Titanium Ester Homoenolates: A Structural and Synthetic Study

Pier Giorgio Cozzi, Tommaso Carofiglio, and Carlo Floriani*

Section de Chimie, Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland

Angiola Chiesi-Villa and Corrado Rizzoli

Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, I-43100 Parma, Italy

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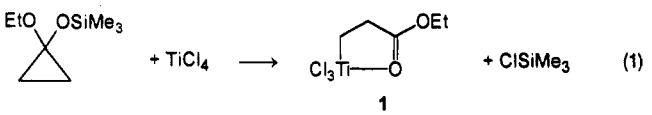
Summary: The synthesis and structural characterization of the novel monomeric titanium homoenolates [(Cl)$_2$(cp)Ti–CH$_2$CH$_2$COOEt] (2), and [(cp)$_2$Ti–CH$_2$CH$_2$COOEt]$^+$ZnI$_3^-$ (3; cp ≡ η^5-C$_5$H$_5$) are reported, along with a structural study on the well-known homoenolate [{(Cl)$_2$Ti–CH$_2$CH$_2$COOEt}$_2$(μ-Cl)$_2$] (1), which is dimeric both in solution and in the solid state. In both classes of titanium homoenolates we observed the presence of a five-membered metallacycle containing a titanium–carbon bond which is significantly longer in 3 than in 1. Crystallographic details: 1 is monoclinic, space group P2$_1$/c, with a = 8.889(2) Å, b = 11.266(2) Å, c = 11.040(2) Å, α = γ = 90°, β = 107.12(2)°, Z = 2, and R = 0.077; 3 is monoclinic, space group P2$_1$/n, with a = 11.814(2) Å, b = 12.084(3) Å, c = 15.182(2) Å, α = γ = 90°, β = 97.95(1)°, Z = 4, and R = 0.052.

While homoenolates are extremely valuable in metal-mediated organic synthesis,[1] some potential drawbacks to using them include (i) the occurrence of side reactions, such as the halogenation of monoaldol products, when titanium homoenolates are used, (ii) the low reactivity with substrates other than aldehydes, and (iii) the stereocontrol of the reactions. Tuning the reactivity and selectivity of the homoenolate functionality may be achieved by an appropriate use of a transition-metal fragment.

We first focused on the structural characterization of the well-known titanium homoenolate 1,[2] both in the solid state and in solution. It has two peculiar characteristics: it contains a Ti–C σ bond not supported by any conventional ancillary ligand, and it is made from a nonorganometallic precursor.



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The stability of 1[3] is ascribed to the intramolecular coordination of the ester group, leading to the production of a metallacycle.[4] Strongly coordinating molecules such as 2,2′-bipyridyl or THF led to the decomposition of 1 to give [TiCl$_3$(bpy)][5] and [TiCl$_3$(THF)$_3$], and a mixture of uncharacterized organic products. The dimeric nature of 1, as suggested by molecular weight determinations in solution,[5] was confirmed by an X-ray analysis. The centrosymmetric dimer is shown in Figure 1, while a selection of bond distances and angles is listed in Table I. The titanium achieves hexacoordination by sharing two chlorine atoms at distances significantly longer (Table I) than those with the terminal chlorines. A similar dimeric structure was found in some platinum β-ketone C-bonded complexes.[6] The metallacycle has the same structural characteristics found for the corresponding Sn(IV) derivative,[7] though the latter is not reactive with electrophiles.

