Synthesis and reactivity of rhodium(I) and iridium(I) complexes of the dianions of 2,3-pyrazinedicarboxylic and 2,5-pyrazinedicarboxylic acid

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Abstract

Rhodium and iridium complexes of the title ligands have been prepared containing cyclooctadiene, carbonyl, phosphine and phosphite ancillary ligands. The complexes are mononuclear or dinuclear depending on the method of preparation and the leaving group basicity. The geometries of the complexes derived from the 2,3- and 2,5-dianions show marked differences owing to differences in the steric interaction between the carboxyl groups. Clear structural assignments were made possible by the symmetry requirements revealed by the infrared and NMR spectra.

Introduction

The anions 2,3-pyrazinedicarboxylato ($cDcp^{2-}$) and 2,5-pyrazinedicarboxylato ($tDcp^{2-}$) have been extensively used as ligands for a wide range of transition metals. In addition to forming mononuclear complexes $M(HcDcp)_2$, in which the ligand behaves as bidentate chelate [1], both dianions have been reported to give hydrated polymeric structures of composition $(M(cDcp) \cdot nH_2O$ [2] and $M(tDcp) \cdot nH_2O$ [3] (M = divalent metal). The structures of the polymeric complexes $Co(cDcp) \cdot 2H_2O$ and $Zn(cDcp) \cdot 3H_2O$ show that different behaviour can be expected for the ligand when it is acting as a bridge. In the cobalt complex, the carboxylato groups are rotated by about 30° each, in opposite directions with respect to the pyrazine ring, to avoid repulsive interaction between the *endo*-oxygens. In this way, the ligand can act as a double N–O chelate [4]. However, in the case of the zinc complex, only one of the sides of the ligand behaves as an N–O chelate, while the other N atom remains uncoordinated. The carboxylato group next to it is rotated by 90° with

respect to the pyrazine ring, and the two oxygens of the group are coordinated to different metal atoms [5]. Polymeric structures containing the VO_2^+ cation [6], and Ag^I–Ag^{II} mixed valence polymers [7] have been also prepared.

The only dinuclear species reported for these ligands are the ruthenium complexes of the $tDcp^{2-}$ ligand [8] and two rhodium complexes of the $cDcp^{2-}$ anion [9]. Recently, $tDcp^{2-}$ and $cDcp^{2-}$ have been used as ancillary ligands for preparing peroxo Ti^{IV} complexes, and show striking differences in their coordination modes [10].

We are engaged in the synthesis of a new type of dinuclear planar complexes which produce stacked structures in the solid state. We have found that the anions of imidazole-4,5-dicarboxylic acid [11] and pyrazole-3,5-dicarboxylic acid [12] are very effective ligands for forming such compounds. Some of the anionic iridium complexes can be chemically or electrochemically oxidized to form conducting materials [12]. An extension of our previous work is the use of H_2cDcp and H_2tDcp as dinucleating ligands for d^8 metal ions, which would allow the study of the influence of the overall charge of the complex in the formation of the stacks in the solid state.

Experimental

All reactions were performed under nitrogen by standard Schlenk techniques. Solvents were purified and dried by standard methods. $[M(\mu\text{-Cl})(cod)]_2$ [13], $[M(\mu\text{-}OMe)(cod)]_2$ (M = Rh, Ir; cod = 1,5 = cyclooctadiene) [14] and pyrazine-2,5-dicarboxylic [15] acid were prepared as previously described. Other reagents were used as received.

Physical measurements

Elemental analyses were performed with a Perkin Elmer 240C instrument. Infrared spectra (4000–400 cm^{-1}) were recorded on a Perkin Elmer Model 1710 Fourier transform spectrometer. Fourier transform ^1H NMR spectra were recorded on a Bruker WP80SY or Bruker AM 400 instrument. Chemical shifts are reported in ppm downfield from tetramethylsilane.

Synthesis of $[Rh_2(tDcp)(cod)_2]$ (Ia). Method A: 4 ml of an 0.1 M solution of Me_4NOH in isopropanol/methanol (0.4 mmol) were added dropwise to a suspension of 100 mg of $[Rh(\mu\text{-Cl})(cod)]_2$ (0.2 mmol) and 34 mg of H_2tDcp (0.2 mmol) in 10 ml of acetonitrile. A dark green solid separated. After 4 h stirring the product was filtered off and rinsed with acetonitrile and ether. Yield 99 mg (83%). Method B: A suspension of 100 mg of $[Rh(\mu\text{-OMe})(cod)]_2$ (0.2 mmol) and 34 mg of H_2tDcp (0.2 mmol) was stirred for 4 h to give a precipitate of 100 mg (83% yield) of the product, which was worked up as in method A. The compound is soluble in CH_2Cl_2 and $CHCl_3$.

