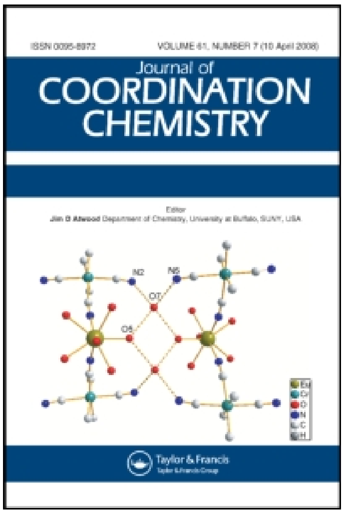

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# Chromium, Molybdenum and Ruthenium Complexes of 2-Hydroxyacetophenone Schiff Bases

S. A. Ali[a]; A. A. Soliman[b]; M. M. Aboaly[c]; R. M. Ramadan[c]
[a] Chemistry Department, University College for Girls, Ain Shams University, Cairo, Egypt [b] Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt [c] Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt

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# CHROMIUM, MOLYBDENUM AND RUTHENIUM COMPLEXES OF 2-HYDROXYACETOPHENONE SCHIFF BASES

S.A. ALI[a], A.A. SOLIMAN[b], M.M. ABOALY[c] and R.M. RAMADAN[c,]*

[a]*Chemistry Department, University College for Girls, Ain Shams University, Cairo, Egypt;*
[b]*Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt;*
[c]*Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt*

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Interaction of the Schiff base 2-hydroxyacetophenonepropylimine (happramH) with $M(CO)_6$, M = Cr or Mo under reduced pressure gave the dicarbonyl complex $M(CO)_2(happramH)_2$. The complex $MoO(appram)_2$ was isolated from the reaction of $Mo(CO)_6$ and happramH in air. $Ru_3(CO)_{12}$ and $RuCl_3$ reacted with the Schiff base bis-(2-hydroxyacetophenone)ethylenediimine ($hapenH_2$) to give $Ru(CO)_2(hapenH_2)$ and $[RuCl_2(hapenH2)]Cl$. Elemental, spectroscopic and magnetic studies of the reported complexes revealed the proposed structures. The thermal properties of the complexes were investigated by thermogravimetric techniques. Cyclic voltammetry of the complexes showed tautomeric redox processes due to ligand-based reduction and metal-based oxidation.

*Keywords:* Schiff base; Chromium; Ruthenium; IR spectra; Thermal decomposition

## INTRODUCTION

In the use of transition metal carbonyls as reactive species in homogeneous catalytic reactions such as hydrogenation, hydroformylation and carbonylation, carbon monoxide serves simply as a ligand providing the complex with the necessary reactivity and/or stability to allow reaction [1]. On the other hand, the presence of ligands having donor atom sets like $N_2O_2$ and $N_4$ have been found to be useful catalysts especially for epoxidation reactions [2]. One of the most interesting ligands is bis-(salicyladehyde)-ethylenediimine, salen [3–5]. In a preceding paper, we have described reactions of chromium and molybdenum hexcarbonyls with the Schiff base bis-(2-hydroxyacetophenone)ethylenediimine, $hapenH_2$ [6]. This ligand is of interest because of its similarity to salen. However, the presence of two methyl groups attached near the donor nitrogen atoms makes the ligand more basic. The oxo derivatives

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*Corresponding author.

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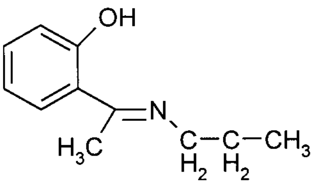
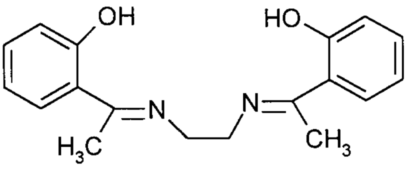
M(O)(hapen), M = Cr and Mo, with a metal atom in + 4 oxidation state were isolated from reactions of $M(CO)_6$ with $hapenH_2$ in air. On the other hand, the dihydride molybdenum complex $MoH_2(CO)(hapen)$ separated from reactions under reduced pressures [6]. A mechanism of formation involved a dicarbonyl intermediate. To further examine the proposed mechanism, reactions of related Schiff base (the bidentate 2-hydroxyacetophenonepropylimine, happramH) were investigated. Also, the reactions of $hapenH_2$ (the quadridentate ligand) with the cluster compound $Ru_3(CO)_{12}$ and $RuCl_3$ were carried out.



