# Titanocene-Based Acetophenone Enolates: Synthesis and Structural Characterization of Mono, Bis, and Cationic Forms of Titanium Enolates and Some Aspects of Their Reactivity

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**Summary:** The reaction of [cp$_2$TiCl$_2$] with potassium enolates derived from 2-MeOC$_6$H$_4$-COMe, 2,4,6-Me$_3$C$_6$H$_2$COMe, and KH led to the metal–enolates [2-MeOC$_6$H$_4$C(CH$_2$)O—Ti-(Cl)cp$_2$] (1), [2,4,6-Me$_3$C$_6$H$_2$C(CH$_2$)O—Ti(Cl)cp$_2$] (2), and [{2-MeOC$_6$H$_4$C(CH$_2$)O}$_2$—Ticp$_2$] (3) where the enolate is $\eta^1$-O-bonded to the metal and the o-methoxy group does not interact with the metal. In order to increase the acidity and the template properties of the metal, complex 2 was ionized with CF$_3$SO$_3$Ag and AgBF$_4$. The cationic form of 2 readily reacts with cyclohexanone to give [2,4,6-Me$_3$C$_6$H$_2$C(O)—CH=C$_6$H$_{10}$] (6) and a titanium oxo species. The cationic form, however, was isolated as an isocyanide adduct with Bu$^t$NC, [2,4,6-Me$_3$C$_6$H$_2$C(CH$_2$)O—Ti-(CNBu$^t$)cp$_2$]$^+$X$^-$ (X$^-$ = CF$_3$SO$_3$, 8; X$^-$ = BF$_4$, 9). The increased reactivity of the enolato functionality in the cationic form of 2 is demonstrated in the reaction with acetonitrile and benzonitrile, where the binding of the nitrile prompted attack by the nucleophilic enolate on the nitrile. The reaction led to β-keto enamine derivatives N,O-bonded to the [cp$_2$Ti]$^{2+}$ fragment, [2-MeOC$_6$H$_4$C(O)CH=C(Me)NH—Ticp$_2$]$^+$CF$_3$SO$_3^-$ (13) and [2,4,6-Me$_3$C$_6$H$_2$C(O)CH=C(R)-NH—Ticp$_2$]$^+$CF$_3$SO$_3^-$ (R = Me, 14; R = Ph, 15). Crystallographic details: 1 is orthorhombic, space group $P2_12_12_1$, $a$ = 7.690(1) Å, $b$ = 14.113(2) Å, $c$ = 15.685(2) Å, $\alpha = \beta = \gamma = 90°$, $Z$ = 4, and $R$ = 0.034; 3 is orthorhombic, space group $Aba2$, $a$ = 9.472(1) Å, $b$ = 20.257(2) Å, $c$ = 12.378(1) Å, $\alpha = \beta = \gamma = 90°$, $Z$ = 4, and $R$ = 0.045; 14 is monoclinic, space group $P2_1/n$, $a$ = 7.765(6) Å, $b$ = 18.386(3) Å, $c$ = 17.677(3) Å, $\alpha = \gamma = 90°$, $\beta$ = 100.6(3)°, $Z$ = 4, and $R$ = 0.088.

## Introduction

Although metal–enolates[1] based on the cp$_2$M fragment [cp = $\eta^5$-C$_5$H$_5$; M = Ti, Zr] are widely used in organic synthesis,[2] their synthetic, structural, and spectroscopic characterization is rather scarce. This may be because they are usually used *in situ*, rather than in the isolated form.[2,3] Some key issues in this area are (i) the experimental conditions allowing the isolation of titanium and zirconium enolates; (ii) the structural parameters associated with an enolato fragment bonded to a titanocene and zirconocene fragment, and its bonding mode to the metal; (iii) the bonding mode and the reactivity of the enolate as depending on the coordination number of the metal. Our investigations led to (a) the synthesis and

structural characterization of mono- and bis(enolato) derivatives of titanocene; (b) the synthesis of an unsaturated cationic titanium enolate, stabilized by isocyanides, and its reactivity with cyclohexanone; (c) the reaction of the cationic form of titanium enolates with nitriles, leading to the formation of metallo–α-keto enamine derivatives.

## Results and Discussion

Numerous past attempts to isolate acetophenone enolate bonded to titanocene or zirconocene fragments gave little

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(1) For general references to metal-assisted enolate chemistry see: (a) Heathcock, C. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 2, Chapters 1.5 and 1.6. (b) Evans, D. A.; Nelson, J. V.; Taber, T. *Top. Stereochem.* 1982, 1. (c) Evans, D. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Pergamon: New York, 1983; Vol. 3, Chapter 1, p 1. (d) Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Pergamon: New York, 1983; Vol. 3, Chapter 2, p 111. (e) Heathcock, C. H. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Verlag Helvetica Chimica Acta: Basle, 1992; p 1. (f) Heathcock, C. H. In *Comprehensive Carbanions Chemistry, Studies in Organic Chemistry 5*; Buncel, E., Durst, T., Eds.; Elsevier: Lausanne, 1984; p 177. (g) Heathcock, C. H. *Aldrichim. Acta* 1990, 23, 99. (h) Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 1.

