REACTIVITY PATTERNS IN THE REACTIONS OF [Rh(CO)₂Cl]₂ WITH CHELATING KETONES

J. WILLIAM SUGGS, MICHAEL J. WOVKULICH, PAUL G. WILLIARD and KEN S. LEE

Department of Chemistry, Brown University Providence, Rhode Island 02912 (U.S.A.)

(Received October 22nd, 1985)

Summary

A survey is made of the reactions of chelating ketones and aldehydes with $[(CO)_2RhCl]_2$. With the enolizable ketone 8-quinolinyl benzyl ketone a rhodium-(I)-vinyl alcohol π-complex forms, whose crystal structure was determined ($C_{18}H_{13}NO_2ClRh$, monoclinic space group $C2/c$, a 14.531(3), b 18.038(3), c 15.257(3) Å, β 111.48(1)°, V 3721 Å³, $Z = 8$, final R_w 4.16%). The non-enolizable ketone 8-quinolinyl phenyl ketone gives oxygen atom transfer to CO, producing CO_2 and a 1,3-dirhodiametallacyclobutane complex. Oxygen atom transfer is also seen from 8-nitroquinoline to give a chelating nitroso ligand. Finally 8-quinoline carboxaldehyde undergoes C–H activation followed by loss of H_2 to give a dimeric acylrhodium(II), whose crystal structure was determined ($C_{26}H_{12}N_2O_8Cl_4Rh_4$, orthorhombic space group $Pccn$, a 9.466(5), b 13.648(9), c 24.124(14) Å, V 3119 Å³, $Z = 4$ final R_w 5.68%).

Introduction

We have reported how 8-substituted quinolinyl aldehydes and ketones can be useful in studies of carbon–hydrogen and carbon–carbon bond activation by transition metals [1,2]. These quinoline ligands bring specific bonds of the ligand into the metal's coordination sphere, resulting in many interesting reactions. We wondered if, by proper choice of ligand and metal, we could isolate stable complexes with agostic metal–C–C interactions [3]. Such interactions recently have been proposed in several organometallic systems [4,5] and they may help to stabilize reduced metal fragments formed upon C–C reductive elimination [6]. A possible agostic M–C–H interaction in the quinolinyl complex *trans*-dichloroquinoline-8-carboxaldehyde triphenylphosphineplatinum(II) was detected by ¹H NMR measurements [7]. However, while an X-ray crystal structure was obtained for this molecule, no precise geometrical information could be extracted concerning the M–H–C interaction since the aldehyde hydrogen could not be located in the heavy-atom

structure. This is an unavoidable (but not insurmountable) difficulty with X-ray crystal structure determination of M–H–C interactions. In contrast, X-ray crystallographic studies of M–C–C interactions should yield accurate structural information. Our attempts to isolate complexes which exhibit such interactions are described below. While we have not yet been successful in our goal of structurally characterizing an agostic M–C–C system, this work does illustrate some of the different kinds of reactivities carbonyl compounds can exhibit when placed into a metal's coordination sphere.

