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Synthesis of Alkoxycarbonyl Complexes by Reaction of the Heterobinuclear Complex [(η⁶-*p*-cymene)RuCl(μ-pz)₂Rh(CO)₂] with Alcohols

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Summary: The reaction of [(η⁶-p-cymene)RuCl(μ-pz)₂-Rh(CO)₂] (pz = pyrazolato; 1) in alcohols with iodine in the presence of an excess of NaI or NaBPh₄ led to alkoxycarbonyl complexes with the formulas [(η⁶-p-cymene)Ru(μ-I)₂(μ-pz)Rh(COOR)I(CO)] (R = Me (2), Et (3), n-Pr (4), i-Pr (5)) and [(η⁶-p-cymene)Ru(μ-Br)₂(μ-Brpz)Rh(Br)(COOMe)(CO)] (Brpz = 4-bromopyrazolato; 6). The new compounds exhibit notable stability. They have been isolated in the solid state and characterized by a combination of elemental analyses and IR and ¹H and ¹³C{¹H} NMR spectroscopy.

Activation of coordinated carbon monoxide by nucleophiles is particularly interesting, since complexes involved in these processes have been invoked as playing a key role in several catalytic reactions.[1] Some representative examples include the water-gas shift reaction,[2] the carbonylation of alcohols,[3] the reductive carbonylation of nitroarenes,[4] the carbonylation of aryl halides,[5] and the carbalkoxylation of vinyl electrophiles.[6]

Alkoxycarbonyls are an important group of activated carbon monoxide species. Several studies have been carried out with compounds of this type in order to prepare and characterize them as stable adducts and to design basic modes of their reactivity.[1a,7] Although several alkoxycarbonyls, in particular those of the group 10 metals, have been prepared by carbonyl insertion into the M–O bond of alkoxy compounds,[6a,7a,8,9] the formation of alkoxycarbonyl complexes has usually been accomplished by nucleophilic attack of coordinated carbon monoxide by alkoxide anions.[7b,c]

However, the synthesis of alkoxycarbonyls by the reaction of metal carbonyl compounds with alcohols is unusual. It is limited to strongly activated cationic metal carbonyls[10] and, frequently, it requires the presence of a base to shift the reactions toward the products.[3a,11]

Following our research into the synthesis and reactivity of binuclear systems with M(μ-pyrazolato)₂M′ (M = Rh(III), Ir(III), Ru(II); M′ = Rh(I), Ir(I)) cores,[12,13] we are now reporting the preparation of RuRh alkoxycarbonyl complexes by the reaction of alcohols with the dicarbonyl complex[13] [(η⁶-*p*-cymene)RuCl(μ-pz)₂Rh(CO)₂] (1) in the presence of halogens.

The reaction of [(η⁶-*p*-cymene)RuCl(μ-pz)₂Rh(CO)₂] (1) with iodine in MeOH, EtOH, *n*-PrOH, or *i*-PrOH, in the presence of an excess of NaI or NaBPh₄, led to the precipitation of the alkoxycarbonyl complexes [(η⁶-*p*-cymene)Ru(μ-I)₂(μ-pz)Rh(COOR)I(CO)] (R = Me (2), Et (3), *n*-Pr (4), *i*-Pr (5), respectively) in a chemical yield of 51–58% (reaction 1). Complex 2 can also be prepared, in poor yield, by reacting 1 with iodine in MeOH in the absence of sodium salts.

It is noteworthy that complex 1 is indefinitely stable in alcohols and that, on addition of iodine to a solution of complex 1 in dichloromethane, IR solution measurements showed a shift of the ν(CO) bands to higher frequencies, indicating an oxidation of the metal from Rh^I to Rh^III.

