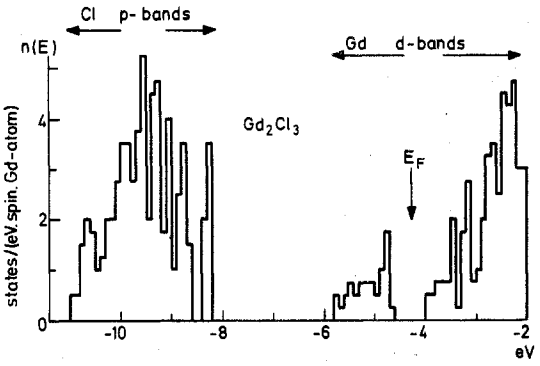

Figure 10. Calculated density of states for a single chain taken from the Gd_2Cl_3 structure. Metal–metal bonding states between −5.8 and −4.6 eV are separated from higher d bands by a 0.7 eV semiconducting gap.

a full band structure calculation would be inconveniently large. Instead we concentrate on the one-dimensional electronic structure of a single chain, $[(Gd_4Cl_8)^{2-}]_n$. This contains the backbone of metal octahedra from one of the chains in the unit cell and the chlorine atoms capping triangular side faces of the octahedra, together with the four bridging chloride ions which are shared between two chains in the full structure (Figure 9). Our single chain preserves the local environment of each metal atom in the real crystal.

The resulting density of states in the Cl p bands and Gd d bands shows the interesting form in Figure 10. The three lowest d bands hybridize to much lower energies than the remaining seventeen, and it is the double occupation of these three low-lying bands that stabilizes the structure. A gap of 0.7 eV separates the highest occupied and lowest unoccupied states of the single chain, and we might therefore expect to find a semiconducting gap which is only slightly smaller in the real crystal. The measurement of the conductivity along the axis of a one-dimensional metal is of course notoriously difficult, but certainly no metallic conduction has been observed in Gd_2Cl_3.[6,7] Very recent experimental evidence from photoemission and from temperature-dependent conductivity studies provide further support that Gd_2Cl_3 is a semiconductor.[39]

No simple covalent bond picture of the three lowest bands appears to be possible in this case. Only one Gd–Gd approach (the 3.35-Å edge shared by adjoining octahedra) per formula unit is perceptibly shorter than the others (~3.8 Å), and the upper two filled bonding states per octahedron are complicated hybrids which cannot be assigned simply to atom pairs.

Conclusion

We conclude that an LCAO calculation of the one-electron band structure can give a good quantitative account of metal–metal bonding in transition-element and rare-earth condensed-cluster halides. For each of the compounds considered the Fermi level lies at or near a deep minimum in the density of states, separating metal–metal bonding states from higher d states. It is the occupation of the metal–metal bands that stabilizes the rather unusual crystal structures formed by some of these compounds, especially Gd_2Cl_3, where the linear chain of edge-sharing distorted Gd octahedra provides a semiconducting gap of 0.7 eV in what one might have expected[7] to be a d band continuum.

Registry No. NbI_4, 13870-21-8; Nb_3I_8, 12030-01-2; ZrCl, 14989-34-5; ScCl, 17775-46-1; GdCl, 40603-48-3; Gd_2Cl_3, 12506-69-3.

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Contribution from the Department of Chemistry, Università della Calabria, 87030 Arcavacata (CS), Italy

Metal Catecholato Complexes: A Source for Metallo-Labeling Antigens

OTTAVIO GANDOLFI,* GIULIANO DOLCETTI,* MAURO GHEDINI, and MICHAEL CAIS

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New Pd(II) and Pt(II) carboxyl- and amine-substituted catecholato complexes of the type $L_2M(1,2\text{-}O_2C_6H_3\text{-}4\text{-}R)$ (L = $^1/_2$ bpy, M = Pt, R = CO_2H; L = $^1/_2$ COD, M = Pt, R = CO_2H or $CH_2CH_2CO_2H$; L = PPh_3, M = Pd or Pt, R = $CH_2CH_2NH_2$) have been prepared and characterized by elemental analysis and IR and NMR spectra. The possibility of forming a covalent bond with organic molecules through the free organic function of metal catecholates, for metallo-immunoassay (MIA) application, has been tested by preparing several amide derivatives. Thus bis(phosphine)palladium(II) and -platinum(II) carboxyl-substituted catecholates have been converted to their respective active esters and subsequently reacted with amines. Amide derivatives were obtained also with the new palladium(II) and platinum(II) amine-substituted catecholates, by reaction with phenylacetic active esters. All the isolated products were characterized by elemental analysis and IR and NMR spectra. A different chemical behavior has been found in the case of the bis(phosphine)palladium(II) catecholato complexes, in which displacement of phosphine occurred in the presence of amines.

Introduction

In the last decade there has been a continuous expansion in the work of metal complexes associated to biological derivatives for medical, pharmacological, and biological applications.

Moreover, a recent nonisotopic system, designated as metalloimmunoassay (MIA),[1] had opened an interesting new dimension for the use of transition-metal atoms in their form of organometallic compounds. The feasibility of MIA has been demonstrated,[2] and its principle is based on the replacement of radioisotopes with organometallic compounds as labeling agents for in vivo and in vitro immunological reactions. A necessary chemical requirement for MIA is the formation of stable "tailor-made" metallo antigens. As already mentioned,[2] one approach for coupling transiton metals to organic mole-

* To whom correspondence should be addressed: O.G., Università della Calabria; G.D., Institute of Chemistry, University of Udine, 33100 Udine, Italy.