**happramH**



**$hapenH_2$**

## EXPERIMENTAL

$Cr(CO)_6$, $MO(CO)_6$, $Ru_3(CO)_{12}$, and $RuCl_3$ were supplied from Aldrich. $RuCl_3$ was dried in an oven at 120°C for 30 min prior to use. (2-hydroxyacetophenone)propylimine (happramH) and bis-(2-hydroxyacetophenone)ethylenediimine ($hapenH_2$) were prepared as described [6,7]. All solvents were of analytical grade and were purified by distillation before use.

IR measurements (KBr discs) were carried out on a Unicam-Mattson 1000 FT-IR. $^1H$ NMR measurements were carried out on a Spectrospin-Bruker AC 200 MHz NMR Spectrometer. The samples were dissolved in deuterated DMSO using TMS as an internal reference. Magnetic susceptibilities of the complexes in the solid state (Gouy method) were recorded on a Sherwood magnetic susceptibility balance. Diamagnetic corrections were made by Pascal's constant and $Hg[Co(SCN)_4]$ was used as a calibrant. Conductivity measurements were made on an YSE conductance meter model 32. Samples of concentration *ca.* $1 \times 10^{-3}$–$1 \times 10^{-6}$ M in DMF were used for the measurements. Potentiometric measurements were carried out on a Horiba pH meter model F-22 with a chloride ion selective electrode (Orion) and a SCE as a reference. Cyclic voltammetrie measurements were performed using a three-electrode configuration cell connected to an EG and G scanning potentiostat model 372. A Pt disk was used as working electrode and a Pt wire as auxiliary electrode. The reference was a Ag–AgCl electrode adjusted to 0.00 V *vs.* SCE. Sample solutions (50 mL) of *ca.* $1 \times 10^{-3}$ M concentration in $CH_2Cl_2$ with 0.1 M $n$-$Bu_4NPF_6$ as supporting electrolyte were used for the measurements. A potential range of + 2000 to − 2000 mV, with a scan rate of 200 $mVs^{-1}$ was used. Thermogravimetric analysis (TG) was carried out under $N_2$ with a heating rate of 10°C/ min using a Shimadzu DT-50 thermal analyzer. Elemental analyses were carried out on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectra of the solid complexes (70 eV, EI) were performed on a Finnigan MAT SSQ 7000 spectrometer. Table I gives the elemental analysis and mass spectrometry data for the complexes.

TABLE I Elemental analysis and mass spectrometry data for the complexes

| *Complex* | *Found (Calcd.) (%)* | | | *Mass spectrometry* | |
|---|---|---|---|---|---|
| | *C* | *H* | *N* | *Mol. wt* | *m/z* |
| Cr(CO)$_2$(happramH)$_2$ | 62.2 (62.3) | 6.6 (6.5) | 5.9 (6.1) | 462.5 | 462 (P–H)$^+$ |
| Mo(CO)$_2$(happramH)$_2$ | 56.7 (56.9) | 6.1 (6.0) | 5.5 (5.5) | 506.5 | 507 (P)$^+$ |
| MoO(happram)$_2$ | 56.8 (56.9) | 6.2 (6.1) | 6.2 (6.0) | 464.4 | 465 (P)$^+$ |
| Ru(CO)$_2$(hapenH$_2$) | 52.8 (53.0) | 4.4 (4.5) | 6.3 (6.2) | 453.4 | 454 (P)$^+$ |
| [RUC1$_2$(hapenH$_2$)]Cl$^a$ | 42.7 (42.9) | 4.2 (4.0) | 5.6 (5.6) | 503.9 | 469 (P–CI)$^+$ |

$^a$% Cl for [RuC1$_2$(hapenH$_2$)]Cl: Found 21.2; Calcd 21.1.

### Synthesis of Cr(CO)$_2$(happramH)$_2$

A mixture of Cr(CO)$_6$ (0.07 g, 0.32 mmol) and happramH (0.11 g, 0.62 mmol) in about 30 mL THF was heated to reflux for *ca.* 9 h. The reaction mixture was then cooled and the solvent was evaporated on a vacuum line. The resulting yellowish green residue was washed several times with hot petroleum ether and recrystallized from hot THF. The yellowish green complex was dried *in vacuo* for a few hours to give a yield of 70%.

