4122 *Organometallics* **1996,** *15,* 4122−4124

New Water-Soluble Ruthenium(II) and Osmium(II) Hydroxo Carbonyl Complexes

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Received April 1, 1996[⊗]

Summary: A high-yield procedure is described for the preparation, from $[M(CO)_3Cl_2]_2$ (M = Ru, Os) and aqueous NaOH, of the new water-soluble and air-stable species $[Ru(CO)_2Cl(OH)]_n$, $[Ru(CO)_2(OH)_2]_n$, $[Os(CO)_3Cl(OH)]_2$, and $[Os(CO)_3(OH)_2]_x$ (x = 2 or n).

Although organotransition-metal hydroxides have been known for a long time, the synthesis and reactivity of late-metal complexes bearing hydroxo ligands have been left relatively unexplored for many years.[1]

Whereas Cr, Mo, W, Mn, and Re hydroxo carbonyl complexes are well-known,[2,3] there has been no report on coordination compounds of group VIII metals with carbonyl and hydroxo ligands *only*. Thus, $[Rh(1,5\text{-}COD)(OH)]_2$,[4a] $[Rh(PPh_3)_2(OH)]_2$,[4b] and $[Rh(CO)(PPh_3)_2(OH)]$[4c] are known but the related $[Rh(CO)_2(OH)]_2$ is not stable enough, in contrast to $[Rh(CO)_2(OR)]_2$ (R = Me,[5a] Ph,[5a] $SiPh_3$[5b]). Similarly, whereas hydroxo complexes of ruthenium(II) and osmium(II) with phosphines,[6,7] cyclopentadiene,[8] or arenes[6,9] as ligands are known, no simple hydroxoruthenium(II) or -osmium(II) carbonyl complexes have been reported, with the exception of some hydroxoruthenium and -osmium carbonyl clusters.[2,6,10] The only related Os(II) compounds are the oxocarbonyl species $[Os_4O_4(CO)_{12}]$ and $[Os_6O_6(CO)_{16}]$, obtained as byproducts of the carbonylation of OsO_4 to $[Os_3(CO)_{12}]$.[11] In addition, the species $[Ru(NH_3)_x(OH)_y(CO)_z]^{n+}$ ($n < 3$) entrapped in zeolite supercages was supposed to be the active catalyst for the water-gas shift reaction, but it has no homogeneous equivalent.[12]

In this communication, we describe a report on the synthesis and characterization of new water-soluble and air-stable chlorohydroxo and dihydroxo Ru(II) and Os(II) carbonyl complexes obtained by reaction of $[M(CO)_3Cl_2]_2$ (M = Ru, Os) with aqueous NaOH.

$[Ru(CO)_2Cl(OH)]_n$ and $[Ru(CO)_2(OH)_2]_n$. Treatment of β-$[Ru(CO)_3Cl_2]_2$[13,14] in dichloromethane with aqueous NaOH (molar ratio NaOH:Ru = 1:1) for 40 min at room temperature, followed by workup,[15] resulted in the clean formation of a new brown ruthenium species, which was characterized by elemental analysis and infrared spectroscopy (Table 1) and by ^1H NMR spectroscopy.[15] The compound is highly soluble in water and has a low volatility.

In addition, we established a simple method to define the number of carbonyl ligands: addition of aqueous HCl to an ethanolic solution of β-$[Ru(CO)_3Cl_2]_2$ or *cis*-$[Ru(CO)_2Cl_2]_n$ cleanly affords *fac*-$[Ru(CO)_3Cl_3]^-$ [16] and $[Ru(CO)_2Cl_2(EtOH)_2]$ (isomer with CO groups in *cis* positions),[6,16,17] respectively (*cis*-$[Ru(CO)_2Cl_4]^{2-}$ is readily

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[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1996.