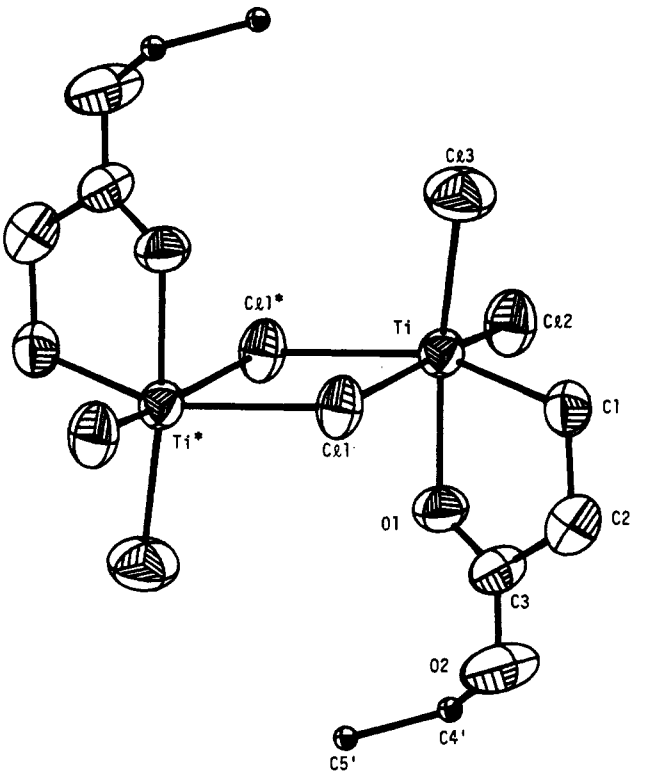

Figure 1. ORTEP view of complex 1 (30% probability ellipsoids).

The solid-state structure of 1 is directly related to the ^{1}H NMR spectrum (CD$_2$Cl$_2$), which shows two triplets at δ 3.43 and 2.78 ppm for the two nonequivalent methylene groups. The room-temperature ^{1}H NMR spectrum in

* To whom correspondence should be addressed.

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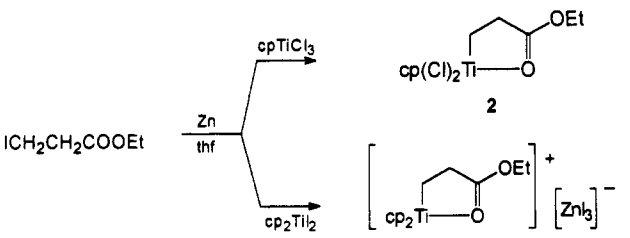
Table I. Relevant Bond Distances (Å) and Angles (deg) for 1[a]

	Distances		
Ti–Cl(1)	2.455(2)	O(2)–C(4)	1.496(20)
Ti–Cl(1)*	2.505(3)	O(2)–C(4)′	1.494(18)
Ti–Cl(2)	2.234(3)	C(1)–C(2)	1.503(15)
Ti–Cl(3)	2.214(4)	C(2)–C(3)	1.503(13)
Ti–O(1)	2.072(6)	C(3)–O(2)	1.283(14)
Ti–C(1)	2.081(9)	C(4)–C(5)	1.535(37)
O1–C(3)	1.235(15)	C(4)′–C(5)′	1.518(24)
	Angles		
O(1)–Ti–C(1)	78.1(3)	Cl(1)*–Ti–Cl(3)	91.1(1)
Cl(3)–Ti–C(1)	92.6(2)	Cl(1)*–Ti–Cl(2)	169.1(1)
Cl(3)–Ti–O(1)	170.2(2)	Cl(1)–Ti–C(1)	156.4(3)
Cl(2)–Ti–C(1)	102.5(2)	Cl(1)–Ti–O(1)	85.5(2)
Cl(2)–Ti–O(1)	87.4(2)	Cl(1)–Ti–Cl(3)	102.6(1)
Cl(2)–Ti–Cl(3)	97.4(1)	Cl(1)–Ti–Cl(2)	93.3(3)
Cl(1)*–Ti–C(1)	83.8(3)	Cl(1)–Ti–Cl(1)*	78.1(1)
Cl(1)*–Ti–O(1)	85.2(2)		

[a] Primes denote a transformation of $-x, -y, -z$.

toluene gave a sharp singlet at 2.67 ppm for the two methylene groups; this split into two triplets on cooling the solution to 199 K. The mechanism by which the two methylene groups become equivalent at room temperature in toluene is still in question.

A significant improvement in the nucleophilicity of the homoenolate functionality, along with a lowering of the chlorination side reaction, was attempted by replacing chlorines in **1** with alkoxo groups.[5] Although this strategy was successful, these were one-pot reactions, without isolation of the species involved. In this context we planned the use of cyclopentadienyl derivatives of titanium instead of $TiCl_4$, where chlorine is replaced by the more donating ligand cp. In addition, the cp ligand provides a better control on the coordination sphere of the metal and on the chemistry of the Ti–C functionality. The synthesis of cyclopentadienyl titanium homoenolates, however, cannot be performed *via* reaction 1. We found that the Rieke methodology[8] gave simple access to zinc homoenolates without using strong donor solvents or extreme reaction conditions[9] which are incompatible with the synthesis of cyclopentadienyl derivatives.