### Synthesis of MO(CO)$_2$(happramH)$_2$

A mixture of MO(CO)$_6$ (0.10 g, 0.38 mmol) and happramH (0.13 g, 0.73 mmol) in a sealed tube charged with about 30 mL THF was degassed and then heated to reflux for *ca.* 3 h. The color of the reaction mixture changed to brown. The reaction mixture was cooled and the solvent was removed on a vacuum line. The residue was washed several times with hot petroleum ether and recrystallized from hot benzene to give brown crystals. The complex was dried under vacuum for several hours (yield 66%).

### Synthesis of MoO(happram)$_2$

Similar procedure was used as for Cr(CO)$_2$(happramH)$_2$. Dark brown crystals with a yield of 89% were obtained.

### Synthesis of Ru(CO)$_2$(hapenH$_2$)

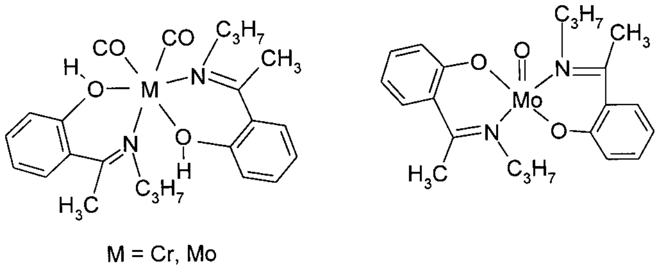
A mixture of Ru$_3$(CO)$_{12}$ (0.10 g, 0.16 mmol) and hapenH$_2$ (0.05 g, 0.16 mmol) in about 40 mL benzene, was heated to reflux under atmospheric pressure for 15 h. The reaction mixture was cooled and the solvent was evaporated under vacuum. The brown residue was washed with hot benzene followed by petroleum ether and then recrystallized from hot ethanol. The brown crystals were left to dry on a vacuum line for several hours (yield 73%; based on the ligand concentration). The complex was found to be air stable.

### Synthesis of [RuCl$_2$(hapenH$_2$)]Cl

The complex was prepared following a similar procedure to that used for synthesis of Ru(Co)$_2$(hapenH$_2$). Dark brown crystals with a yield of 85% were obtained.

## RESULTS AND DISCUSSION

Reactions of $Cr(CO)_6$ with 2-hydroxyacetophenonepropylimine (happramH) in THF either in the presence of air or under reduced pressure resulted in the formation of the dicarbonyl complex $Cr(CO)_2(happramH)_2$. The corresponding reactions of $MO(CO)_6$ were found to be dependent on the reaction conditions. When the reaction proceeded in the absence of oxygen under reduced pressure, the dicarbonyl complex $Mo(CO)_2(happramH)_2$ was isolated. On the other hand, an oxomolybdenum complex, $MoO(happram)_2$, separated from reactions in presence of air. The IR spectrum of happramH showed characteristic bands due to the functional groups OH, C=N and C–O. The IR spectrum of the chromium and molybdenum complexes displayed the ligand characteristic bands with appropriate shifts due to complex formation (Table II). In addition, the IR spectra of the two complexes $Cr(CO)_2(happramH)_2$ and $Mo(CO)_2(happramH)_2$ exhibited two bands in the terminal metal carbonyl range due to symmetric and asymmetric stretching frequencies of two CO groups [8]. The presence of two CO bands in the IR spectra suggested that they were bound to the metal in *cis* positions [8]. The IR spectrum of the oxo complex, $MoO(happram)_2$, showed that $\nu$(OH) of the ligand disappeared, Table II. The elimination of hydrogen from the OH group, which was also confirmed by the disappearance of the OH signal in the $^1$H NMR spectrum (Table III), indicated that ligand coordinated oxidatively to the metal [1,9]. The IR spectrum of the complex also showed a strong band at 967 cm$^{-1}$ due to the Mo=O bond [8]. Therefore, the diamagnetic oxo complex has a Mo(IV) with a low-spin $d^2$ configuration. Such diamagnetism might arise from further splitting of the $t_{2g}$ orbitals in the low symmetry complex, *i.e.*, $d_{xy}^2\ d_{xz}^0\ d_{yz}^0\ d_{x2-y2}^0\ d_{z2}^0$ [6,10]. Scheme 1 gives the proposed structure of the chromium and molybdenum complexes.