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0020-1669/80/1319-1785$01.00/0

cules of immunological importance can be achieved by anchoring the metals directly into the biological molecule. An example can be provided by the important and extensive work on palladium(II) and platinum(II) complexes with nucleobases and nucleosides in the frame of metal coordination complexes in cancer chemotherapy.[3-12] Recently, the synthesis of several complexes with steroids was accomplished by using (π-allyl)palladium chemistry.[13-16] Nevertheless, since biological molecules anchored to metal complexes have to undergo immunological reactions in vitro and/or in vivo, the reactivity with nucleophiles[17] of the π-allyl complexes and their possible oxidation to allylic alcohols[18] may discourage their use in MIA. A second approach for the synthesis of metallo antigens can be achieved by covalently coupling specific functionalized organometallic complexes with appropriate haptens containing complementary organic functions. Thus, sulfonyl- and amine-substituted η^5-cyclopentadienyl complexes of Mn, Fe, and Co, or amine- and carbonyl-substituted 4,5-pentanedionato complexes of Cr, Rh, and Pt anchored to functionalized steroids, have been prepared in this way.[1]

In the present work we have investigated the possibility for MIA applications of a new series of stable amine- and carboxyl-functionalized palladium(II) and platinum(II) catecholato complexes. Substituted catecholato ligands with carboxylic and amine functions, provided their corresponding complexes are still capable of binding organic molecules and satisfy the condition of stability in biological fluids, may offer an interesting source for metallo-labeling antigens.

Pursuing the work initiated in our laboratory, we report here an extension of our study on the preparation and characterization of new palladium and platinum carboxyl-substituted catecholato complexes. Bis(phosphine)palladium(II) and -platinum(II) amine-substituted catecholates have been prepared in high yield, and their spectrophotometric data provided useful information for the palladium and platinum catecholato complexes investigated so far. Some of the compounds, which appeared more suitable for MIA applications, have been tested by preparing their respective active esters and consequently forming their corresponding amide-substituted catecholato derivatives.

Experimental Section

Apparatus. All the reactions were performed in an atmosphere of nitrogen which had been purified by passing it through a column of R3-11 BASF deoxygenating catalyst and then drying it over molecular sieves. The subsequent workup of the reaction mixture was carried out in air. Infrared spectra were recovered with a Perkin-Elmer 180 instrument. The solid samples were run as KBr pellets. Proton NMR spectra were obtained by using a Varian EM 360 spectrometer with $CDCl_3$ as solvent and tetramethylsilane as internal standard. The elemental analyses were determined by the Microanalysis Laboratory of the Istituto di Farmacia of the University of Pisa, Pisa, Italy.

Solvents and Chemicals. All the solvents were deoxygenated prior to use, and the transfers were carried out with the flexible needle or syringe technique. Diethyl ether and hexane were purified by distillation over Na; tetrahydrofuran (THF) was purified by distillation over $LiAlH_4$. Chlorinated solvents were purified as described in the literature.[19]

N-Hydroxysuccinimide (NHS), *N*,*N*-dicyclohexylcarbodiimide (DCC), 3,4-dihydroxyphenylacetic acid, 3,4-dihydroxycinnamic acid, 3-hydroxytyramine hydrobromide (all 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. Propylamine and benzylamine (Fluka A. G. puriss. product and Aldrich reagent grade product, respectively) were distilled prior to use. The complexes $[M(PPh_3)_2Cl_2]$ (M = Pd,[20] Pt[21]), $[M(bpy)Cl_2]$ (M = Pd,[22] Pt[23]), and $[M(COD)Cl_2]$[24] (M = Pd, Pt) were prepared as described in the literature: complexes **1**–**6** as previously reported.[25]

Preparation of Pt(1,2-$O_2C_6H_3$-4-CO_2H)(bpy) (7). To a suspension of 0.34 mmol of $[Pt(bpy)Cl_2]$ in 2 mL of THF was added 4 mL of a methanolic solution containing 0.4 mmol of 3,4-dihydroxybenzoic acid and 1.2 mmol of potassium hydroxide. The mixture was stirred at room temperature for 60 h. After removal of the solvent at reduced pressure, the brown product was dissolved in H_2O and filtered from unreacted starting material. The product was precipitated with 0.5 N CH_3COOH and washed with H_2O and acetone. The product was insoluble in most organic solvents.

Preparation of Pt(1,2-$O_2C_6H_3$-4-R)(COD) (R = CO_2H (8), R = $CH_2CH_2CO_2H$ (9)). To a suspension of 0.27 mmol of $[Pt(COD)Cl_2]$ in 3 mL of THF was added 5 mL of an ethanolic solution containing a stoichiometric amount of the appropriate catechol and 0.8 mmol of potassium hydroxide. The mixture was stirred at room temperature for 20 h. After removal of the solvent at reduced pressure, the product was washed on a suction filter with a few milliliters of H_2O, 0.5 N CH_3COOH, and H_2O.

Workup of 8. The product was dissolved in CH_2Cl_2, and the solution was dried over $MgSO_4$ and filtered on a small silica-gel column (Kieselgel 60 Merck, 70–230 mesh ASTM); the solvent was removed at reduced pressure and the solid washed with ether.

Workup of 9. The product was directly dried in vacuo over $CaCl_2$ and washed with ether. The products were soluble in chlorinated solvents and slightly soluble in other polar solvents.

