Inorganica Chimica Acta, 141 (1988) 169–171

Synthetic Routes to Rhodium(III) Corrolates

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(Received July 10, 1987)

The extremely rich chemistry of porphyrins has developed a large interest in other tetrapyrrolic macrocycles [1]. One of the most interesting among them is corrole which contains an 18 electron π system, thus maintaining an aromatic character.

The direct link between the A and D pyrrole rings leads to a deformation effect on the macrocycle so that it cannot have a complete planar structure although the hybridization of carbon atoms at the 1- and 19-positions is considered to be sp^2 [2]. The presence of three amino nitrogens could ease the formation of metal(III) corrolates, however their chemistry has not been widely investigated as yet.

The first synthesis of metal corrole complexes dates back to 1965 [3], but, as far as rhodium complexes are concerned, the only example reported in the literature is an out of plane dicarbonyl rhodium(I) derivative obtained by reaction of dichlorotetracarbonyldirhodium with free corrole in chloroform [4].

The purpose of the present work was to synthesize rhodium corrolates with the metal atom lying in the macrocycle plane in order to compare the behaviour of such complexes with that of the related porphyrin systems [5, 6].

The totally symmetric octamethyl-biladiene-a,c dihydrobromide has been chosen as a precursor for the preparation of metallocorrolates in order to obtain simply and easily assignable NMR spectra.

We now report the first examples of rhodium(III) correlates bearing one or two axial ligands.

Experimental

IR spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer as nujol mulls. NMR spectra were recorded on a Bruker WP 80 SY instrument as C_6D_6 solutions with tetramethylsilane (TMS) as internal standard. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer as diethyl ether or tetrahydrofurane solutions.

Hydrated rhodium trichloride was purchased from Engelhardt S.p.A. and used as received. Dichlorotetracarbonyldirhodium was prepared following the procedure reported by McCleverty and Wilkinson [7]. 1,19-dideoxy-2,3,7,8,12,13,17,18-octamethylbiladiene-a,c dihydrobromide (BD) was prepared following the procedure reported for the 3,6-dimethyl-hexaethyl derivative as well as octamethylcorrole [3]. All solvents (Farmitalia) were reagent grade and were used without further purification.

Synthesis of [RhcorroleLL'] Complexes

(a) $L = PPh_2Me, PPh_3, AsPh_3, NEt_3; L' = -$

Hydrated rhodium trichloride (1 mmol), sodium acetate (10 mmol) and L (2 mmol) are dissolved in 150 ml of methanol and refluxed for 15 min. BD (1, 2 mmol) is added to the dark brown solution and the mixture is further refluxed for 3 h. The solution colour turns from green to dark red. The solvent is evaporated under vacuum and the residue extracted (soxhlet) with diethyl ether. The dark red ethereal solution is concentrated to about 10 ml and n-hexane (50 ml) is added. Complexes precipitate as dark red powders. Analytically pure products can be obtained by column chromatography on grade I type T basic alumina (eluant: Et_2O) although such purification procedure leads to extensive decomposition.

(b) $L = NHMe_2; L' = -$

Hydrated rhodium trichloride (1 mmol) and corrole (1.2 mmol) are refluxed, under nitrogen, in *N,N*-dimethylformamide (100 ml) for 2 h. The solvent is evaporated under vacuum and the residue chromatographed on a Florisil column eluting with diethyl ether. The crude product can be recrystallized from diethyl ether/n-hexane 1:2.

(c) $L = PPh_3; L' = CO$

Dichlorotetracarbonyldirhodium (1 mmol), sodium acetate (10 mmol) are dissolved in methanol (150 ml) and refluxed for about 10 min. BD (1.2 mmol) is added and the solution kept refluxing for one hour. On addition of PPh_3 (1.2 mmol) the solution turns to dark red. The solvent is evaporated under vacuum and the residue worked up as in procedure (a).

(d) L = L' = t-butylisocyanide; benzylisocyanide

(Triphenylphosphine)octamethyl-corrolato rhodium(III) (200 mg) is dissolved in diethyl ether (50 ml) and excess of isocyanide is added. The solution is stirred, under a nitrogen atmosphere, for 1 h. The solvent is evaporated under vacuum and the residue column chromatographed on Florisil eluting with diethyl ether. Recrystallization from diethyl ether/n-hexane 1:2 affords pure products.

0020-1693/88/$3.50

TABLE I. Elemental Analyses for [RhcorroleLL′] Complexes

L	L′	C(%)		H(%)		N(%)	
		Calc.	Found	Calc.	Found	Calc.	Found
PPh_2Me		66.65	66.05	7.00	6.75	7.75	7.40
PPh_3		69.95	69.70	5.50	5.65	7.25	6.90
PPh_3	CO	69.00	68.70	5.30	5.25	7.00	7.10
$AsPh_3$		66.20	66.00	5.20	5.25	6.85	6.45
NEt_3		64.80	65.00	6.90	6.95	11.45	11.20
$NHMe_2$		62.70	61.80	6.15	5.90	12.60	12.35
t-buNC	t-buNC	65.65	65.30	6.70	6.50	12.40	12.35
BzNC	BzNC	70.60	69.95	3.85	3.65	11.50	11.20