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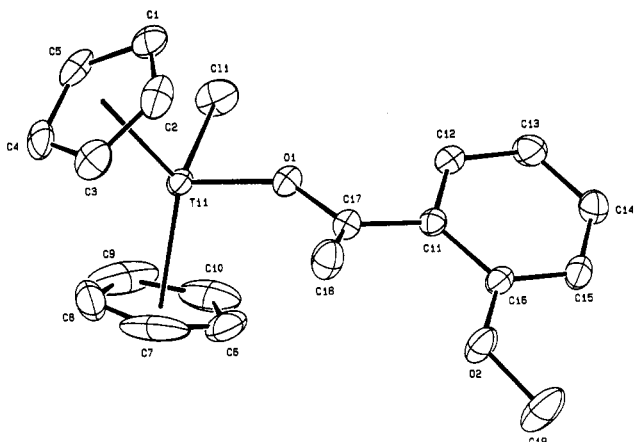
**Figure 1.** ORTEP view of complex 1 (30% probability ellipsoids).

characterized noncrystalline solids, and mixtures of mono- and dienolato derivatives derived from the reaction with $cp_2MCl_2$[cp = $\eta^5$-$C_5H_5$; M = Ti, Zr].[3,4]

The use of 2-methoxy- or 2,4,6-trimethylacetophenone as the source of the enolate (eq 1) allowed characterization of pure and crystalline solids in the case of titanium.



$$R_1 = R_2 = H; R_3 = OMe, 1$$
$$R_1 = R_2 = R_3 = Me, 2$$
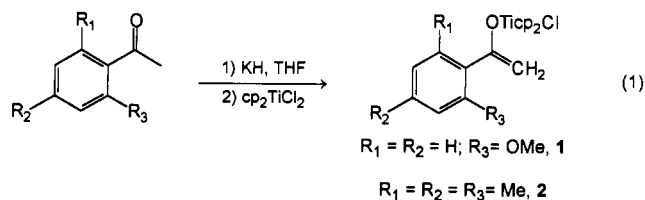
Both compounds 1 and 2 were isolated as red crystalline solids.[5] The ^{1}H NMR spectrum of both compounds shows the two heterotopic methylene protons as two singlets, due to the small $J_{HH}$ coupling constant. In the case of complex 1, the methoxy group does not coordinate titanium, in spite of the favorable geometry, as seen in the X-ray crystal structure, Figure 1. A list selected bond distances and angles is reported in Table V. The bent [cp$_2$Ti] fragment has an angle cp1–Ti–cp2 of 131.7(3)° and accommodates in the equatorial plane the Cl and the $\eta^1$-enolato ligands. The CH$_2$ nucleophilic site is *trans* to the Cl atom, the Cl–Ti···C17–C18 torsional angle being –166.2(4)°. The enolato group O1,C17,C18,C11 is twisted with respect to the C11···C16 aromatic ring, the torsion angle around the C11···C17 bond being 20.5(1)°. It forms a dihedral angle of 152.5(1)° with the equatorial plane Ti1,O1,C11. The C17 carbon atom and the O2 oxygen atom are slightly but significantly out of the ring plane, being displaced by +0.075(4) and –0.043(3) Å, respectively. The C17–C18 and C17–O1 bond distances are almost identical and support a significant double bond character of the C–C and C–O bonds in the enolato moiety. The Ti1–O1 distance [1.861(3) Å] and the Ti1–O1–C17 [147.3-(2)°] angle suggest a rather poor donation from the oxygen to the metal.[6]

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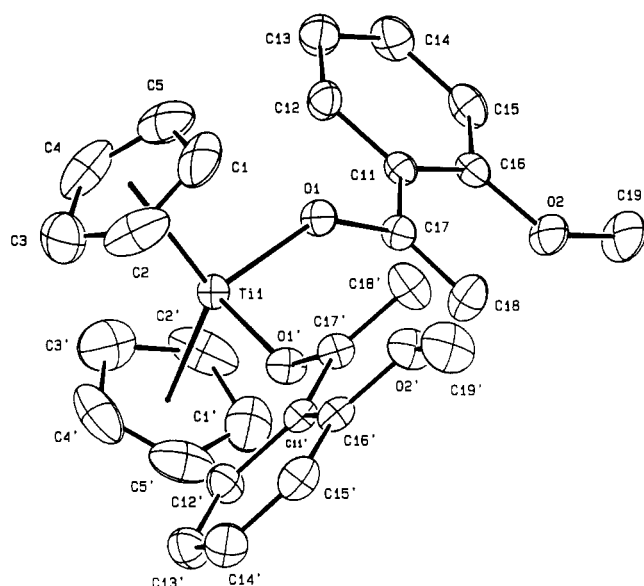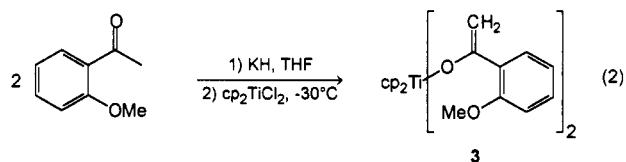(6) Curtis, M. D.; Thanedar, S.; Butler, W. M. *Organometallics* **1984**, *3*, 1855.



