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Carbonyl Complexes of Rh(I), Ir(I) and Mo(0) Containing Substituted Derivatives of 1,10-Phenanthroline and 2,2′-Bipyridine

G. CLAUTI, G. ZASSINOVICH and G. MESTRONI

Dipartimento di Scienze Chimiche, Università di Trieste, Piazzale Europa 1, 34127 Trieste, Italy

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Abstract

The A_1 symmetry ν_{CO} of the carbonyl complexes [Mo(chel)$(CO)_4$], [M(chel)$(CO)_2$][PF_6] (M = Rh, Ir; chel = bipy, phen and substituted derivatives) are used for determining the electron donor–acceptor properties of the title ligands. The steric hindrance of the methyl groups in positions 2 and 9 of the phenanthroline favours the formation of Rh(I) and Ir(I) pentacoordinated derivatives.

Introduction

Transition metal complexes with 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) act as catalysts in several reactions, and the interest in this field is gradually increasing [1–11]. Nevertheless, the study of this catalytic activity is often restricted to simple bipy and phen derivatives, although some substituted derivatives of these ligands are commercially available and the synthesis of many others can be found in the literature.

On the other hand, we have reported that complexes of the type [M(chel)(L–L)][X] (**I**) are catalyst precursors for hydrogen transfer reactions [12–14] and that complexes of the type [M(chel)$(CO)_2$][X] (**II**) promote the selective reduction of nitroaromatics to amines using CO + H_2O as hydrogen source [15] (M = Rh, Ir; L–L = 1,5-cyclooctadiene (COD), 1,5-hexadiene (HD); X^- = PF_6^-, BPh_4^-; chel = bipy, 4,4′-Me_2bipy, phen, 4,7-Me_2phen, 4,7-Ph_2phen, 3,4,7,8-Me_4phen (TMphen), 3,4,5,6,7,8-Me_6phen (HMphen)). The last reaction can be also accomplished using the $Rh_6(CO)_{16}$ + chel [15] and the $Ru_3(CO)_{12}$ + chel [16] systems as catalyst precursors. The catalytic activity of these catalysts depends strongly on the chel nature [12–16].

A correlation between the catalytic activity and the pK_a of the ligand has generally been found with the unhindered methyl-substituted phenanthrolines, but a correlation is not found, for instance, when the 4,7-Ph_2phen or the hindered 2,9-Me_2phen are used.

In order to rationalize the activity data as a function of the chel nature and to discriminate between their steric and electronic properties, we decided, in agreement with Tolman's work [17], to use the A_1 carbonyl stretching frequency of the complexes [M(chel)$(CO)_2]^+$ (M = Rh, Ir) and [Mo(chel)$(CO)_4]^0$ as a measure of the electron donor–acceptor properties of all the available chelating ligands. In particular, the Mo complexes, due to their geometry and solubility in non-coordinating solvents, are well-suited to this kind of analysis.

Experimental

Synthesis of Complexes

3,4,5,6,7,8-Me_6phen and 4,7-Cl_2phen were prepared by the literature methods [18, 19]. The complexes [Mo(chel)$(CO)_4$], (M(chel)(COD)$]^+X^-$ (M = Rh, Ir; X^- = Cl^-, PF_6^-, BPh_4^-) and [M(chel)$(CO)_2]^+$-X^- (M = Rh, Ir; X^- = PF_6^-, BPh_4^-) have been synthesized following procedures already reported [20–22].

[M(chel)(COD)Cl] (M = Rh, Ir; chel = 2,9-Me₂-phen, 2,9-Me₂-4,7-Ph₂phen)

0.41 mmol of [M(COD)Cl$]_2$ dissolved in deaerated CH_2Cl_2 (10 ml) are treated with 0.87 mmol of chel; the yellow product is precipitated by addition of ether, filtered off and washed with ether.

[M(chel)(COD)(Mid)][PF₆] (M = Rh, Ir; chel = 2.9-Me₂phen, 2,9-Me₂-4,7-Ph₂phen)

To a deaerated solution of 87 mmol of [M(COD)-$(Mid)_2$][PF_6] [21] in 25 ml of ethanol, a stoichiometric amount of chel is added and the solution is heated at reflux for 5 min. On cooling the complex precipitates; it is filtered off and washed with ethanol.