(2)

Complexes **2** and **3** have been fully characterized, including the X-ray analysis on **3**. Its structure is shown in Figure 2 with selected structural parameters listed in Table II. In both compounds **1** and **3** the metallacycle has a boat envelope conformation with the metal out of plane (0.281(1) and 0.589(3) Å in **1** and **3**, respectively). The formally higher coordination number of titanium in **3** leads to a significant elongation of the titanium–carbon bond

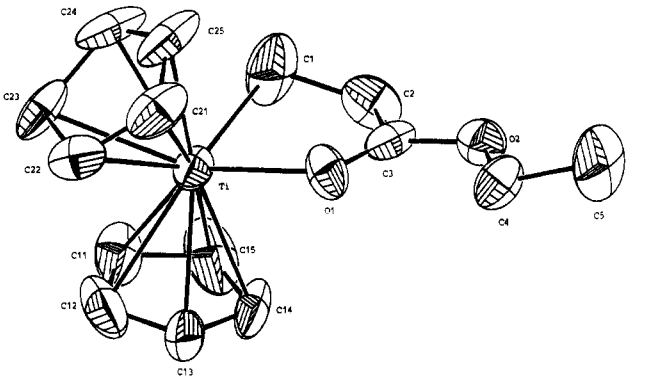


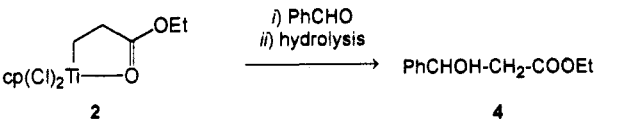
Figure 2. ORTEP view of complex **3** (30% probability ellipsoids).

Table II. Relevant Bond Distances (Å) and Angles (deg) for 3[a]

	Distances		
Ti(1)–cp(1)	2.04(4)	O(2)–C(3)	1.344(26)
Ti(1)–cp(2)	2.01(3)	O(2)–C(4)	1.470(28)
Ti(1)–O(1)	2.067(15)	C(1)–C(2)	1.483(39)
Ti(1)–C(1)	2.197(32)	C(2)–C(3)	1.504(33)
O(1)–C(3)	1.200(32)	C(4)–C(5)	1.470(36)
	Angles		
cp(1)–Ti(1)–cp(2)	134.2(15)	O(1)–Ti(1)–C(1)	78.4(9)

[a] cp1 and cp2 refer to the centroids of the cyclopentadienyl rings C11–C15 and C21–C25, respectively.

(2.197(32) *vs* 2.081(9) Å) in **1**. The IR band for the carbonylic function around 1600 cm^{-1} is diagnostic for the chelation of the ester group to titanium in complexes **1–3**. The very low solubility of **3** prevented inspection by NMR, while the ^1H NMR spectrum of **2** is neither solvent- nor temperature-dependent. Preliminary studies have shown that **2** reacts with carbonyl groups, leading to a C–C bond without side chlorination. The reaction of **2** with PhCHO was carried out both in the presence and in the absence of a Lewis acid ($BF_3{\cdot}Et_2O$), the major difference being the much higher speed of the reaction in the presence of the Lewis acid.



(3)

Compound **4** has been obtained in greater than 60% yield without any chlorinated side product.

Experimental Section

All operations were carried out under an atmosphere of purified nitrogen. All solvents were purified by standard methods and freshly distilled prior to use. NMR spectra were recorded on a 200-AC Bruker instrument.

