

Rhodium Complexes Containing 1-(4-Pyridylmethylene)-4-alkoxyanilines as Ligands: Crystal Structure of an Unusual Square-Planar Cluster of 64 Electrons, $\text{Rh}_4(\text{OOCCH}_3)_4(\text{CO})_4(\text{NC}_5\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{OC}_{14}\text{H}_{29})_4$

Fernando J. Lahoz, Alberto Martín, Miguel A. Esteruelas, Eduardo Sola, J. Luis Serrano, and Luis A. Oro*

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

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$\text{Rh}(\text{OOCOR}_3)(\text{cod})\text{L}^n$ (1-6) and *cis*- $\text{Rh}(\text{OOCOR}_3)(\text{CO})_2\text{L}^n$ (7-12) (R = H, F; cod = 1,5-cyclooctadiene; $\text{L}^n = \text{NC}_5\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ with $n = 2, 8, 14$) complexes have been prepared by the reaction of the L^n ligands with the corresponding dimers $[\text{Rh}(\text{OOCOR}_3)(\text{cod})]_2$ or $[\text{Rh}(\text{OOCOR}_3)(\text{CO})_2]_2$ (R = H, F). The *cis*-dicarbonyl compounds 7-12 decompose in dichloromethane solution to form square-planar clusters of 64 electrons, $\text{Rh}_4(\text{OOCCH}_3)_4(\text{CO})_4\text{L}^n_4$ (13-18). The molecular structure of $\text{Rh}_4(\text{OOCCH}_3)_4(\text{CO})_4\text{L}^{14}_4$ (15) has been determined by X-ray investigation. The complex is centrosymmetric, and the four rhodium atoms define a rectangle. Two alternant metal-metal bonds of the rectangle are bridged by two carbonyl groups; the other two remaining Rh-Rh bonds are bridged by two acetate groups. Each metal completes its coordination sphere with the pyridinic ligand $\text{NC}_5\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{OC}_{14}\text{H}_{29}$. Crystal data for 15: space group $P\bar{1}$, $a = 10.300$ (1) Å, $b = 11.166$ (1) Å, $c = 26.216$ (3) Å; $\alpha = 89.29$ (1)°, $\beta = 88.68$ (1)°, $\gamma = 72.17$ (1)°; 4491 reflections, $R = 0.041$, $R_w = 0.041$. The complexes $[\text{Rh}_4(\text{OOCCH}_3)_4(\text{CO})_4(\text{py})_4]$ (19, 20; R = H, F; py = pyridine) are also reported.

Introduction

As a part of a broad study of the chemistry and properties of rhodium and iridium complexes with 1-(4-pyridylmethylene)-4-alkoxyanilines ($\text{L}^n = \text{NC}_5\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$), we have recently reported the preparation of compounds of the type *cis*- $\text{MCl}(\text{CO})_2\text{L}^n$ (M = Rh, Ir).¹ Continuing with our work in this field, we can now report the synthesis of the unusual square-planar clusters $\text{Rh}_4(\text{OOCOR}_3)_4(\text{CO})_4\text{L}^n_4$, which are formed by the decomposition of the compounds *cis*- $\text{Rh}(\text{OOCOR}_3)(\text{CO})_2\text{L}^n$ (R = H, F) in dichloromethane solutions.

In four-metal-atom clusters, the most symmetric and compact arrangement is the tetrahedron, found in many organometallic clusters.² Since 1977 there has been a dramatic increase in the number of molecules synthesized and studied that contain an M_4 butterfly structure.³ Butterfly clusters represent an intermediate arrangement between tetrahedral and square-planar structures.⁴ However, the examples of clusters with square-planar geometry are less common; this structure has been found in complexes with capped ligands (e.g. PR, NEt, GeMe) containing Fe,⁵ Co,⁶ or Rh.⁷ For the complexes $\text{Os}_4(\text{CO})_{16}$ ⁸

and $\text{Ir}_4(\text{CO})_4[(\text{MeCO})_2\text{C}_2]$,⁹ a distorted-square-planar arrangement has also been observed.

There is only a small number of compounds of this type with carboxylate ligands. Sasaki et al. have recently reported that the complex $\text{Pt}_4(\text{OOCCH}_3)_8$ reacts with acetylacetonate ions to give the tetrakis(acetylacetonate) complex $\text{Pt}_4(\text{OOCCH}_3)_4(\text{acac})_4$,¹⁰ which retains the $\text{Pt}_4(\text{OOCCH}_3)_8$ square-planar core.¹¹ Previously, Moiseev et al. had described the structure of the complex $\text{Pd}_4(\text{CO})_4(\text{OOCCH}_3)_4$. The Pd_4 framework of this cluster is a parallelogram with angles differing markedly from the perpendicular. The CO ligands bond two palladium atoms, forming $\text{Pd}_2(\text{CO})_2$ fragments that are connected by acetate groups.¹²

The M_4 square-planar clusters have 64 valence electrons in their polyhedra according to the effective atomic number rule.¹³ This rule is followed by some complexes such as $\text{Fe}_4(\text{CO})_{11}[\text{P}(\text{OMe})_3](\text{PTol})_2$, $\text{Os}_4(\text{CO})_{16}$, $\text{Co}_4(\text{CO})_{10}(\text{PPh})_2$, $\text{Ir}_4(\text{CO})_8[(\text{MeCO})_2\text{C}_2]_4$, and $\text{Pt}_4(\text{OOCCH}_3)_4(\text{acac})_4$. However, no Rh_4 square-planar compound with 64 valence electrons has been previously reported; our complexes $\text{Rh}_4(\text{OOCCH}_3)_4(\text{CO})_4\text{L}^n_4$ represent the first examples of rhodium complexes of this type, and to the best of our knowledge only a related rhodium square-planar cluster with 60 electrons, $\text{Rh}_4(\text{PPh})_2(\text{cod})_4$,⁷ has been characterized by X-ray diffraction.