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[15] *Preparation of $[Ru(CO)_2Cl(OH)]_n$.* A dichloromethane solution (50 mL) of β-$[Ru(CO)_3Cl_2]_2$ (0.775 mmol) was *vigorously* stirred at room temperature with aqueous NaOH (5 mL; 1.557 mmol of NaOH); the hydrolysis was followed by IR, with monitoring of the decrease in intensity of the carbonyl bands in the organic phase. When the conversion of β-$[Ru(CO)_3Cl_2]_2$ was complete (40 min), the yellow water solution was dried under vacuum, affording a brown residue. Treatment of this residue with acetone (50 mL), followed by filtration to remove NaCl, gave a yellow-brown solution which, after evaporation, afforded *cis*-$[Ru(CO)_2Cl(OH)]_n$ as a brown powder (308 mg; 95% yield). The same species was obtained by stirring a slurry of β-$[Ru(CO)_3Cl_2]_2$ and aqueous NaOH (50 mL; 1:1 NaOH:Ru molar ratio) until all the solid dissolved. In this latter case, 3 h 30 min was required for completion of the reaction. At room temperature, the ^1H NMR spectrum of *cis*-$[Ru(CO)_2Cl(OH)]_n$, $(CD_3)_2CO$, shows many resonances which can be attributed to hydroxide protons in the range δ 2.26−3.38 ppm (most intense signals at 2.26, 2.34, 2.41, 2.56 (br), and 3.38 ppm), suggesting a mixture of isomers; at −40 °C the signals are shifted to lower field (δ 2.41−4.20 ppm; most intense signals at 2.41, 2.45, 2.71 (br), and 4.20 ppm), as expected.[32] Addition of HCl to the sample, at room temperature, causes the disappearance of these signals, as expected for the reaction of hydroxo ligands to form $[Ru(CO)_2Cl_4]^{2-}$.

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Table 1. Yields[a] and Infrared and Analytical Data of New Ruthenium and Osmium Complexes

compd	yield (%)	ν_{CO} (cm^{-1})	ν_{OH} (cm^{-1}) (KBr)	ν_{MCl} (cm^{-1})[b] (polyethene)	elem anal. calcd	elem anal. found
$[Ru(CO)_2Cl(OH)]_n$	95	2068 (s), 1995 (s) (KBr)	3422 (br)	322 (m)	C, 11.5	C, 11.5
		2062 (s), 1991 (s) (ethanol)			H, 0.5	H, 0.5
		2050 (s), 1979 (s), 1944 (w) (acetone)			Cl, 16.9	Cl, 17.4
$[Ru(CO)_2(OH)_2]_n$	85	2041 (s), 1968 (s) (KBr)	3415 (br)	no abs	C, 12.5	C, 12.3
		2040 (s), 1964 (s) (ethanol)			H, 1.1	H, 1.3
$[Os(CO)_3Cl(OH)]_2$	90	2129 (m), 2031 (s), 1947 (m) (KBr)	3445 (br)	320 (w), 287 (m)	C, 11.0	Cl, 11.1
		2122 (m), 2117 (sh), 2029 (vs), 1961 (m) (ethanol)			H, 0.3	H, 0.4
		2121 (m), 2111 (sh), 2027 (vs), 1947 (m) (acetone)			Cl, 10.9	Cl, 10.9
$[Os(CO)_3(OH)_2]_x$ ($x = 2, n$)	81	2123 (m), 2024 (vs), 1933 (m) (KBr)	3416 (br)	no abs	C, 11.7	C, 11.9
		2115 (m), 2024 (vs), 1946 (s) (ethanol)			H, 0.6	H, 0.9
		2117 (m), 2021 (vs), 1938 (m) (acetone)				

[a] Yields are of pure materials. [b] M = Ru, Os.

converted to $[Ru(CO)_2Cl_2(EtOH)_2]$ in ethanol).[18] Addition of aqueous HCl to an ethanolic solution of our new brown ruthenium complex causes a shift of the carbonyl bands from 2062 (s) and 1991 (s) cm^{-1} to 2066 (s) and 1996 (s) cm^{-1}, characteristic of $[Ru(CO)_2Cl_2(EtOH)_2]$ with *cis* CO groups. Evaporation of the solvent affords *cis*-$[Ru(CO)_2Cl_2]_n$.[19] These observations, elemental analysis, and the evidence of the presence of hydroxo ligands by infrared and ^{1}H NMR spectroscopy, together with the typical insolubility in nondonor solvents and the low volatility, would suggest a polymeric $[Ru(CO)_2Cl(OH)]_n$ structure with a chloride- and hydroxide-bridged chain. The carbonyl groups are probably in *cis* positions, by analogy with the known structures of the related polymeric halides $[Ru(CO)_2X_2]_n$[20] and alkyl sulfides $[Ru(CO)_2(S_2R_2)]_n$,[21] which show a similar infrared pattern in the carbonyl region. In agreement with the presence of bridging chlorine, the Ru−Cl absorption of the new complex is in the range of frequencies reported for the bridging chlorine ligands of *cis*-$[Ru(CO)_2Cl_2]_n$.[19]

