

Nucleophilic Substitution Reactions of *o*-Catechols with Iridium(III) Carbonyl Complexes: Novel Series of Functionalized Ir(III) Complexes

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Complexes of $\text{Ir}(\text{CO})\text{X}_2\text{Y}(\text{PPh}_3)_2$: $\text{X} = \text{Y} = \text{I}, \text{Cl}$; $\text{X} = \text{I}, \text{Y} = \text{Cl}$; and $[\text{Ir}(\text{CO})(\text{CH}_3)(\text{CH}_3\text{CN})(\text{PPh}_3)_2]^+$ undergo nucleophilic substitutions with *o*-catechols, yielding a variety of carbonyl-Ir(III)-*o*-catecholato species. Following a preliminary investigation using tetrabromopyrocatechol and pyrocatechol as the reacting ligands, a new series of carbonyl-Ir(III)-(amine- and carboxyl-substituted)-*o*-catecholates of the type $[\text{Ir}(\text{CO})\text{X}(1,2\text{-O}_2\text{C}_6\text{H}_3\text{-4-R})(\text{PPh}_3)_2]$; $\text{R} = \text{CH}_2\text{CH}_2\text{NH}_2$, $\text{X} = \text{I}, \text{CH}_3$; $\text{R} = \text{CO}_2\text{H}$, $\text{X} = \text{CH}_3$; $\text{R} = \text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, $\text{X} = \text{I}$ have been prepared and characterized by elemental analysis, and IR and NMR spectra.

The stability of the complexes and the anchoring potentiality of the functionalized derivatives toward a variety of complementary functionalized organic species have been investigated by preparing amide-substituted-*o*-catecholato species.

Introduction

Covalently anchoring transition metals to organic structures of biological interest has been recently achieved by the use of organometallic compounds having a free organic function [1–3]. A specific application of such complexes is metallo-immunoassay (MIA), in which stable transition metal complexes, anchored to bioinorganic molecules, undergo *in vitro* immunological reactions [1, 3, 4].

We have recently reported the preparation and characterization of a series of stable functionalized tetracoordinated palladium(II) and platinum(II) *o*-catecholato complexes [5, 6]. The presence of the free amine or carboxyl function in the *o*-catecholato ligand was found to be a potential tool for covalently coupling either simple organic molecules [6] or

more elaborate organic structures (such as derivatives of estrone, estradiol and testosterone), conveniently functionalized in different positions of the steroid molecule [3].

The encouraging results obtained so far for the Pd(II) and Pt(II) *o*-catecholato species [3, 6] have prompted us to extend our investigations to the preparation of other functionalized *o*-catecholato complexes within the VIII group, which, being coordinatively saturated, may satisfy the requirement of stability necessary in biological fluids.

Six-coordinated iridium(III) and rhodium(III)-carbonyl-*o*-catecholato complexes have been prepared in the last decade by oxidative addition reaction of *o*-quinone with square planar d^6 complexes of formula $[\text{M}(\text{CO})\text{X}(\text{PPh}_3)_2]$, $\text{M} = \text{Rh}, \text{Ir}$; $\text{X} = \text{halogen}$ [7–9]. This method was limited to the synthesis of *o*-catecholates from *o*-quinones with high oxidation potentials, such as tetrahalo-*o*-quinones.

To the best of our knowledge, nucleophilic substitution reaction of *o*-catechols on coordinatively saturated octahedral complexes has been reported only in the case of iridium(III)-nitrosyl complexes [10] and ruthenium(II)-biscarbonyl complexes [11, 12].

The alternative synthetic procedure, starting from high oxidation state metal complexes, is independent from the quinone oxidation potential or from the nature of the complex itself. Therefore it may offer the possibility of preparing specific *o*-catecholato species.