Results and Discussion

The halogen bridges in the dimeric compounds $[\text{MCl}(\text{cod})]_2$ (M = Rh, Ir; cod = 1,5-cyclooctadiene) are readily

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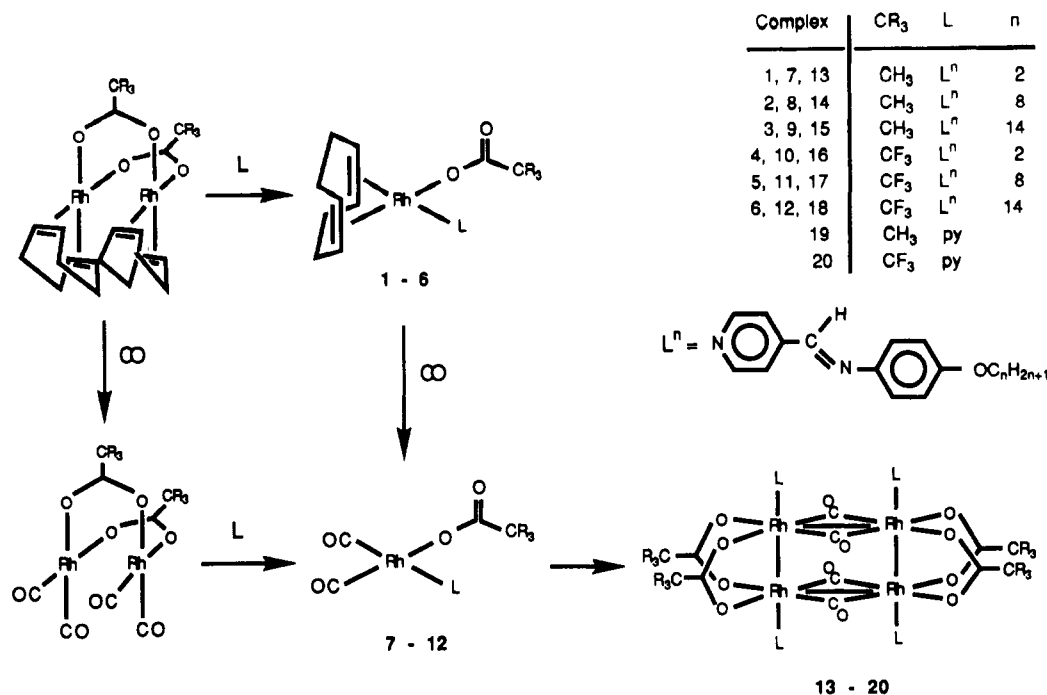
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Scheme I



split by ligands of the type 1-(4-pyridylmethylene)-4-alkoxyaniline (Lⁿ) to give square-planar mononuclear complexes with the formula MCl(cod)Lⁿ.¹ Similarly, the reactions of the dimeric carboxylate compounds [Rh(OOCCR₃)L'₂]₂ (R = H, F; L'₂ = 2 CO, cod) with the ligands Lⁿ (Lⁿ = NC₅H₄CH=NC₆H₄OC_nH_{2n+1} with n = 2, 8, 14) lead to the species Rh(OCO₂CR₃)(cod)Lⁿ (1-6) or *cis*-Rh(OCO₂CR₃)(CO)₂Lⁿ (7-12). The latter can also be prepared by means of the reaction of the corresponding diolefin compounds 1-6 with CO (Scheme I) or, alternatively, by the treatment of chloro dicarbonyl complexes *cis*-RhCl(CO)₂Lⁿ with silver acetate or trifluoroacetate. We note that previous studies of the reaction of the complexes [Rh(OOCCR₃)(CO)₂]₂ with other Lewis bases such as pyridine or triphenylphosphine have been carried out. The reaction with pyridine leads to the mononuclear compound Rh(OCOCH₃)(CO)₂(py),¹⁴ while the reaction with triphenylphosphine gives the dimeric [Rh(OOCCCH₃)(CO)(PPh₃)₂]₂;¹⁵ an analogous complex, [Rh(OOCCCH₃)(CO)(PCy₃)₂]₂, has recently been isolated in our laboratory.¹⁶

We formulate products 1-12 as square-planar derivatives containing unidentate carboxylate ligands on the basis of assignments for $\nu_{\text{asym}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ at ca. 1580-1710 and 1370-1380 cm⁻¹, respectively. Mitchell et al.¹⁷ and Robinson et al.¹⁸ also formulate similar complexes as four-coordinate species with unidentate carboxylate ligands on the basis of similar IR spectra. Furthermore, the values found for $\Delta\nu$ ($\nu_{\text{asym}}(\text{OCO}) - \nu_{\text{sym}}(\text{OCO})$) (Table I) coincide with those established by Deacon et al. for the unidentate coordination of carboxylate groups.¹⁹ In order to corroborate the monomeric character of these compounds, the molecular weights of two representative examples, complexes 2 and 12, were determined osmotically in

Table I. IR Data for the Complexes (Nujol)

complex	$\nu(\text{CO}), \text{cm}^{-1}$	$\nu(\text{CR}_3\text{COO}), \text{cm}^{-1}$		$\Delta\nu$
		$\nu_{\text{asym}}(\text{OCO})$	$\nu_{\text{sym}}(\text{OCO})$	
1		1595	1380	215
2		1585	1380	205
3		1585	1380	205
4		1680		
5		1680		
6		1690		
7	2065, 2005	1630	1370	260
8	2050, 1990 (2005, 2085) ^a	1625	1370	255
9	2060, 1995	1625	1370	255
10	2100, 2025	1710		
11	2100, 2023 (2025, 2100) ^a	1710		
12	2095, 2020	1710		
13	1820, 1798	1570	1425	145
14	1815, 1790	1565	1415	150
15	1818, 1795 (1828, 1805) ^a	1570	1425	145
16	1850, 1820	1655		
17	1835, 1813 (1850, 1830) ^a	1650		
18	1845, 1835	1650		
19	1825, 1800	1580	1425	155
20	1848, 1830	1650		

^a In CH₂Cl₂ solution.

CHCl₃; the values obtained (561 for 2 and 653 for 12) agree well with those calculated for the formulas Rh(OCOCH₃)(cod)L⁸ (580.6) and Rh(OCO₂CF₃)(CO)₂L¹⁴ (666.5).