The new complex dissolves only in donor solvents which cleave chloro and hydroxo bridges, affording soluble monomeric species such as $[Ru(CO)_2Cl(OH)L_2]$ (L = donor solvent) with *cis* CO groups, as suggested by the infrared spectrum (Table 1 and by analogy with the behavior of *cis*-$[Ru(CO)_2Cl_2]_n$ or β-$[Ru(CO)_3Cl_2]_2$.[13] The monomeric nature of the chlorohydroxoruthenium carbonyl species dissolved in water has been confirmed by molecular weight determination using both gel permeation chromatography and osmometry techniques.[22]

A related brown non-chlorinated complex of ruthenium(II) is obtained by following the same procedure,[15] but with a 2:1 NaOH:Ru molar ratio. With the biphasic system CH_2Cl_2/NaOH in H_2O, the reaction is already complete after 15 min.[23] The low solubility in nondonor solvents of this compound, its low volatility, and the presence of hydroxo and carbonyl infrared absorptions, together with the lack of a Ru−Cl infrared absorption band, elemental analysis (Table 1), and finally the reaction of an ethanolic solution with aqueous HCl, which selectively affords $[Ru(CO)_2Cl_2(EtOH)_2]$ with *cis* CO groups, would suggest also in this case a polymeric *cis*-$[Ru(CO)_2(OH)_2]_n$ structure, with bridging hydroxo ligands.

However, the species initially formed in water by reaction of aqueous NaOH with β-$[Ru(CO)_3Cl_2]_2$ (molar ratio NaOH:Ru = 2:1) has probably three carbonyl ligands per ruthenium, as suggested by the reaction with HCl of the water solution, obtained when the reaction is completed and diluted with ethanol, which affords mainly *fac*-$[Ru(CO)_3Cl_3]^-$ and only traces of $[Ru(CO)_2Cl_2(EtOH)_2]$ with *cis* CO groups. Therefore, the species initially formed in water is probably a water-soluble complex such as *mer*-$[Ru(CO)_3(OH)_2(H_2O)]$, as suggested also by the infrared carbonyl absorptions in ethanol at 2041 (s) and 1966 (s) cm^{-1}.[13,19] By evaporation of the solvent to dryness, this ruthenium species polymerizes, losing CO to give a solid residue consisting of a mixture of $[Ru(CO)_3(OH)_2]_n$ and $[Ru(CO)_2(OH)_2]_n$. Only further thermal treatment, for instance under vacuum for 4 h at 120 °C, gives pure $[Ru(CO)_2(OH)_2]_n$. As expected, the tendency to polymerize is much higher with hydroxide than with chloride ligands; for instance β-$[Ru(CO)_3Cl_2]_2$ must be heated at 200 °C under vacuum in order to generate the polymer *cis*-$[Ru(CO)_2Cl_2]_n$.[13]

By analogy with the infrared spectrum in the carbonyl region of polymeric species such as *cis*-$[Ru(CO)_2X_2]_n$[20] and *cis*-$[Ru(CO)_2(S_2R_2)]_n$,[21] $[Ru(CO)_2(OH)_2]_n$ also has presumably a hydroxide-bridged chain structure with *cis* carbonyl groups. The degree of polymerization increases on standing in the solid state, as shown by the decrease with time of solubility in donor solvents. In water the hydroxo bridges are cleaved, affording monomeric $[Ru(CO)_2(OH)_2(H_2O)_2]$ species, as shown by both gel permeation chromatography and osmometry.[22]

Unfortunately, we are unable at the moment to obtain for both of the new compounds suitable crystalline samples for X-ray investigations.

$[Os(CO)_3Cl(OH)]_2$ and $[Os(CO)_3(OH)_2]_x$ (x = 2 or n). By the procedure described for the ruthenium dimer analogue, α-$[Os(CO)_3Cl_2]_2$[14,24] dissolved in dichloromethane is hydrolyzed at room temperature by aqueous

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[22] The molecular weights in water of the hydroxoruthenium and -osmium carbonyl species prepared in this work were determined (i) with a vapor pressure osmometer, Perkin-Elmer Model 115, and (ii) with a gel permeation chromatography (GPC) Waters Modular System consisting of a Model 600E pump, Model 717 autoinjector, Model 996 diode array, Model 410 differential refractive index, and Model 120 column ultrahydrogen. Both techniques were in agreement with the presence of only monomeric species in water solution ($[Ru(CO)_2(OH)Cl(H_2O)_2]$, $[Ru(CO)_2(OH)_2(H_2O)_2]$, $[Os(CO)_3(OH)Cl(H_2O)]$, and $[Os(CO)_3(OH)_2(H_2O)]$).