SCHEME 1

Heating a mixture of bis-(2-hydroxyacetophenone)ethylenediimine and $Ru_3(CO)_{12}$ in benzene resulted in the formation of a brown complex of molecular formula $Ru(CO)_2(hapenH_2)$. The IR spectrum of $hapenH_2$ displayed characteristic bands due to $\nu$(OH), $\delta$(OH), $\nu$(C=N), $\nu$(C–O) at 3450, 1449, 1615 and 1245 cm$^{-1}$, respectively [6]. The IR spectrum of the complex showed a $\nu$(OH) stretching frequency at 3250 cm$^{-1}$ (Table II). This band was shifted 200 cm$^{-1}$ and occurred in hydrogen bonding region [11]. The C–O stretching band of the C–OH group of ligand was also shifted to 1223 cm$^{-1}$ in the spectrum of $Ru(CO)_2(hapenH_2)$ complex. In addition, the $\delta$(OH) frequency was shifted to 1434 cm$^{-1}$. The shifts in $\nu$(OH), $\nu$(C–O) and $\delta$(OH) to lower frequencies indicates participation of the OH groups in bonding [12]. Furthermore, the presence of $\nu$(OH) bands in the spectrum showed that the two

TABLE II Important IR data for happramH, hapenH$_2$ and their complexes

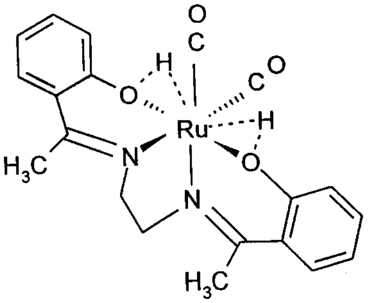
| *Compound* | *IR data* (cm$^{-1}$) | | | | |
|---|---|---|---|---|---|
| | $\nu(OH)$ | $\delta(OH)$ | $\nu(C{=}O)$ | $\nu(C\text{–}O)$ | $\nu(C{=}N)$ |
| HappramH | 3456 m | 1453 m | – | 1241 m | 1619 s |
| Cr(CO)$_2$(happramH)$_2$ | 3443 s | 1445 m | 1950 m<br>1862 m | 1237 m | 1607 s |
| Mo(CO)$_2$(happramH)$_2$ | 3432 s | 1457 m | 1974 m<br>1897 m | 1249 m | 1599 m |
| MoO(happram)$_2$$^a$ | – | – | – | 1249 m | 1586 m |
| hapenH$_2$ | 3450 s | 1449 m | – | 1245 m | 1615 m |
| Ru(CO)$_2$(hapenH$_2$) | 3250 s | 1434 m | 2043 s<br>1967 s | 1223 m | 1605 m |
| [RuCl$_2$(hapenH$_2$)]Cl | 3430 s | 1414 m | – | 1210 m | 1598 m |

$^a\nu$(Mo = O) = 967 s cm$^{-1}$.