The IR and ¹H NMR spectra of the complexes 1-12 are listed in Tables I and II and are in good agreement with the structures proposed; the IR spectra in Nujol of the dicarbonyl compounds 7-12 show two strong $\nu(\text{CO})$ bands at about 2000 cm⁻¹ (Table I), consistent with the *cis* geometry. The ¹H NMR spectra show the resonances expected for the ligands Lⁿ (Table II); the displacement of the pyridinic proton resonances of the ligands Lⁿ in the complexes observed, in relation to those resonances for the free ligands, confirms that the pyridinic nitrogen is linked to the rhodium atom. For the 1,5-cyclooctadiene ligand in the diolefinic compounds 1-6, only a single vinylic resonance is observed at room temperature, which suggests the existence of a rapid exchange process, as has been observed in other similar systems.²⁰

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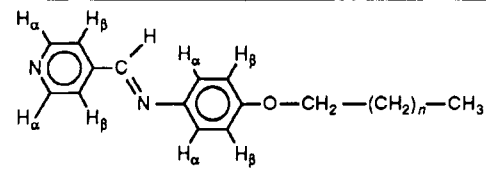
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Table II. ¹H NMR Spectra (CDCl₃) for the Complexes^a


complex	cod									
	H _a	H _b	-CH=N-	H _a , H _b	-OCH ₂	-(CH ₂) _n -	-CH ₃	=CH	CH ₂	OOCCH ₃
1	8.81 <i>J</i> _{ab} = 6.3	7.72	8.44 (s)	7.28, 6.93 <i>J</i> _{αβ} = 8.8	4.05 (q) <i>J</i> = 7.0		1.43 (t) <i>J</i> = 7.0	4.0 (br)	2.5 (br) 1.8 (br)	1.75 (s)
2	8.81 <i>J</i> = 6.0	7.73	8.44 (s)	7.28, 6.93 <i>J</i> _{αβ} = 8.8	3.98 (t) <i>J</i> = 6.6	1.8-1.3	0.88 (m)	4.0 (br)	2.5 (br) 1.8 (br)	1.76 (s)
3	8.81 <i>J</i> _{ab} = 6.3	7.73	8.44 (s)	7.28, 6.93 <i>J</i> _{αβ} = 8.8	3.97 (t) <i>J</i> = 6.5	1.8-1.2	0.87 (m)	4.1 (br)	2.5 (br) 1.8 (br)	1.76 (s)
4	8.79 <i>J</i> _{ab} = 6.1	7.74	8.43 (s)	7.28, 6.93 <i>J</i> _{αβ} = 8.8	4.06 (q) <i>J</i> = 7.1		1.43 (t) <i>J</i> = 7.1	4.1 (br)	2.5 (br) 1.8 (br)	
5	8.79 <i>J</i> _{ab} = 6.5	7.75	8.43 (s)	7.28, 6.93 <i>J</i> _{αβ} = 8.8	3.97 (t) <i>J</i> = 6.4	1.8-1.2	0.88 (m)	4.1 (br)	2.5 (br) 1.8 (br)	
6	8.79 <i>J</i> _{ab} = 6.1	7.75	8.43 (s)	7.30, 6.93 <i>J</i> _{αβ} = 8.9	3.98 (t) <i>J</i> = 6.4	1.8-1.2	0.87 (m)	4.1 (br)	2.5 (br) 1.8 (br)	
7	8.73 <i>J</i> _{ab} = 6.1	7.88	8.51 (s)	7.33, 6.94 <i>J</i> _{αβ} = 8.2	4.08 (q) <i>J</i> = 7.0		1.44 (t) <i>J</i> = 7.0			2.00 (s)
8	8.72 <i>J</i> _{ab} = 6.3	7.88	8.50 (s)	7.32, 6.94 <i>J</i> _{αβ} = 8.8	3.98 (t) <i>J</i> = 6.4	1.8-1.3	0.88 (m)			2.00 (s)
9	8.73 <i>J</i> _{ab} = 5.9	7.88	8.51 (s)	7.33, 6.94 <i>J</i> _{αβ} = 8.4	3.98 (t) <i>J</i> = 6.3	1.8-1.3	0.88 (m)			2.00 (s)
10	8.67 <i>J</i> _{ab} = 6.2	7.94	8.53 (s)	7.35, 6.95 <i>J</i> _{αβ} = 8.8	4.08 (q) <i>J</i> = 7.1		1.44 (t) <i>J</i> = 7.1			
11	8.67 <i>J</i> _{ab} = 6.4	7.95	8.53 (s)	7.35, 6.96 <i>J</i> _{αβ} = 8.8	4.00 (t) <i>J</i> = 6.6	1.8-1.3	0.89 (m)			
12	8.68 <i>J</i> _{ab} = 5.9	7.95	8.53 (s)	7.35, 6.96 <i>J</i> _{αβ} = 8.8	4.00 (t) <i>J</i> = 6.5	1.8-1.2	0.87 (m)			
15	8.31 <i>J</i> _{ab} = 6.3	7.30	8.13 (s)	7.01, 6.70 <i>J</i> _{αβ} = 8.8	3.91 (t) <i>J</i> = 6.5	1.8-1.2	0.88 (m)			2.29 (s)
17	8.20 <i>J</i> _{ab} = 6.3	7.38	8.15 (s)	7.02, 6.76 <i>J</i> _{αβ} = 8.8	3.92 (t) <i>J</i> = 6.5	1.8-1.2	0.89 (m)			
18	8.19 <i>J</i> _{ab} = 6.5	7.38	8.15 (s)	7.02, 6.76 <i>J</i> _{αβ} = 8.8	3.92 (t) <i>J</i> = 6.5	1.8-1.3	0.89 (m)			

^aChemical shifts are in ppm and *J* values in Hz. ^bComplexes 13, 14, 16, 19, and 20 are not soluble enough for NMR recording.