In the present work our attention has been focused on the preparation of iridium(III)-carbonyl-*o*-catecholato adducts, these being usually more stable than their rhodium(III) analogues [9]. Preliminary nucleophilic substitution reactions using tetrabromopyrocatechol and pyrocatechol, as the reacting ligands, have been carried out in order to find the optimal reaction conditions and to avoid incidental interferences caused by the presence of a third organic function in the ligand. These two

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TABLE I. Analytical Data for Carbonyl-Iridium(III)-*o*-Catecholato Complexes and their Amide Derivatives. L = PPh₃; R = Ph; R' = CH₂CH₃.

No.	Compound	Yield %	Found (Calcd.) %			
			C	H	N	P
1	Ir(CO)I(1,2-O ₂ C ₆ Br ₄)L ₂	72	39.5(39.6)	2.7(2.3)		4.8(4.8)
2	Ir(CO)Cl(1,2-O ₂ C ₆ Br ₄)L ₂	31	42.9(42.9)	2.6(2.5)		5.3(5.1)
3	Ir(CO)(CH ₃)(1,2-O ₂ C ₆ Br ₄)L ₂	63	44.3(44.6)	2.8(2.8)		5.7(5.4)
4	Ir(CO)I(1,2-O ₂ C ₆ H ₄)L ₂	56	52.2(52.7)	3.4(3.5)		6.1(6.3)
5	Ir(CO)(CH ₃)(1,2-O ₂ C ₆ H ₄)L ₂	53	61.2(60.9)	4.5(4.3)		6.9(7.1)
6	Ir(CO)I(1,2-O ₂ C ₆ H ₃ -4-CH ₂ CH ₂ NH ₂)L ₂	54	52.7(52.8)	3.5(3.8)	1.5(1.4)	
7	Ir(CO)Cl(1,2-O ₂ C ₆ H ₃ -4-CH ₂ CH ₂ NH ₂)L·CH ₂ Cl ₂	35	44.3(44.6)	3.7(3.5)	1.2(1.8)	
8	Ir(CO)I(1,2-O ₂ C ₆ H ₃ -4-CH ₂ CH ₂ CO ₂ H)L ₂	33	52.8(52.5)	3.9(3.6)		6.2(5.9)
9	Ir(CO)(CH ₃)(1,2-O ₂ C ₆ H ₃ -4-CH ₂ CH ₂ NH ₂)L ₂	68	60.8(60.6)	4.6(4.6)	1.5(1.5)	
10	Ir(CO)(CH ₃)(1,2-O ₂ C ₆ H ₃ -4-CO ₂ H)L ₂	39	58.6(59.2)	4.1(4.1)		6.7(6.8)
11	Ir(CO)I(1,2-O ₂ C ₆ H ₃ -4-CH ₂ CH ₂ COHNCH ₂ R)L·3/2CHCl ₃	51 ^a	41.8(41.4)	3.4(3.0)	1.6(1.3)	
12	Ir(CO)I(1,2-O ₂ C ₆ H ₃ -4-CH ₂ CH ₂ NHCOCH ₂ R)L·1/2CHCl ₃	27 ^a	45.2(45.4)	3.7(3.3)	1.6(1.5)	
13	Ir(CO)(Cl)(1,2-O ₂ C ₆ H ₃ -4-CH ₂ CH ₂ NHCOR')L·2CH ₂ Cl ₂	53 ^a	42.4(43.0)	3.1(3.5)	1.8(1.6)	
14	Ir(CO)I(1,2-O ₂ C ₆ H ₃ -4-CH ₂ CH ₂ NHCOR)L·2CH ₂ Cl ₂	48 ^a	41.4(41.8)	3.1(3.0)	1.6(1.4)	

^aBased on the metal functionalized catecholates.

catechols represent two extreme cases of electron withdrawing *o*-catecholato ligands. The stereochemistry of the products has been investigated by IR methods and the results compared with those obtained by other synthetic pathways.

In a second step, we have extended our investigation to the synthesis of carbonyl-Ir(III)-(amine- and carboxyl-substituted) *o*-catecholato complexes.

The reactivity of the coordinated organic ligands has been studied by preparing amide derivatives in accordance with classic organic procedures. Although mild conditions were used, displacement of a phosphine ligand in the products was observed.

