		
	H(1)	H(2)	H(3)	H(1)/H(2)	H(1)/H(3)	H(2)/H(3)
	5.86	4.93	4.96	10.8	18.0	1.3
13.2	3.134	1.660	2.935	6.8	12.8	~0
12.8	3.617	2.689	2.763	7.2	12.4	~0
13.2	3.170	2.087	2.931	7.2	10.8	~0
12.8	3.139	2.056	2.819	7.2	9.6	~0
12.2	[e]	2.034	2.687	7.2	10.1	~0
13.4	4.193	3.387	3.239	7.6	13.2	~0

[e] Overlapped by N—Me signals of free and complexed 4-dimethylaminopyridine. [f] Additional fine structure is observed due to coupling to H(2) and ^{103}Rh, see text.

^{103}Rh NMR

^{103}Rh NMR shift values for **2**—**6** are recorded in Table 2. As two of us have noted earlier [4] such data are more readily obtainable than has been implied in the earlier literature [10,11]. Although the number of data are limited, one may note that on going from a poor σ-donor/good π-acceptor in **2** to increasingly better σ-donor/weaker π-acceptors the metal resonances shift to progressively lower field. The relatively large chemical shifts and reasonably narrow line widths observed for these resonances give promise that as more such data are collected, structure-shift correlations will be possible and may help to clarify the nature of the bonding in rhodium(I) complexes.

Experimental

General

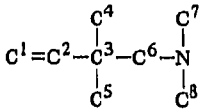
Acetonitrile was purified by distillation, once from CaH_2 and four times from P_2O_5. Commercial $CHCl_3$, CH_2Cl_2, $CDCl_3$, CD_2Cl_2 and CD_3CN were used without purification. 2,2,*N*,*N*-tetramethyl-3-buten-1-amine (**1**) was prepared as described previously [3]. μ-Dichlorotetraethylenedirhodium(I) was prepared by Cramer's procedure [5]. NMR spectra were measured on a Bruker WH-400 (9.39 T) spectrometer using solutions of the complexes at a concentration of about 0.2 molar in 5 mm tubes for ^1H and 10 mm tubes for ^{13}C and ^{103}Rh resonances. Chemical shifts of ^1H and ^{13}C signals were measured relative to internal TMS. Those for ^{103}Rh were measured relative to external $Rh(CO)_2acac$ which has a chemical shift of 1660 ppm downfield of rhodium metal at 298 K [4]. Conditions for the acquisition of FT rhodium spectra are: pulse angle, about 30°; acquisition time, 1.024 sec; relaxation delay, 0.1 sec; number of scans, about 1000. Typically less than 20 min of signal averaging were required to obtain a ^{103}Rh spectrum.

Complexes

Although the ethylene and acetonitrile complexes are reasonably stable in

TABLE 2

CARBON-13 AND RHODIUM-103 NMR DATA (ppm, J(Hz)) FOR COMPLEXES



Compound	Solvent	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	J(C(1)—Rh)	J(C(2)—Rh)	^{103}Rh
1	$CDCl_3$	110.6	147.9	38.5	25.5	25.5	71.5	48.4	48.4			
2 [a]	$CDCl_3$	52.09	86.9	42.3	28.4	28.4	70.6	52.4	52.4	15	15	652.4
3	CD_3CN	40.9	73.0	42.1	29.2	28.4	72.6	54.5	53.5	15	15	1696.3
4	CH_2Cl_2	41.8	73.9	41.7	29.2	28.5	73.0	54.6	53.8	19	19	2029.5
5	CH_2Cl_2	40.2	72.4	41.7	29.2	28.5	73.0	54.6	53.7	21	19	2050.9
6	CH_2Cl_2	38.8	71.0	41.7	29.3	28.5	73.0	54.5	53.5	19	20	2095.1
Rh_2Cl_2(**1**)$_2$	CD_2Cl_2	50.5	85.6	42.1	29.0	28.4	69.4	52.0	51.3	14	12	—

[a] Carbon-13 NMR data for ethylene: δ 66.1 ppm, $J(^{13}C—^{103}Rh)$ 11 Hz.

the solid state, all manipulations were performed under nitrogen and the complexes were stored in a refrigerator. The pyridine complexes are very air-sensitive and undergo slow decomposition in $CHCl_3$. They are stable in CH_2Cl_2 solution, such solutions having survived storage for several months in sealed NMR tubes in a refrigerator.

Chloro(ethylene)(2,2,N,N-tetramethyl-3-buten-1-amine)rhodium(I) (**2**)

μ-Dichlorotetraethylenedirhodium(I) (0.778 g, 2 mmol) was placed in a nitrogen-filled flask and air-free $CHCl_3$ (1 cm^3) was added. The resulting solution was stirred and **1** (0.508 g, 4 mmol) in chloroform (5 cm^3) was added dropwise. After 1 h the reaction mixture was stored in a refrigerator overnight. It was then filtered and the solvent removed first by bubbling nitrogen through the solution and finally under reduced pressure. At this stage, a brown-yellow solid (1.068 g) was obtained. A fraction (0.8 g) of this material was dissolved in pure acetonitrile (4 cm^3), and the resulting solution was then cooled in an acetone-solid CO_2 bath. The yellow crystals (0.32 g) obtained were filtered off quickly and washed with cold acetonitrile (1 cm^3). The filtrate gave another crop (0.1 g) of less pure (pale brown) product. The ^1H NMR spectra of both crystalline fractions and of the initial crude product were devoid of resonances attributable to impurities. The yellow crystals had m.p. 113°C (dec.) (Found: C, 39.07; H, 7.17; N, 4.72. $C_{10}H_{21}ClNRh$ calcd.: C, 40.89; H, 7.22; N, 4.71%.)

Chloro(acetonitrile)(2,2,N,N-tetramethyl-3-buten-1-amine)rhodium(I) (**3**)

Crude **2** obtained from μ-dichlorotetraethylenedirhodium(I) (1.17 g, 3 mmol) as above, was dissolved in acetonitrile (3 cm^3) and the resulting solution was heated under N_2 at 45°C for 7 h and then 55°C for a further 7 h. At this time the NMR signal from bonded ethylene was no longer observable and the solution was filtered, partially evaporated and then placed in a refrigerator overnight. A yellow solid (0.3 g) precipitated. After evaporation of more acetonitrile a further amount (0.3 g) of the product was obtained. It had m.p. 138—142°C (dec.) (Found: C, 38.96; H, 6.79; N, 8.90. $C_{10}H_{20}ClN_2Rh$ calcd.: C, 39.15; H, 6.59; N, 9.14%.)

Pyridine complexes (**4—6**)

Complex **3** (0.122 g, 0.4 mmol) was placed in an NMR tube and kept under vacuum at 40°C for 30 min. The tube was then filled with N_2 and a solution (0.5 ml) of CD_2Cl_2 in CH_2Cl_2 (20%) was added. It was then cooled in liquid nitrogen and a solution of the appropriate pyridine (0.4 mmol) in the same solvent mixture (1.5 cm^3) was added. The tube was then outgassed four times and sealed under N_2. The progress of the ligand exchange reaction was followed by ^1H NMR. Equilibrium was reached at room temperature after 3 days for **6** and 5 days for **4** and **5**. Estimates of the extent of conversion were made on the basis of the intensities of the aromatic signals arising from free and complexed pyridines. The values obtained were: for **4**, >90%; for **5** and **6**, ~70%.

Acknowledgement

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