Interestingly, the *cis*-dicarbonyl compounds 7-12 decompose in dichloromethane solutions into the square-planar clusters Rh₄(OOCCH₃)₄(CO)₄L₄ (13-18). The decomposition can easily be monitored by IR spectroscopy. Dichloromethane solutions of 7-9 initially show an orange color that progressively becomes dark green; their IR spectra contain the bands of 7-9 together with two new absorptions at about 1820-1790 cm⁻¹, which can be assigned to carbonyl bridges. Under reflux and after 3 days, the IR spectra have, in the carbonyl region, only the absorption resulting from carbonyl bridges. The trifluoroacetate compounds 10-12 are more stable than the analogues acetates 7-9, and thus, the presence of ONMe₃ was necessary for the formation of 16-18.

Lawson and Wilkinson¹⁴ had previously reported that the complexes of the type Rh(OCOR)₂(CO)₂L (L = amine ligand) were decomposed by moisture to *ill-defined straw-colored solids*. We suspected that these solids should contain square-planar clusters similar to 13-18; this prompted us to investigate the decomposition of the complexes Rh(OCOR)₂(CO)(py) (R = H, F), generated "in situ" by adding pyridine to the dichloromethane solutions

of the tetracarbonyl compounds [Rh(OOCCR₃)(CO)₂]₂ (R = H, F). Thus, working under conditions similar to those mentioned above for 7-12, we have isolated dark green solids with empirical formulas [Rh(OOCCF₃)(CO)(py)]_x and [Rh(OOCCF₃)(CO)(py)]_x. The low solubility of these solids in most solvents prevented the obtainment of NMR spectra, which is necessary for their characterization. However, they can be described as the square-planar clusters 19 and 20 (Scheme I), on the basis of their IR spectra in Nujol (see Table I).

Molecular Structure of Rh₄(OOCCH₃)₄(CO)₄(NC₅-H₄CH=NC₆H₄OC₁₄H₂₉)₄ (15). The definitive characterization of 15 as a square-planar cluster came from an X-ray diffraction experiment. A partial view of the molecular geometry of this compound is shown in Figure 1; for clarity, only the pyridine ring of the L¹⁴ ligand is represented. Selected bond distances and angles are listed in Table III.

The complex is centrosymmetric, with two crystallographically independent dinuclear Rh₂(OOCCH₃)₂(CO)₂L¹⁴₂ moieties held together by two Rh-Rh metal bonds (2.577 (1) Å) and four bridging acetate ligands, giving rise to a tetranuclear cluster with the metal atoms defining a slightly distorted square plane. Within each independent dinuclear half, both rhodium atoms also show a metal-metal bond (2.633 (1) Å) and are additionally

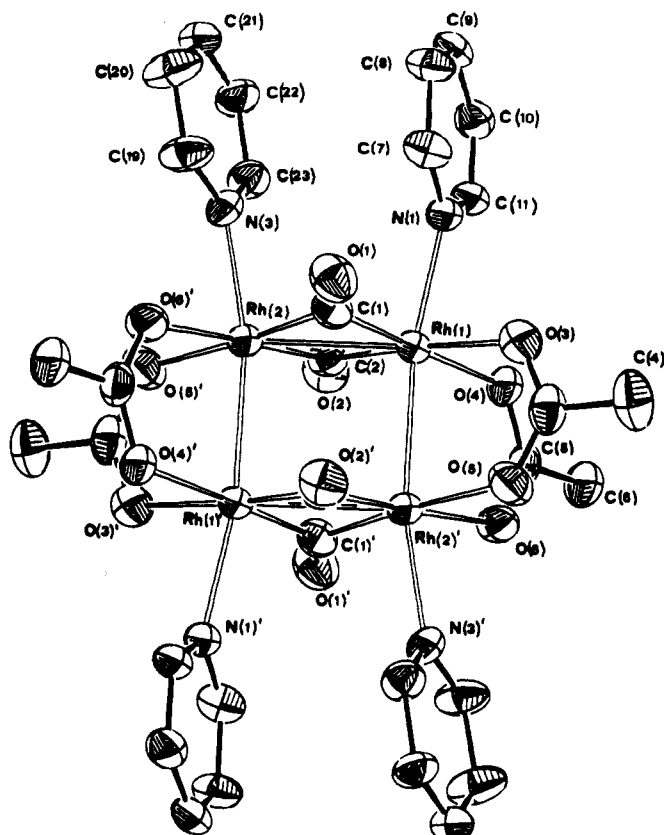


Figure 1. ORTEP diagram of $\text{Rh}_4(\text{OOCCH}_3)_4(\text{CO})_4(\text{NC}_5\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{OC}_{14}\text{H}_{26})_4$ (15) showing the numbering scheme used. Hydrogen atoms and a part of the 1-(4-pyridylmethylene)-4-alkoxyanilines ($-\text{CH}=\text{NC}_6\text{H}_4\text{OC}_{14}\text{H}_{26}$) have been omitted for clarity.

bridged by two carbonyl groups. Both metal-metal distances are similar to those found for complexes with a relatively short Rh-Rh single bond bridged by a carbonyl group and by a bidentate



ligand (e.g. X = N, 1*H*-pyrrolo[2,3-*b*]pyridinate, 2.686 (2) Å;²¹ X = O, 2-pyridonate, 2.6197 (8) Å;²² X = P, 2-(di-phenylphosphino)pyridine, 2.612 (1) Å²³) and are shorter than those observed in the related cluster $\text{Rh}_4(\mu\text{-PPh})_2(\text{cod})_4$ (2.850 (1), 2.836 (1) Å).⁷ The slight distortion of the metal cluster from an ideal square plane arises from the different Rh-Rh distances and the values of the angles Rh(2)-Rh(1)-Rh(2)' (88.88 (5)°) and Rh(1)-Rh(2)-Rh(1)' (91.12 (6)°).