Experimental

Apparatus

All the reactions were performed in an atmosphere of nitrogen, purified by passing through a column of R3-11 BASF deoxygenating catalyst and then drying over molecular sieves. The subsequent work-up of the reaction mixture was carried out in air. Infrared spectra were recorded with a Perkin-Elmer 180 (4000–180 cm⁻¹) instrument. The solid samples were run as KBr pellets, unless stated otherwise. Proton NMR spectra were obtained using a Varian EM 360 spectrometer with CDCl₃ as solvent and tetramethylsilane as internal standard. The elemental analyses were determined by the Micro-

analysis Laboratory of the Istituto di Farmacia dell'Universita di Pisa, Pisa, Italy.

Solvents and Chemicals

All the solvents were deoxygenated prior to use and transfers were carried out with the flexible needle or syringe technique. Benzene, diethyl-ether and hexane were purified by distillation over Na; tetrahydrofuran (THF) over LiAlH₄. Chlorinated solvents were purified as described in the literature [13].

N-Hydroxysuccinimide (NHS), N,N'-dicyclohexylcarbodiimide (DCC), 3,4-dihydroxycinnamic acid, 3-hydroxytyramine hydrobromide, pyrocatechol, tetrabromopyrocatechol (Aldrich reagent grade products); 3,4-dihydroxybenzoic acid (Fluka A.G. purum grade product) and phenylacetic acid (Merck-Schuchardt purum grade product) were used throughout. Propionylchloride (Merck-Schuchardt, purum grade product), benzylamine (Fluka A.G. Puriss.) and triethylamine (C. Erba R.P.E.) were distilled prior to use.

The complex [Ir(CO)(CH₃)I(CH₃CN)(PPh₃)₂]⁺ was prepared by addition of CH₃I to [Ir(CO)(CH₃-CN)(PPh₃)₂]⁺ [14] in CH₂Cl₂. Ir(CO)X₂Y(PPh₃)₂, X = Y = I, Cl; X = I, Y = Cl; were prepared as described in the literature [15].

Compounds 1–5, 9, 10

In a typical preparation, to 1 ml of a benzene solution containing 0.133 mmol of catechol, was added 1.064 ml of a methanolic solution containing a

TABLE 2. Selected IR Bands^a and NMR Data^b for the Carbonyl-Ir(III)-*o*-Catecholato Complexes and their Amide Derivatives.

Compound	$\nu(\text{C}\equiv\text{O})$ cm^{-1}	$\nu(\text{catecholato}$ skeletal bands) cm^{-1}	other absorptions cm^{-1}	NMR (τ)		
				C_6H_5	1,2- C_6H_3	other resonances
1	2042	1420, 1260 1231, 922				
2	2038	1430, 1260 1240, 925	320 ($\nu\text{Ir}-\text{Cl}$) ^c			
3	2018	1431, 1260 1238, 924		2.60(m)		9.08(t, CH_3)
4	2025	1474, 1265		2.65(m)	4.0–4.6(m)	
5	1998	1480, 1255		2.66(m)	4.2–5.1(m)	8.85(t, CH_3)
6	2020	1480, 1267	1566(σCNH)	2.6(m)	3.6–4.9(m)	7.2–7.9(m, CH_2CH_2)
7	2020	1480, 1265	1570(σCNH) 322($\nu\text{Ir}-\text{Cl}$) ^c	2.62(m)	3.7–4.4(m)	7.4–7.9(m, CH_2CH_2)
8	2020	1480, 1260	1700, 1560(CO_2H)	2.7(m)	3.9–4.9(m)	7.72(m, CH_2CH_2)
9	1992	1480, 1270	1570(σCNH)	2.65(m)	3.9–4.8(m)	7.4–8.0(m, CH_2CH_2) 8.83(t, CH_3)
10	1990	1480, 1284	1651, 1577(CO_2H)	2.56(m)	3.7–4.6(m)	8.80(t, CH_3)
11	2020	1480, 1265	1620, 1550(CONH)	2.57(m)	4.0–4.8(m)	5.68(d, OCNCH_2) 7.35–8.1(m, OCCH_2CH_2)
12	2020	1480, 1267	1640, 1565(CONH)	2.53(m)	3.8–4.7(m)	7.0(m, OCNCH_2) 6.2–7.05(m, OCCH_2 ; PhCH_2)
13	2020	1480, 1283	1670, 1565(CONH) 320($\nu\text{Ir}-\text{Cl}$)	2.62(m)	3.8–4.5(m)	6.6–7.1(m, $\text{OCNCH}_2\text{CH}_2$) 7.7(m, OCCH_2); 1.1 (m, CH_3)
14	2020	1480, 1270	1670, 1565(CONH)	2.58(m)	3.9–4.6(m)	6.5–7.3(m, $\text{OCNCH}_2\text{CH}_2$)