Preparation of M(1,2-$O_2C_6H_3$-4-$C_2H_4NH_2$)($P(C_6H_5)_3$)$_2$ (M = Pd (10), M = Pt (11)). To a suspension of 4 mmol of $[M(P(C_6H_5)_3)Cl_2]$ in 20 mL of THF and 20 mL of ethanol was added 50 mL of a methanolic solution containing a stoichiometric amount of 3-hydroxytyramine hydrobromide and a threefold amount of potassium hydroxide. The mixture was stirred at room temperature overnight (for **10**) and for 3 days (for **1**). A small amount of unreacted metal halide complex was recovered by filtration. After removal of the solvent at reduced pressure, the solid was washed with H_2O and dissolved in EtOH, and the solution was filtered and evaporated to dryness. The product was dissolved in methylene chloride, the solution was dried over $MgSO_4$ and filtered on a small silica-gel column, and the solid was crystallized from chlorinated solvent–hexane to give dark blue (**10**) and brown (**11**) crystals. Both products were soluble in chlorinated solvents, THF, ethanol, and acetone.

Preparation of the Amide Derivatives. (A) Metal Carboxyl-Substituted Catecholato Active Esters. In a typical preparation, a stoichiometric amount of DCC, dissolved in 2 mL of THF, was added

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Table I. Physical and Analytical Data for Palladium(II) and Platinum(II) Carboxyl- and Amine-Substituted Catecholato Complexes and Their Amide Derivatives (L = PPh_3, $R^1 = HNCH_2CH_2CH_3$, $R^2 = HNCH_2Ph$, $R^3 = COCH_2Ph$, COD = Cyclooctadiene, bpy = 2,2′-Bipyridine)

					% found (calcd)			
no.	compd	yield,[a] %	color	mp, °C	C	H	N	P
1	$Pd(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CO_2H)L_2\cdot 2C_6H_{14}$ [b]	88	dark brown	124				
2	$Pd(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CO_2H)L_2\cdot CH_2Cl_2$ [b]	86	dark brown	98				
3	$Pd(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CH_2CO_2H)L_2\cdot CH_2Cl_2$ [b]	71	brown	103				
4	$Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CO_2H)L_2$ [b]	81	yellow	251[c]				
5	$Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CO_2H)L_2\cdot{}^1/_2CH_2Cl_2$ [b]	90	yellow-brown	174				
6	$Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CH_2CO_2H)L_2\cdot{}^1/_2CH_2Cl_2$ [b]	94	orange-brown	172				
7	$Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CO_2H)(bpy)$	28	brown	224[c]	40.35 (40.56)	2.28 (2.39)	5.64 (5.57)	
8	$Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CO_2H)(COD)\cdot CH_2Cl_2$	23	bright yellow	198	35.69 (35.56)	2.29 (2.33)		
9	$Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CH_2CO_2H)(COD)$	70	bright yellow	187	42.20 (42.43)	4.39 (4.14)		
10	$Pd(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CH_2NH_2)L_2\cdot CH_2Cl_2$	66	dark blue	122	62.39 (62.35)	4.69 (4.73)	1.61 (1.61)	
11	$Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CH_2NH_2)L_2\cdot{}^1/_2CH_2Cl_2$	89	yellow-brown	142	52.30 (52.04)	3.76 (3.86)	1.40 (1.37)	
12	$Pd(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2COR^1)L_2\cdot{}^3/_2CH_2Cl_2$	14	brown	172[c]	60.69 (60.34)	4.80 (4.97)	1.74 (1.45)	
13	$Pd(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2COR^2)LR^2\cdot CH_2Cl_2$	34	brown	137[c]	60.18 (60.37)	4.97 (4.78)	3.40 (3.43)	4.19 (3.80)
14	$Pd(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CH_2COR^1)L_2\cdot CH_2Cl_2$	12	orange-brown	129	58.02 (58.76)	4.65 (4.80)	1.31 (1.28)	
15	$Pd(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CH_2COR^1)LR^1\cdot{}^1/_2CH_2Cl_2$	31	brown	80[c]	58.18 (58.21)	5.79 (5.50)	3.82 (4.06)	5.29 (5.18)
16	$Pd(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CH_2COR^2)LR^2\cdot CH_2Cl_2$	42	yellow-brown	117	59.78 (60.80)	5.09 (4.94)	4.38 (4.12)	4.09 (3.87)
17	$Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}COR^1)L_2\cdot{}^1/_2CH_2Cl_2$	45	yellow	142	58.43 (58.46)	4.49 (4.40)	1.67 (1.46)	
18	$Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}COR^2)L_2\cdot CH_2Cl_2$	46	yellow	114	58.22 (58.56)	4.38 (4.11)	1.68 (1.34)	
19	$Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2COR^1)L_2$	49	brown	126	60.00 (60.91)	4.64 (4.64)	1.44 (1.51)	
20	$Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2COR^2)L_2\cdot CH_2Cl_2$	75	yellow-brown	123	58.95 (59.92)	4.52 (4.24)	1.75 (1.32)	
21	$Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CH_2COR^1)L_2\cdot{}^1/_2CH_2Cl_2$	61	orange	120	58.50 (59.23)	4.74 (4.68)	1.41 (1.42)	
22	$Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CH_2COR^2)L_2$	68	orange	117	62.51 (63.16)	4.48 (4.55)	1.51 (1.42)	
23	$Pd(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CH_2NHR^3)L_2\cdot 3CH_2Cl_2$	15	dark brown	120	57.44 (57.19)	4.40 (4.41)	1.25 (1.21)	
24	$Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CH_2NHR^3)L_2\cdot{}^1/_2CH_2Cl_2$	75	yellow	160	60.96 (61.14)	4.03 (4.46)	1.37 (1.35)	

[a] Based on the metal-functionalized catecholate. [b] From ref 25. [c] Decomposition.

to a 13-mL THF solution containing 0.384 mmol of metal carboxyl-substituted catecholate containing a stoichiometric amount of NHS at 0 °C. The solution was stirred for 2 h at 0 °C and for a further 20 h at room temperature. The white precipitate formed in the reaction was filtered off and characterized as *N,N′*-dicyclohexylurea by comparison with an authentic sample. After removal of the solvent at reduced pressure, the product was dried in vacuo and dissolved in methylene chloride, and the solution was allowed to stand at 4 °C for 2 h. A small amount of white solid (a residue of *N,N′*-dicyclohexylurea) was removed by filtration; the solution was poured into a flask containing hexane and the mixture was evaporated to dryness. The product was washed with ether and characterized by the IR absorptions at 1810 w, 1780 m, and 1740 vs cm^{-1} and by the appearance of an NMR singlet at $\tau = 7.2$ ($OCCH_2CH_2CO$).