TABLE III Important $^1$H NMR data for happramH and its complexes

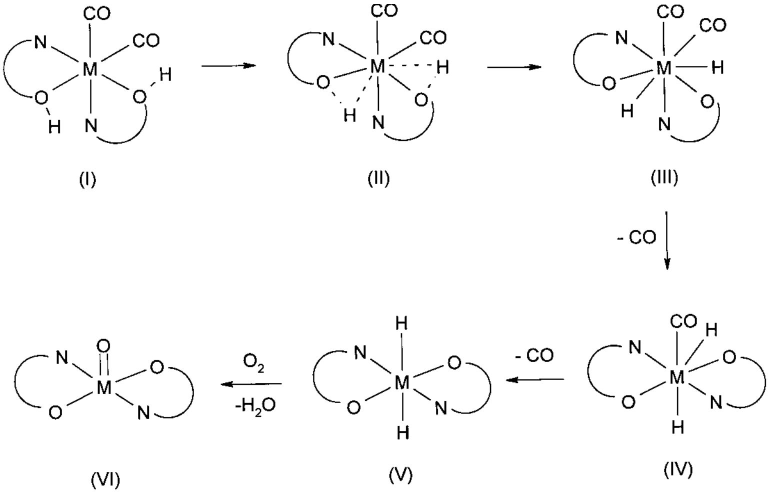
| *Compound* | *$^1$H NMR data* (p.p.m.) |
|---|---|
| HappramH | 10.30s (1H; OH), 7.3 m (4H; Ph), 4.13 t (J = 6 Hz, 2H; CH$_2$ 2.24 h (J = 6 Hz, 2H; CH$_2$), 1.38 s (3H; CH$_3$), 1.04 t (J = 6 Hz, 3H; CH$_3$) |
| Cr(CO)$_2$(happramH)$_2$ | 10.32 s (1H; OH), 7.4m (4H; Ph), 4.15 t (J = 6 Hz, 2H; CH$_2$), 2.28 h (J = 6 Hz, 2H; CH$_2$) 1.42 s (3H; CH$_3$), 1.07t (J = 6 Hz, 311; CH$_3$) |
| Mo(CO)$_2$(happramH)$_2$ | 10.28 s (1H; OH), 7.4 m (4H; Ph), 4.19 t (J = 7 Hz, 2H; CH$_2$), 2.22 h (J = 7 Hz, 2H; CH$_2$), 1.53 s (3H; CH$_3$), 1.18 t (J = 7 Hz, 3H; CH$_3$) |
| MoO(happram)$_2$ | 7.5 m (4H; Ph), 4.09 t ( J= 6 Hz, 2H; CH$_2$), 2.33 h (J = 6 Hz, 2H; CH$_2$), 1.40 s (3H; CH$_3$) 0.941 (J = 6 Hz, 3H; CH$_3$) |

OH groups coordinate to the ruthenium atom without proton displacement. The participation of the two azomethine nitrogen atoms was obviously indicated from the IR spectrum of the complex. In the far IR spectrum of the complex, the non-ligand bands observed at 530 cm$^{-1}$ due to Ru–O and 422 cm$^{-1}$ due to Ru–N bond gave conclusive evidence regarding the bonding of azomethine nitrogen and phenolic oxygen of the Schiff base to the metal ion [13,14]. The IR spectrum of Ru(CO)$_2$(hapenH$_2$) also displayed two strong bands in the metal carbonyl region at 2043 and 1967 cm$^{-1}$ due to symmetric and asymmetric stretching frequencies of the two CO groups [8]. This may indicate that the two CO groups were bound *cis* to each other in a distorted octahedral arrangement. The distortion of the octahedral arrangement may be explained based on the non-coplanar characteristics of the Schiff base molecule [13]. The lower frequency band at 1967 cm$^{-1}$ had two shoulders at 1937 and 1902 cm$^{-1}$, which may be due to coupled M–H bonds [8,9]. Attempts to synthesize the deuterated species were unsuccessful. However, no additional information could be abstracted from such an experiment because the expected $\nu$(Ru–D) bands might interfere with the other bands of the Schiff base in the range 1400–1550 cm$^{-1}$. A zerovalent ruthenium complex is expected to be five coordinate In fact, the isolated six-coordinate complex showed that it was paramagnetic and gave no $^1$H NMR spectra. Magnetic susceptibility measurement of the complex at 304 K showed a value of $1.75 \times 10^{-6}$ e.m.u.g$^{-1}$ with an effective magnetic moment $\mu_{\text{eff}}$ of 1.39 BM. The $\mu_{\text{eff}}$ value is smaller than the spin-only moment of an unpaired electron (1.73 BM). Thus, one can conclude that a probable change in oxidation state of the ruthenium atom from zero to +1 was achieved from partial hydrogen bonding to the ruthenium to give a low-spin $d^7$ electronic configuration, *i.e.*, $t_{2g}^6\ d_{z2}^1\ d_{x2-y2}^0$ [10]. This bonding can account for the large shift of the $\nu$(OH) in the IR spectrum of the complex. Accordingly, the complex may have the following structure (Scheme 2):