Reaction of [Rh(CO)₂Cl]₂ with 8-quinolinyl benzyl ketone

8-Quinolinyl benzyl ketone (**1**) reacts at or below room temperature with [Rh(C₂H₄)₂Cl]₂ to give an acylrhodium(III) benzyl complex, which arises from
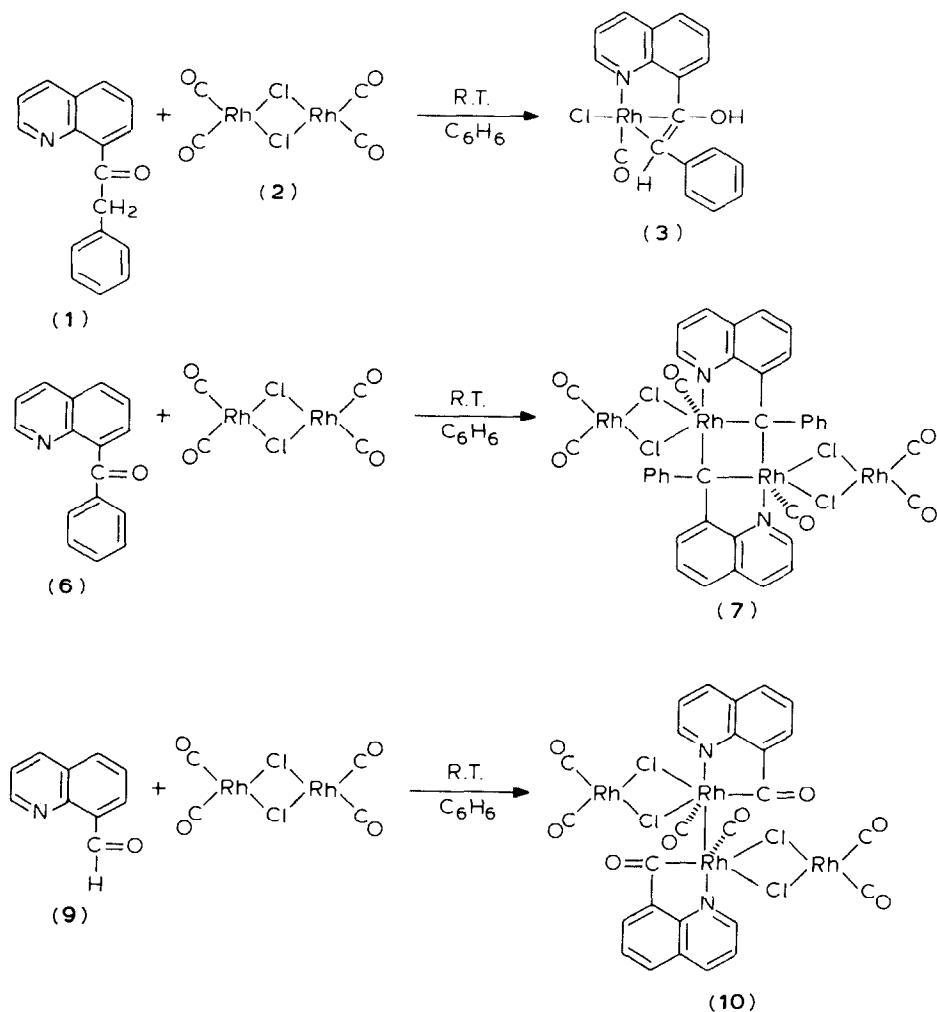
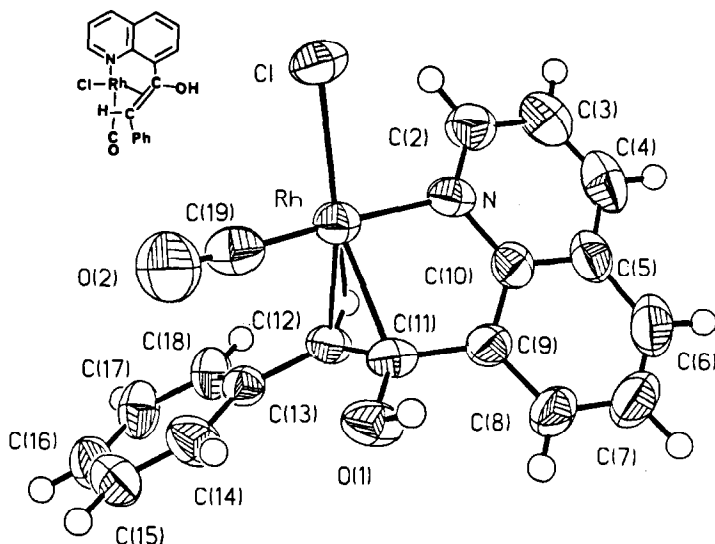SCHEME 1. Summary of the reactions of **2** with 8-substituted quinoline derivatives.

Fig. 1. Molecular structure of **3**. Bond lengths and angles are given in Tables 2 and 3.

rhodium(I) insertion into the $CO-CH_2Ph$ bond of the ligand [1]. When this and related alkyl acylrhodium(III) complexes are treated with CO or phosphines, they undergo ligand-induced reductive elimination back to the starting quinoline ligand and a rhodium(I) CO or phosphine complex [8]. We thus began our search for an agostic Rh–C–C interaction by looking at the reaction of $[Rh(CO)_2Cl]_2$ (**2**) (a complex with ligands that stabilize the rhodium(I) oxidation state) with **1**, a ligand with a reatively weak C–C bond. Upon mixing these two compounds in benzene at 25°C the solution turned orange, CO was evolved and after a few hours orange needles formed. After 24 h these were collected (52% yield).

The product, **3**, was discovered to be the η^2-enol complex, whose X-ray crystal structure is shown in Fig. 1. Tables 1–4 give atomic coordinates, bond lengths, bond angles and collection data. This complex appears to form **3** by trapping out the small equilibrium amount of the enol form of **2**. When the synthesis of **3** was carried out in CD_3OD, the vinylic resonance at δ 4.80 ppm in the product was absent, showing that proton exchange via enolization was faster than π-complex formation. No exchange of the vinylic proton in **3** took place at 25°C over 24 h when **3** in acetone-d_6 was mixed with excess CD_3OD.