Measurements

The IR spectra were recorded on a Perkin-Elmer 983G spectrophotometer; the ^1H NMR spectra were obtained with a Bruker WP-80 spectrometer. Catalytic activity data were obtained as previously described [16].

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TABLE I Selected Analytical and NMR Data

Compound	Elemental analysis[a]			^1H NMR[b] (δ)
	%C	%H	%N	
$Mo(HMphen)(CO)_4$	55.80	3.87	5.90	
	(55.94)	(4.27)	(5.93)	
$[Rh(TMphen)(CO)_2]PF_6$	40.00	2.89	5.29	
	(40.02)	(2.99)	(5.19)	
$[Rh(TMphen)(CO)_2]BPh_4$	69.30	5.04	3.91	
	(70.60)	(5.08)	(3.92)	
$[Rh(HMphen)(CO)_2]PF_6$	42.00	3.22	5.06	
	(42.27)	(3.55)	(4.93)	
$[Ir(HMphen)(CO)_2]PF_6$	36.80	3.02	4.16	
	(36.53)	(3.07)	(4.26)	
$[Rh(2,9\text{-}Me_2phen)(COD)Cl]$[c]	57.90	5.29	6.18	2,9-Me_2phen $-CH_3$ 3.99 $H^{5,6}$ 7.83 $H^{3,4,7,8}$ 7.88, 8.24, 8.34, COD =CH 3.61
	(58.19)	(5.32)	(6.16)	
$[Rh(2,9\text{-}Me_2\text{-}4,7\text{-}Ph_2phen)(COD)Cl]$	65.70	5.21	4.53	
	(67.27)	(5.31)	(4.62)	
$[Rh(2,9\text{-}Me_2phen)(COD)(Mid)]PF_6$[d]	48.00	4.54	8.63	Mid $-CH_3$ 3.58 H^4 6.59 H^5 7.03 H^2 7.60
	(48.31)	(4.68)	(8.67)	
$[Ir(2,9\text{-}Me_2phen)(COD)Cl]$	48.00	3.99	4.87	
	(48.56)	(4.45)	(5.15)	
$[Ir(2,9\text{-}Me_2\text{-}4,7\text{-}Ph_2phen)(COD)Cl]$	57.70	4.57	4.02	
	(58.65)	(4.63)	(4.02)	

[a] Calculated values in parentheses. [b] Values in ppm downfield from TMS. [c] NMR solvent deuterochloroform. [d] NMR solvent acetone-d^6

Results

The $[Mo(chel)(CO)_4]$ derivatives of all the available chelating ligands were obtained following previously reported procedures [20].

The complexes $[M(chel)(CO)_2]^+X^-$ (M = Rh, Ir, $X^- = PF_6^-$, BPh_4^-, chel = phen, 4,7-Me_2phen, 4,7-Ph_2phen, TMphen, HMphen) were synthesized as shown in eqn (1)

$$[M(chel)(COD)] + Cl^- + X^- \longrightarrow [M(chel)(COD)]^+X^- + Cl^- \qquad (1)$$

$$[M(chel)(COD)]^+X^- + 2CO \longrightarrow [M(chel)(CO)_2]^+X^- + COD$$

With the sterically-hindered phenanthrolines 2,9-Me_2phen and 2,9-Me_2-4,7-Ph_2phen, the dicarbonyl derivatives could not be obtained, due to the formation of stable pentacoordinated COD chloroderivatives which did not exchange the coordinated chloride with non-coordinating anions (eqn 2)

$$\begin{tikzcd} & {[M(phen)(COD)]^+Cl^-} \\ {[M(COD)Cl]} \arrow[ur, "phen"] \arrow[dr, "2,3\text{-}Me_2phen"'] & & (2) \\ & {[M(2,9\text{-}Me_2phen)(COD)Cl]^0} \end{tikzcd}$$

Then we tried the synthesis of $[M(2,9\text{-}Me_2phen)(COD)][PF_6]$ derivatives following an alternative route which did not require the use of the chloroderivatives (eqn 3) [21]

$$\begin{tikzcd} & {[M(phen)(COD)]^+PF_6^-} \\ {[M(Mid)_2(COD)]^+PF_6^-} \arrow[ur, "phen"] \arrow[dr, "2,9\text{-}Me_2phen"'] & & (3) \\ & {[M(2,9\text{-}Me_2phen)(COD)(Mid)]^+PF_6^-} \end{tikzcd}$$