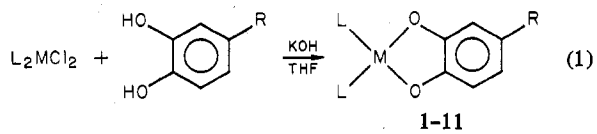
(B) Reaction with Amines: Compounds 12–22. In a typical preparation, to a 5-mL THF solution containing 0.3 mmol of a metal carboxyl-substituted *o*-catecholato active ester was added a 3-mL THF solution containing 0.5 mmol of amine. The reaction mixture was stirred at room temperature for 6 h. After filtration, the solvent was removed at reduced pressure and the product kept in vacuo for 2 h. The solid was washed with H_2O, the solution was dissolved in CH_2Cl_2, dried over $MgSO_4$, and filtered, and the product was precipitated with hexane. The platinum derivatives were further chromatographed on a silica-gel column by eluting with CH_2Cl_2/CH_3OH (19:1).

(C) Reaction of 10 and 11 with Phenylacetic Active Ester: Compounds 23 and 24. In a typical preparation, a 2-mL THF solution containing a stoichiometric amount of phenylacetic active ester, prepared with the same procedure as for the metal–active ester derivatives, was added to a 5-mL THF solution containing 0.2 mmol of **10** or **11** and 0.8 mmol of triethylamine. After being stirred overnight at room temperature, the reaction mixture was filtered and the solution evaporated to dryness. The solid was washed with H_2O, dried in vacuo, and chromatographed on a silica-gel column, by eluting with CH_2Cl_2/CH_3OH (24:1).

Results and Discussion

Preparation of New Metal-Functionalized Catecholates. In a recent communication[25] we have reported that the interaction between bis(phosphine)palladium(II) and -platinum(II) halide complexes with carboxyl-substituted catechols in the presence of a base leads to the formation of stable *o*-catecholato species.

In accordance with the same procedure, new palladium(II) and platinum(II) catechol complexes (**7–11**) of the type $[L_2M(cat)]$, in which L is an uncharged ligand as reported below, were obtained following the general preparation in reaction 1.



(1)

1–11

M = Pd, L = Ph_3P: **1**, R = CO_2H; **2**, R = CH_2CO_2H; **3**, R = $CH_2CH_2CO_2H$; **10**, R = $CH_2CH_2NH_2$
M = Pt, L = Ph_3P: **4**, R = CO_2H; **5**, R = CH_2CO_2H; **6**, R = $CH_2CH_2CO_2H$; **11**, R = $CH_2CH_2NH_2$
M = Pt, L = $^1/_2$ bpy: **7**, R = CO_2H
M = Pt, L = $^1/_2$ COD: **8**, R = CO_2H; **9**, R = CH_2CO_2H

When a third organic function such as a carboxyl group or an amine group is present in the reacting catechol, the availability of an extra binding site can potentially lead to a metal–carboxylato or to a metal–nitrogen bond formation, respectively.[26–32] The possibility that an O-metalation with the carboxyl group should occur instead, therefore, leading to a metal–carboxylato bond (as either mono- or bidentate coordination), can be excluded on the basis of IR and NMR measurements.[25–27,33–37]

Physical properties, analytical data, selected infrared bands, and NMR data for the catechol–metal complexes are reported in Tables I and II and compared with those of the bis(phosphine)palladium(II) and -platinum(II) carboxyl-substituted catechols.[25]

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Table II. Selected IR Bands[a,b] and NMR Data[c] for Palladium(II) and Platinum(II) Carboxyl- and Amine-Substituted Catecholato Complexes and Their Amide Derivatives