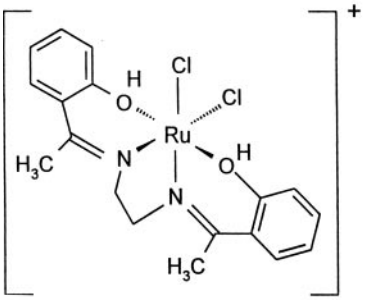
SCHEME 2

A proposed mechanism for formation of the oxo complexes M(O)(hapen), M = Cr or Mo, suggested formation through a six coordinate intermediate M(CO)$_2$(hapenH$_2$) [6]. We were not able to isolate such a complex which underwent loss of a CO group due to *trans* effect to give M(CO)(hapenH$_2$) [6]. In the case of Ru(CO)$_2$(hapenH$_2$), the presence of two CO groups in a *cis* position to each other as well as the occurrence of hydrogen bonding might cause stabilization of that complex. As can be seen from Scheme 3, this species could change to the dihydride intermediate III with one of the hydride ligand *trans* to a CO group. *Trans* labilization of the hydride ligand might cause CO loss to give the intermediate IV [1]. Further loss of the other CO group would give intermediate V which could easily react with an oxygen molecule to give the oxo derivative VI.



SCHEME 3

$RuCl_3$ reacted with hapen$H_2$ to give the complex Ru(hapen$H_2$)$Cl_3$. Conductivity measurements of dilute solutions of the complex in DMF showed a weak electrolyte. Also, potentiometric titration of solutions of the complex using, a chloride selective electrode, showed that there was only one ionizable chloride ion present in the complex. Thus, it can be concluded that the complex had the formula [Ru(hapen$H_2$)$Cl_2$]Cl. The IR spectrum of the complex exhibited $\nu$OH at $3430\,cm^{-1}$. This band was found to be slightly shifted from that of the ligand which indicated that no hydrogen bonding to ruthenium took place, Table II. (Recall the large shift in the $\nu$OH of the Ru$(CO)_2$(hapen$H_2$) complex.) The participation of the two OH groups in coordinate bond formation was further confirmed from the shifts in the $\delta$OH and $\nu$C–O to lower wavenumbers ($1414\,cm^{-1}$ and $1210\,cm^{-1}$, respectively). These bands appeared at lower frequency relative to that of Ru$(CO)_2$(hapen$H_2$) which is consistent with the difference in charge distribution of the two complexes. The IR spectrum of the chloro complex also displayed distinctive bands due to Ru–O and Ru–N bonds. Magnetic susceptibility measurements of the solid complex at 304 K showed a value of $4.167 \times 10^{-6}$ e.m.u.$g^{-1}$ with an effective magnetic moment of 2.27 BM. The value is higher than the spin-only moment for one unpaired electron ($d_{xz}^2\ d_{yz}^2\ d_{xy}^2\ e_g^0$), which indicates considerable spin-orbit coupling in the complex [10]. Accordingly, the complex may have the following structure, Scheme 4:



SCHEME 4

## Thermogravimetric Analysis

The reported chromium, molybdenum and ruthenium complexes were found to be air stable and have high thermal stability. These properties along with their possibility to use as catalysts in epoxidation reactions have prompted us to investigate their thermal decomposition. This study was carried out using the thermogravimetric technique with a heating rate of 10°C/min. The decomposition ranges along with the corresponding mass losses are given in Table IV. The TG plot of Cr$(CO)_2$(happramH$)_2$ showed that it decomposed in three resolved and well-defined steps. The first and second decomposition steps occurred in the temperature ranges 337–392 and 415–642 K with a net weight loss of 6.14 and 24.93%, respectively. The percentage weight losses were consistent with the elimination of a CO group in the first step, and a CO and two $C_3H_8$ groups in the second stage. On the other hand, the third decomposition peak occurred in the temperature range 654–915 K with a net weight loss of 50.82%. This decomposition step corresponded to the material decomposition of $C_{16}H_{14}N_2$ to give finally the residue $CrO_2$ [15].