TABLE II. Spectral Properties for [RhcorroleLL′] Complexes

L	L′	λ_{max} (nm)	IR (cm^{-1})		^1H NMR (ppm)			
			ν(CO)	ν(NC)	5,15 CH	10 CH	Pyr Me	L
PPh_2Me		550 410			9.49(s, 2H)	9.45(s, 1H)	3.53(s, 6H) 3.49(s, 6H) 3.39(s, 12H)	6.87–6.20(m, 6H) 4.39–4.15(m, 4H) 1.94(d, 6H), J(PH) = 12 Hz)
PPh_3		550 400			9.39(s, 2H)	9.41(s, 1H)	3.45(s, 6H) 3.39(s, 6H) 3.33(s, 12H)	6.62–6.38(m, 9H) 4.71–4.45(m, 6H)
PPh_3	CO	554 404	1985		9.09(s, 2H)	9.14(s, 1H)	3.42(s, 6H) 3.35(s, 6H) 3.27(s, 12H)	6.96–6.52(m, 9H) 4.65–4.35(m, 6H)
$AsPh_3$		562 532 400			9.40(s, 2H)	9.48(s, 1H)	3.41(s, 12H) 3.33(s, 12H)	6.89–6.35(m, 9H) 4.81–4.72(m, 6H)
NEt_3		580 566 400			9.22(s, 2H)	9.06(s, 1H)	3.65(s, 6H) 3.52(s, 6H) 3.48(s, 12H)	−2.12(t, 9H) −3.54(q, 6H)
$NHMe_2$		566 531 400			9.23(s, 6H)	9.04(s, 1H)	3.67(s, 6H) 3.55(s, 6H) 3.49(s, 12H)	−3.37(d, 6H) −5.80(br,m, 1H)
t-buNC	t-buNC	574 564 410		2200	9.96(s, 2H)	9.74(s, 1H)	4.04(s, 6H) 3.91(s, 6H) 3.81(s, 12H)	−0.96(s, 9H)
BzNC	BzNC	578 566 410		2215	10.00(s, 2H)	9.79(s, 1H)	4.12(s, 6H) 3.96(s, 6H) 3.87(s, 12H)	7.04–6.83(m, 6H) 4.62–4.45(m, 4H) 2.08(s, 4H)

All complexes gave satisfactory elemental analyses (see Table I). Spectral properties are reported in Table II.

Results and Discussion

The synthesis of novel rhodium(III) corrole derivatives has been achieved by means of three different procedures.

The first synthetic method involves cyclization of octamethylbiladiene with hydrated rhodium trichloride in the presence of a ligand, such as a phosphine, in a buffered methanolic solution. Neutral pentacoordinated corrolates are thus obtained in good yields.

Although the electronic spectrum of the reaction mixture demonstrates that cyclization of the biladiene and formation of metallocorrolate occurs even in the absence of these ligands, all our efforts to isolate the axially unsubstituted rhodium corrolate were unsuccessful.

Square planar cobalt(III) corrolates have been isolated, but the stabilizing effect of a coordinated triphenylphosphine ligand on such complexes has been previously observed by other authors [8]. The behaviour of rhodium closely resembles that of cobalt in this respect, and it appears to be even more sensitive to the presence of axial ligands.

When dichlorotetracarbonyldirhodium is used instead of rhodium trichloride, in the same experimental conditions, in plane rhodium(III) corrolate of formula [Rhcorrole(CO)(PPh_3)] is obtained. In this complex the coordination sphere of the metal atom is complete and carbon monoxide occupies the sixth position.

The last synthetic procedure is an extension of the 'classic' Adler's method for the metallation of porphyrins [9]. Thus corrole reacts with hydrated rhodium trichloride in *N,N*-dimethylformamide leading to decarboxylation of the solvent and incorporation of one molecule of dimethylamine in the resulting metal complex, following a pathway already observed in the case of porphyrins [10].

This latter synthetic procedure is the only one by which we achieved metallation of a preformed corrole ring.

Pentacoordinated rhodium corrolates easily react with isocyanides, at room temperature, like their analogous cobalt complexes; however, in this case, we do not observe a simple substitution reaction of the axial ligand but the formation of bis-isocyanides derivatives [Rhcorrole($CNR)_2$].

In the IR spectra of these complexes the stretching absorptions of the coordinated isocyanides fall at 2200 cm^{-1} when R = t-butyl, and at 2215 cm^{-1} when R = benzyl. Their energies are lower than those of the corresponding bands in the spectra of the related bis-isocyanide rhodium(III) porphyrinates. This is probably due to the higher electronic density on the rhodium atom induced by the corrole ring, thus enhancing the back donation from the filled d orbitals of the metal to the antibonding ones of the ligand.

The same effect is observed in the IR spectrum of [Rhcorrole(CO)(PPh_3)]: the carbonyl stretching appears as a sharp band centered at 1985 cm^{-1} and is thus 100 cm^{-1} lower than the corresponding band in the spectrum of [RhTPP(CO)Cl] [11].

As far as the ligands resonances are concerned, ^1H NMR spectra show a strong upfield shift. The similarity of spectral properties between corrolates and porphyrinates demonstrates, again, the aromatic character of the corrole ring. The upfield shift can then be explained in terms of the anisotropic effects due to the macrocycle ring current.

The resonances of the *meso* protons at the 5-, 10- and 15-positions appear as two signals 2:1 in the spectra of rhodium corrolates; their relative intensity is reversed when the axial ligands are triphenylphosphine or triphenylarsine.

Modifications of the *meso* protons signals in the NMR spectra of metalloporphyrinates have been attributed to concentration effects or, obviously, to conformational equilibria [12]. In the case of rhodium corrolates, spectra recorded between 300 and 340 K, in a concentration range between 10^{-4} and 10^{-2} M, are identical. The variation of intensity of the resonances of the *meso* protons in the case of [Rhcorrole(PPh_3)] and [Rhcorrole($AsPh_3$)] can then be explained as a contribution of the shielding effect of the phenyl rings of the axial ligands to that of the macrocycle.

Further investigations on the reactivity and on the spectroscopic properties of rhodium corrolates are in progress.

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