^aKBr pellets. ^bIn CDCl_3 . ^cNujol mulls.
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two-fold amount of potassium hydroxide. The benzene–methanolic solution was syringed to 0.089 mmol of the appropriate parent complex, suspended in 2 ml of benzene. The mixture was stirred at room temperature for 6 h, and filtered. MeOH was added to the filtrate and on concentration at reduced pressure microcrystals precipitated, which were washed with MeOH, ether, and dried *in vacuo*.

Compounds 6, 7, 8

In a typical preparation, to 2 ml of a benzene solution containing 0.356 mmol of the appropriate catechol, was added 2.84 ml of a methanolic solution containing two-fold amount of potassium hydroxide. The benzene–methanolic solution was then syringed to 0.356 mmol of $\text{Ir}(\text{CO})\text{I}_3(\text{PPh}_3)_2$ suspended in 2 ml of benzene. The mixture was stirred in the dark at room temperature for 20 h. The resultant dark-red suspension was partially concentrated at reduced pressure and the brown product collected on a suction filter was washed with a few ml of benzene. From the filtrate and the benzene washing a small amount of unreacted $\text{Ir}(\text{CO})\text{I}_3(\text{PPh}_3)_2$ was recovered. The product was therefore washed thoroughly with H_2O , dissolved in CH_2Cl_2 , dried over MgSO_4 and filtered through a small deactivated neutral alumina column. The solvent was removed at reduced pressure and the brown solid thus

obtained was washed with hexane and dried *in vacuo*. For compound 8 an additional washing with $\text{CH}_3\text{CO}_2\text{H}$ 0.5 N, followed by H_2O , was necessary before treatment with MgSO_4 , in CH_2Cl_2 .

Compounds 11, 12

These were prepared as described for the palladium and platinum *o*-catecholato analogues [3, 6]. Purification of the crude reaction product was performed in this case by column chromatography with deactivated neutral alumina, eluting with CHCl_3 . The dark brown eluate yielded, on evaporation of the solvent, a brown solid, which was washed with *n*-hexane and dried *in vacuo*.

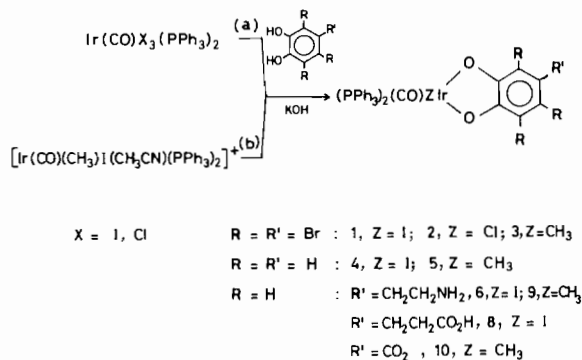
Compounds 13, 14

In a typical preparation, 1 ml of a THF solution containing 0.128 mmol of the appropriate acyl chloride, followed by 1 ml THF solution containing a stoichiometric amount of Et_3N , were syringed to 0.107 mmol of 7 or 8, partially dissolved in 3 ml of THF, at 0 °C. The solution was stirred for 20 min, at 0 °C and then for 1 h at room temperature. The solvent was removed at reduced pressure and the product washed with H_2O and dried *in vacuo*. The solid, dissolved in CH_2Cl_2 , was chromatographed on a silica gel column with CH_2Cl_2 containing 1% MeOH.