Each rhodium atom is also coordinated to a pyridinic ligand with the nitrogen atom of the ligands contained in the plane determined by the four metals (maximum deviation from this plane 0.013 (5) Å for N(1)). Surprisingly, both Rh-N bond distances (2.234 (6) and 2.196 (7) Å) are different within the estimated error, for no apparent reason. These distances compare well with those found in the dimeric complex $\text{Rh}_2(\text{OOCCH}_3)_4(\text{py})_2$ (2.227 (3) Å), where the pyridinic nitrogen is also trans to a Rh-Rh single bond.²⁴

Table III. Selected Bond Lengths (Å) and Angles (deg) for 15^a

Rh(1)-Rh(2)	2.633 (1)	Rh(2)-Rh(1)'	2.577 (1)
Rh(1)-C(1)	1.954 (7)	Rh(2)-C(1)	1.957 (8)
Rh(1)-C(2)	1.947 (8)	Rh(2)-C(2)	1.947 (6)
Rh(1)-N(1)	2.235 (6)	Rh(2)-N(3)	2.196 (7)
Rh(1)-O(3)	2.147 (6)	Rh(2)-O(5)'	2.124 (5)
Rh(1)-O(4)	2.138 (5)	Rh(2)-O(6)'	2.118 (5)
C(1)-O(1)	1.175 (9)	C(2)-O(2)	1.179 (9)
C(3)-O(3)	1.259 (11)	C(5)-O(4)	1.266 (11)
C(3)-O(5)	1.257 (10)	C(5)-O(6)	1.254 (10)
C(3)-C(4)	1.534 (12)	C(5)-C(6)	1.502 (9)
Rh(2)-Rh(1)-Rh(2)	88.88 (5)	Rh(1)-Rh(2)-Rh(1)	91.12 (6)
Rh(2)-Rh(1)-C(1)	94.3 (2)	Rh(1)-Rh(2)-C(1)	95.8 (2)
Rh(2)-Rh(1)-C(2)	93.0 (2)	Rh(1)-Rh(2)-C(2)	94.5 (2)
Rh(2)-Rh(1)-N(1)	170.3 (2)	Rh(1)-Rh(2)-N(3)	168.4 (2)
Rh(2)-Rh(1)-O(3)	85.0 (2)	Rh(1)-Rh(2)-O(5)'	85.9 (2)
Rh(2)-Rh(1)-O(4)	86.1 (2)	Rh(1)-Rh(2)-O(6)'	84.7 (2)
Rh(2)-Rh(1)-C(1)	47.8 (2)	Rh(1)-Rh(2)-C(1)	47.6 (2)
Rh(2)-Rh(1)-C(2)	47.5 (2)	Rh(1)-Rh(2)-C(2)	47.5 (2)
Rh(2)-Rh(1)-N(1)	100.8 (2)	Rh(1)-Rh(2)-N(3)	100.5 (2)
Rh(2)-Rh(1)-O(3)	138.8 (2)	Rh(1)-Rh(2)-O(5)'	137.8 (2)
Rh(2)-Rh(1)-O(4)	134.9 (2)	Rh(1)-Rh(2)-O(6)'	135.8 (2)
C(1)-Rh(1)-C(2)	94.5 (3)	C(1)-Rh(2)-C(2)	94.4 (3)
C(1)-Rh(1)-N(1)	92.6 (3)	C(1)-Rh(2)-N(3)	92.2 (3)
C(1)-Rh(1)-O(3)	92.1 (3)	C(1)-Rh(2)-O(5)'	174.4 (3)
C(1)-Rh(1)-O(4)	177.4 (3)	C(1)-Rh(2)-O(6)'	89.0 (3)
C(2)-Rh(1)-N(1)	93.4 (3)	C(2)-Rh(2)-N(3)	93.3 (3)
C(2)-Rh(1)-O(3)	173.2 (3)	C(2)-Rh(2)-O(5)'	90.8 (3)
C(2)-Rh(1)-O(4)	88.1 (3)	C(2)-Rh(2)-O(6)'	176.6 (3)
N(1)-Rh(1)-O(3)	87.9 (2)	N(3)-Rh(2)-O(5)'	85.4 (2)
N(1)-Rh(1)-O(4)	86.8 (2)	N(3)-Rh(2)-O(6)'	87.0 (2)
O(3)-Rh(1)-O(4)	85.3 (2)	O(5)'-Rh(2)-O(6)'	85.9 (2)
Rh(1)-C(1)-Rh(2)	84.6 (3)	Rh(1)-C(2)-Rh(2)	85.1 (3)
Rh(1)-C(1)-O(1)	138.2 (6)	Rh(1)-C(2)-O(2)	137.6 (6)
Rh(2)-C(1)-O(1)	137.1 (6)	Rh(2)-C(2)-O(2)	137.2 (6)

^a Primed atoms refer to symmetry-related ones through the operation 1 - x, -y, -z. Estimated standard deviations in the least significant figure are given in parentheses.

Without consideration of the Rh(1)-Rh(2) bond, the coordination environment of each rhodium could be formally described as a slightly distorted octahedron, showing cis-interligand angles ranging from 84.7 (2) to 95.8 (2)° and the trans analogues from 168.4 (2) to 177.4 (3)°. The Rh(1)-Rh(2) bond approximately bisects the C(1)-Rh-C(2) angles (Rh-Rh-C angles range 47.4-47.8 (2)°).

Concluding Remarks. This study has shown that ligands of the type 1-(4-pyridylmethylene)-4-alkoxyaniline split the bridge of the complexes $[\text{Rh}(\mu\text{-OOCRR}_3\text{L}'_2)_2$ (R = H, F; L'₂ = 2 CO, cod), giving mononuclear species of the type $\text{Rh}(\text{OOCRR}_3)(\text{cod})\text{L}$ and *cis*- $\text{Rh}(\text{OOCRR}_3)(\text{CO})_2\text{L}$. The latter are not stable in dichloromethane solutions and decompose to the unusual square-planar clusters $\text{Rh}_4(\text{OOCRR}_3)_4(\text{CO})_4\text{L}_4$, where the four rhodium atoms define a rectangle. The total molecular structure of the clusters can be described as two $\text{Rh}_2(\text{CO})_2\text{L}_2$ fragments connected by carboxylate ligands. The complexes $\text{Rh}(\text{OOCRR}_3)(\text{CO})_2(\text{py})$, reported by Lawson and Wilkinson, also decompose into the square-planar clusters $\text{Rh}_4(\text{OOCRR}_3)_4(\text{CO})_4(\text{py})_4$ under similar conditions.