**Figure 2.** ORTEP view of complex 3 (30% probability ellipsoids). Prime refers to a transformation of –*x*, –*y*, *z*.

The use of 2 mol of potassium enolate in the reaction with cp$_2$TiCl$_2$ led to the formation (64%) of a rare[3,4,7] and well characterized bis(enolato) derivative, isolated as an orange crystalline solid:



The ^{1}H NMR spectrum of the methylene group shows the same two singlets observed for 1 and 2. The structure of 3 is shown in Figure 2, with a list of selected bond distances and angles in Table VI. Complex 3 has an imposed $C_2$ crystallographic symmetry. Coordination at the Ti atom involves two symmetry related O-bonded enolato ligands in a geometry usual for cp$_2$Ti derivatives. The Ti1–O1 bond distance [1.901(2) Å] is significantly longer than that found in complex 1 [1.861(3) Å], and this corresponds to a narrowing of the Ti1–O1–C17 bond angle [138.9(2) *vs* 147.3(2)° in complex 1] and a further decreasing of the $\pi$ donation from the oxygen to titanium.[6]

The enolato group (O1,C17,C18,C11) is nearly coplanar with the C11···C16 aromatic ring, the torsion angle around the C11···C17 bond being 2.9(1)°. It forms a dihedral angle of 141.6(1)° with the equatorial plane (Ti1,O1,O1'). The C17 carbon atom and the O2 oxygen atoms are slightly displaced by the ring plane [0.031(3) and 0.030(3) Å, respectively]. The two symmetry related enolato groups are roughly perpendicular each other, the dihedral angle they form being 108.3(1)°. Bond distances and angles within the enolate ligand are in good agreement with those observed in complex 1, with C17–C18 [1.334(6) Å] and O1–C17 [1.351(4) Å] having important double bond character.

We have not yet found appropriate conditions for studying the reactivity of titanium enolates 1–3, a major problem being the formation of a complex mixture of organic compounds and of [(cp$_2$TiCl)$_2$($\mu$-O)] in the reaction with aldehydes and ketones. The formation of the ($\mu$-

(7) Collins, S.; Ward, D. G. *J. Am. Chem. Soc.* **1992**, *114*, 5460.

oxo)titanium species occurs as well when 1 and 2 are used in the cationic form. In order to increase the acidity of the metal center and its potential as a template for bringing together the substrate and the enolate functionality, we used an ionized form of 2 in the reaction with cyclohexanone, as reported in reaction 3.
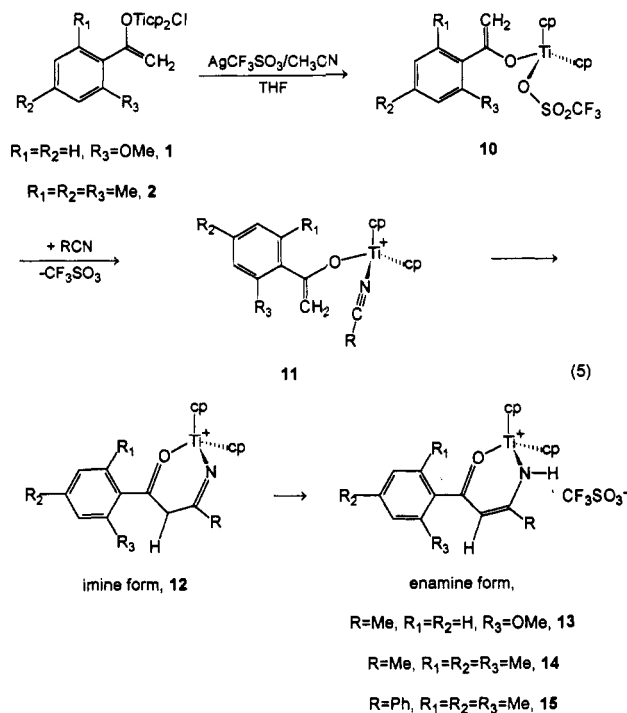


$$R_1 = R_2 = R_3 = Me$$

(3)
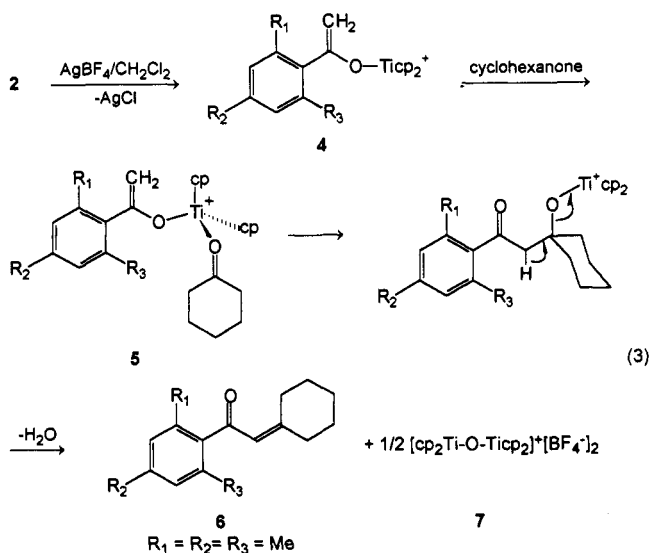
Under the experimental conditions reported (see the Experimental Section) we isolated neither the ionized form, 4, nor the precursor, 5, in the aldol condensation, due to the fast reaction between the enolate and the ketone. The product we isolated in significant yield is 6. If 6 forms as in reaction 3, this would require the elimination of $H_2O$ from 5, and in fact a partial hydrolysis of 2 is observed, giving 2,4,6-trimethylacetophenone. The full characterization of 6 is detailed in the Experimental Section, but 7 has been identified only as a cyclopentadienyl–oxo–titanium derivative. The identification of the cationic form of the titanium enolate 4 was achieved when the ionization was carried out in the presence of Bu$^t$NC (reaction 4).