Preparation of 1. $TiCl_4$ (19.52 g, 103 mmol) was added dropwise to a solution of 1-ethoxy-1-((trimethylsilyl)oxy)cyclopropane[10] (17.9 g, 103 mmol) in hexane (20 mL). The initially yellow mixture turned purple, and a microcrystalline solid formed. After the mixture was stirred for 30 min, the solid was filtered off, washed with hexane (50 mL), and dried under vacuum overnight (70%). Recrystallization by pentane extraction gave crystals suitable for X-ray analysis. ^1H NMR (CD_2Cl_2, room temperature): δ 4.68 (q, 2 H, Et, J = 7.13 Hz), 3.43 (t, 2 H, CH_2,

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Table III. Experimental Data for the X-ray Diffraction Studies

complex	1	3
formula	$C_{10}H_{18}Cl_6O_4Ti_2$	$C_{15}H_{19}I_3O_2TiZn$
M_r	504.8	725.3
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
cell params at 295 K[a]		
a, Å	8.889(2)	11.814(2)
b, Å	11.266(2)	12.084(3)
c, Å	11.040(2)	15.182(2)
α, γ, deg	90	90
β, deg	107.12(2)	97.95(1)
V, Å^3	1056.6(4)	2146.6(7)
Z	2	4
D_{calcd}, g cm^{-3}	1.605	2.244
$F(000)$	512	1344
linear abs coeff, cm^{-1}	15.24	57.89
cryst dimens, mm	0.23 × 0.35 × 0.47	0.21 × 0.28 × 0.38
diffractometer	Philips PW 1100	Rigaku AFC6S
radiation	[b]	[b]
2θ range, deg	6–54	6–50
scan type	$\omega/2\theta$	$\omega/2\theta$
scan width, deg	1.20 + 0.35 tan θ	1.42 + 0.30 tan θ
scan speed, deg min^{-1}	3–10	4–8
total no. of unique data	2316	4007
criterion for observn	$I > 2\sigma(I)$	$I > 2\sigma(I)$
no. of unique obsd data	1185	1433
$R = \sum\|\Delta F\|/\sum\|F_o\|$	0.077	0.052
$R_w = \sum w^{1/2}\|\Delta F\|/\sum w^{1/2}\|F_o\|$	0.079	0.057
GOF = $[\sum w\|\Delta F\|^2/(NO - NV)]^{1/2}$	4.03	1.91

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 25 carefully centered reflections chosen from diverse regions of reciprocal space. [b] Graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å).

J = 7.01 Hz), 2.78 (t, 2 H, CH_2, J = 7.02 Hz), 1.50 (q, 3 H, Et, J = 7.13 Hz). ^{1}H NMR (toluene, 199 K): δ 4.10 (q, 2 H, Et, J = 7.2 Hz), 3.10 (t, 2 H, CH_2, J = 7.05 Hz), 2.48 (t, 2 H, CH_2, J = 7.05 Hz), 1.09 (t, 3 H, Et, J = 7.2 Hz). ^{1}H NMR (toluene, 283 K): δ 4.10 (q, 2 H, J = 7.2 Hz), 2.67 (s, 4 H), 1.09 (t, 3 H, J = 7.2 Hz). ^{13}C NMR (CD_2Cl_2): δ 14.51, 44.59, 69.06, 101.55, 190.55. IR: 1590, 1607 (CH_2Cl_2) cm^{-1}.

Preparation of [IZnCH$_2$CH$_2$COOEt]. In a 500-mL flask under argon freshly cut lithium (1 g, 144.3 mmol) was added to a THF (50 mL) solution of naphthalene (19.97 g, 155.79 mmol). The mixture was stirred at room temperature until all of the lithium had reacted. Separately, $ZnCl_2$ (16.61 g, 72.92 mmol) was heated under vacuum to its melting point and cooled back to room temperature under argon. THF (150 mL) was then added, and the suspension was stirred at room temperature until the $ZnCl_2$ was completely dissolved. The solution was then transferred to a pressure-equalized dropping funnel and added over a period of 3 h to the lithium naphthalene solution. The activated zinc thus formed was separated from the mother liquor by decantation and washed with THF (3 × 150 mL). Finally 100 mL of freshly distilled THF was added and the zinc suspension utilized for the preparation of the zinc homoenolate. To a THF (100 mL) suspension of activated zinc (72.93 mmol), was added ethyl 3-iodopropionate (obtained from 3-chloropropionate by exchange with NaI) (16 g, 70.21 mmol) by syringe. The resulting yellow-brown suspension was stirred at room temperature for 2 h and then filtered into a pressure-equalized dropping funnel. The molarity of the organozinc solution obtained was determined by titration with EDTA. The zinc homoenolate was characterized by NMR. ^{1}H NMR (CD_2Cl_2): δ 4.16 (q, 2H, Et, J = 7.1 Hz), 3.97 (m, THF), 2.62 (t, 2H, J = 7 Hz), 1.96 (m, THF), 1.28 (t, 3H, Et, J = 7.1 Hz), 0.46 (t, 2H, J = 7 Hz). ^{13}C NMR: 183.03, 62.05, 33.82, 14.45, 6.28. IR (CH_2Cl_2) 1704 cm^{-1}.