A few examples of vinyl alcohols stabilized by complexation to transition metals have been reported, including $PtCl(acac)(CH_2=CHOH)$ (**4**) [9], $PdCl_2(Me_2N-CH_2CMe_2CH=CHOH)$ (**5**) [10] and Fe, W and Mo examples [11]. Complex **3** is unusual, however, in that the interaction between rhodium and the enol double bond carbons is symmetric. Other η^2-vinyl alcohol complexes whose structures have been determined have the terminal M–C distance shorter than the M–C(OH) distance. For **4** these distances are 2.10 vs. 2.22 Å and for **5** 2.11 vs. 2.26 Å. In the case of **3**, the analogous M–C distances are both 2.14 Å (unless otherwise noted, all distances discussed herein have uncertainties of less than 0.004 Å). The greater electron density at the β-carbon of a vinyl ether would be expected to shorten that M–C bond in an η^2-vinyl alcohol complex. The fact that this does not occur in **3**

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($\mathring{A}^2 \times 10^3$) OF **3**

Atom	x	y	z	U [a]
Rh	1494(1)	3143(1)	2396(1)	46(1)
Cl	2112(1)	3414(1)	4016(1)	62(1)
O(1)	−259(3)	3130(2)	524(2)	61(2)
O(2)	900(4)	4719(2)	1993(3)	92(2)
N	1764(3)	2015(3)	2680(3)	49(2)
C(2)	2429(5)	1697(4)	3415(4)	62(3)
C(3)	2496(5)	930(4)	3537(5)	76(3)
C(4)	1824(5)	487(3)	2897(5)	78(4)
C(5)	1085(5)	804(4)	2117(4)	61(3)
C(6)	325(6)	393(4)	1442(5)	83(4)
C(7)	−388(5)	759(5)	733(5)	82(4)
C(8)	−362(4)	1520(4)	615(4)	66(3)
C(9)	387(4)	1933(3)	1227(4)	50(2)
C(10)	1084(4)	1570(3)	2007(4)	51(2)
C(11)	566(4)	2722(3)	1056(4)	47(2)
C(12)	1484(4)	2914(3)	1019(3)	46(2)
C(13)	1741(4)	3500(3)	476(3)	43(2)
C(14)	1119(4)	4076(4)	2(4)	65(3)
C(15)	1414(5)	4577(4)	−527(4)	73(3)
C(16)	2333	4518	−581	71
C(17)	2953	3973	−102	66
C(18)	2662	3471	416	56
C(19)	1135	4118	2131	61
C(20)	0(24)	8283(11)	2705(15)	362(17)
C(21)	341(11)	7852(11)	1877(8)	215(12)
C(22)	231(13)	7111(7)	2103(14)	260(16)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

may be due to the rigidity of the chelate ring. The stronger than usual rhodium–olefin bond in **3** that results also shows up in the C=C and C–O bond lengths. The C=C distances in **4** and **5** are 1.39 Å, while the same distance in the chelated enol **3** is 1.41

TABLE 2

BOND LENGTHS (Å) IN **3**

Rh–Cl	2.352(1)	Rh–C(19)	1.837
O(1)–C(11)	1.378(6)	O(2)–C(19)	1.333(4)
N–C(2)	1.313(7)	N–C(10)	1.390(6)
C(2)–C(3)	1.395(10)	C(3)–C(4)	1.359(9)
C(4)–C(5)	1.400(8)	C(5)–C(6)	1.414(9)
C(5)–C(10)	1.391(9)	C(6)–C(7)	1.363(10)
C(7)–C(8)	1.388(11)	C(8)–C(9)	1.366(8)
C(9)–C(10)	1.409(7)	C(9)–C(11)	1.485(8)
C(11)–C(12)	1.413(8)	C(12)–C(13)	1.473(8)
C(13)–C(14)	1.393(8)	C(13)–C(18)	1.374(6)
C(14)–C(15)	1.380(10)	C(15)–C(16)	1.372(7)
C(16)–C(17)	1.353	C(17)–C(18)	1.366
C(20)–C(20a)	0.626(55)	C(20)–C(21a)	1.220(34)
C(21)–C(22)	1.405(24)	C(21)–C(20a)	1.220(34)

TABLE 3

BOND ANGLES (°) IN **3**

Cl–Rh–C(19)	90.0	C(2)–N–C(10)	118.7(5)
N–C(2)–C(3)	122.7(5)	C(2)–C(3)–C(4)	119.3(6)
C(3)–C(4)–C(5)	119.8(6)	C(4)–C(5)–C(6)	123.8(6)
C(4)–C(5)–C(10)	118.3(5)	C(6)–C(5)–C(10)	117.9(5)
C(5)–C(6)–C(7)	119.2(7)	C(6)–C(7)–C(8)	122.2(6)
C(7)–C(8)–C(9)	120.2(5)	C(8)–C(9)–C(10)	118.1(6)
C(8)–C(9)–C(11)	123.0(5)	C(10)–C(9)–C(11)	118.6(4)
N–C(10)–C(5)	121.0(5)	N–C(10)–C(9)	116.9(5)
C(5)–C(10)–C(9)	122.1(5)	O(1)–C(11)–C(9)	117.0(4)
O(1)–C(11)–C(12)	118.2(5)	C(9)–C(11)–C(12)	117.6(5)
C(11)–C(12)–C(13)	129.9(4)	C(12)–C(13)–C(14)	125.2(6)
C(12)–C(13)–C(18)	117.6(4)	C(14)–C(13)–C(18)	117.2(5)
C(13)–C(14)–C(15)	120.6(6)	C(14)–C(15)–C(16)	120.2(5)
C(15)–C(16)–C(17)	119.6(3)	C(16)–C(17)–C(18)	120.6
C(13)–C(18)–C(17)	121.8(2)	Rh–C(19)–O(2)	177.6(3)
C(20a)–C(20)–C(21a)	132.1(28)	C(22)–C(21)–C(20a)	111.9(19)

Å. The C–OH distance is 1.38 Å in **3**, significantly longer than the 1.32 and 1.30 Å distance in **4** and **5**. Thus, there is less interaction of the oxygen's nonbonding electrons with the olefin π-system in **3** than with other η^2-vinyl alcohol complexes.