$$R_1=R_2=R_3=Me, X=CF_3SO_3, 8$$

$$R_1=R_2=R_3=Me, X=BF_4, 9$$

(4)
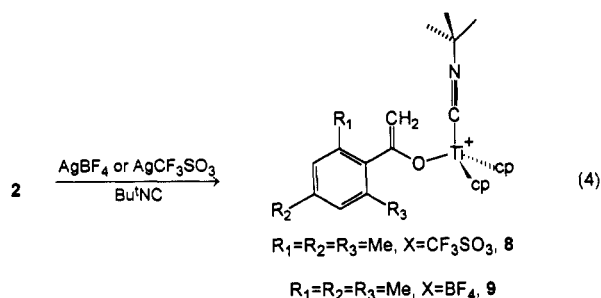
Complexes 8 and 9 have been isolated (~70%) as light red crystalline solids. The $\nu$(NC) band is shifted from 2138 cm$^{-1}$ for the free Bu$^t$NC to 2229 and 2223 cm$^{-1}$ upon binding to an acidic center. The methylene did not show significant changes compared to 2 in the $^1$H NMR spectrum. Isocyanides are good inserting groups in migratory insertion reactions involving metal–carbon bonds,[8] but this is not the case with metal–enolates containing M–O bonds. We expected a Lewis acid activated isocyanide to be attacked by a nucleophile such as the enolate. This was not observed with isocyanides, but only with nitriles.

The latter reaction (equation 5) was carried out by adding an acetonitrile or benzonitrile solution of silver triflate to a THF solution of 1 or 2.



$$R_1=R_2=H, R_3=OMe, 1$$

$$R_1=R_2=R_3=Me, 2$$

(5)

imine form, 12                    enamine form,

$$R=Me, R_1=R_2=H, R_3=OMe, 13$$

$$R=Me, R_1=R_2=R_3=Me, 14$$

$$R=Ph, R_1=R_2=R_3=Me, 15$$

The addition of silver triflate was followed by the sudden formation of solid AgCl and a red-orange solution, which became red-violet in a few hours. The reaction is much faster when AgBF$_4$ is employed, which is in agreement with a weak precoordination of the triflate anion in 10, before substitution by the nitrile in 11. The same effect was observed for the analogous isocyanide complexes 8 and 9. The nucleophilic attack by the enolate on the metal-bonded nitrile leads to the $\beta$-keto imino derivative 12. This later tautomerizes to the stable $\alpha$-keto enamine form which has been isolated as complexes 13–15. Analogous compounds have been obtained by the reaction of a nitrile with rhenium C-bonded enolates reported by Bergman and Heathcock,[9] as exemplified in reaction 6.



$$R = Me, Ph, NEt_2$$

(6)
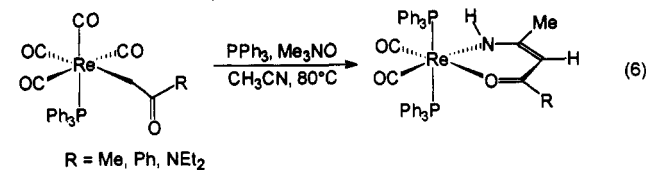
The IR spectroscopic data for 13–15 are in agreement with those reported for the rhenium derivatives, including the absence of any carbonylic band and the appearance of the N–H vibration around 3250 cm$^{-1}$. The structure of the $\alpha$-keto enamine form was unquestionably supported

(8) Iminoacyl formation from migratory insertion of RNC with M–C bonds is a well-known reaction: Singleton, E.; Ossthnizen, H. E. *Adv. Organomet. Chem.* 1983, 22, 209. Otsuka, S.; Nakamura, A.; Yoshida, T.; Naruto, M.; Ataba, K. *J. Am. Chem. Soc.* 1973, 95, 3180. Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* 1974, 13, 438. Aoki, K.; Yamamoto, Y. *Inorg. Chem.* 1976, 15, 48. Bellachioma, G.; Cardaci, G.; Zanazzi, P. *Inorg. Chem.* 1987, 26, 84. Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: London, U.K., 1982; Vol. 8, Chapter 38.4. Crociani, B. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; Chapter 9.

(9) Stack, J. G.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *Organometallics* 1990, 9, 453 and references therein.
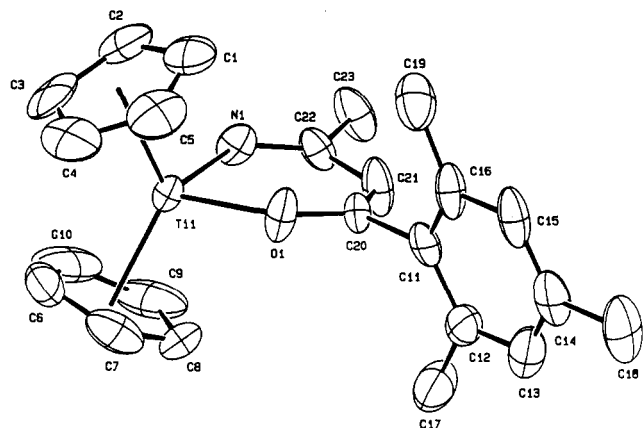
**Figure 3.** ORTEP view of complex **14** (30% probability ellipsoids).

by an X-ray analysis on **14**. The structure consists of the packing of complex cations and $CF_3SO_3^-$ anions in the molar ratio 1/1. A perspective view of the cation showing the atomic numbering scheme is presented in Figure 3. Selected bond distances and angles are given in Table VII. The coordination geometry is similar to that found in complexes **1** and **3**. The organic ligand is N,O-bonded to titanium, giving rise to a six-membered chelation ring. The ring assumes a half-boat conformation, the metal being displaced by 0.218(2) Å from the mean plane through O1, C20, C21, C22, and N1 atoms. The folding angle of the chelation ring along the N1···O1 line is 171.7(3)°. (The folding angle is the dihedral angle between the equatorial plane (Ti,O1,N1) and the mean plane through O1,C20,-C21,C22,N1.)