The hindered phenanthrolines react with the cationic square planar complexes and again form five-coordinated species with one molecule of N-methyl imidazole in the fifth coordination position; these complexes exchange, with difficulty, with carbon monoxide to give the carbonyl derivatives only in poor yield

Selected analytical data for the previously unknown complexes are reported in Table I, the elemental analysis, the IR and ^{1}H NMR spectra are in agreement with the proposed structures. In particular, the ^{1}H NMR spectrum of the [Rh(2,9-Me$_2$-phen)(COD)Cl]$^{\circ}$ derivative shows a singlet at 3.99 δ ascribable to the two equivalent methyl groups, a singlet at 7.83 δ due to the 5,6-protons, and two doublets centered at 8.29 δ and 7.85 δ, respectively, assigned to the 4,7- and 3,8-protons of the substituted phenanthroline. COD olefinic protons show up as a singlet at higher field (3.61 δ) than in the free COD (4.3 δ), and the aliphatic COD protons are present as two multiplets centered at 1.66 δ and 2.56 δ. In the spectrum of the [Rh(2,9-Me$_2$-phen)(COD)(Mid)] [PF$_6$] complex, the 2,9-Me$_2$-phen and the COD signals show the same pattern as that observed for the chloroderivative. Furthermore, the hydrogens and the methyl group of the N-methyl imidazole are easily assigned (Table I); the 2-hydrogen of the coordinated Mid is shifted downfield in comparison with the free ligand. No signal attributable to the free Mid can be detected, confirming the stability of the pentacoordinated species even in solution. The behaviour of 2,9-substituted phenanthrolines is clearly different from that showed for all the other phenanthrolines having both lower and higher pK_a values (see Table II). Such behaviour can be rationalized in terms of steric hindrance: the presence of the methyl groups in 2- and 9-positions causes a distortion from the planar geometry favouring the pentacoordination. These distortions have been previously observed and quantitatively determined in the case of Pd(II) derivatives of the type [Pd(chel)$_2$]$^{++}$ with chel = bipy [23, 24] and phen [25], respectively, where the steric hindrance occurs between the H^2 and H^9 protons of the two ligands. Wernberg and Hazell suggest that these steric interactions play an important role in the affinity for pentacoordination and, in fact, pentacoordinated complexes of the type [Pt(phen)$_2$X]$^+$ (X$^-$ = CN$^-$, SH$^-$; OH$^-$) have been obtained as stable compounds [26].

TABLE II. Carbonyl Stretching Frequencies of [Mo(chel)(CO)$_4$] Complexes [a]

chel	pK_a	ν_{CO} (cm^{-1})[b]	
4,7-Cl$_2$phen	3.03	2017.5	
5,6-Cl$_2$phen	3.47		(2016)
phen	4.86	2016.7	(2014)
4,7-Ph$_2$phen	4.84	2015.5	(2013)
4,7-Me$_2$phen	5.94	2015.4	
TMphen	6.31	2015.0	(2012)
HMphen	7	2013.7	
2,9-Me$_2$phen	6.17	2017.5	
2,9 Me$_2$-4,7-Ph$_2$phen		2016.5	
bipy	4.44	2016.7	
4,4'-Me$_2$bipy	5.32	2015.3	
4,4'-Ph$_2$bipy		2015.0	

[a] Solvent CHCl$_3$. [b] Values in parentheses, see ref. 27.

IR Spectra

In agreement with their symmetry, [Mo(chel)(CO)$_4$] derivatives both in the solid state and in CHCl$_3$ solution show the expected four ν_{CO} bands (2A$_1$ + B$_1$ + B$_2$). In Table II we have collected the highest ν_{CO} frequencies (A$_1$ symmetry) for the phen, bipy and their substituted derivatives; they are arranged in order of ν_{CO} decrease: that is, the increase of the electron density on the metal atom. We have also reported in parentheses some of the ν_{CO} values previously found by Angelici and Graham [27]; in spite of the differences between their results and ours, the same trend is observed.