Preparation of 2. A THF solution of [IZnCH$_2$CH$_2$COOEt] (22.2 mL, 20.62 mmol) was added dropwise to a benzene (85 mL) solution of cpTiCl$_3$ (4.52 g, 20.62 mmol). The resulting red solution was stirred for 2 h; then a red solid crystallized (56%). Anal. Calcd for $C_{10}H_{14}Cl_2O_2Ti$: C, 42.14; H, 4.85. Found: C, 42.05; H, 4.61. ^{1}H NMR (CD_2Cl_2): δ 6.60 (s, 5 H, cp), 4.43 (q, 2 H, Et, J. = 7.14 Hz), 3.06 (t, 2 H, CH_2, J = 6.50 Hz), 2.09 (t, 2 H, CH_2, J = 6.53 Hz), 1.39 (t, 3 H, Et, J = 7.14 Hz). ^{13}C NMR (CD_2Cl_2): δ 14.54, 44.74, 66.94, 79.79, 120.60, 188.07. IR: 1615, 1621 (CH_2CH_2) cm^{-1}.

Table IV. Atomic Coordinates (×10^4) for Complex 1[a]

atom	x/a	y/b	z/c	U_{eq}
Ti	963(2)	1056(1)	1382(1)	662(6)
Cl(1)	419(3)	904(2)	−925(2)	806(11)
Cl(2)	1861(3)	2914(2)	1447(2)	982(13)
Cl(3)	3274(4)	162(3)	2100(3)	1222(15)
O(1)	−1278(7)	1770(5)	979(6)	822(30)
O(2)	−3442(10)	2054(8)	1574(9)	1359(51)
C(1)	500(11)	897(8)	3116(7)	776(41)
C(2)	−1192(13)	1147(8)	3021(9)	869(46)
C(3)	−2027(13)	1686(9)	1756(10)	848(49)
C(4)	−4551(33)	2056(23)	258(17)	
C(5)	−4463(40)	3383(23)	−29(30)	
C(4)′	−4109(27)	2899(15)	508(15)	
C(5)′	−4974(26)	2002(16)	−478(19)	

[a] U_{eq} is in the form $^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$. The site occupation factors for primed and unprimed C(4) and C(5) atoms are 0.6 and 0.4, respectively.

Table V. Atomic Coordinates (×10^4) for Complex 3[a]

atom	x/a	y/b	z/c	U_{eq}
Zn(1)	682(2)	778(2)	4233(2)	682(9)
Ti(1)	5144(3)	−53(3)	2449(2)	640(13)
I(1)	282(1)	411(1)	2570(1)	791(6)
I(2)	1310(1)	−1089(1)	5123(1)	885(7)
I(3)	2084(1)	2350(1)	4683(1)	1046(8)
O(1)	3739(14)	323(12)	1529(10)	807(62)
O(2)	2426(13)	1596(13)	1046(10)	846(66)
C(1)	5112(23)	1762(26)	2527(21)	1313(151)
C(2)	3893(25)	2051(18)	2261(16)	980(110)
C(3)	3369(19)	1244(24)	1568(13)	714(98)
C(4)	1900(19)	781(20)	396(16)	861(102)
C(5)	1022(25)	1381(25)	−200(21)	1420(149)
C(11)	5408(25)	−424(35)	3950(15)	1034(141)
C(12)	5129(37)	−1436(32)	3560(26)	1342(189)
C(13)	4112(30)	−1351(33)	3182(22)	1237(167)
C(14)	3659(23)	−412(48)	3252(24)	1545(214)
C(15)	4493(44)	247(31)	3815(19)	1436(184)
C(21)	5760(24)	−775(31)	1172(18)	1040(134)
C(22)	6271(23)	−1394(18)	1896(20)	838(110)
C(23)	7015(17)	−737(27)	2453(15)	883(116)
C(24)	6184(23)	204(32)	1294(19)	1127(151)
C(25)	6893(26)	393(30)	2007(24)	1274(154)