Bond distances and angles in the chelation ring are consistent with double bonds localized on the N1—C22 [1.271(15) Å] and C20—C21 [1.342(17) Å] bonds, even if a significant shortening of the O1—C20 distance [1.266-(13) Å], if compared with the analogous distances in complexes **1** and **3** (Tables V and VI), and of the C21—C22 distance [1.431(18) Å] with respect to a single $C_{sp^2}$—$C_{sp^2}$ bond, along with the planarity of the O1,C20,C21,C22,N1 system, suggest some $\pi$ delocalization which is, however, considerably less than that observed in [(CO)₂(PPh₃)₂-Re(NH—C(CH₃)=CH—C(R)=O)].[9] The mesityl ring is nearly perpendicular to the mean plane through the chelation ring (including titanium), the dihedral angle being 80.7(2)°.

We conclude by comparing the reactions of the O-bonded enolate **10** with those of Re–carbon-bonded enolates. The reaction of nitriles with titanium complexes occurs under milder conditions, as expected from the polarization induced on the nitrile by the cationic metal center. That the nitrile coordinates the metal center in **11** is supported by the isolation of the analogous isocyanide complexes **8** and **9**, while in the case of the rhenium complexes the potential conversion of the C-bonded to O-bonded form does not allow a clear choice between a migratory insertion reaction (Re–C bonded) and the external nucleophilic attack on the coordinated nitrile (Re–O bonded) to be made. Such two reaction modes exemplify respectively a four- and a six-electron pathway for C–C bond formation. In our case, the O-bonded enolate on an oxophilic metal strongly favors an external nucleophilic attack on the nitrile.[3,4,9]

## Experimental Section

**Synthesis of 1.** 2-Methoxyacetophenone (6.67 g, 44 mmol) was added with a syringe to a suspension of KH (1.78 g, 44 mmol) in THF (250 mL) and the mixture stirred for 3–4 h. At –50 °C cp₂TiCl₂ (10.50 g, 42 mmol) was added and the solution stirred for 10 h at that temperature. The solvent was evaporated and the red residue suspended in ether (200 mL). After a 1-day extraction, large red crystals, suitable for X-ray analysis, were collected (50%). Anal. Calcd for C₁₉H₁₉ClO₂Ti: C, 62.92; H, 5.28. Found: C, 62.98; H, 5.21. ¹H NMR (CD₂Cl₂): δ 3.89 (s, OMe, 3 H), 4.36 (s, =CH₂, 1 H), 4.81 (s, =CH₂, 1 H), 6.40 (s, cp, 10 H), 6.9–7.35 (m, Ar, 4 H). ¹³C NMR (CD₂Cl₂): δ 56.0 (OMe), 92.9 (=CH₂), 120 (Ar), 117.9 (cp), 168.8 (ketone).

**Synthesis of 2.** 2,4,6-Trimethylacetophenone (7.60 g, 47 mmol) was added with a syringe to a THF (200 mL) suspension of KH (1.90 g, 47 mmol) and the mixture stirred for 3–4 h. At –60 °C cp₂TiCl₂ (10.50 g, 42 mmol) was added and the solution stirred for 12 h at that temperature. The solvent was evaporated and the red residue suspended in ether (200 mL). After a 1-day extraction a red microcrystalline solid was collected (63%). Anal. Calcd for C₂₁H₂₃ClOTi: C, 67.30; H, 6.19. Found: C, 66.67; H, 6.38. ¹H NMR (CD₂Cl₂): δ 2.26 (s, Me, 3 H), 2.35 (s, Me, 6 H), 3.89 (s, =CH₂, 1 H), 4.17 (s, =CH₂, 1 H), 6.41 (s, cp, 10 H), 6.85 (s, Ar, 2 H).

**Synthesis of 3.** 2-Methoxyacetophenone (4.50 g, 30 mmol) was added with a syringe to a suspension of KH (1.20 g, 30 mmol) in THF (200 mL) and the mixture stirred for 3–4 h. At –30 °C cp₂TiCl₂ (3.61 g, 14.50 mmol) was added and the solution stirred overnight allowing the temperature to rise slowly. The solvent was evaporated and the orange residue redissolved in benzene (100 mL). The solution was concentrated to half-volume, and then heptane (50 mL) was added. A red microcrystalline solid was collected (64%). Crystals suitable for X-ray analysis were obtained by recrystallization from benzene. Anal. Calcd for C₂₈H₂₈O₄Ti: C, 70.59; H, 5.92. Found: C, 70.85; H, 5.93. ¹H NMR (CD₂Cl₂): δ 3.37 (s, OMe, 6 H), 4.42 (s, =CH₂, 2 H), 5.20 (s, =CH₂, 2 H), 6.14 (s, cp, 10 H), 6.6–7.8 (m, Ar, 8 H).