While this experiment did not provide an example of an agostic M–C–C interaction, we believe it is relevant to the study of C–C bond activation. In **3** there is a rhodium(I) center interacting with two sp^2 carbon atoms located at the 8-position of a quinoline ligand. [Rh(C$_2$H$_4$)$_2$Cl]$_2$ reacts with 8-quinolinyl phenyl ketone (**6**) to break the CO–Ph bond, producing an phenylacylrhodium(III) complex. The bond that is broken in **6** is between two sp^2 hybridized carbons. It seems

TABLE 4

CRYSTALLOGRAPHIC DATA FOR **3**

Molecular formula	C$_{18}$H$_{13}$NO$_2$ClRh
Crystal system	Monoclinic
Cell dimensions	*a* 14.531(3), *b* 18.038(3), *c* 15.257(3) Å
	β 111.48(1)°
	V 3721.35(114) Å^3
Wavelength	0.71069 Å (Mo-K_α, graphite monochromator)
Range of 2θ	3.5–42°
Space group	*C*2/*c*
Z	8
Calculated density	1.48 g/cm^3
Linear absorption coefficient (cm^{-1})	10.38
Number of unique reflections	2666
Structure factor weights	$W = 1/[\sigma^2(F) + 0.00020 F^2]$
	with $\sigma^2(F)$ from counting statistics
Final *R* factors	$R = 0.0417$, $R_w = 0.0416$
Goodness of fit (Nominal)	1.483
Goodness of fit (Divided by slope of normal probability plot)	1.078
Crystal dimensions (mm)	0.3×0.3×0.2

possible that the geometry found in **3** is very much like the geometry that occurs during the insertion of a rhodium(I) complex into the sp^2-C–sp^2-C bond in **6**. The structure of **3**, therefore, presents a very clear picture of how an 8-substituted quinoline can direct a metal to a specific C–C bond in the ligand.

Reaction of [Rh(CO)$_2$Cl]$_2$ with other 8-quinolinyl carbonyl compounds

To avoid problems with enolization we next investigated the reaction of [Rh(CO)$_2$Cl]$_2$ with the non-enolizable phenyl ketone **6**. This, however, gave an unexpected product arising from carbon–oxygen bond activation, **7** in which the ketone carbonyl has transferred its oxygen to coordinated CO, giving CO$_2$ and ultimately **7**. This reaction is described in more detail elsewhere [12], and is mentioned here for the sake of completeness. Since **7** could, in principle, arise by dimerization of a alkylidenerhodium we investigated the reaction of **2** with 8-quinolinyl-N,N-dimethyl amide, expecting that the nucleophilic amide oxygen could be transferred to coordinated CO more easily than a ketone oxygen. However, no CO$_2$ formed and the decrease in the amide carbonyl stretch by 12 cm^{-1} in the resulting complex indicated the rhodium was coordinated to the amide oxygen. With the good oxygen atom donor 8-nitroquinoline, **2** gave chlorocarbonyl-8-nitrosoquinolinerhodium(I) (**8**) by oxygen atom transfer from NO$_2$ to CO.

Since neither enolizable nor non-enolizable ketones gave agostic M–C–C products with **2**, we next investigated its reaction with the chelating aldehyde 8-quino-
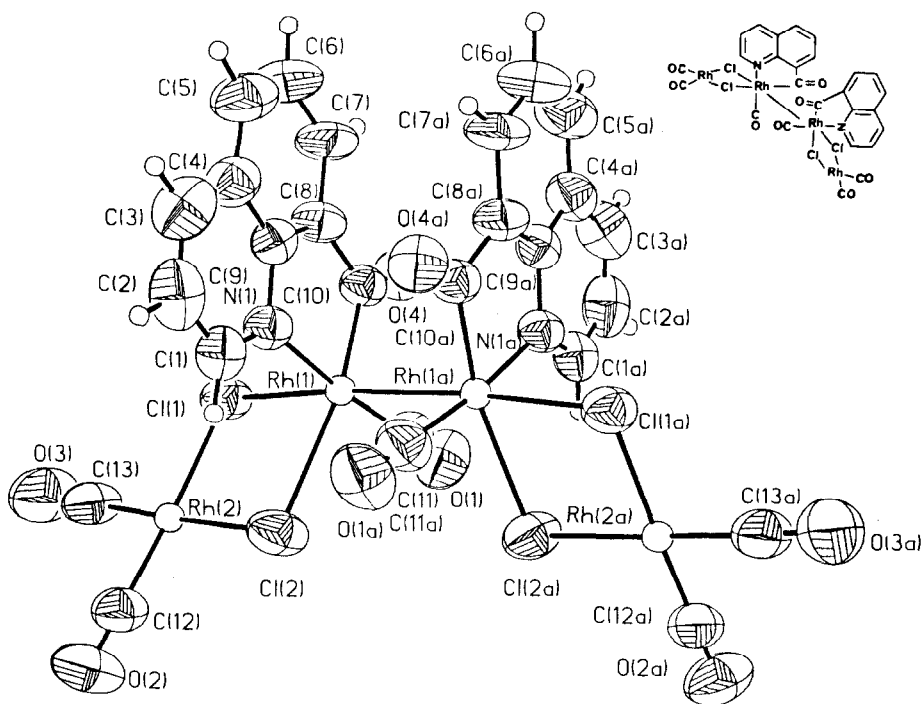