[23] In the absence of CH_2Cl_2, the reaction is slower, 3 h being required for conversion. Because the dihydroxoruthenium carbonyl complex is much less soluble in acetone than $[Ru(CO)_2Cl(OH)]_n$, it was purified by column chromatography (Sephadex G10) using water as eluent; the ruthenium complex being less retained by Sephadex than NaCl, it was eluted first.

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NaOH (molar ratio NaOH:Os = 1:1 or 1:2).[25] In this latter case, the alkaline hydrolysis is slower than with the Ru complex, 5 and 3 h being necessary to hydrolyze one and two Os−Cl bonds, respectively.

The new complexes were characterized by elemental analysis and by infrared spectroscopy (Table 1), by ^{1}H NMR spectroscopy, which gives further evidence for OH ligands,[25] and by their reaction with aqueous HCl, which affords *fac*-$[Os(CO)_3Cl_3]^-$ [19] in both cases, as occurs with α-$[Os(CO)_3Cl_2]_2$. As expected for a dimer,[21c,26] the white chlorinated complex is very soluble in donor solvents such as acetone, ethanol, and water, even after a long time under vacuum, whereas the beige non-chlorinated derivative has a lower solubility, being only slightly soluble in weak donor solvents such as acetone although rather soluble in ethanol and in water.

The dimeric structure $[Os(CO)_3Cl(OH)]_2$ was confirmed by a peak at *m*/*e* 652 in the mass spectrum. In this spectrum, there was also the molecular ion peak of $[Os(CO)_3O]_4$ at *m*/*e* 1160, associated with its known fragmentation pattern.[11] No higher polynuclear species such as $[Os_6O_6(CO)_{16}]$[11] was detected. Freshly prepared $[Os(CO)_3Cl(OH)]_2$ was not contaminated with $[Os(CO)_3O]_4$, as shown by elemental analysis and by infrared spectroscopy, the spectrum of $[Os(CO)_3O]_4$ in the carbonyl region[11] being very different from that of $[Os(CO)_3Cl(OH)]_2$ (see Table 1). In addition, we could not separate any $[Os(CO)_3O]_4$ by treatment with $CHCl_3$; this latter compound is soluble, while $[Os(CO)_3Cl(OH)]_2$ is totally insoluble. Therefore, it appears that some $[Os(CO)_3Cl(OH)]_2$ condenses to $[Os(CO)_3O]_4$, with elimination of HCl, under the conditions used to measure the mass spectrum (high vacuum and temperature of about 200 °C). The beige dihydroxoosmium carbonyl complex condenses even more easily to $[Os(CO)_3O]_4$, with elimination of water, since only this species could be observed by mass spectroscopy, no molecular ion peak corresponding to $[Os(CO)_3(OH)_2]_2$ being detected. Also in this case, the compound was not originally contaminated by $[Os(CO)_3O]_4$ on the basis of both infrared spectra and lack of extraction with $CHCl_3$. As a matter of fact, mass spectra confirm the presence of three carbonyl ligands per osmium atom in both complexes.

We cannot at the moment clearly distinguish, on the basis of only infrared spectra, a dimeric structure with chloride or hydroxide bridges for $[Os(CO)_3Cl(OH)]_2$, because we cannot definitely assign the Os−Cl stretching frequencies (Table 1) to bridging chloride ligands. Besides, the dimeric or polymeric nature of the dihydroxoosmium species cannot be well established. The similarity of its infrared carbonyl absorption bands with those of $[Os(CO)_3Cl(OH)]_2$ (Table 1) and the easy formation of $[Os(CO)_3O]_4$ by thermal treatment would suggest, at least initially, a dimeric structure with hydroxide bridges. However, the relatively low solubility even in donor solvents, which decreases with time, would suggest a progressive polymerization. In water, $[Os(CO)_3Cl(OH)]_2$ and $[Os(CO)_3(OH)_2]_x$ ($x = 2$ or n) are converted to monomeric $[Os(CO)_3Cl(OH)(H_2O)]$ and $[Os(CO)_3(OH)_2(H_2O)]$, respectively, as shown by gel permeation chromatography and by osmometry.[22]