**Synthesis of 6.** To a CH₂Cl₂ (50-mL) solution of **2** (1.05 g, 2.80 mmol) was added AgBF₄ (0.55 g, 2.80 mmol) and the suspension stirred for 30 min. Cyclohexanone (0.275 g, 2.80 mmol) was then added with a syringe and the solution turned orange-yellow. The solvent was evaporated to dryness, and the residue redissolved in ether (50 mL) and filtered. The light yellow filtrate was concentrated to dryness, yielding a brown oil. When this oil was treated with CH₂Cl₂ (20 mL) and ether (50 mL), a product, **7**, was isolated (27%). From the solution, **6** was recovered as an oil (50%). IR (neat): (**6**) ν(CO) 1671 (m), ν(C=C) 1613 cm⁻¹. ¹H NMR (CDCl₃): δ 1.6–1.8 (m, CH₂, 8 H), 2.25 and 2.28 (2s, Me, 9 H), 2.6 (m, CH₂, 2 H), 6.22 (s, CH, 1 H), 6.87 (s, Ar, 2 H). MS: M⁺, 242.15 for C₁₇H₂₂O. GC–MS and ¹H NMR show the presence of 2,4,6-trimethylacetophenone. The IR spectrum of **7** does not show any carbonylic band, while the ¹H NMR spectrum in CD₂-Cl₂, in which **7** is sparingly soluble, shows only the presence of a cyclopentadienyl peak at 6.50 ppm.

**Synthesis of 8.** A THF (30-mL) solution of silver triflate (0.99 g, 3.8 mmol) was added dropwise to a THF (50 mL) solution of **2** (1.44 g, 3.84 mmol) and the mixture stirred for 30 min. Butᵗ-NC (0.45 mL, 3.85 mmol) was then added, the solvent was evaporated to dryness, the residue was dissolved in CH₂Cl₂ (50 mL), and AgCl was filtered off. The filtrate was concentrated to 20 mL and ether (50 mL) was added dropwise, yielding a light red microcrystalline solid (73%). IR (Nujol): ν(NC) 2229 (s) cm⁻¹. Anal. Calcd for C₂₇H₃₂F₃NO₄STi: C, 56.74; H, 5.64; N, 2.45. Found: C, 56.28; H, 5.79; N, 3.10. ¹H NMR (CD₂Cl₂): δ 1.49 (s, Buᵗ, 9 H), 2.25 and 2.29 (2s, Me, 9 H), 3.98 and 4.28 (2s, =CH₂, 2 H), 6.47 (s, cp, 10 H), 6.87 (s, Ar, 2 H).

**Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Compounds 1, 3, and 14**

| compd | 1 | 3 | 14 |
|---|---|---|---|
| formula | $C_{19}H_{19}ClO_2Ti$ | $C_{28}H_{28}O_4Ti$ | $C_{23}H_{26}NOTiKCF_3O_3S$ |
| cryst syst | orthorhombic | orthorhombic | monoclinic |
| space group | $P2_12_12_1$ (No. 19) | $Aba2$ (No. 41) | $P2_1/n$ (No. 14) |
| cell params at 295 K | | | |
| $a$, Å | 7.690(1) | 9.472(1) | 7.765(6) |
| $b$, Å | 14.113(2) | 20.257(2) | 18.386(3) |
| $c$, Å | 15.685(2) | 12.378(1) | 17.677(3) |
| $\alpha$, deg | 90 | 90 | 90 |
| $\beta$, deg | 90 | 90 | 100.6(3) |
| $\gamma$, deg | 90 | 90 | 90 |
| $V$, Å$^3$ | 1702.3(4) | 2375(4) | 2480.8(20) |
| $Z$ | 4 | 4 | 4 |
| $D_{calcd}$, g cm$^{-3}$ | 1.415 | 1.332 | 1.418 |
| mol wt | 362.7 | 476.4 | 529.4 |
| linear abs coeff, cm$^{-1}$ | 6.60 | 33.1 | 4.72 |
| transm factor range | 0.942–1.000 | 0.850–1.000 | 0.957–1.000 |
| $t$, °C | 22 | 22 | 22 |
| radiation | a | b | a |
| $R = \Sigma|\Delta F|/\Sigma|F_o|$ | 0.034 [0.038]$^c$ | 0.045 [0.073]$^c$ | 0.088 |
| $R_w = \Sigma w^{1/2}|\Delta F|/\Sigma w^{1/2}|F_o|$ | 0.038 [0.042]$^c$ | 0.048 [0.077]$^c$ | |
| $R_G = [\Sigma w|\Delta F|^2/\Sigma w|F_o|^2]^{1/2}$ | 0.046 [0.050]$^c$ | 0.058 [0.099]$^c$ | |

$^a$ Graphite monochromated Mo K$\alpha$ ($\lambda$ = 0.710 69 Å). $^b$ Ni-filtered Cu K$\alpha$ ($\lambda$ = 1.541 78 Å). $^c$ Values in square brackets refer to the the "inverted" structure.

**Table II. Fractional Atomic Coordinates ($\times 10^4$) for Complex 1**

| atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Ti1 | 2751.9(8) | 27.9(5) | 4746.7(4) |
| Cl1 | 5065.3(15) | -1066.6(9) | 4994.1(7) |
| O1 | 3747(3) | 1053(2) | 5311(2) |
| O2 | 2862(5) | 2893(2) | 7332(2) |
| C1 | 4485(6) | 357(4) | 3501(3) |
| C2 | 3382(7) | 1122(4) | 3607(3) |
| C3 | 1659(7) | 822(4) | 3532(3) |
| C4 | 1701(6) | -156(4) | 3314(3) |
| C5 | 3437(7) | -431(3) | 3307(3) |
| C6 | 976(8) | 133(5) | 5990(3) |
| C7 | -44(9) | 264(7) | 5316(6) |
| C8 | -94(12) | -552(13) | 4888(5) |
| C9 | 939(16) | -1182(5) | 5278(9) |
| C10 | 1607(8) | -726(7) | 5992(5) |
| C11 | 4667(5) | 1816(3) | 6574(2) |
| C12 | 6145(5) | 1252(3) | 6567(3) |
| C13 | 7339(6) | 1252(3) | 7227(3) |
| C14 | 7026(6) | 1816(3) | 7932(3) |
| C15 | 5537(6) | 2364(3) | 7979(3) |
| C16 | 4363(5) | 2374(3) | 7308(3) |
| C17 | 3500(5) | 1817(3) | 5812(3) |
| C18 | 2399(6) | 2489(3) | 5589(3) |
| C19 | 2428(9) | 3366(4) | 8095(3) |