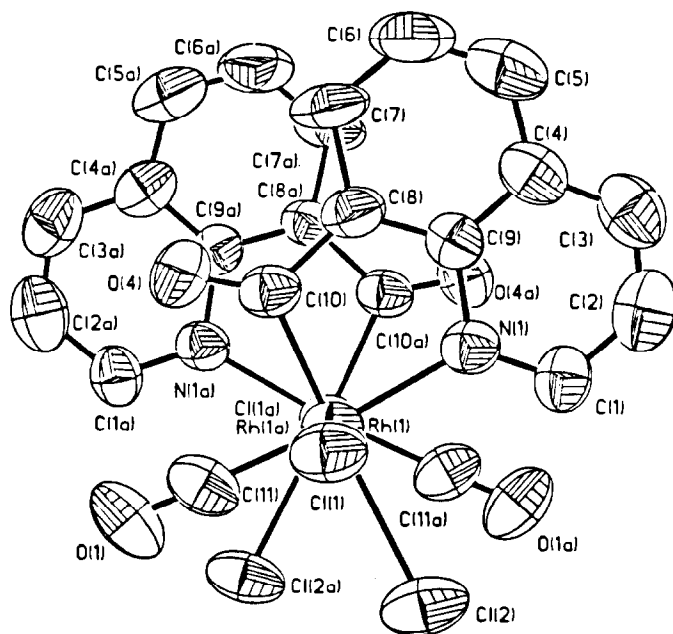Fig. 2. Molecular structure of **10**. Bond lengths and angles are given in Tables 6 and 7.

Fig. 3. A different view of **10** through the Rh–Rh bond, showing the stacking of the carbonyl groups on the aromatic rings. The terminal rhodium atoms are omitted.

TABLE 5

ATOMIC COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($\text{Å} \times 10^3$) OF **10**

Atom	x	y	z	U^a
Rh(1)	8414(1)	1754(1)	1309(1)	57(1)
Rh(2)	11156(1)	766(1)	393(1)	64(1)
Cl(1)	10032(2)	293(1)	1229(1)	70(1)
Cl(2)	9607(3)	2117(2)	341(1)	88(1)
O(1)	6064(7)	599(4)	796(3)	100(3)
O(2)	12677(9)	1434(5)	−611(3)	109(3)
O(3)	13128(11)	−890(7)	496(3)	141(4)
O(4)	6963(7)	682(4)	2147(3)	78(2)
N(1)	9935(6)	2548(4)	1739(2)	59(2)
C(1)	10893(8)	3161(5)	1563(4)	67(3)
C(2)	11744(9)	3694(6)	1937(4)	89(4)
C(3)	11619(9)	3592(7)	2487(5)	91(4)
C(4)	10650(9)	2896(6)	2692(4)	77(3)
C(5)	10420(12)	2682(8)	3261(4)	97(4)
C(6)	9509(13)	2021(8)	3427(4)	108(5)
C(7)	8629(10)	1521(7)	3056(3)	87(4)
C(8)	8812(8)	1717(5)	2478(3)	65(3)
C(9)	9806(7)	2409(5)	2321(3)	57(2)
C(10)	7847(9)	1278(5)	2051(3)	60(3)
C(11)	6906(9)	1056(6)	984(4)	78(3)
C(12)	12097(9)	1191(7)	−233(3)	78(3)
C(13)	12355(12)	−265(7)	455(3)	88(4)