Complexes 2–5 were obtained as dark red, air-stable powders, and their formulations were ascertained by analytical and spectroscopic means. Thus, the presence of carbonyl and alkoxycarbonyl groups was inferred from

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Table I. ^{1}H and Relevant ^{13}C NMR Data for the Reported Complexes

complex	^{1}H NMR/$\delta^{a,b}$	^{13}C{^{1}H} NMR/δ^a
[(η^6-p-cymene)Ru(μ-I)$_2$-(μ-pz)Rh(COOMe)I(CO)] (2)	8.34 (d, 1H), 7.91 (d, 1H), 6.18 (t, 1H, $^3J_{HH}$ = 2.2), 5.60, 5.52 (2H, J_{AB} = 6.0), 5.43, 5.35 (2H, J_{AB} = 6.3), 3.73 (s, 3H), 2.96 (sp, 1H), 2.41 (s, 3H), 1.27 (d, 3H, $^3J_{HH}$ = 6.9), 1.28 (d, 3H, $^3J_{HH}$ = 6.9)	181.8 (d, J_{RhC} = 59.0), 173.2 (d, J_{RhC} = 31.3)
[(η^6-p-cymene)Ru(μ-I)$_2$-(μ-pz)Rh(COOEt)I(CO)] (3)	8.33 (d, 1H), 7.91 (d, 1H), 6.17 (t, 1H, $^3J_{HH}$ = 2.2), 5.59, 5.50 (2H, J_{AB} = 5.9), 5.41, 5.34 (2H, J_{AB} = 6.2), 4.22 (q, 2H, $^3J_{HH}$ = 7.1), 2.95 (sp, 1H), 2.40 (s, 3H), 1.27 (d, 3H, $^3J_{HH}$ = 6.8), 1.27 (t, 3H), 1.28 (d, 3H), $^3J_{HH}$ = 6.7)	182.0 (d, J_{RhC} = 56.0), 172.4 (d, J_{RhC} = 31.2)
[(η^6-p-cymene)Ru(μ-I)$_2$-(μ-pz)Rh(COO-n-Pr)I(CO)] (4)	8.33 (d, 1H), 7.91 (d, 1H), 6.17 (t, 1H, $^3J_{HH}$ = 2.2), 5.59, 5.51 (2H, J_{AB} = 5.8), 5.40, 5.33 (2H, J_{AB} = 5.4), 4.14 (t, 2H, J = 6.4), 2.95 (sp, 1H), 1.59 (m, 2H), 2.39 (s, 3H), 1.26 (d, 3H, $^3J_{HH}$ = 6.8), 1.27 (d, 3H, $^3J_{HH}$ = 6.9), 0.92 (t, 3H, $^3J_{HH}$ = 7.4)	181.9 (d, J_{RhC} = 55.9), 172.3 (d, J_{RhC} = 30.9)
[(η^6-p-cymene)Ru(μ-I)$_2$-(μ-pz)Rh(COO-i-Pr)I(CO)] (5)	8.33 (d, 1H), 7.90 (d, 1H), 6.16 (t, 1H, $^3J_{HH}$ = 2.2), 5.58, 5.50 (2H, J_{AB} = 5.8), 5.40, 5.33 (2H, J_{AB} = 6.0), 3.73 (s, 3H), 2.95 (sp, 1H), 2.39 (s, 3H), 1.27 (d, 6H, $^3J_{HH}$ = 7.1), 1.24 (d, 3H, $^3J_{HH}$ = 6.3), 1.19 (d, 3H, $^3J_{HH}$ = 6.8), 1.10 (m, 1H)	182.1 (d, J_{RhC} = 55.9), 171.6 (d, J_{RhC} = 30.7)
[(η^6-p-cymene)Ru(μ-Br)$_2$-(μ-Brpz)Rh(Br)(COOMe)(CO)] (6)	8.10 (s, 1H), 8.02 (s, 1H), 5.64, 5.58 (2H, J_{AB} = 5.9), 5.47, 5.42 (2H, J_{AB} = 6.3), 3.81 (s, 3H), 2.86 (sp, 1H), 2.41 (s, 3H), 1.28^c (d, 6H, $^3J_{HH}$ = 7.0)	