**Table III. Fractional Atomic Coordinates ($\times 10^4$) for Complex 3**

| atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Ti1 | 0(-) | 0(-) | 0(-) |
| O1 | 1325(2) | -355(1) | 996(2) |
| C1 | 1360(7) | 995(3) | 117(5) |
| C2 | 192(6) | 1133(2) | -488(7) |
| C3 | 329(7) | 765(4) | -1446(6) |
| C4 | 1569(9) | 419(3) | -1359(6) |
| C5 | 2185(5) | 568(3) | -446(6) |
| C11 | 2655(3) | -1301(1) | 1531(3) |
| C12 | 3577(4) | -1147(2) | 684(3) |
| C13 | 4769(4) | -1515(2) | 449(4) |
| C14 | 5062(4) | -2064(2) | 1069(4) |
| C15 | 4174(4) | -2240(2) | 1899(3) |
| C16 | 2986(4) | -1868(2) | 2138(3) |
| C17 | 1412(3) | -851(1) | 1723(3) |
| C18 | 478(5) | -910(2) | 2524(4) |
| O2 | 2105(3) | -2019(1) | 2980(3) |
| C19 | 2433(5) | -2592(2) | 3611(5) |

**Table IV. Fractional Atomic Coordinates ($\times 10^4$) for Complex 14**

| atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Ti1 | 6206(2) | 3045(1) | 6538(1) |
| S1 | 529(7) | 767(3) | 8363(4) |
| O2 | -422(16) | 139(6) | 8223(10) |
| O3 | -207(18) | 1387(6) | 8035(9) |
| O4 | 1642(30) | 856(12) | 9187(9) |
| F1 | 3169(15) | -5(9) | 8262(11) |
| F2 | 3516(20) | 1093(11) | 8183(14) |
| F3 | 1745(37) | 591(19) | 7254(9) |
| O1 | 5457(11) | 2335(4) | 5754(5) |
| N1 | 4492(12) | 3744(5) | 5826(6) |
| C1 | 8321(16) | 3321(12) | 5735(5) |
| C2 | 8203(16) | 3942(12) | 6201(5) |
| C3 | 8765(16) | 3737(12) | 6982(5) |
| C4 | 9230(16) | 2990(12) | 6999(5) |
| C5 | 8956(16) | 2733(12) | 6228(5) |
| C6 | 6454(15) | 2955(13) | 7901(6) |
| C7 | 5807(15) | 2280(13) | 7577(6) |
| C8 | 4139(15) | 2405(13) | 7111(6) |
| C9 | 3755(15) | 3158(13) | 7148(6) |
| C10 | 5186(15) | 3498(13) | 7636(6) |
| C11 | 4107(11) | 1578(4) | 4763(4) |
| C12 | 2759(11) | 1095(4) | 4832(4) |
| C13 | 2641(11) | 429(4) | 4447(4) |
| C14 | 3869(11) | 247(4) | 3994(4) |
| C15 | 5217(11) | 730(4) | 3925(4) |
| C16 | 5335(11) | 1396(4) | 4309(4) |
| C17 | 1446(20) | 1272(9) | 5344(9) |
| C18 | 6765(18) | 1902(10) | 4187(8) |
| C19 | 3674(26) | -484(7) | 3577(9) |
| C20 | 4268(14) | 2301(6) | 5160(6) |
| C21 | 3202(19) | 2862(7) | 4919(7) |
| C22 | 3378(17) | 3583(7) | 5229(7) |
| C23 | 2165(19) | 4153(7) | 4815(7) |
| C24 | 2363(47) | 572(15) | 8003(27) |

Bu$^t$NC (0.50 mL, 4.30 mmol) was then added, the solvent was evaporated to dryness, the residue was dissolved in $CH_2Cl_2$ (50 mL), and AgCl was filtered off. The filtrate was concentrated to 10 mL and ether (25 mL) was added dropwise, yielding a light red microcrystalline solid (67%). IR (Nujol): $\nu$(NC) 2223 (s) cm$^{-1}$. Anal. Calcd for $C_{28}H_{32}BF_4NOTi$: C, 61.32; H, 6.33; N, 2.75. Found: C, 60.78; H. 6.51; N, 3.03. $^1$H NMR ($CD_2Cl_2$): $\delta$ 1.49 (s, Bu$^t$, 9 H), 2.25 and 2.29 (2s, Me, 9 H), 3.98 and 4.28 (2s, =CH$_2$, 2 H), 6.47 (s, cp, 10 H), 6.87 (s, Ar, 2 H).

**Synthesis of 13.** An acetonitrile (25-mL) solution of silver triflate (0.43 g, 1.65 mmol) was added dropwise to a $CH_2Cl_2$ (30 mL) solution of 1 (0.60 g, 1.65 mmol). A red solution was obtained, which was stirred for 3 h and turned violet. AgCl was filtered

**Synthesis of 9.** A THF (30-mL) solution of AgBF$_4$ (0.83 g, 4.30 mmol) was added dropwise to a THF (50-mL) solution of 2 (1.60 g, 4.27 mmol), and the mixture was stirred for 30 min.