^{a} Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 6

BOND LENGTHS (Å) IN **10**

Rh(1)–Cl(1)	2.522(2)	Rh(1)–Cl(2)	2.642(2)
Rh(1)–N(1)	2.079(6)	Rh(1)–C(10)	1.979(7)
Rh(1)–C(11)	1.887(9)	Rh(1)–Rh(1a)	2.671(1)
Rh(2)–Cl(1)	2.370(2)	Rh(2)–Cl(2)	2.359(3)
Rh(2)–C(12)	1.846(8)	Rh(2)–C(13)	1.814(10)
O(1)–C(11)	1.110(11)	O(2)–C(12)	1.114(11)
O(3)–C(13)	1.128(14)	O(4)–C(10)	1.190(10)
N(1)–C(1)	1.305(10)	N(1)–C(9)	1.421(9)
C(1)–C(2)	1.411(13)	C(2)–C(3)	1.338(15)
C(3)–C(4)	1.410(13)	C(4)–C(5)	1.420(13)
C(4)–C(9)	1.372(11)	C(5)–C(6)	1.311(16)
C(6)–C(7)	1.400(14)	C(7)–C(8)	1.429(11)
C(8)–C(9)	1.387(10)	C(8)–C(10)	1.502(11)

linecarboxaldehyde (**9**). The reaction between **2** and **9**, in benzene at 25°C, gave red crystals similar in appearance to **7**. However, the product, **10**, which is a rhodium(II) dimer, was shown by X-ray crystallography to be the product of C–H and not $R_2C=O$ bond activation. Figures 2 and 3 are depictions of **10**'s structure and Tables 5–8 contain atom coordinates, bond lengths, bond angles and collection data.

Apparently, **10** is formed by displacement of CO from **2** by **9**, oxidative addition of the aldehyde C–H bond and finally intermolecular reductive elimination of H_2.

TABLE 7

BOND ANGLES (°) IN **10**

Cl(1)–Rh(1)–Cl(2)	79.7(1)	Cl(1)–Rh(1)–N(1)	91.7(2)
Cl(2)–Rh(1)–N(1)	92.7(2)	Cl(1)–Rh(1)–C(10)	88.5(2)
Cl(2)–Rh(1)–C(10)	167.9(2)	N(1)–Rh(1)–C(10)	84.7(3)
Cl(1)–Rh(1)–C(11)	91.6(3)	Cl(2)–Rh(1)–C(11)	92.9(3)
N(1)–Rh(1)–C(11)	173.9(3)	C(10)–Rh(1)–C(11)	90.3(3)
Cl(1)–Rh(1)–Rh(1a)	174.8(1)	Cl(2)–Rh(1)–Rh(1a)	97.7(1)
N(1)–Rh(1)–Rh(1a)	93.0(2)	C(10)–Rh(1)·Rh(1a)	94.3(2)
C(11)–Rh(1)–Rh(1a)	83.9(3)	Cl(1)–Rh(2)–Cl(2)	88.8(1)
Cl(1)–Rh(2)–C(12)	176.4(3)	Cl(2)–Rh(2)–C(12)	90.6(3)
Cl(1)–Rh(2)–C(13)	90.0(3)	Cl(2)–Rh(2)–C(13)	178.3(3)
C(12)–Rh(2)–C(13)	90.5(4)	Rh(1)–Cl(1)–Rh(2)	97.0(1)
Rh(1)–Cl(2)–Rh(2)	94.1(1)	Rh(1)–N(1)–C(1)	130.8(5)
Rh(1)–N(1)–C(9)	111.3(4)	C(1)–N(1)–C(9)	117.8(6)
N(1)–C(1)–C(2)	121.2(8)	C(1)–C(2)–C(3)	122.0(8)
C(2)–C(3)–C(4)	118.3(9)	C(3)–C(4)–C(5)	125.3(9)
C(3)–C(4)–C(9)	118.4(8)	C(5)–C(4)–C(9)	116.2(8)
C(4)–C(5)–C(6)	122.5(9)	C(5)–C(6)–C(7)	122.1(9)
C(6)–C(7)–C(8)	117.4(8)	C(7)–C(8)–C(9)	118.5(7)
C(7)–C(8)–C(10)	121.4(7)	C(9)–C(8)–C(10)	119.8(7)
N(1)–C(9)–C(4)	122.0(7)	N(10–C(9)–C(8)	114.8(6)
C(4)–C(9)–C(8)	123.1(7)	Rh(1)–C(10)–O(4)	126.3(6)
Rh(1)–C(10)–C(8)	109.0(5)	O(4)–C(10)–C(8)	124.5(7)
Rh(1)–C(11)–O(1)	176.0(8)	Rh(2)–C(12)–O(2)	178.9(8)
Rh(2)–C(13)–O(3)	178.3(10)		

TABLE 8

CRYSTALLOGRAPHIC DATA FOR 10

Molecular formula	$C_{26}H_{12}N_2O_8Cl_4Rh_4$
Crystal system	Orthorhombic
Cell dimensions	a 9.466(5), b 13.648(9), c 24.124(14) Å
	$\alpha = \beta = \gamma = 90.00°$
	$V = 3119.64(500)$ Å^3
Wavelength	0.71069 Å (Mo-K_α, graphite monochromator)
Range of 2θ	2.7–45°
Space group	$Pccn$
Z	4
Calculated density	2.201 g/cm^3
Linear absorption coefficient (cm^{-1})	24.07 cm^{-1}
Number of unique reflections	2360
Structure factor weights	$W = 1/[\sigma^2(F) + 0.00178F^2]$
	with $\sigma^2(F)$ from counting statistics
Final R factors	$R = 0.0508$, $R_w = 0.0568$
Goodness of fit (Nominal)	1.336
Goodness of fit (Divided by slope of normal probability plot)	1.155
Crystal dimensions (mm)	0.3 × 0.3 × 0.6