compd	ν(C=O), cm^{-1}	ν(C-O-H) and ν(C-N-H) bending, cm^{-1}	ν(catecholato) skeletal band, cm^{-1}	τ values					
				C_6H_5	$1,2\text{-}O_2C_6H_3$	$OCNCH_2$	CH_3	NH	other resonances
1[d]	1670 m	1563 m	1282 s	2.45–2.75 (m)	3.3–3.65 (m)				
2[d]	1650 m	1560 m	1290 s	2.4–2.65 (m)	3.1–3.6 (m)				
3[d]	1620 m	1555 m	1270 s	2.45–2.65 (m)	3.3–3.8 (m)				
4[d]	1655 m	1568 m	1285 s	2.45–2.75 (m)	3.65 (m)				
5[d]	1660 s	1570 m	1270 s	2.45–2.75 (m)	3.64 (m)				6.6 (s, $OCCH_2$)
6[d]	1720 m	1570 m	1270 s	2.45–2.75 (m)	3.74 (m)				7.4 (q, $OCCH_2CH_2$)
7	1680 m	1585 m	1285 s	*e*	*e*				*e*
8	1665 s	1575 m	1270 s		3.4 (m)				4.1–5.25 (m, HC=CH), 7.2–7.8 (m, CH_2)
9	1718 s	1580 m	1277 s		3.35–3.35 (m)				4.5–5.4 (m, HC=CH), 6.85–7.85 (m, $OCCH_2CH_2$, CH_2)
10		1558 w	1269 s	2.1–2.9 (m)	3.8 (m)			*f*	7.35 (m, NCH_2CH_2)
11		1560 m	1270 s	2.71 (m)	3.79 (m)			9.44 (s)	7.35 (m, NCH_2CH_2)
12	1665 m	1568 w	1273 m	2.2–2.3 (m)	3.2–4.2 (m)	7.0 (m)	9.1 (m)	*f*	8.6 (m, CH_2)
13	1637 m	1570 m	1283 m	2.1–2.9 (m)	2.9–3.8 (m)	5.7 (m)		*f*	
14	1640 m	1565 m	1280 s	2.1–2.9 (m)	3.1–3.6 (m)	6.8 (m)	9.15 (t)	*f*	8.6 (m, CH_2)
15	1646 m	1571 w	1278 s	2.1–2.9 (m)	3.1–3.6 (m)	6.8 (m)	9.15 (t)	*f*	8 6 (m, CH_2)
16	1642 m	1570 w	1281 s	2.2–2.9 (m)	3.1–3.8 (m)	5.8 (m)		*f*	
17	1649 m	1572 m	1285 s	2.7 (m)	3.58 (m)	6.7 (m)	9.1 (t)	9.3 (s)	8.58 (m, CH_2)
18	1651 m	1570 w	1285 s	2.72 (m)	3.6 (m)	5.62 (d)		*f*	
19	1656 m	1570 m	1276 s	2.68 (m)	3.7 (m)	6.88 (q)	9.1 (t)	9.18 (m)	6.58 (s, $OCCH_2$), 8.68 (m, CH_2)
20	1648 w	1571 m	1278 s	2.76 (m)	3.72 (m)	5.65 (d)		9.1 (m)	6.52 (s, $OCCH_2$)
21	1632 m	1564 m	1272 s	2.72 (m)	3.68 (m)	6.83 (m)	9.1 (t)	9.17 (m)	7.4 (q, $OCCH_2CH_2$), 8.65 (m, CH_2)
22	1650 m	1560 w	1271 s	2.7 (m)	3.7 (m)	5.63 (d)		9.22 (s)	7.37 (q, $DCCH_2CH_2$)
23	1640 s	1559 w	1270 s	2.75 (m)	3.55–4.3 (m)	7.5 (m)		9.15 (s)	6.6 (m, CH_2)
24	1650 s	1562 w	1270 s	2.8 (m)	3.6–4.2 (m)	7.45 (m)		9.18 (s)	6.65 (m, CH_2)

[a] As KBr pellets. [b] Other particular infrared absorptions are reported in the text. [c] In $CDCl_3$ with Me_3Si as internal standard. [d] From ref 25. [e] Low solubility in $CDCl_3$. [f] See text.

In the polyolefin case the formation of alkoxy halides of general formula $[(diene\text{-}OR)_2M_2X_2]$, where M = Pd or Pt, from reaction of their corresponding $[(diene)MX_2]$ complexes in alcoholic solution in the presence of a base, has been largely recognized in the literature.[38-40] Nevertheless, in the case of (1,5-diene)platinum dihalides, drastic conditions such as treatment with anhydrous sodium carbonate in boiling methanol are usually necessary in order to achieve the dimeric species bis(8-alkoxycyclooct-4-enyl)di-μ-halo-diplatinum.[38] When (cyclo-1,5-octadiene)platinum dichloride was allowed to react at room temperature in THF solution with a stoichiometric amount of potassium catecholato salt, the diene–metal–catechol derivative, instead of the alkoxide derivative, was obtained. IR absorptions in the carbonyl region (at 1680 cm^{-1} for **8** and at 1718 cm^{-1} for **9**) are indicative for the presence of uncoordinated carboxyl group of the ring-substituted catechol.[25,27,31] Moreover, the two strong absorptions at ca. 1275 cm^{-1} and at ca. 1494 cm^{-1} are indicative of coordinated *o*-catechol.[25,41-49] No NMR resonances due to ethoxy protons, as a consequence of a possible interaction with the solvent, have been observed. The retention of the double bond relative to a π-olefin–metal system is indicated by the olefinic proton resonances at τ = 4.5–5.6.

On the other hand, because of the greater reactivity of the analogous palladium cyclooctadiene complexes, partial decomposition occurred with $[(COD)PdCl_2]$, and the majority of the starting complex was recovered unchanged. Attempts to achieve the analogous palladium catecholato derivative were carried out by first forming the intermediate $[(COD)PdS_2^{2+}][BF_4^-]_2$, where S = solvent, with $AgBF_4$ and then reacting the dicationic complex with catechol in methylene chloride solution, but no formation of the expected product was obtained, even when pyrocatechol was used as the reacting ligand.

When $[(bpy)PtCl_2]$ was reacted with the series of carboxyl-substituted catechols, only the benzoic-substituted catecholato complex **7** was obtained, and it was in very low yield, as shown from the IR absorptions of the coordinated *o*-catechol and of the free carboxyl group (see Table II) and from the two bands at 768 and 724 cm^{-1} characteristic of a coordinated bpy.[50]

Although the reaction appeared to go also with other carboxyl-substituted catechols, as seen from the typical change in color from yellow to dark-brown, the products were unstable and a remarkable amount of starting $[(bpy)PtCl_2]$ was recovered. The minor acidity of the 3,4-dihydroxyphenylacetic acid and of the 3,4-dihydroxycinnamic acid, as catecholato ligands, may be responsible for the instability of their corresponding metal complexes.