Experimental Section

General Data. All reactions were carried out with use of standard Schlenk procedures. Solvents were dried and purified by known procedures and distilled prior to use. Anhydrous ONMe₃ was obtained by drying commercial ONMe₃·2H₂O for 24 h, at 100 °C, under reduced pressure. Elemental analyses were performed with a Perkin-Elmer 240 microanalyzer. ¹H NMR spectra were recorded on a Varian XL 200 spectrometer at room temperature. Chemical shifts are expressed in parts per million upfield from Si(CH₃)₄. Infrared spectra were run on a Perkin-

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Table IV. Elemental Analyses, Yields, and Color of the Complexes

complex	anal. found (calcd), %			yield, %	color
	C	H	N		
1	57.79 (58.07)	6.01 (5.89)	5.52 (5.64)	50	orange
2	61.97 (62.06)	7.37 (7.11)	5.04 (4.82)	38	yellow
3	64.58 (65.04)	8.07 (8.03)	4.46 (4.21)	54	yellow
4	52.83 (52.37)	4.92 (4.76)	5.20 (5.08)	70	yellow
5	57.04 (56.78)	6.31 (6.03)	4.35 (4.41)	72	yellow
6	60.29 (60.16)	7.25 (7.01)	4.16 (3.89)	61	yellow
7	48.15 (48.66)	3.87 (3.85)	6.66 (6.30)	75	orange
8	54.53 (54.55)	5.78 (5.53)	5.52 (5.30)	68	orange
9	58.55 (58.82)	6.76 (6.74)	4.70 (4.57)	75	orange
10	43.82 (43.39)	3.09 (2.83)	5.51 (5.62)	82	yellow
11	49.39 (49.49)	4.64 (4.50)	4.80 (4.81)	88	yellow
12	54.04 (54.06)	6.08 (5.74)	4.21 (4.20)	88	yellow
13	48.93 (49.05)	3.95 (4.11)	6.66 (6.73)	53	green
14	54.69 (55.20)	6.12 (5.84)	5.54 (5.60)	60	green
15	59.30 (59.58)	7.12 (7.58)	4.66 (4.79)	56	green
16	43.85 (43.42)	3.27 (3.00)	5.94 (5.95)	15	green
17	49.37 (49.83)	5.26 (4.72)	5.02 (5.05)	38	green
18	55.15 (54.55)	6.53 (6.00)	4.58 (4.32)	21	green
19	35.15 (35.71)	3.12 (2.99)	5.35 (5.20)	41	green
20	29.71 (29.74)	1.59 (1.56)	4.07 (4.33)	25	green

Elmer 783 spectrophotometer, either as solids (Nujol mulls on polyethylene sheets) or solutions (NaCl cell windows). Molecular weights were determined in chloroform solutions on a Knauer vapor pressure osmometer (isopiestic method).

Starting Materials. Starting complexes were prepared as follows.

[Rh(OOCCH₃)(cod)]₂. A suspension of [Rh(OMe)(cod)]₂²⁵ (2.8 g, 5.8 mmol) in hexane (5 mL) was treated with an excess of acetic acid (0.5 mL) and stirred for 30 min. The resulting orange crystalline precipitate was filtered off, washed with hexane, and dried in vacuo; yield 2.70 g (85%). Anal. Calcd for C₂₀H₃₀O₄Rh₂: C, 44.46; H, 5.59. Found: C, 44.39; H, 5.79.

[Rh(OOCCF₃)(cod)]₂. The complex was prepared by using the procedure described for [Rh(OOCCH₃)(cod)]₂, with [Rh(OMe)(cod)]₂ (1 g, 1.68 mmol) and trifluoroacetic acid (0.5 mL). [Rh(OOCCF₃)(cod)]₂ was obtained as orange crystals in 89% (1 g) yield. Anal. Calcd for C₂₀H₂₄O₄F₆Rh₂: C, 37.05; H, 3.73. Found: C, 37.58; H, 3.99.

[Rh(OOCCH₃)(CO)]₂. Bubbling of CO through a suspension of [Rh(OOCCH₃)(cod)]₂ (2.4 g, 4.4 mmol) in hexane (5 mL) for 5 min gave a dichroic brown crystalline solid, which was filtered off, washed with hexane, and dried in vacuo; yield 1.70 g (88%). Anal. Calcd for C₈H₈O₅Rh₂: C, 22.04; H, 1.38. Found: C, 22.25; H, 1.41.

[Rh(OOCCF₃)(CO)]₂. The complex was prepared by using the procedure described for [Rh(OOCCH₃)(CO)]₂, with [Rh(OOCCF₃)(cod)]₂ (0.8 g, 1.23 mmol). [Rh(OOCCF₃)(CO)]₂ was obtained as dichroic brown crystals in 88% (0.55 g) yield. Anal. Calcd for C₈O₅F₆Rh₂: C, 17.66. Found: C, 17.84.

Preparation of the Complexes. The synthesis of the compounds is described as a general procedure for each type of complex. Details of the analytical data, yields, and colors are given in Table IV.

Rh(OCOCR₃)(cod)Lⁿ (R = H, n = 2 (1), 8 (2), 14 (3); R = F, n = 2 (4), 8 (5), 14 (6)). The stoichiometric amount of Lⁿ (2/1 molar ratio) was added to a suspension of [Rh(OOCCR₃)(cod)]₂ (100 mg) in acetone (5 mL) and the mixture stirred at room temperature for 5 h. The resulting solution was taken to dryness in vacuo, producing an orange residue, which was treated with pentane to yield an orange (or yellow) powder. This powder was filtered off, washed with pentane, and dried in vacuo.

cis-Rh(OCOCR₃)(CO)₂Lⁿ (R = H, n = 2 (7), 8 (8), 14 (9); R = F, n = 2 (10), 8 (11), 14 (12)). These complexes can be prepared in high yield by using two different procedures.