Synthesis of $[Ir_2(tDcp)(cod)_2]$ (Ib). The procedure A used for Ia, but on a 0.15 mmol scale gave a 50% yield of a dark brown product. The yield was increased to 77% when method B was used. The complex is soluble in CH_2Cl_2 and $CHCl_3$.

Synthesis of $(NMe_4)[Rh(cDcp)(cod)]$ (IIa). 4 ml of an 0.1 M solution of Me_4NOH (0.4 mmol) in methanol/isopropanol were added dropwise to a stirred suspension of 50 mg of $[Rh(\mu\text{-Cl})(cod)]_2$ (0.1 mmol) and 34 mg of H_2cDcp (0.2 mmol) in 10 ml of acetonitrile. The dark orange solution was evaporated to dryness. The residue was dissolved in a mixture of 8 ml of acetonitrile and 2 ml of methanol, and the solution

was slowly evaporated under vacuum to give an orange precipitate. This was filtered off and rinsed with acetonitrile and ether to give 62 mg of the product (68% yield). This solid is hygroscopic and soluble in methanol.

Synthesis of (NMe₄)[Ir(cDcp)(cod)] (IIb). When 1.6 ml of a 0.1 ml of a solution of Me₄NOH in methanol/isopropanol (0.16 mmol) were added to a suspension of 50 mg of [Ir(μ-OMe)(cod)]$_2$ (0.075 mmol) and 25 mg of H$_2$cDcp (0.15 mmol) in 10 ml of acetonitrile. A red solution was formed. The volume was reduced by one half and 15 ml of ether were added to give a precipitate of 69 mg (85% yield) of the orange product. The compound is very hygroscopic, and soluble in methanol and acetonitrile.

Synthesis of [Rh₂(cDcp)(cod)₂] (IIIa). Mixing of 100 mg of [Rh(μ-OMe)(cod)]$_2$ (0.2 mmol) and 34 mg of H$_2$cDcp (0.2 mmol) in 10 ml of acetonitrile immediately produced a precipitate of the brown product. After 4 h stirring to ensure completion of the reaction, the solid was filtered off and rinsed with methylene chloride; yield 101 mg (83%). The product is only soluble in DMF and DMSO.

Synthesis of [Ir₂(cDcp)(cod)₂] (IIIb). Treatment of 100 mg of [Ir(μ-OMe)(cod)]$_2$ (0.15 mmol) with 25 mg of H$_2$cDcp (0.15 mmol) in acetonitrile as described for the preparation of IIIa gave 70 mg of the dark brown product (60%). It is soluble in methylene chloride.

Synthesis of [Rh₂(tDcp)(CO)₂(PPh₃)₂] (IVa). A red solution was formed when carbon monoxide was bubbled through a solution of 50 mg of Ia (0.085 mmol) and 45 mg of PPh$_3$ (0.17 mmol) in 5 ml of methylene chloride. Layering of the solution with hexane produced 68 mg of red crystals (84%). The well-formed crystals lose solvent after a few seconds exposure to the atmosphere, even inside a capillary. The solid is very soluble in chlorinated solvents.

Synthesis of [Ir₂(tDcp)(CO)₂(PPh₃)₂] (IVb). 30 mg Ib was treated as described for the rhodium complex IVa, to yield 32 mg (72%) of a brown product. It is very soluble in chlorinated solvents.

Synthesis of [Rh₂(tDcp)(CO)₂(P(OR)₃)₂] (R = Ph, Va; R = Me, VIa). The procedure described for the preparation of the complex IVa, but starting with 40 mg of Ia gave 59 mg (83%) of the red crystals in the case of R = Ph, and 39 mg (85%) of green crystals when R was Me. Both solids are very soluble in chlorinated solvents.

Synthesis of [Rh₂(cDcp)(CO)₂(PPh₃)₂] (VIIa). Treatment of 20 mg of IIIa as in the preparation of IVa gave 25 mg of a brick-red complex (77%).

Synthesis of [Rh₂(cDcp)(CO)₂(P(OR)₃)₂] (R = Ph, VIIIa; R = Me, IXa). 30 mg IIIa were treated similarly to give 26 mg (49%) of the triphenylphosphite complex or 24 mg (70%) of the trimethylphosphite complex. Both products are pale brown.