A slight difference in the NMR spectra for the amine-substituted catechol complexes **10** and **11** should be pointed out. While compound **11** showed a slightly broad singlet for the amine protons (disappearing after addition of D_2O), not even a broad resonance for the amine protons was detected in the case of **10**. As already discussed,[25] intramolecular hydrogen interactions are very likely to occur with catecholato derivatives. It is well-known that the most indicative infrared region of catechol coordination is the region from 1200 to 1500 cm^{-1}, in which two characteristic bands at 1450–1480 cm^{-1} and at about 1250 cm^{-1} occur.[41,42,45-48] This is in agreement with our data, also in the case of palladium and platinum amine-substituted catecholato derivatives **10** and **11** (very strong absorptions at ca. 1270 cm^{-1} and an increase of the ν(phosphine) at 1480 cm^{-1} due to the ν(C–O) stretching frequency of the *o*-diolato). Although the band at 1480 cm^{-1} was not always visible, because of overlap with the ν(phosphine), strong absorptions for the COD and the bpy derivatives at ν = 1491, 1495, and 1494 cm^{-1} for **7**, **8**, and **9**, respectively, were observed.

No absorptions in the 1460–1310-cm^{-1} region were detected for compounds **7–9**—which is in accordance with the absence of a $\nu(C{=}O)_{sym}$ stretching vibration of a coordinated carboxyl group and is in favor of the free carboxylic system.[25,26,28,33-37] In addition, for compounds **10** and **11**, a weak infrared absorption assigned to the ν(N–H) stretching vibration was detected at 3290 cm^{-1}, which is usually too high a value for coordinated amines.[37,51] The IR and NMR results for the new (cyclooctadiene)- and (bipyridyl)metal carboxyl-substituted *o*-catecholato complexes **7–9** and for the bis(phsophine)metal amine-substituted *o*-catecholato complexes **10** and **11** draw further support for the formation of *o*-catecholato species having a free organic function and, therefore, exclude the formation of a metal–carboxylato bond or a nitrogen–metal bond, as discussed in our previous communication.[25]

Anchoring Properties of Functionalized Metal Catecholates. In order to test the capability of the series of metal-functionalized *o*-catecholato complexes to couple with organic molecules having a complementary organic function, we transformed some of the carboxyl-substituted derivatives into their respective active esters, by reaction with *N*-hydroxysuccinimide (NHS) in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC). The criteria of choice for the complexes was mostly dictated by reasons of stability and solubility. As mentioned before, the bpy comples **7** appeared unstable during the crystallization operations. On the other hand, although the stability was in favor of the (cyclooctadiene)metal *o*-catecholato complexes **8** and **9**, their low solubility in polar solvents discouraged a further application. The general preparation reaction for the bis(phosphine)palladium(II) and -platinum(II) carboxyl-functionalized *o*-catecholato active ester intermediates is reported in eq 2.

IR spectra of the isolated products show absorptions in the carbonyl region at 1810 w, 1780 m, and 1740 vs cm^{-1}, typical for active ester derivatives, and no variation of the *o*-catecholato frequencies is detected. NMR spectra show a new resonance at τ = 7.2 (s, $OCCH_2CH_2CO$), which is shifted from τ = 7.5 for the free NHS. The carbonyl absorptions of the active ester derivatives disappeared after reaction with amines. Similar to their functionalized precursors, almost all the palladium (**12–16**) and platinum derivatives (**17–22**) retain

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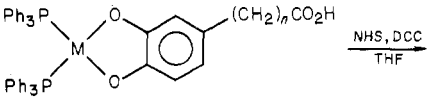
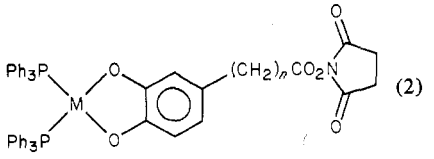


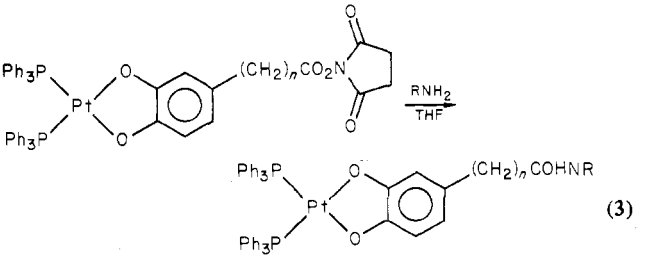
1-6



(2)

M = Pd: **1**, $n = 0$; **2**, $n = 1$; **3**, $n = 2$
M = Pt: **4**, $n = 0$; **5**, $n = 1$; **6**, $n = 2$

tenaciously chlorinated solvents, used during the workup, and, therefore, they were characterized as solvates. Physical and analytical data are given in Table I and spectroscopic data in Table II. It is noteworthy to underline that no remarkable variation of the strong infrared absorption at ca. 1275 cm^{-1}, due to the catecholato skeletal vibration, was observed, therefore indicating the retention of the catecholato ligand. The isolated products showed two new IR absorptions at approximately 1650 and 1570 cm^{-1}, which are usually characteristic of a ν(C=O) amide and of a ν(C–N–H) bending mode. In the case of the platinum derivatives,[17-22] elemental analysis and proton NMR integration are consistent with the formation of 1:1 adducts in accordance with eq 3. Whereas the platinum



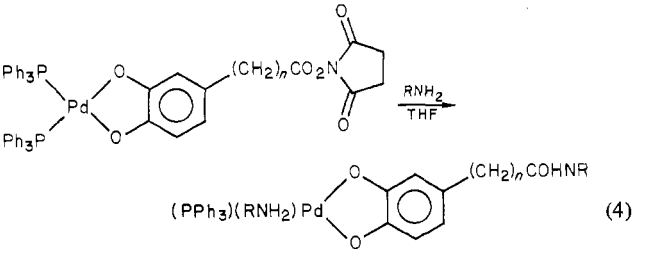
(3)