(a) The stoichiometric amount of Lⁿ (2/1 molar ratio) was added to a solution of [Rh(OOCCR₃)(CO)]₂ (100 mg) in CH₂Cl₂ (5 mL) and the resulting solution stirred for 5 min. The solution was concentrated under reduced pressure to 0.5 mL, and hexane

Table V. Summary of Crystal Data and Details of Intensity Collection for 15

formula	C ₁₁₆ H ₁₆₄ N ₈ O ₁₆ Rh ₄ H ₂ O
fw	2356.25
cryst shape	dark green needles
cryst size, mm	0.10 × 0.65 × 0.07
space group	P $\bar{1}$
cell params	
a, Å	10.300 (1)
b, Å	11.166 (1)
c, Å	26.216 (3)
α, deg	89.29 (1)
β, deg	88.68 (1)
γ, deg	72.17 (1)
V, Å ³	2869.5 (5)
Z	1
ρ(calcd), g cm ⁻³	1.364
temp, °C	20
radiation (λ, Å)	graphite-monochromated Mo Kα (0.710 69)
collect mode	ω/2θ
2θ limits, deg	3 ≤ 2θ ≤ 43
no. of unique data collected	6009
no. of unique data used	4491, F ≥ 5.0σ(F)
linear abs coeff, μ, cm ⁻¹	6.19
final no. of params refined	519
weighting scheme	w = 1.626/[σ ² (F) + 0.000292F ²]
R ^a	0.041
R _w ^b	0.041

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}.$$

was added to give a microcrystalline solid, which was filtered off, washed with hexane, and dried in vacuo.

(b) A dichloromethane solution (5 mL) of Rh(OCOCR₃)(cod)Lⁿ (1–6) was stirred under CO for 10 min and the resulting solution concentrated under reduced pressure to 0.5 mL. Addition of hexane caused the precipitation of a microcrystalline solid, which was filtered off, washed with hexane, and dried in vacuo.

Rh₄(OOCCH₃)(CO)₄Lⁿ (n = 2 (13), 8 (14), 14 (15)). A dichloromethane solution (10 mL) of cis-Rh(OCOCH₃)(CO)₂Lⁿ (7–9) was refluxed under N₂ for 3 days. During this time the initial orange solution changed to a dark green suspension. The suspension was concentrated under reduced pressure to 4 mL and cooled, causing the precipitation of a green microcrystalline solid, which was filtered off, washed with cold CH₂Cl₂, and dried in vacuo.

Rh₄(OOCCF₃)(CO)₄Lⁿ (n = 2 (16), 8 (17), 14 (18)). An acetone solution (10 mL) of cis-Rh(OCOCF₃)(CO)₂Lⁿ (10–12) was treated with the stoichiometric amount of ONMe₃ (1/1 molar ratio) and the mixture refluxed under N₂. The reaction mixture changed from yellow to dark green after 1 h. At this point, the suspension was concentrated under reduced pressure to 1 mL and methanol was added to complete the precipitation of a green powder. After filtration the powder was recrystallized from CH₂Cl₂/pentane to give a microcrystalline green solid.

Rh₄(OOCCH₃)(CO)₄(py)₄ (19). A dichloromethane solution (10 mL) of cis-Rh(OCOCH₃)(CO)₂(py)—prepared in situ by mixing pyridine (54 μL, 0.68 mmol) and [Rh(OOCCH₃)(CO)]₂ (150 mg, 0.34 mmol)—was refluxed for 3 days under N₂. The resulting green suspension was concentrated under reduced pressure to 4 mL, causing the precipitation of a green solid, which was filtered off, washed with cold CH₂Cl₂, and dried in vacuo.

Rh₄(OOCCF₃)(CO)₄(py)₄ (20). An acetone solution (10 mL) of cis-Rh(OCOCF₃)(CO)₂(py)—prepared in situ by mixing pyridine (30 μL, 0.36 mmol) and [Rh(OOCCF₃)(CO)]₂ (100 mg, 0.18 mmol)—was treated with ONMe₃ (22.0 mg, 0.36 mmol), and the mixture was stirred for 24 h at room temperature. The resulting suspension was concentrated under reduced pressure to 2 mL and methanol added to give a green precipitate, which was filtered off, washed with methanol, and dried in vacuo.

X-ray Data Collection. Compound 15 crystals suitable for X-ray diffraction studies were obtained by the slow diffusion of methanol into a saturated dichloromethane solution of the com-

Table VI. Atomic Coordinates ($\times 10^4$) for the Non-Hydrogen Atoms and U_{eq} Values ($\times 10^3$) with Esd's in Parentheses for 15