The eluate was evaporated to dryness and the brown solid washed with petroleum ether (40–60).

Results and Discussion

Six-coordinated Ir(III) complexes of formula $\text{Ir}(\text{CO})\text{X}_3(\text{PPh}_3)_2$ where $\text{X} = \text{I}, \text{Cl}$, and the cationic species $[\text{Ir}(\text{CO})(\text{CH}_3)\text{I}(\text{CH}_3\text{CN})(\text{PPh}_3)_2]^+$ undergo nucleophilic substitution reactions at ambient temperature with tetrabromopyrocatechol and pyrocatechol in the presence of a base in accordance with eqns. (1 a,b):



Analytical data, selected infrared bands and NMR data for the catechol iridium adducts 1–5 are reported in Table I and Table II. The typical strong IR absorptions in the 1480–1430 cm^{-1} region and at ca. 1260 cm^{-1} are consistent with the formation of *o*-diolato species [3, 5, 6, 9–12].

A first comparison between the two types of catecholato ligands is outlined by an average 20 cm^{-1} decrease in the carbonyl stretching frequencies, when pyrocatechol replaces tetrabromopyrocatechol in complexes having the same σ donor ligand. The lower values for the carbonyl absorptions of the pyrocatecholato complexes, reflect the reduced electron withdrawing power of the pyrocatecholato ligand in respect to the tetrabromopyrocatecholato, as has been observed in other cases [5, 6, 9, 11, 12, 16].

Octahedral tetrahalocatecholato complexes of Ir(III), having a *cis*-phosphine geometry (form A), are the sole products obtained by the direct oxidative addition method of tetrahalo-1,2-benzoquinones on Vaska's complex [9]. On the other hand, carbonyl-tetrahalocatecholato complexes of Ir(III) with a *trans*-phosphine arrangement (form B) have been achieved with a multi-step reaction by Blake *et al.* [17]. The possibility of obtaining *cis*- or *trans*-phosphine arrangement is therefore dependent upon the synthetic pathway.

It should be pointed out that in our case the parent complexes $\text{Ir}(\text{CO})\text{X}_3(\text{PPh}_3)_2$, $\text{X} = \text{halogen}$ and $[\text{Ir}(\text{CO})(\text{CH}_3)\text{I}(\text{CH}_3\text{CN})(\text{PPh}_3)_2]^+$ have been prepared by oxidative addition reactions of X_2 and CH_3I with

trans- $[\text{Ir}(\text{CO})\text{X}(\text{PPh}_3)_2]$ and *trans*- $[\text{Ir}(\text{CO})(\text{CH}_3\text{CN})(\text{PPh}_3)_2]^+$ respectively. It is known that in solution, *trans* addition on planar tetracoordinated Ir(I) complexes takes place with the two phosphines remaining in the *trans* arrangement [15].

If interconversion from a *trans*- to a *cis*-geometry does not take place during the nucleophilic substitution of the halide ligands, and as isomers A and B are also known not to interconvert [17], the carbonyl-Ir(III)-*o*-catecholates (1–5) obtained in our reaction conditions should result in form B.

A criterion for distinguishing between *cis*- and *trans*-phosphine geometries was outlined by Mastin [18] for tetracoordinated complexes and extended by Blake *et al.* [17] to octahedral complexes. The principle in the latter case is based on the intensity of an absorption at $520 \pm 5 \text{ cm}^{-1}$ in the infrared spectra of Rh(III) and Ir(III) carbonyl-tetrahalo-*o*-catecholato-bistriphenylphosphine complexes. A weak intensity is indicative for *trans* phosphine ligands, a strong intensity for *cis* phosphine ligands.

In our case a small shoulder in the 520–550 cm^{-1} region was observed for 1–5.