[a] U_{eq} is in the form $^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

Preparation of 3. A THF solution of [IZnCH$_2$CH$_2$COOEt] (22.7 mL, 10.0 mmol) was added dropwise to a benzene (70 mL) solution of cp$_2$TiI$_2$ (4.79 g, 10.0 mmol). As the cp$_2$TiI$_2$ was consumed, 3 formed as a red crystalline solid (62%). Anal. Calcd for $C_{15}H_{19}I_3O_2TiZn$: C, 24.84; H, 2.64. Found: C, 24.80; H, 2.68. IR: ν(C=O) 1590 cm^{-1} (Nujol). When the reaction was carried out in CH_2Cl_2, 3 crystallized on standing for 2–3 weeks at −20 °C.

Reaction of 2 with PhCHO. 2 (0.25 g, 0.874 mmol) was added to a CH_2Cl_2 solution (10 mL) of PhCHO containing BF_3·Et$_2$O (0.874 mmol) cooled to −78 °C. The red suspension was warmed to room temperature and stirred for 2 h. The red solid disappeared, and a yellow solution formed. The solution was quenched with a $NaHCO_3$ solution (10 mL), and the crude product was purified by flash chromatography (n-hexane/Et$_2$O, 4:6) to give PhCHOH–CH$_2$CH$_2$COOEt (60%). ^{1}H NMR ($CDCl_3$): δ 7.37–7.30 (m, 5 H, Ph); 4.80 (t, 1 H, CH, J = 6.94, 3.65 Hz), 4.17 (q, 2 H, CH_2, J = 7.31 Hz), 2.46 (t, 2 H, CH_2, J = 6.94 Hz), 2.42 (d, 1 H, OH, J = 3.65 Hz), 2.17 (q, 2 H, CH_2, J = 6.94 Hz), 1.25 (t, 3 H, Me, J = 7.31 Hz). M$^+$: m/e 162.05 (see the corresponding lactone). We did not observe the formation of any chlorinated product.

Crystallography.[11] Intensity data were collected at room temperature on a single-crystal four-circle diffractometer. Crystal data and details are given in Table III. The reduced cells were

obtained with use of TRACER.[12] For intensities and background individual reflection profiles were analyzed.[13] Intensity data were corrected for Lorentz and polarization effects and for absorption.[14] The function minimized during the full-matrix least-squares refinement was $\Delta w|\Delta F|^2$ using a weighting scheme based on counting statistics. Anomalous scattering corrections were included in all structure factor calculations.[15b] Scattering factors for neutral atoms were taken from ref 15a for non-hydrogen atoms and from ref 16 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary.

Complex 1. The structure was solved by the heavy-atom method (Patterson and Fourier syntheses). Refinement was first done isotropically for all the non-H atoms, except for the carbon atoms (C(4) and C(5)) of the one independent ethyl group. This was found statistically distributed over two positions isotropically refined with site occupation factors of 0.6 and 0.4 for the primed and unprimed atoms, respectively. During the refinement a constraint was applied to the distances involved (O–C, 1.48(1) Å; C–C, 1.54(1) Å). The H atoms, except for those associated with the disordered carbons, were put in geometrically calculated positions and introduced in refinement as fixed contributors with isotropic U values fixed at 0.08 Å^2. The final difference map showed no unusual features, with no significant peak above the general background. Final atomic coordinates of the non-hydrogen atoms are given in Table IV.

Complex 3. The structure was solved by the heavy-atom method (Patterson and Fourier syntheses). Refinement was first done isotropically for all the non-H atoms. The H atoms were put in geometrically calculated positions and introduced in refinement as fixed contributors with isotropic U values fixed at 0.10 Å^2. The final difference map showed three residual peaks of about 1 e Å^{-3} close to the iodine atoms. Final atomic coordinates of the non-hydrogen atoms are given in Table V.

Acknowledgment. We thank the Fonds National Suisse de la Recherche Scientifique (Grant No. 20-33420-92) for financial support.

Supplementary Material Available: Listings of anisotropic thermal parameters, atomic coordinates for hydrogen atoms, and bond distances and angles (Tables S1–S6) for complexes 1 and 3 (6 pages). Ordering information is given on any current masthead page.

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