atom	x/a	y/b	z/c	$U_{eq}, \text{\AA}^2$	atom	x/a	y/b	z/c	$U_{eq}, \text{\AA}^2$
Rh(1) ^b	3890 (1)	1243 (1)	421 (0)	336 (3)	C(23)	6536 (7)	3338 (7)	291 (3)	43 (3)
Rh(2) ^b	6416 (1)	643 (1)	64 (0)	331 (3)	C(24)	8334 (9)	5022 (7)	1108 (3)	53 (4)
O(1)	6032 (5)	-233 (5)	1098 (2)	56 (2)	C(25)	9500 (8)	5827 (7)	1690 (3)	49 (4)
O(2)	4369 (5)	2563 (5)	-502 (2)	49 (2)	C(26)	10667 (9)	5516 (8)	1973 (3)	61 (4)
O(3)	2752 (5)	681 (5)	1024 (2)	56 (2)	C(27)	10994 (9)	6441 (8)	2262 (3)	62 (4)
O(4)	1941 (5)	2289 (5)	134 (2)	47 (2)	C(28)	10106 (8)	7653 (8)	2262 (3)	48 (4)
O(5)	7460 (5)	980 (5)	-604 (2)	52 (2)	C(29)	8968 (8)	7956 (8)	1979 (3)	60 (4)
O(6)	8316 (5)	-633 (5)	275 (2)	48 (2)	C(30)	8646 (8)	7061 (7)	1693 (3)	57 (4)
O(7)	6177 (6)	9843 (5)	3054 (2)	72 (3)	C(31)	7039 (9)	9537 (8)	3486 (3)	65 (2)
O(8)	10323 (6)	8600 (5)	2539 (2)	67 (3)	C(32)	7048 (9)	10763 (8)	3713 (3)	67 (3)
O(9) ^c	1527 (11)	2385 (10)	1818 (4)	67 (5)	C(33)	7920 (9)	10607 (8)	4187 (3)	66 (2)
N(1)	3784 (6)	2943 (5)	881 (2)	37 (3)	C(34)	7895 (8)	11874 (8)	4405 (3)	65 (2)
N(2)	4984 (7)	6096 (6)	1955 (3)	53 (3)	C(35)	8766 (9)	11785 (8)	4882 (3)	65 (2)
N(3)	7096 (6)	2124 (6)	410 (2)	39 (2)	C(36)	8682 (9)	13073 (8)	5079 (3)	68 (3)
N(4)	9247 (7)	4803 (6)	1436 (2)	54 (3)	C(37)	9543 (9)	13041 (8)	5549 (3)	68 (3)
C(1)	5629 (7)	276 (7)	712 (3)	37 (3)	C(38)	9426 (9)	14364 (8)	5740 (3)	67 (2)
C(2)	4718 (7)	1823 (6)	-169 (3)	36 (3)	C(39)	10277 (9)	14349 (8)	6214 (3)	65 (2)
C(3)	2297 (7)	-236 (8)	975 (3)	46 (3)	C(40)	10138 (8)	15665 (8)	6412 (3)	63 (2)
C(4)	1359 (8)	-450 (8)	1406 (3)	64 (4)	C(41)	11077 (9)	15659 (8)	6853 (3)	66 (3)
C(5)	8699 (7)	-1773 (8)	154 (3)	41 (3)	C(42)	10931 (9)	16941 (8)	7066 (3)	65 (2)
C(6)	10019 (7)	-2603 (7)	362 (3)	55 (3)	C(43)	11894 (9)	16943 (8)	7494 (3)	72 (3)
C(7)	4534 (8)	2853 (7)	1295 (3)	48 (4)	C(44)	11823 (9)	18229 (8)	7689 (3)	72 (3)
C(8)	4702 (8)	3901 (7)	1534 (3)	48 (4)	C(45)	11453 (8)	8322 (8)	2877 (3)	63 (2)
C(9)	4052 (7)	5096 (7)	1343 (3)	43 (3)	C(46)	11353 (9)	9551 (8)	3136 (3)	67 (3)
C(10)	3207 (7)	5179 (7)	927 (3)	48 (3)	C(47)	12393 (9)	9422 (8)	3548 (3)	65 (2)
C(11)	3097 (7)	4101 (7)	710 (3)	46 (3)	C(48)	12201 (9)	10664 (8)	3811 (3)	69 (3)
C(12)	4266 (8)	6216 (7)	1564 (3)	50 (3)	C(49)	13176 (9)	10623 (8)	4239 (3)	67 (3)
C(13)	5269 (8)	7109 (7)	2204 (3)	47 (4)	C(50)	12942 (9)	11893 (8)	4489 (3)	69 (3)
C(14)	6034 (9)	6770 (8)	2632 (3)	62 (4)	C(51)	13921 (9)	11875 (8)	4919 (3)	68 (3)
C(15)	6380 (9)	7649 (8)	2931 (3)	64 (4)	C(52)	13725 (9)	13166 (8)	5144 (3)	77 (3)
C(16)	5937 (8)	8883 (8)	2789 (3)	52 (4)	C(53)	14708 (8)	13140 (8)	5574 (3)	66 (3)
C(17)	5171 (9)	9248 (8)	2355 (3)	63 (4)	C(54)	14518 (9)	14441 (8)	5796 (3)	69 (3)
C(18)	4842 (9)	8349 (8)	2067 (3)	61 (4)	C(55)	15505 (9)	14428 (8)	6223 (3)	67 (3)
C(19)	8098 (8)	1842 (7)	743 (3)	53 (3)	C(56)	15325 (9)	15720 (8)	6450 (3)	65 (2)
C(20)	8567 (9)	2731 (7)	977 (3)	63 (4)	C(57)	16230 (9)	15682 (8)	6901 (3)	72 (3)
C(21)	7963 (8)	3997 (7)	865 (3)	43 (3)	C(58)	16090 (10)	16975 (8)	7111 (4)	85 (3)
C(22)	6939 (7)	4298 (7)	509 (3)	48 (3)					

^a U_{eq} = one-third of the trace of the orthogonalized U_{ij} tensor. ^b Atomic coordinates for these atoms are expressed $\times 10^5$ and U_{eq} values $\times 10^4$. ^c This atom was included in the analysis as a water solvent molecule.

pound. Data were collected on a Stoe-Siemens AED-2 diffractometer at 20 °C using graphite-monochromated Mo $K\alpha$ radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 60 reflections in the range $20 \leq 2\theta \leq 34^\circ$. A triclinic crystal system was established by the usual peak search and reflection indexing programs. One complete set of independent reflections was collected in the range $3 \leq 2\theta \leq 43^\circ$. The intensities of the standard reflections, measured every 1 h, showed no variation. Table V collects pertinent crystal data and details of the intensity collection. Data reduction procedures included the usual Lorentz and polarization corrections and an empirical absorption correction²⁶ (minimum and maximum corrections 0.848, 1.150).

Structure Solution and Refinement. The structure was solved by using Patterson techniques to locate the metals and by successive least-squares and difference Fourier calculations to obtain the other atom positions. All non-hydrogen atoms (excepting alkyl chains of 1-(4-pyridylmethylene)-4-alkoxyaniline ligands) were refined with anisotropic thermal parameters. Hydrogen atoms were assigned to calculated positions in the last

cycles of refinement and refined riding on their carbon atoms with a common thermal parameter. At this stage a clear residual peak in the difference Fourier map ($\sim 7-8 \text{ e}/\text{\AA}^3$) was assigned to a crystallization water molecule. Hydrogen atoms for this solvent molecule were not included. The largest remaining peak in the final difference map was equivalent to about $0.47 \text{ e}/\text{\AA}^3$ and was located in the vicinity of Rh(1). In the final cycles of refinement a weighing scheme, $w = k[\sigma^2(F_o) + gF_o^2]$, was used with $k = 1.626$ and $g = 0.000292$. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 27. Refinement in the centrosymmetric space group $P\bar{1}$ converged at $R = 0.041$ and $R_w = 0.041$. The final positional parameters for all non-hydrogen atoms are given in Table VI.

Supplementary Material Available: Tables of anisotropic thermal parameters, positional parameters of the hydrogen atoms, and full experimental details of the X-ray analysis (6 pages); a table of structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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