Hydrogen was detected above the reaction using GLC. The most interesting feature of 10's structure is the presence of a Rh^{II}–Rh^{II} single bond, unsupported by any bridging groups. Several other unbridged Rh^{II}–Rh^{II} complexes have been reported, and the metal–metal bond in them ranges in length from 2.936(2) to 2.775(4) Å [13]. In our structure the Rh^{II}–Rh^{II} distance is only 2.67(1) Å, not much longer than in a Rh^{II}–Rh^{II} complex with two bridging acetates [13]. Two reasons for this short metal–metal single bond can be advanced. First, the atoms *trans* to the bond, Cl, have a weak *trans* influence, unlike, for example, the $Rh_2(DMG)_4(PPh_3)_2$ structure (DMG = dimethylglyoximato) in which the PPh_3 groups *trans* to the Rh^{II}–Rh^{II} bond help to lengthen it to 2.936(2) Å. Second, stacking interactions between the acylquinoline ligands act to shorten the metal–metal distance. As Fig. 3 shows, each acyl group sits over the C_5N ring of the opposite quinoline. This stacking is similar to what is seen in crystal structures of purines and pyrimidines [14], in which dipole-induced dipole interactions between a C=O group and an aromatic ring stabilize base stacks. The rings are staggered by a dihedral angle (C(10)–Rh(1)–Rh(1a)–C(10a)) of 50° to keep the aromatic rings apart, while the two quinoline rings are almost parallel (the ring planes [C(10)–Rh(1)–N(1)/C(10a)–Rh(1a)–N(1a)] make a dihedral angle of 9.9° with one another). This ring geometry maximizes the C=O–C_5N overlap. As a result of this stacking, there are close non-bonded contacts of the atoms along the edge of the quinoline rings: C(8)–C(8a), 3.275 Å; C(10–C(9a), 3.151; O(4)–C(9a), 3.125 Å. The rhodium–acyl bond distance (Rh(1)–C(10), 1.979(7) Å) is somewhat longer than similar distances in other chelating acylrhodium structures we have determined (1.938(6) Å for an ethyl-acylrhodium(III) complex [8] and 1.949(4) Å for an benzylacylrhodium(III) complex) [1]. This lengthening in 10 may be due to the interaction of the acyl group with the nearby ring.

These results, coupled with other work, allow us to detect some tendencies in the reactions of 8-substituted quinolines with rhodium(I) complexes. Where there are good electron-donating groups at the 8-position, such as 8-quinolinyl styryl ketone or the enol form of **1**, formation of a rhodium(I) π-complex is to be expected. 8-Quinolinyl ketones undergo C–C bond cleavage with an olefin rhodium(I) complex, but when better π-acid ligands are present on the metal (such as phosphines or CO), C–C activation does not occur at least to give isolable alkylacylmetals. Finally, the aldehyde C–H bond in **9** reacts with a range of rhodium(I) systems (including $RhCl(PPh_3)_3$, $[Rh(C_2H_4)_2Cl]_2$ and $[Rh(CO)_2Cl]_2$ and this bond is more easily activated than either C–C or ketone C=O bonds.

Experimental

General procedures

All manipulations involving rhodium(I) were carried out under N_2, either in a glove box or using Schlenk techniques. ^1H NMR were taken at 250 MHz on a Bruker WM-250 and chemical shifts are given as δ values. Ligands were made by literature procedures or were of commercially available reagent quality. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, New York.

Synthesis of the η^2-enol complex 3

To 42 mg of $[(CO)_2RhCl]_2$ in 2 ml of benzene was added 53 mg of 8-quinolinyl benzyl ketone. The solution turned orange and after 24 h orange crystals of **3** were recovered (53 mg), m.p. 168–170°C. IR (Nujol): 3250, 2022 cm^{-1}. ^1H NMR (acetone-d_6) 9.04(dd), 8.60(dd), 8.14(dd), 8.02(dd), 7.94(dd), 7.74(m), 7.25(m), 4.80(d, J 2.5 Hz). Also formed, as yellow needles, when water was present (which came from incomplete drying of the quinoline ligand) was the salt $[C_{17}H_{14}NO]^+$ $[(CO)_2RhCl_2]^-$ where the cation is the protonated ketone form of **1**, m.p. 153–155°C. IR (Nujol) 2060(s), 1997(s), 1653(m), 1624(m), 1592(m), 1555(m) cm^{-1}. ^1H NMR (acetone-d_6) 9.72(dd), 9.55(d), 9.29(d), 8.83(m), 8.46(dd), 8.27(dd), 7.5(m), 4.86(s). This was also characterized by X-ray crystallography.