Moreover, positions of the $\nu(\text{C}\equiv\text{O})$ below 2045 cm^{-1} are in support of isomer B. Such values are in fact consistent with these groups being *trans* to a σ donor ligand or to a diolato ligand, and not *trans* to strong π -acceptor ligands (*e.g.* PPh_3), for which higher values are usually expected [17, 19]. In addition, the $\nu(\text{Ir}-\text{Cl})$ at 320 cm^{-1} for 2 is also in agreement with the chlorine being *trans* to oxygen, but not to phosphorus [17, 20].

Functionalized-*o*-catecholato-iridium(III) complexes have been prepared under the same reaction conditions in accordance with equations (1a, b). Experimental data for compounds 6–10 (Tables I and II), compared with those of the unfunctionalized iridium(III)-*o*-catecholates reported herein (1–5), and of the functionalized Pd(II)- and Pt(II)-*o*-catecholates [5, 6], are in accordance with a coordination mode *via* the phenolic groups of the catechol. NMR resonances for the H-catechols of the Ir(III) complexes 4–10 are slightly shifted to higher fields in respect of the values found for the Pd(II)- and Pt(II)-*o*-catecholates (Table II). Furthermore, the IR values of the $\nu(\text{C}\equiv\text{O})$ for the alkyl-substituted-*o*-catecholato complexes, which are lower in respect to those of the tetrabromopyrocatecholato analogues, are in agreement with the minor electron withdrawing property of the chelating ligand, as mentioned previously.

A second comparative study of the tetrabromopyrocatechol ligand and the less electron-withdrawing catechols, such as pyrocatechol or the 4-alkyl-substituted catechols, has been shown by the following results. While tetrabromopyrocatechol reacted with $\text{Ir}(\text{CO})\text{X}_3(\text{PPh}_3)_2$, where X is either iodide or chloride and with $[\text{Ir}(\text{CO})(\text{CH}_3)\text{I}(\text{CH}_3\text{CN})(\text{PPh}_3)_2]^+$

yielding the respective stable carbonyl-Ir(III)-*o*-catecholato complexes 1–5, no carbonyl-Ir(III)-*o*-catecholato derivative was achieved in the reaction of pyrocatechol with Ir(CO)Cl₃(PPh₃)₂. IR investigation of the crude product, isolated from the latter reaction, showed the loss of the carbonyl group. Broad IR absorptions at 3400 cm⁻¹ and at 1580 cm⁻¹, which are indicative of the presence of an aquato ligand, have been observed for the crude product in addition to the two strong IR absorptions at 1480, 1225 cm⁻¹ characteristic of an *o*-catecholato moiety. The results obtained in this case suggest the formation of species analogous to those achieved by an irreversible addition of H₂O to unsaturated pentacoordinate Ir(III)-*o*-catecholates [17].

The failure of obtaining a carbonyl-iridium(III)-pyrocatecholato complex, starting from Ir(CO)Cl₃(PPh₃)₂ can be explained by the greater ability as a leaving group of the iodide ligand in respect to the chloride together with the minor electron-withdrawing power of the pyrocatechol. This is supported also by the fact that, when Ir(CO)Cl₂(PPh₃)₂ was used as the parent complex, retention of the chloride ligand in the product (compound 7) was observed. It should be pointed out that in this case dissociation of a phosphine ligand occurred and the formation of a five-coordinated species (which strongly retained a solvent molecule) was obtained. Easy dissociation of a phosphine ligand has been also reported recently in work on oxidative addition reactions leading to the formation of six-coordinated Ir(III) complexes [21].

Although there are so far no kinetic data in order to enter into a detailed study on the possible intermediates originated during the course of the nucleophilic substitution reaction with *o*-catechols, it may be mentioned that in the resulting 4-alkyl substituted-*o*-catecholato complexes the iridium–phosphorous bond appeared characteristically labile.