^{a} Measured in CDCl$_3$ at room temperature: chemical shifts relative to SiMe$_4$ as external standard, with J in Hz. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet. ^{b} Two AB systems and two doublets are observed for the aromatic and isopropyl methyl protons, respectively, of the p-cymene in each case. ^{c} Only one doublet is observed for the two isopropyl methyls of this complex.
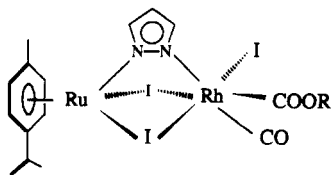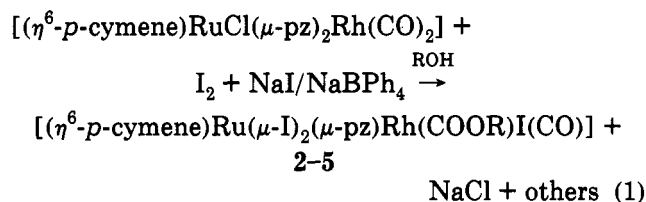

Figure 1. Proposed structure for complexes 2–5.

$$[(\eta^6\text{-}p\text{-cymene})RuCl(\mu\text{-pz})_2Rh(CO)_2] +$$
$$\overset{ROH}{I_2 + NaI/NaBPh_4 \rightarrow}$$
$$[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-I})_2(\mu\text{-pz})Rh(COOR)I(CO)] +$$
$$2\text{--}5$$
$$NaCl + \text{others} \quad (1)$$

R = Me (2), Et (3), n-Pr (4), i-Pr (5)

their IR spectra. They showed one terminal ν(C≡O) band at ca. 2090 cm^{-1} and two strong absorptions in the 1700–1705- and 1050–1065-cm^{-1} regions, which were assigned respectively to ν(C=O) and ν(C—O) vibrations of an alkoxycarbonyl group. The ν(C=O) frequencies come into the upper range of those observed for alkoxycarbonyl complexes (1580–1703 cm^{-1})^{7b,c} and are indicative of low dπ–pπ back-bonding from rhodium, consistent with oxidation of this atom during the reaction.^{10b}

The ^{1}H NMR spectra of complexes 2–5 showed the presence of only one pyrazolato group per p-cymene ligand. Furthermore, two AB systems and two doublets were assigned to the aromatic and isopropyl methyl protons of the p-cymene ligand, respectively, which indicate that the ruthenium is a chiral center.^{14} The appropriate resonances of the R substituent of the coordinated alkoxycarbonyl group were also observed in each case (Table I).

Besides the resonances of the pyrazolato, R, and p-cymene groups, the ^{13}C{^{1}H} NMR spectra of 2–5 showed two doublets (due to ^{103}Rh–^{13}C coupling) at ca. 182 and 172 ppm, which correspond to the carbonyl carbon nucleus of the CO and COOR ligands, respectively.

All attempts to obtain suitable crystals of these complexes for diffractometric purposes have been unsuccessful. However, we have recently determined the molecular

structure of the related IrRh alkoxycarbonyl species [(η^5-C$_5$Me$_5$)Ir(μ-I)$_2$(μ-pz)Rh(COOMe)I(CO)] by diffractometric methods.^{15} Interestingly, its spectroscopic data are comparable to those of complexes 2–5 and, therefore, these complexes probably adopt similar structures. Consequently, although several binuclear geometries are in accord with the analytical and spectroscopic data, we propose the structure schematically shown in Figure 1 (found for the IrRh alkoxycarbonyl^{15}) for the new complexes. The metals are bridged by two iodides and one pyrazolato ligand. The terminal ligands iodide, carbonyl, and alkoxycarbonyl are linked to the rhodium atom, the carbonyl group being *trans* to the pyrazolato bridging ligand.

Reaction 1 was performed using other oxidants such as chlorine and bromine as well as methyl iodide, with the following results. The addition of chlorine or methyl iodide to solutions of complex 1 in MeOH, EtOH, or i-PrOH, in the presence of NaBPh$_4$, afforded complex mixtures of products which we have not been able to separate or characterize. However, the addition of bromine in carbon tetrachloride to a solution of 1 in methanol gave a single compound (6) whose IR spectrum is analogous to those recorded for compounds 2–5. Analytical data and the observation by ^{1}H NMR of only two singlets, at 8.02 and 8.10 ppm, for the protons of the pyrazolato ligand, indicate that bromination of the 4-position of the pyrazolato ring has taken place.^{16} Consequently, complex 6 has been formulated as [(η^6-p-cymene)Ru(μ-Br)$_2$(μ-Brpz)Rh(Br)-(COOMe)(CO)] (Brpz = 4-bromopyrazolato) and, given the similarity of spectroscopic data, we propose a structure comparable to those of complexes 2–5.