Structure solution of 3

An orange crystal, 0.3 × 0.3 × 0.2 mm was mounted on top of a glass rod in a random orientation with epoxy glue. All constants and orientation matrix were obtained from centering 9 reflections of low 2 θ angle. The axis lengths which came from the indexing of 9 reflections were confirmed by an axial photograph, and all cell constants and orientation matrix were refined by least squares on 25 reflections in the range 26–28° of 2 θ. Crystal and collection data are given in Table 4. The reflection data were collected with the 2 θ–θ scan technique at 21 ± 1°. The structure was solved using direct methods with the SHELXTL series of programs supplied with our Nicolet R3m/E diffractometer. Separate ψ scans of 8 strong representative reflections were recorded to determine an empirical absorption correction. Structure factor magnitudes were extracted from raw intensities by application of the Lorenz and polarization factors. An ellipsoidal empirical absorption correction was applied using the ψ-scan data. The maximum transmission was 0.739, the minimum was 0.668. The enol hydrogen was located in a difference map and all the other hydrogens were inserted at calculated positions and constrained to

ride with the appropriate carbon atom. The temperature factors of all non-hydrogen atoms were anisotropic.

Synthesis of the rhodium(II) dimer 10

The rhodium carbonyl **2** (20 mg) was dissolved in 2 ml of benzene and a solution of 8-quinoline carboxaldehyde (8 mg) in 3 ml of benzene was added. The flask was capped. After 3 days at room temperature deep red crystals formed (16 mg). IR ($CHCl_3$) 2083(s), 2060(m, sh) 2015(s), 1675(m) cm^{-1}. ^1H NMR ($CDCl_3$) 9.86(d), 8.69(dd) 7.4–8.4(m). One of these crystals was used in the X-ray structure determination.

Structure solution of 10

A deep red crystal, $0.3 \times 0.3 \times 0.6$ mm, was mounted on the top of a glass rod in a random orientation with epoxy glue. Data collection and refinement were carried out as with **3**. Table 8 summarizes the crystal and collection data.

Synthesis of chlorocarbonyl-8-nitrosoquinolinerhodium(I) (8)

To 10 mg of **2** in 7 ml of benzene was added 9 mg of 8-nitroquinoline in 3 ml of benzene. Vigorous gas evolution took place. In a separate experiment this gas was shown to contain CO_2 by its IR spectrum and by absorption onto Ascarite (66% yield of CO_2 based on **8**). A black powder precipitated which was soluble in $CHCl_3$, 11 mg, (m.p. 219°C (dec). Anal. Found: C, 36.56; H, 1.89; N, 8.65. $C_{10}H_6N_2O_2ClRh$ calcd.: C, 36.98; H, 1.86; N, 8.63%. IR (Nujol) 2030(s), 1580(m), 1495(m) cm^{-1}. ^1H NMR ($CDCl_3$) 10.28(d), 8.73(d), 8.48(d), 8.28(d), 7.96(m), 7.60(m). The downfield shift of the proton at C(2) in the quinoline ring to 10.28 indicates rhodium coordination to the quinoline nitrogen and the IR band at 1495 cm^{-1} is consistent with an arylnitrosylrhodium complex bonded through nitrogen [15,16].

Acknowledgements

References

1 J.W. Suggs and C.-H. Jun, J. Am. Chem. Soc., 106 (1984) 3054.
2 J.W. Suggs, J. Am. Chem. Soc., 100 (1978) 640.
3 M. Brookhart and M.L.H. Green, J. Organomet. Chem., 250 (1983) 395.
4 R. Periana and R.G. Bergman, J. Am. Chem. Soc., 106 (1984) 7272.
5 R.H. Crabtree, Chem. Rev., 85 (1985) 245.
6 W.D. Jones and F.J. Feher, J. Am. Chem. Soc., 106 (1984) 1650.
7 A. Albinati, C.G. Anklin and P.S. Pregosin, Inorg. Chim. Acta, 90 (1984) L37.
8 J.W. Suggs, M.J. Wovkulich and S.D. Cox, Organometallics, 4 (1985) 1101.
9 F.A. Cotton, J.N. Francis, B.A. Frenz and M. Tsutsui, J. Am. Chem. Soc., 95 (1973) 2483.
10 R. McCrindle, G. Perguson, A.J. McAlees and B.L. Ruhl, J. Organomet. Chem., 204 (1981) 273.
11 J. Hillis, M. Ishaq, B. Gorewit and M. Tsutsui, J. Organomet. Chem., 116 (1976) 91.
12 J.W. Suggs, M.J. Wovkulich and K.S. Lee, J. Am. Soc., 107 (1985) 5546.

13 T.R. Felthouse, Prog. Inorg. Chem. 29 (1982) 73.
14 W. Saenger, Principles of Nucleic Acid Structure, Springer Verlag, New York, 1984, p. 132–140.
15 G. Vasapollo, P. Giannoccaro, C.F. Nobile and F. Allegretta, J. Organomet. Chem., 270 (1984) 109; R.G. Little and R.J. Doedens, Inorg. Chem., 12 (1973) 537.
16 H.A. Morrison, in H. Fever (Ed.), Chemistry of the NO_2 and NO Groups, Part 1, John Wiley and Sons, New York, 1969, p. 165–213.