TABLE IV Thermal analysis data for the chromium, molybdenum and ruthenium complexes

| *Molecular formula* | *Decomposition steps,* K | *% Weight loss* | *Mol. wt* | *Speices eliminated* | *% Solid residue* |
|---|---|---|---|---|---|
| $Cr(CO)_2(happramH)_2$ | 337–392 | 6.14 | 28.01 | CO | 18.16 |
| | 415–642 | 24.93 | 28.01 + 88.19 | $CO + 2C_3H_8$ | |
| | 654–915 | 50.82 | 234.30 | $C_{16}H_{14}N_2$ | |
| $Mo(CO)_2$ $(happramH)_2$ | 325–375 | 5.98 | 28.01 | CO | 18.00 |
| | 382–612 | 24.83 | 28.01 + 88.19 | $CO + 2C_3H_8$ | |
| | 624–953 | 51.12 | 234.30 | $C_{16}H_{14}N_2$ | |
| $MoO(happram)_2$ | 456–928 | 68.83 | 320.48 | $C_{22}H_{28}N_2$ | 30.86 |
| $Ru(CO)_2(hapenH_2)$ | 406–680 | 58.5 | 264.00 | hapen-$O_2$ | 41.65 |
| $[RuCl_2(hapenH_2)Cl$ | 323–423 | 7.05 | 35.50 | $1/2Cl_2$ | 40.70 |
| | 436–579 | 26.0 | 130.90 | $C_9H_9N$ | |
| | 583–769 | 26.44 | 133.1 | $C_9H_{11}N$ | |

The thermal analysis of the $Mo(CO)_2(happramH)_2$ complex was similar to that of the chromium analog. The TG plot of the complex displayed three decomposing steps in the temperature range 325–953 K (Table IV). The first and second decomposition steps were consistent with the loss of two CO and two propanes. The third decomposition step occurred in a wide temperature range and corresponded to material decomposition of $C_{16}H_{14}N_2$ to yield the metallic residue $MoO_2$.

The $MoO(happram)_2$ complex was thermally decomposed in a single step with a broad temperature range (456–928 K). The percentage weight loss, 68.83%, was consistent with complete ligand decomposition ($C_{22}H_{28}N_2$) to yield the metallic oxide $MoO_3$ [15].

$[Ru(hapenH_2)Cl_2]Cl$ decomposed in three separated and well-defined steps with a total mass loss of 59.49%, Table IV. The first decomposition peak occurred in the temperature range 323–423 K and corresponded to the loss of $1/2Cl_2$. The thermal decomposition also involved the cleavage of the hapen moiety into two nearly equal parts, which were removed in two successive decomposition steps as indicated by two separated DTG peaks. This can be explained on the basis that the cleavage and removal of the first ($C_9H_9N$), followed by rearrangement of the coordination sphere around ruthenium before the removal of the second ($C_9H_{11}N$) to leave the residue $RuCl_2$ [15].

$Ru(CO)_2(hapenH_2)$ complex decomposed in a broad temperature range starting at 406 K and ending at 680 K (Table IV). The DTG peak was found to be slightly split, indicating that decomposition took place in two close and successive steps. This broad and split decomposition peak was not separated even at a heating rate of 2°C/min. This can be explained on the basis that the decomposition process of this complex was more complicated, and might involve, in addition to the cleavage and removal of the hapen as two nearly equal species as in case of $[Ru(hapenH_2)Cl_2]Cl$ the cleavage of the two hydrogen bridges and rearrangement of the coordination sphere around ruthenium. This might result in broadening of the decomposition range to about 250 K and explain the undefined DTG decomposition peaks compared with those of the $[Ru(hapenH_2)Cl_2]Cl$ complex where no hydrogen bridges were included.

## Electrochemical Studies

The cyclic voltammogram measurements of the reported complexes were carried out in $CH_2Cl_2$ using 0.1 M $n$-$Bu_4NPF_6$ as supporting electrolyte and at a scan rate of

200 mVs$^{-1}$. The CV of the Cr(CO)$_2$(happramH)$_2$ complex was consistent with one *quasi*-reversible ($E_{1/2} = -0.62$ V) and one irreversible ($E$pc $= -0.04$ V) ligand-based reduction, Table V. These two ligand-based reductions corresponded to the reduction of the two azomethine groups of the happram Schiff base

$$[\mathrm{Cr(CO)_2(happramH)_2}] \overset{e^-}{\rightleftharpoons} [\mathrm{Cr(CO)_2(happramH)_2}] \xrightarrow{-e^-} [\mathrm{Cr(CO)_2(happramH)_2}]^{2-}$$

In addition, the CV of the complex showed only one irreversible anodic peak potential without cathodic coupling, due to metal-based oxidation. This oxidation indicated that the zerovalent chromium in the complex underwent oxidation to the + 1 oxidation state.