The low tendency of chlorohydroxo- and dihydroxoosmium(II) carbonyl complexes to lose CO, in comparison to their ruthenium analogues, is expected, since the conversion of $[Os(CO)_3I_2]_2$ to $[Os(CO)_2I_2]_n$ requires more drastic conditions[26] than the conversion of $[Ru(CO)_3I_2]_2$ to $[Ru(CO)_2I_2]_n$.[13] It is worth pointing out the great tendency of both osmium complexes, as opposed to the related ruthenium complexes, to lose thermally either HCl or H_2O, with retention of three carbonyl ligands, affording μ-oxo bridges.

Preliminary experiments show that an excess of base (for example, a 3:1 NaOH:M molar ratio) leads to water-soluble species, probably anions of the type $[Os(CO)_3(OH)_3]^-$ and $[Ru(CO)_x(OH)_3(H_2O)_{3-x}]^-$ ($x = 2$, 3), as suggested by their rather low carbonyl stretching frequencies in KBr (Os, 2022 (sh), 2005 (s), 1935 (sh), 1905 (s) cm^{-1}; Ru, 2028 (s), 1935 (s) cm^{-1}) and by the reaction of their solutions with aqueous HCl, which affords *fac*-$[Os(CO)_3Cl_3]^-$ and a mixture of *fac*-$[Ru(CO)_3Cl_3]^-$ and $[Ru(CO)_2Cl_2(EtOH)_2]$, respectively. The stability of the carbonyl ligands in these Os(II) compounds toward nucleophilic attack of OH^- is quite unexpected.[27]

Conclusion. The new hydroxoruthenium and -osmium carbonyl complexes described here are a new class of stable, water-soluble carbonyl compounds. We have preliminary evidence[28] that they could be the active species involved in the high-yield silica-mediated synthesis of various osmium[29] and ruthenium[30] carbonyl clusters starting from $[M(CO)_3Cl_2]_2$ (M = Ru, Os) in the presence of alkali-metal carbonates. In addition, they could find application as homogeneous catalysts, by analogy with other Ru(II) and Os(II) complexes, in particular for the water-gas shift reaction[1,12,27] and for the hydration of unsaturated organic compounds.[1,31]

Acknowledgment. We are grateful to the Consiglio Nazionale delle Ricerche and to the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Rome) for support in this research. We deeply thank Dr. R. Mendichi and A. Giacometti Schieroni (Istituto di Chimica delle Macromolecole, CNR) for gel permeation chromatography measurements and molecular weight determinations.

OM960248Q

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(25) The chlorohydroxo- and the dihydroxoosmium(II) carbonyl complexes were prepared like their ruthenium analogues but with 5-fold quantities of CH_2Cl_2 and H_2O, due to the lower solubility of α-$[Os(CO)_3Cl_2]_2$ compared to β-$[Ru(CO)_3Cl_2]_2$. In addition, $[Os(CO)_3(OH)_2]_x$ was purified by column chromatography (Sephadex LH 20) using acetone/water (25/1) as eluent; the osmium complex being less retained by Sephadex than NaCl, it was eluted first. At room temperature, the ^{1}H NMR spectrum of $[Os(CO)_3Cl(OH)]_2$, in $(CD_3)_2CO$, shows many distinct resonances of various intensities for the hydroxide protons in the range δ 3.62−3.97 ppm (the most intense signals are at 3.62, 3.74, 3.80, and 3.95 ppm), suggesting a mixture of monomeric and/or dimeric species, as expected for a weak donor solvent such as acetone. A gradual decrease of the temperature leads to a shift of the resonances to lower field, as expected[32] ($T = -80$ °C, δ 4.06−4.83 ppm, most intense signals at 4.06, 4.38, 4.46, 4.65, and 4.83 ppm). As in the case of ruthenium,[15] addition of HCl to the sample causes the disappearance of the hydroxide protons in the ^{1}H NMR spectrum. $[Os(CO)_3(OH)_2]_x$ was insufficiently soluble in $(CD_3)_2CO$ for ^{1}H NMR measurements.

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