Results and discussion

A list of the compounds prepared and their analytical data is given in Table 1. Infrared and NMR data are shown in Tables 2 and 3, respectively. The compound VIIa has been previously reported [9].

The pyrazinedicarboxylic acids H$_2$cDcp and H$_2$tDcp differ remarkably in their reactions with the dinuclear species [M(μ-Cl)(cod)]$_2$ (M = Rh, Ir) in the presence of two molar equivalents of base. The ligand H$_2$tDcp forms the expected dinuclear complexes Ia and Ib, but H$_2$cDcp yields the mononuclear compounds IIa and IIb, plus the complex anions [MCl₂(cod)]$^-$. The infrared spectra of the species IIa and

Table 1

Analytical data for compounds I–IX

Compound	Analyses (found (calcd.)) (%)		
	C	N	H
$[Rh_2(tDcp)(cod)_2]$ (Ia)	44.9	4.88	4.43
	(44.9)	(4.76)	(4.45)
$[Ir_2(tDcp)(cod)_2]$ (Ib)	32.9	3.58	3.36
	(34.5)	(3.65)	(3.42)
$[NMe_4][Rh(cDcp)(cod)]$ (IIa)	47.6	9.21	5.95
	(47.9)	(9.31)	(5.81)
$[NMe_4][Ir(cDcp)(cod)]$ (IIb)	38.5	7.63	5.16
	(40.0)	(7.77)	(4.85)
$[Rh_2(cDcp)(cod)_2]$ (IIIa)	44.5	4.81	4.46
	(44.9)	(4.76)	(4.45)
$[Ir_2(cDcp)(cod)_2]$ (IIIb)	33.3	3.86	3.38
	(34.5)	(3.65)	(3.42)
$[Rh_2(tDcp)(CO)_2(PPh_3)_2]$ (IVa)	53.5	2.92	3.39
	(55.5)	(2.94)	(3.39)
$[Ir_2(tDcp)(CO)_29PPh_3)_2]$ (IVb)	46.8	2.22	3.31
	(46.7)	(2.48)	(2.85)
$[Rh_2(tDcp)(CO)_2(P(OPh)_3)_2]$ (Va)	50.4	2.68	3.06
	(50.4)	(2.67)	(3.08)
$[Rh_2(tDcp)(CO)_2(P(OMe)_3)_2]$ (VIa)	24.5	4.04	2.94
	(24.9)	(4.14)	(2.98)
$[Rh_2(cDcp)(CO)_2(PPh_3)_2]$ (VIIa)	53.6	2.94	3.53
	(55.5)	(2.94)	(3.39)
$[Rh_2(cDcp)(CO)_2(P(OPh)_3)_2]$ (VIIIa)	50.4	2.90	3.22
	(50.4)	(2.67)	(3.08)
$[Rh_2(cDcp)(CO)_2(POMe)_3)_2]$ (IXa)	24.4	4.50	2.63
	(24.9)	(4.14)	(2.98)

IIb, in the COO^- region, show bands at 1628 cm^{-1} (M = Rh) and 1626 cm^{-1} (M = Ir) characteristic of free carboxylate groups, in addition to the bands of the in-plane coordinated carboxylate at 1672 cm^{-1} (M = Rh) and 1680 cm^{-1} (M = Ir).

Table 2

Infrared data (cm^{-1}) (in CH_2Cl_2) for compounds I–IX

Compound	$\nu(OCO)_{as}$		$\nu(CO)$
Ia	1663		
IIa	1672	1628	
IIIa	1664	1686	
IVa	1669		1988
VIIa	1670	1694	1984
Va	1675		2014
VIIIa	1677	1700	2011
VIa	1674		2005
IXa	1673	1695	2003
Ib	1681		
IIb	1680	1626	
IIIb	1684	1712	
IVb	1686	1709	1969

Table 3

^{1}H NMR data (ppm) for compounds I–IX ^{a}

Compound	H(ring)	CH(cod)	CH$_2$(cod) exo	endo	
Ia ^{b}	8.22(s)	4.43(s,b)	2.55(m)	2.01(d,b)	J 8.9 Hz
IIa ^{c}	8.23(s,b)	4.33(s,b)	2.48(m)	1.97(d,b)	J 8.0 Hz
IIIa ^{d}	8.18(s,b)	4.37(s,b)	^{e}	1.95(d,b)	J 8.0 Hz
Ib ^{b}	8.47(s)	4.44(b)	2.34(m)	1.91(d,b)	J 8.0 Hz
IIb ^{c}	8.83(s,b) 8.08(s,b)	4.19(b)	2.32(m)	1.83(d,b)	J 7.9 Hz
IIIb ^{b}	8.59(s,b)	4.16(s,b)	2.29(m)	1.73(d,b)	J 8.0 Hz