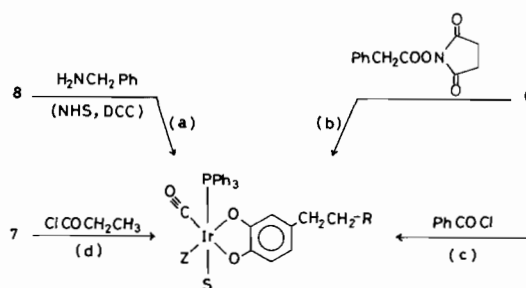
On the other hand, when Ir(CO)Cl₂(PPh₃)₂ was treated with two fold amounts of AgPF₆ in CH₃CN and subsequently reacted either with tetrabromopyrocatechol, pyrocatechol or 4-alkyl-substituted catechol, displacement of the chloride as well as of the iodide occurred, yielding the six-coordinated species: compounds 1, 4 and 6 in about 80%, 80% and 45% yield respectively.

Although the use of AgPF₆ resulted in a faster reaction, favouring the elimination of both the two groups (Cl and I) mutually *cis* in the parent complex, interference by the presence of Ag⁺ in the reaction with tyramine was observed.

Anchoring properties

Following the same procedure outlined for the functionalized Pd(II)- and Pt(II) complexes [3, 6] and by using acylchlorides as the coupling reagents,

some of the (amino- or carboxyl-functionalized)-iridium(III) complexes have been transformed into their respective amide derivatives in accordance with eqns. (2a–d).



- (a) Z = I : 11, R = COHNCH₂Ph
 (b) : 12, R = H₂CCOCH₂Ph
 (c) : 14, R = H₂CCOPh
 (d) Z = Cl : 13, R = H₂CCOCH₂CH₃

IR and NMR measurements of the crude product, isolated from the reaction of 8 with N-hydroxy-succinimide (NHS) in the presence of N,N'-dicyclohexylcarbodiimide (DCC), (eqn. 2a), are in support of the formation of an active ester derivative (*i.e.* absorptions at 1810w, 1780m, 1740vs cm⁻¹ and NMR resonance at $\tau = 7.2$ ppm (s, OCCH₂CH₂CO) [3, 6]). IR spectra of the TLC pure products 11–14 show, in addition to the general IR pattern of the carbonyl-Ir(III)-*o*-catecholato moiety, new absorptions of medium intensity at *ca.* 1670 cm⁻¹ and 1560 cm⁻¹, indicative of amide bonds in *o*-catecholato complexes [3, 6]. On the other hand, while new NMR resonances characteristic of the anchored moiety have been observed, NMR integrations and analytical data (Tables I and II) indicate the displacement of a phosphine ligand in all the amide derivatives. As has been mentioned previously for compound 7, the potentially facile release of a phosphine ligand in the six-coordinated-*o*-catecholato complexes may have been enhanced by the presence of stabilizing nucleophilic reagents in the coupling reaction.

Since the IR absorptions of individual substituted catechols occur in the 550–520 cm⁻¹ region, assignment of a phosphine geometry for complexes 6, 8–10 was not feasible by the method reported by Blake *et al.* [17]. Nevertheless, evidence for an analogous *trans*-phosphine arrangement is supported by the lower IR values of the $\nu(\text{C}\equiv\text{O})$, as it has been discussed previously. Moreover, the achievement of five-coordinate species may be also a consequence of a *trans*-phosphine geometry of the parent complexes. Strong π -acceptor ligands (such as phosphines) are known to labilize one another, when mutually *trans*. The retention of the positions of the IR

carbonyl absorptions at *ca.* 2020 cm^{-1} for all the amide derivatives 11–14, and of the $\nu(\text{Ir}-\text{Cl})$ at 320 cm^{-1} for 13, suggest that these groups remain *trans* to the *o*-diolato ligand after the coupling reaction.

In conclusion the satisfactory yields obtained in the preparation of the amide derivatives clearly stress the distinguished reactivity of the new series of functionalized-iridium(III)-catecholates.

The possibility of anchoring these complexes to more elaborate organic structures, such as derivatives of estrogens [3], is currently being investigated.

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