17-22

R = $CH_2CH_2CH_3$: **17**, $n = 0$; **19**, $n = 1$; **21**, $n = 2$
R = CH_2Ph: **18**, $n = 0$; **20**, $n = 1$; **22**, $n = 2$

derivatives **17–22** were easily eluted through a Florisil or silica-gel column, difficult purification was encountered in the case of the palladium derivatives **12–16**. No matter the extent of deactivation of the chromatographic material used for the column purification, retention of the complex always occurred. Furthermore, the palladium derivatives could not be crystallized in order to improve purity, and they are reported as crude products. For the complexes **13**, **15**, and **16** proton NMR integrations showed a ratio of 1:2 phosphine:amine and are consistent with a loss of phosphine. Only in two experiments (preparation of **12** and **14**) were the expected products successfully isolated, although in very low yield, phosphine: amine being 2:1. In repetition of the synthesis of **12** and **14** and in all the other experiments, although equivalent IR spectra were obtained in all cases, an increase of the percentage of nitrogen and a decrease of the percentage of phosphorus were found.

It is well-known that palladium(II) complexes are more reactive than the corresponding platinum (II) species. Fast nucleophilic displacement by amines of different basicity of a variety of organic sulfides in complexes of the type *trans*-$[Pd(RSR')_2Cl_2]$ and the influence of their steric hindrance have been studied.[52] Easy ligand-exchange reactions have been found to occur even with (phosphine)palladium(II) complexes, and the tertiary phosphine rate displacement increases with the basicity of the phosphine itself.[53] Owing to the slight excess of amine used during the reaction, a monosubstitution of the triphenylphosphine with the amine was likely to occur, leading to complexes **13**, **15**, and **16** as shown in eq 4.

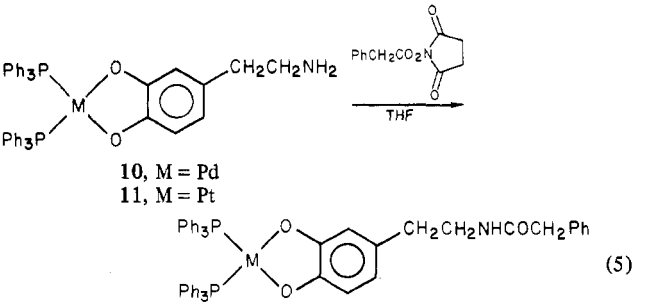


(4)

13, R = CH_2Ph, $n = 1$
15, R = $CH_2CH_2CH_3$, $n = 2$
16, R = CH_2Ph, $n = 2$

The formation of monophosphine–monoamine–palladium catecholato species **13**, **15**, and **16** is in accordance with spectroscopic and analytical data. No remarkable difference in the IR spectra was observed with respect to the platinum derivatives **17–22**, except for a slight increase in the ν(C–H) stretching absorption. Equivalent spectra were obtained also when complex **1** in the form of the active ester was reacted with the amines. Nevertheless, on this occasion, no pure product was obtained, analytical and NMR data showing only an increase of the amine moiety and a decrease of the phosphine ligand.

The formation of an amine–palladium coordination bond may explain also the strong interaction occurring during the chromatographic operations. On the other hand, amide derivatives **23** and **24** were easily obtained from the palladium(II) and platinum(II) amine-functionalized catecholato complexes **10** and **11** by reacting them with phenylacetic active ester, as is shown in eq 5.



(5)

23, M = Pd
24, M = Pt

IR and NMR spectra are consistent with the formation of the amide bond and the retention of the catecholato ligand. No remarkable difference was noticed between the platinum complex **24** and the palladium complex **23**, except for the very low yield obtained in the case of complex **23**, which is probably due to the loss during column chromatography purification.

Remarks on the Applicability for MIA. It is noteworthy to point out a few considerations on the choice of palladium(II) and platinum(II) functionalized *o*-catecholato complexes for metallo-labeling antigens. As has been already mentioned, reasons of solubility and stability may lead to the bis(phosphine)metal *o*-catecholato species **1–6**, **10**, and **11**. Relatively high yields were obtained in the case of the platinum derivatives **17–22** and **24**. Should it be possible to increase the yield in the case of the analogous palladium–amide–*o*-catecholato derivatives, the risk of phosphine displacement by electron-

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donor species during their preparation or, furthermore, in biological fluids, as is the case of immunological reactions, may discourage their use.

No chemical differences were observed when the acidity of the carboxyl-substituted catechol was varied or when the amine-substituted catechol was used as the chelating ligand. Therefore, the series of platinum *o*-catecholates may be an interesting source for an investigation on the only immunological changes in a series of similar metallo antigens.

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Registry No. **1**, 73296-00-1; **2**, 73296-01-2; **3**, 73296-02-3; **4**, 73308-29-9; **5**, 73296-03-4; **6**, 73296-04-5; **7**, 73296-05-6; **8**, 73296-06-7; **9**, 73296-07-8; **10**, 73296-08-9; **11**, 73296-09-0; **12**, 73308-30-2; **13**, 73296-10-3; **14**, 73296-11-4; **15**, 73296-12-5; **16**, 73296-13-6; **17**, 73296-14-7; **18**, 73296-15-8; **19**, 73296-16-9; **20**, 73296-17-0; **21**, 73296-46-5; **22**, 73296-47-6; **23**, 73296-48-7; **24**, 73296-49-8; $Pd(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CO_2N(COCH_2CH_2CO))(PPh_3)_2$, 73296-50-1; $Pd(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CO_2N(COCH_2CH_2CO))(PPh_3)_2$, 73323-94-1; $Pd(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CH_2CO_2N(COCH_2CH_2CO))(PPh_3)_2$, 73296-51-2; $Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CO_2N(COCH_2CH_2CO))(PPh_3)_2$, 73296-52-3; $Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CO_2N(COCH_2CH_2CO))(PPh_3)_2$, 73296-53-4; $Pt(1,2\text{-}O_2C_6H_3\text{-}4\text{-}CH_2CH_2CO_2N(COCH_2CH_2CO))(PPh_3)_2$, 73296-54-5; $CH_3CH_2CH_2NH_2$, 107-10-8; $PhCH_2NH_2$, 100-46-9; NHS, 6066-82-6; 1-[(phenylacetyl)oxy]-2,5-pyrrolidinedione, 23776-85-4; $Pt(bpy)Cl_2$, 13965-31-6; $Pt(COD)Cl_2$, 12080-32-9; $Pd(PPh_3)_2Cl_2$, 15604-37-2; $Pt(PPh_3)_2Cl_2$, 15604-36-1.