We have also attempted the preparation of alkoxycarbonyl complexes of RuIr by treating the dicarbonyl complex [(η^6-p-cymene)RuCl(μ-pz)$_2$Ir(CO)$_2$] (7) with iodine and NaBPh$_4$ in MeOH, EtOH, i-PrOH, or n-PrOH. In all cases the reaction led to the precipitation of red-brown solids, which are mixtures of several products. In most cases the major component, according to ^{1}H NMR

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measurements, was the decomposition product $[\{(\eta^6\text{-}p\text{-}cymene)RuI\}_2(\mu\text{-}I)_2]$.[17]

In summary, the addition of iodine or bromine to solutions of $[(\eta^6\text{-}p\text{-}cymene)RuCl(\mu\text{-}pz)_2Rh(CO)_2]$ in different alcohols increases the electrophilicity of the carbon atom of the coordinated carbon monoxide due to the oxidation of the rhodium center. Thus, one of the carbon monoxide carbons can be selectively attacked by the alcohol used as solvent, affording alkoxycarbonyl complexes. However, the whole process is more complex since, according to the stoichiometry of the final products, the mechanism also includes the substitution of the chloride atom, favored by the presence of sodium salts, and the displacement of one of the two bridging pyrazolato groups by an iodide ligand. On the other hand, the reaction is not a general one. Thus, the related iridium complex $[(\eta^6\text{-}p\text{-}cymene)RuCl(\mu\text{-}pz)_2Ir(CO)_2]$, under the same conditions, gives a complex mixture of reaction and/or decomposition products. Additionally, the use of chlorine or methyl iodide as oxidants, instead of iodine, affords intractable mixtures of reaction products and, finally, bromine produces not only the oxidation of the rhodium atom in 1 but also the substitution of the proton of the 4-position of the remaining pyrazolato group.

Experimental Section

General Comments. $[(\eta^6\text{-}p\text{-}cymene)RuCl(\mu\text{-}pz)_2Rh(CO)_2]$ was prepared as previously reported.[13] IR spectra were recorded on a Perkin-Elmer 783 spectrophotometer, using Nujol mulls between polyethylene sheets, or dichloromethane solutions between NaCl plates. NMR spectra (external standard SiMe₄) were measured at room temperature on a Varian XL 200 spectrometer (50.3 (^{13}C) and 200.0 (^{1}H) MHz). Elemental analyses were carried out with a Perkin-Elmer 240C microanalyzer.

Synthesis of $[(\eta^6\text{-}p\text{-}cymene)Ru(\mu\text{-}I)_2(\mu\text{-}pz)Rh(COOR)I(CO)]$ (R = Me (2), Et (3), n-Pr (4), i-Pr (5)). A solution of $[(\eta^6\text{-}p\text{-}cymene)RuCl(\mu\text{-}pz)_2Rh(CO)_2]$ (1; 0.125 g, 0.22 mmol) in