The highest ν_{CO} value is found with the 4,7-Cl$_2$-phen, the ligand with the lowest pK_a value. As the pK_a increases, going along the series of the unhindered phenanthrolines, a gradual ν_{CO} decrease is observed until a minimum is reached when chel = HMphen. The ν_{CO} *vs.* pK_a correlation is not found only with the 4,7-Ph$_2$phen, giving a ν_{CO} value almost identical to that of the 4,7-Me$_2$phen, although its pK_a value is slightly lower than that of phen. Even in the case of hindered ligands the correlation between pK_a and ν_{CO} is not found. In fact, the 2,9-Me$_2$phen, having a pK_a value comparable to that of the 4,7-dimethyl isomer, shows a ν_{CO} value equal to that of 4,7-Cl$_2$phen.

The ν_{CO} lowering when a phenyl group is in *para* position to the nitrogen atom seems to be a general phenomenon, since it is also observed in the hindered phenanthrolines and in the bipy series. As expected, the ν_{CO} decreases going from bipy to 4,4'-Me$_2$bipy; it is remarkable that the carbonyl stretching frequencies of these two derivatives are practically the same as those of phen and 4,7-Me$_2$-phen, respectively, in spite of the lower pK_a value of the flexible ligands compared to that of the rigid ones.

The same trend of the ν_{CO} frequencies with the chel nature has also been observed in the case of the carbonyl derivatives of the type [M(chel)(CO)$_2$]-[PF$_6$] (M = Rh, Ir) (Table III), although the study has been restricted to the compounds with the unhindered phenanthrolines. All these complexes show, in CO saturated CH$_3$CN solution, two ν_{CO} bands of comparable intensity, typical of the *cis* arrangement of the two-coordinated carbonyl groups. The IR spectra of the HMphen derivatives in the solid state show two carbonyl bands, as was seen in solution. In the case of the complexes with the TMphen and the 4,7-Me$_2$phen, these are split into four bands, while a more complex pattern is observed in the spectra of the phen derivatives. The results reported suggest that the correlation between

TABLE III. Carbonyl Stretching Frequencies of $[M(chel)(CO)_2]PF_6$ (M = Rh, Ir) Complexes [a]

chel	pK_a	ν_{CO} (cm^{-1})			
		Rh		Ir	
phen	4.86	2102.4	2042.7	2091.0	2025.6
4,7-Ph_2phen	4.84	2101.4	2042.5	2088.9	2024.5
4,7-Me_2phen	5.94	2100.0	2039.7	2088.1	2022.4
TMphen	6.31	2099.5	2039.3	2087.5	2021.9
HMphen	7	2098.8	2038.4	2086.5	2020.9

[a] Solvent CH_3CN.

ν_{CO} and the electron donor–acceptor properties of the ligands could be obtained whatever the nature of the metal atom, at least for the carbonyl complexes of the second and third transition row.

Comparison between Catalytic Activity and ν_{CO}

As reported in the introduction, the correlation between the catalytic activity and the pK_a of the ligands is not found in the case of 4,7-Ph_2phen. On the other hand, a good agreement between catalytic activity and ν_{CO} can be observed using complexes with unhindered phenanthrolines as catalyst precursors. As an example, we report in Table IV the trends observed in the reduction of nitrobenzene with CO + H_2O using both the rhodium and ruthenium carbonyl clusters in the presence of various ligands as catalyst precursors; other examples with iridium complexes can be found in the literature [12, 13].

TABLE IV. Catalytic Reduction of Nitrobenzene to Aniline with CO/H_2O; Catalyst Precursors: (a) $Ru_3(CO)_{12}$ + chel; (b) $Rh_6(CO)_{16}$ + chel [a]

chel	ν_{CO} (cm^{-1})	% Conversion	
		a (1 h)	b (2 h)
phen	2016.7	73	7.5
4,7-Ph_2phen	2015.5	65.5	12.5
4,7-Me_2phen	2015.4	67.5	25
TMphen	2015.0	46	53

[a] $[M] = 1 \times 10^{-4}$ M; Sub/metal = 1000; chel/metal = 1; T = 180 °C; p_{CO} = 30 atm; EtOH 95% = 50 ml.

The ν_{CO} seems to be a better parameter than the pK_a of the ligand, allowing the evaluation of the relationship between catalytic activity and electron density on the active site. The easy determination of this parameter suggests the use of the ν_{CO} to estimate the relative electron donor–acceptor ability of Schiff bases obtained by condensation of pyridin-2-aldehyde with primary amines. Rhodium and iridium complexes of such ligands are, in fact, catalyst precursors in asymmetric transfer hydrogenations [14] and hydrosilylation reactions of ketones [28].

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