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520

Reactions of Imines with $(\mu\text{-}H)_2Os_3(CO)_{10}$. Competitive Addition and Abstraction of Hydrogen Atoms to and from an Iminyl Group

RICHARD D. ADAMS*[1] and JOHN P. SELEGUE

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$(\mu\text{-}H)_2Os_3(CO)_{10}$ was found to react with $C_6H_5(H)C{=}NCH_3$ in refluxing hexanes solution to produce the compounds $(\mu\text{-}H)_2(\mu\text{-}N(CH_3)CH_2C_6H_4)Os_3(CO)_9$, A, and $(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}C_6H_5C{=}NCH_3)Os_3(CO)_{10}$, B. A has been studied by IR, ^1H NMR, and X-ray crystallographic analyses. Crystal data: space group *Pbca* (D_{2h}^{15}, No. 61; a = 13.198 (4), b = 21.254 (6), c = 15.129 (5) Å, V = 4244 (4) Å^3, mol wt 943.88; Z = 8; ρ_{calcd} = 2.95 g cm^{-3}. For 2228 reflections ($F^2 \geq 3.0\sigma(F^2)$), collected by counter techniques, R_1 = 0.052 and R_2 = 0.057. A contains a triangular cluster of osmium atoms, nine terminal carbonyl ligands, two bridging hydride ligands, and a μ-$N(CH_3)CH_2C_6H_4$ ligand which bridges an *edge* of the cluster through the nitrogen atom and contains an ortho-metalated phenyl ring. The complex was evidently formed by the addition of one molecule of imine to the cluster, transfer of one hydrogen atom from the cluster to the iminyl group, loss of a carbonyl ligand, and ortho metalation of the phenyl ring. B was apparently formed by addition of the imine to the cluster, abstraction of a hydrogen atom from the iminyl carbon, and loss of H_2 from the cluster.

Introduction

The cluster hydride complex $(\mu\text{-}H)_2Os_3(CO)_{10}$ has now been shown to react and transfer hydrogen to a variety of unsaturated small molecules including alkenes,[2] alkynes,[3] carbon disulfide,[4] isocyanides,[5] arylisocyanates and isothiocyanates,[6] ketene,[7] and methylene.[8] We have presented evidence that indicates the hydrogen transfer can occur by either intramolecular or dissociative processes.[5] $(\mu\text{-}H)_2Os_3(CO)_{10}$[9,10] and $Os_3(CO)_{12}$[8,11,12] have also been shown to abstract hydrogen atoms readily from alkyl groups. It appears that there may be a delicate balance between hydrogen addition and hydrogen abstraction reactions in the chemistry of triosmium cluster compounds.

Imines are potential products of isocyanide reductions; thus in connection with our earlier work[5] we have investigated the nature of the reaction of imines with $(\mu\text{-}H)_2Os_3(CO)_{10}$. In this paper we wish to present the results of our studies of the reaction of the imine $C_6H_5(H)C{=}NCH_3$ with $(\mu\text{-}H)_2Os_3(CO)_{10}$. In this system we have found that both addition and abstraction reactions are important processes.

Experimental Section

Reactions were performed under a nitrogen atmosphere. Solvents were dried by refluxing over sodium–benzophenone and distilling just prior to use. $H_2Os_3(CO)_{10}$ was prepared by the method of Kaesz.[13] $C_6H_5(H)C{=}NCH_3$ was obtained commercially and vacuum distilled prior to use. $Os_3(CO)_{12}$ was obtained from Strem Chemicals Inc., Newburyport, Mass., and was used without further purification. Infrared spectra were recorded on a Perkin-Elmer 237 spectrometer and were calibrated with polystyrene. ^1H NMR spectra were recorded at the Southern New England High-Field NMR facility operating at 270 MHz. Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected.

Reaction of $H_2Os_3(CO)_{10}$ with $C_6H_5CH{=}NCH_3$. $H_2Os_3(CO)_{10}$ (0.296 g, 0.347 mmol), $C_6H_5CH{=}NCH_3$ (0.6 mL), and hexanes (40 mL) were stirred at reflux for 18 h. After being cooled to room temperature, the yellow solution was decanted and the residue (containing largely $Os_3(CO)_{12}$, 11.6 mg, 4%) was rinsed with ca. 20 mL of benzene. The combined supernatant and washings were chromatographed over silica gel. Hexanes eluted a yellow band which yielded 121.2 mg (36%) of $(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}C_6H_5C{=}NCH_3)Os_3(CO)_{10}$, B. Benzene eluted a yellow band which gave 42.0 mg (13%) of $(\mu\text{-}H)_2(\mu\text{-}N(CH_3)CH_2C_6H_4)Os_3(CO)_9$, A, as yellow crystals. A third band, eluted by THF, gave $Os_3(CO)_{12}$ (1 mg, 0.33%), benzaldehyde,

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