The cyclic voltammogram of Mo(CO)$_2$(happramH)$_2$ was consistent with two *quasi*-reversible ligand-based reductions (Table V). These two reductions of the molybdenum complex, due to reduction of the two azomethine groups of the two happram ligands, occurred at slightly higher negative values relative to those observed for the chromium analog,

$$[\mathrm{Mo(CO)_2(happram)_2}] \overset{e^-}{\rightleftharpoons} [\mathrm{Mo(CO)_2(happram)_2}]^- \xrightarrow{e^-} [\mathrm{Mo(CO)_2(happram)_2}]^{2-}$$

The CV of the molybdenum complex also exhibited an anodic potential peak at + 1.08 V due to metal-based oxidation from M$^0$ to M$^+$. This oxidation peak appeared at lower positive value than that of the chromium complex.

The cyclic voltammogram of the Ru(CO)$_2$(hapenH$_2$) complex was consistent with two *quasi*-reversible ligand-based reductions and one *quasi*-reversible metal-based oxidation (Table V). The two *quasi*-reversible reductions corresponded to reduction of the two C = N moieties of the hapen ligand. These reductions occurred at more negative values than those of the reductions of azomethine groups of happram moieties in the chromium and molybdenum complexes. The *quasi*-reversible metal-based oxidation, which indicated that the zerovalent metal in the complex underwent oxidation to the + 1 oxidation state, appeared at more positive values for the oxidation

TABLE V Cyclic voltammetric data for the chromium, molybdenum and ruthenium complexes

| *Complex* | *Epa* (V) | *Epc* (V) | $E_{1/2}$ (V) | $\Delta Ep^a$ |
|---|---|---|---|---|
| Cr(CO)$_2$(happramH)$_2$ | − 0.50 | − 0.73 | − 0.62 | 0.23 |
| | | − 0.04 | | |
| | + 1.27 | | | |
| Mo(CO)$_2$(happramH)$_2$ | − 0.65 | − 0.77 | − 0.71 | 0.12 |
| | + 0.08 | − 0.04 | + 0.02 | 0.12 |
| | + 1.08 | | | |
| Ru(CO)$_2$(hapenH$_2$) | − 0.58 | − 0.86 | − 0.72 | 0.28 |
| | + 0.04 | − 0.11 | − 0.40 | 0.15 |
| | + 1.17 | + 0.96 | + 1.07 | 0.21 |
| [RuCl$_2$(hapenH$_2$)}Cl | − 0.53 | − 0.71 | − 0.62 | 0.18 |
| | | − 0.19 | | |

[a] $\Delta E\mathrm{p} = E\mathrm{pa} - E\mathrm{pc}$

of the $Ru(CO)_3(PBI)$ and $[Ru(CO)_3(HPBI)Py$, HPBI = 2-(2′-pyridyl)benzimidazole; Py = pyridine [16] and for the $Ru(CO)_3(DPQ)$ and $Ru(CO)_2(DPQ)(Py)$, DPQ = 2,3-bis(2′-pyridyl)-quinoxaline complexes [17]. This could be related to the basicity of HPBI, DPQ and Py with respect to the hapen ligand.

The cyclic voltammogram of $[RuCl_2(hapenH_2)]Cl$ was consistent with two (a *quasi*-reversible and an irreversible) ligand-based reductions. The first *quasi*-reversible reduction ($E_{1/2} = -0.62\,V$) corresponded to reduction of one of the azomethine groups of the hapen moiety. The irreversible cathodic peak at −1.19 V was due to reduction of the second C = N moiety.

## CONCLUSION

The bidentate 2-hydroxyacetophenonepropylimine and tetradentate bis-(2-hydroxyacetophenone)ethylenediimine Schiff bases are related to each other. However, the interactions of both ligands with chromium and molybdenum carbonyls under reduced pressure are different. The happramH afforded the dicarbonyl derivative $M(CO)_2(happramH)_2$ with the CO groups in a *cis* configuration while the molybdenum dihydride complex $MoH_2(CO)(hapen)$ was the only isolated product. On the other hand, in the presence of $O_2$ both ligands gave similar oxo complexes with $Mo(CO)_6$. $Ru_3(CO)_{12}$ with $hapenH_2$ gave a dicarbonyl derivative with two hydrogen bonded OH groups. All these species are proposed to be involved in the mechanism of formation of the finally oxo derivative.

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