ROH (25 mL) was allowed to react at room temperature with the NaA salt (A = I, BPh₄; 0.33 mmol) and I_2 (0.44 mmol) for 24 h. During this time a dark red solid precipitated, which was removed by filtration, washed with ROH, and dried under vacuum. All complexes were recrystallized from dichloromethane–hexane. **2:** yield 56%. Anal. Calcd for $C_{16}H_{20}N_2I_3O_3RhRu$: C, 22.01; H, 2.31; N, 3.21. Found: C, 22.63; H, 2.44; N, 3.48. ^{13}C NMR (CDCl₃, δ): 181.8 (d, J_{RhC} = 59.0 Hz, CO); 173.2 (d, J_{RhC} = 31.3, COOR); 145.2, 143.1, 106.3 (pz); 105.8, 98.8, 82.0, 81.6, 81.4, 32.0, 22.7, 22.6, 18.4 (p-cymene); 56.0 (COOMe). IR (cm⁻¹): 2090 (s), 1700 (s), 1065 (m). **3:** yield 51%. Anal. Calcd for $C_{17}H_{22}N_2I_3O_3$-RhRu: C, 23.02; H, 2.50; N, 3.16. Found: C, 23.18; H, 2.56; N, 3.43. ^{13}C NMR (CDCl₃, δ): 182.0 (d, J_{RhC} = 56.0 Hz, CO); 172.4 (d, J_{RhC} = 31.2, COOR); 145.1, 143.1, 106.3 (pz); 105.8, 98.8, 82.0, 81.7, 81.4, 32.0, 22.8, 22.6, 18.4 (p-cymene); 65.1, 14.7 (COOEt). IR (cm⁻¹): 2090 (s), 1705 (s), 1050 (m). **4:** yield 58%. Anal. Calcd for $C_{18}H_{24}N_2I_3O_3RhRu$: C, 23.99; H, 2.68; N, 3.11. Found: C, 24.23; H, 2.48; N, 3.18. ^{13}C NMR (CDCl₃, δ): 181.9 (d, J_{RhC} = 55.9, CO); 172.3 (d, J_{RhC} = 30.9, COOR); 145.1, 143.1, 106.3 (pz); 105.8, 98.8, 82.0, 81.7, 81.6, 81.5, 32.0, 22.7, 22.6, 18.4 (p-cymene); 70.9, 22.5, 10.7 (COOn-Pr). IR (cm⁻¹): 2090 (s), 1705 (s), 1055 (m). **5:** yield 52%. Anal. Calcd for $C_{18}H_{24}O_3N_2I_3$-RhRu: C, 23.99; H, 2.68; N, 3.11. Found: C, 24.48; H, 2.75; N, 3.24. ^{13}C NMR (CDCl₃, δ): 182.1 (d, J_{RhC} = 55.9, CO); 171.6 (d, J_{RhC} = 30.7, COOR); 145.0, 143.1, 106.2 (pz); 105.7, 98.8, 82.0, 81.8, 81.7, 81.4, 32.0, 22.8, 22.6, 18.4 (p-cymene); 72.9, 22.25, 22.2 (COOi-Pr). IR (cm⁻¹): 2090 (s), 1700 (s), 1055 (m).

Complex 2 was prepared as above, but in the absence of sodium salts, in 15% yield.

Synthesis of $[(\eta^6\text{-}p\text{-}cymene)Ru(\mu\text{-}Br)_2(\mu\text{-}Brpz)Rh(Br)(COOMe)(CO)]$ (6). To a solution of 0.150 g (0.27 mmol) of $[(\eta^6\text{-}p\text{-}cymene)RuCl(\mu\text{-}pz)_2Rh(CO)_2]$ (1) and 0.135 g (0.39 mmol) of NaBPh₄ in methanol (25 mL) was added 2.10 mL (0.64 mmol) of a 0.31 M solution of Br_2 in CCl₄. The mixture was stirred at room temperature for 2 days, and during this time an orange solid precipitated which was filtered off, washed with methanol, and dried under vacuum. The solid was recrystallized from dichloromethane–hexane; yield 28%. Anal. Calcd for $C_{16}H_{19}N_2Br_4O_3RhRu$: C, 23.70; H, 2.36; N, 3.45. Found: C, 24.25; H, 2.39; N, 3.46. IR (cm⁻¹): 2110 (s), 1710 (s), 1065 (m).

(17) An authentic sample of $[\{(\eta^6\text{-}p\text{-}cymene)RuI\}_2(\mu\text{-}I)_2]$ was prepared by treating the chloride $[\{(\eta^6\text{-}p\text{-}cymene)RuCl\}_2(\mu\text{-}Cl)_2]$ with excess NaI in MeOH over 24 h. Anal. Calcd for $C_{20}H_{28}I_4Ru_2$: C, 24.56; H, 2.85. Found: C, 24.82; H, 2.92. ^{1}H NMR (CDCl₃, 300.0 MHz, 25 °C, δ): 5.53, 5.43 (AB system, 4H, phenyl ring protons, J_{AB} = 6.0 Hz); 3.01 (sp, 1H, i-Pr CH); 2.35 (s, 3H, CH₃); 1.24 (d, 6H, i-Pr CH₃, J_{HH} = 6.8 Hz).