		H(phenyl)	H(methyl)		
IVa ^{b}	9.11(s)	7.71(m) 7.48(m)			
Va ^{b}	8.86(s)	7.32(m) 7.36(m)			
VIa ^{b}	9.10(s)		3.83(d)	J(H–P) 12.7 Hz	
VIIa ^{b}	8.51(s,b)	7.71(m) 7.48(m)			
VIIIa ^{b}	8.27(s,b)	7.32(m) 7.19(m)			
IXa ^{b}	9.21(s,b) 8.68(s,b)		3.84(d) 3.78(d)	J(H–P) 12.0 Hz J(H–P) 12.0 Hz	
IVb ^{b}	9.15(s)	7.68(m) 7.47(m)			

^{a} b, broad; d, doublet; m, multiplet; s, singlet. ^{b} in CDCl$_3$. ^{c} in CD$_3$OD. ^{d} in DMSO. ^{e} multiplet obscured by solvent signals.

These bands appear at nearly the same frequency of the single band observed for each of the dinuclear compounds Ia and Ib, for which coplanarity of the pyrazine ring and a square-planar coordination environment of the metals is expected.

Dinuclear complexes derived from H$_2$cDcp can be prepared by use of [M(μ-OMe)(cod)]$_2$ (M = Rh, Ir) as starting materials. The complexes IIIa (M = Rh) and IIIb (M = Ir), again show bands for in-plane coordinated carboxylato groups, together with a high frequency band at 1686 cm^{-1} (M = Rh) or 1712 cm^{-1} (M = Ir), which can be assigned to coordinated out-of-plane (and therefore non conjugated) carboxylato groups. The basic starting materials also react with H$_2$tDcp to yield the dinuclear complexes Ia and Ib. All these reactions are summarized in Scheme 1.

The implications of the difference in behaviour between the two isomeric ligands are that when one of the carboxylato groups of the cDcp^{2-} anion has formed a chelate with the N of the pyrazine, the other is forced to rotate out of the plane of the aromatic ring to avoid the steric hindrance. It should be noted that the structure of the acid form of the ligand shows a dihedral angle of 34° between the pyrazine ring and the plane defined by one of the carboxylic groups [16]. The potential chelate fragment formed by the pyrazine ring and the rotated carboxylato group is a much weaker ligand than the corresponding in-plane chelate. This poor coordinating ability of the former can be inferred from the second reaction in Scheme 1, in which no substitution of the labile chloro ligands of the anions [MCl$_2$(cDcp)]$^-$ takes place. Similar behaviour has been observed in the case of Zn(cDcp) · 3H$_2$O, [5] although there the polymeric structure allows coordination to the metal of both oxygens of the twisted carboxylato group.

$[M_2(cod)_2Cl_2] + 2 Me_4NOH + H_2tDcp$ ⟶ $+ 2 NMe_4Cl + 2 H_2O$

$[M_2(cod)_2(\mu-OMe)_2] + H_2tDcp$ ⟶ $+ 2MeOH$

M=Rh (Ia)
M=Ir (Ib)

$[M_2(cod)_2Cl_2] + 2 Me_4NOH + H_2cDcp$ ⟶ NMe_4^+ $\left[\right]^-$ $+ NMe_4^+[M(cod)_2Cl_2]^- + 2 H_2O$

M=Rh (IIa)
M=Ir (IIb)

$[M_2(cod)_2(\mu-OMe)_2] + H_2cDcp$ ⟶ $+ 2 MeOH$

M=Rh (IIIa)
M=Ir (IIIb)
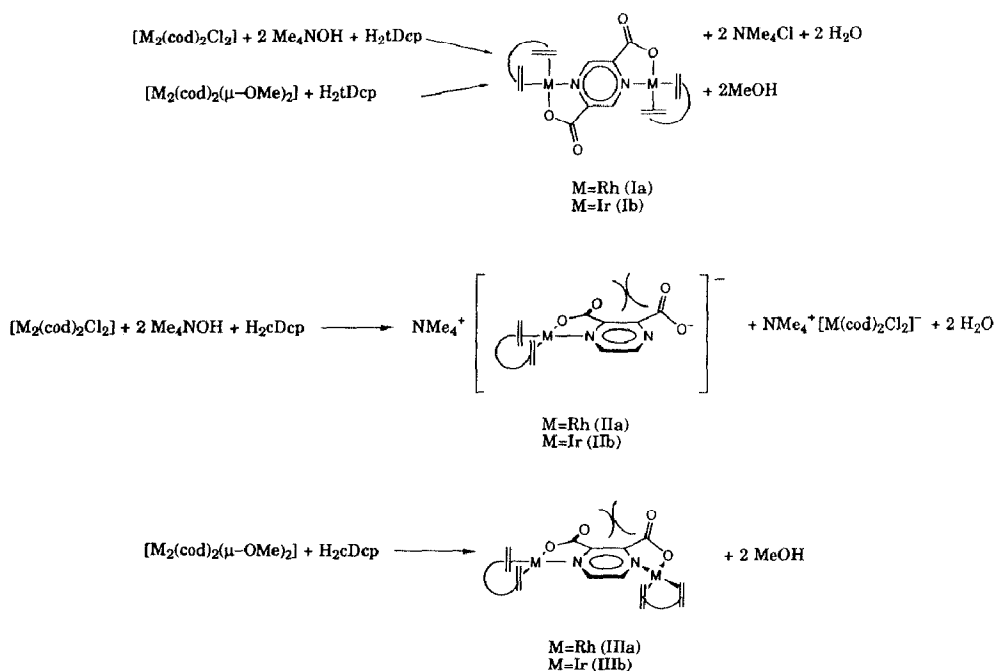
Scheme 1. Preparation of compounds I–III.

When $[M(\mu-OMe)(cod)]_2$ is used as starting material the very poorly coordinating MeOH is formed as side product rather than Cl$^-$. In this case, the out-of-plane chelate is able to replace the alcohol molecules of the solvato complex to form the dinuclear species IIIa and IIIb. It is significant that the infrared spectra of the latter complexes are consistent with the presence of both a chelate in-plane and a twisted chelate ligand, which contrasts with the structure of the complex $Co(cDcp) \cdot 2H_2O$, in which both carboxylato groups are rotated out of the plane of the pyrazine [4]. ^1H NMR spectra of the dinuclear rhodium and iridium complexes of $cDcp^{2-}$ show a broad signal for the two heterocyclic protons, indicating a dynamic equilibrium between the in-plane and out-of-plane chelates. On the other hand, the dinuclear complexes of $tDcp^{2-}$ show a single absorption for these protons, consistent with a symmetrical structure.

Steric interaction between the carboxylato groups at the 2 and 3 positions of the pyrazine six member ring has not been observed for any of the complexes of the ligands imidazole-4,5-dicarboxylic acid [11] and triazole-4,5-dicarboxylic acid [17]. The obvious conclusion is that the slight increment (ca. 12°) in the opening of the angle formed by the bonds between the heterocycle atoms and the carboxylate carbons is sufficient to preclude such distortion in the five member heterocycles.

When carbon monoxide was bubbled through solutions of the compounds Ia, Ib, IIIa, and IIIc the impure carbonyl derivatives were obtained in very low yield as insoluble dark materials. Because of the intractability of these solids, no further characterization was attempted. However, in the presence of a phosphine or phosphite ligand, the reaction with CO yields quantitatively the compounds $[M_2(tDcp)(CO)_2(PR_3)_2]$ and $[M_2(cDcp)(CO)_2(PR_3)_2]$ (M = Rh, Ir; R = Ph, OPh, OMe). A single CO absorption was observed in the infrared spectra of these

compounds, which is consistent with a CO *trans*-O-structure, related to that found for the mononuclear [Rh(pic)(CO)(PPh$_3$)] (pic = 2-carboxypyridine) [18].

Conclusions

The ligands cDcp^{2-} and tDcp^{2-} differ markedly in their dinucleating properties. With the former the coordination ability of the second chelate is drastically reduced when one chelate has been formed, as a result of the repulsive interaction between the two carboxylate groups, whereas the ligand tDcp^{2-} readily forms dinuclear species. Neither ligand gave characterizable dinuclear tetracarbonyl species similar to those reported for dinucleating five member ring dicarboxyazolates. The lower basicity of the pyrazine ligands may be responsible for this difference.

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