**Table V. Selected Bond Distances (Å) and Angles (deg) for Complex 1**

| | | | |
|---|---|---|---|
| Ti1–Cp1 | 2.083(5) | C11–C12 | 1.388(6) |
| Ti1–Cp2 | 2.074(9) | C11–C16 | 1.414(6) |
| Ti1–Cl1 | 2.388(1) | C11–C17 | 1.495(6) |
| Ti1–O1 | 1.861(3) | C12–C13 | 1.384(6) |
| O1–C17 | 1.348(5) | C13–C14 | 1.384(6) |
| O2–C16 | 1.368(5) | C14–C15 | 1.384(6) |
| O2–C19 | 1.410(6) | C15–C16 | 1.387(6) |
| C17–C18 | 1.319(6) | | |
| | | | |
| Cl1–Ti1–O1 | 96.8(1) | C12–C11–C16 | 117.5(4) |
| Cp2–Ti1–O1 | 106.3(3) | C11–C12–C13 | 122.5(4) |
| Cp2–Ti1–Cl1 | 106.7(3) | C12–C13–C14 | 118.8(4) |
| Cp1–Ti1–O1 | 105.7(2) | C13–C14–C15 | 120.5(4) |
| Cp1–Ti1–Cl1 | 104.3(2) | C14–C15–C16 | 120.3(4) |
| Cp1–Ti1–Cp2 | 131.7(3) | C11–C16–C15 | 120.3(4) |
| Ti1–O1–C17 | 147.3(2) | O2–C16–C15 | 122.3(4) |
| C16–O2–C19 | 118.5(4) | O2–C16–C11 | 117.4(3) |
| C16–C11–C17 | 123.4(4) | O1–C17–C11 | 112.4(3) |
| C12–C11–C17 | 119.1(4) | C11–C17–C18 | 126.7(4) |
| O1–C17–C18 | 120.7(4) | | |

**Table VI. Selected Bond Distances (Å) and Angles (deg) for Complex 3**

| | | | |
|---|---|---|---|
| Ti1–Cp1 | 2.101(7) | C11–C16 | 1.408(5) |
| Ti1–O1 | 1.901(2) | C11–C17 | 1.508(4) |
| O1–C17 | 1.351(4) | C12–C13 | 1.384(6) |
| O2–C16 | 1.370(5) | C13–C14 | 1.379(6) |
| O2–C19 | 1.433(6) | C14–C15 | 1.375(6) |
| C11–C12 | 1.400(5) | C15–C16 | 1.386(6) |
| C17–C18 | 1.334(6) | | |
| | | | |
| O1–Ti1–O1' $^a$ | 99.1(1) | C11–C12–C13 | 123.1(3) |
| Cp1'–Ti1–O1 | 109.2(2) | C12–C13–C14 | 118.8(4) |
| Cp1–Ti1–O1 | 103.0(2) | C13–C14–C15 | 120.1(4) |
| Cp1–Ti1–Cp1' | 129.5(3) | C14–C15–C16 | 121.0(4) |
| Ti1–O1–C17 | 138.9(2) | C11–C16–C15 | 120.7(3) |
| C16–O2–C19 | 117.6(3) | O2–C16–C15 | 122.4(3) |
| C16–C11–C17 | 125.7(3) | O2–C16–C11 | 116.9(3) |
| C12–C11–C17 | 118.1(3) | O1–C17–C11 | 113.1(2) |
| C12–C11–C16 | 116.3(3) | C11–C17–C18 | 125.5(3) |
| O1–C17–C18 | 121.4(3) | | |

$^a$ ′ = –x, –y, z.

off and the solvent evaporated. The residue was redissolved in CH₂Cl₂ (20 mL) and ether (20 mL), yielding a dark red microcrystalline solid (70%). IR (Nujol): $\nu$(NH) 3265 (m) cm⁻¹. Anal. Calcd for $C_{22}H_{22}F_3NO_5STi$: C, 51.07; H, 4.29; N, 2.70. Found: C, 50.87; H, 4.02; N, 2.70. ¹H NMR (CD₂Cl₂): $\delta$ 2.40 (s, Me, 3 H), 3.94 (s, OMe, 3 H), 5.51 (d, =CH, 1 H, $J$ = 1.5 Hz), 6.55 (s, cpTi, 10 H), 7.03 and 7.47 (2d, Ar, 4 H). ¹³C NMR (CD₂Cl₂): $\delta$ 27.9 (s, Me), 56.4 (s, OMe), 107.0 (s, CF₃), 119.8 (s, cp), 121.3, 130.6, 133.2, and 158.6 (4s, Ar), 175.2 and 176.2 (2s, ketone).

**Synthesis of 14.** An acetonitrile (25-mL) solution of silver triflate (1.26 g, 4.90 mmol) was added dropwise to a CH₂Cl₂ (30 mL) solution of 2 (1.83 g, 4.90 mmol). A red solution was obtained, which was stirred for 3 h and turned violet. AgCl was filtered off and the solvent evaporated. The residue was redissolved in CH₂Cl₂ (10 mL) and ether (50 mL), yielding a dark red microcrystalline solid (71%). IR (Nujol): $\nu$(NH) 3265 (m) cm⁻¹. Anal. Calcd for $C_{24}H_{26}F_3NO_4STi$: C, 54.44; H, 4.95; N, 2.65. Found: C, 54.74; H. 5.11; N, 2.86. ¹H NMR (CD₂Cl₂): $\delta$ 2.29 and 2.35 (2s, Me, 9 H), 2.36 (s, Me, 3 H), 5.58 (d, =CH, 1 H, $J$ = 1.4 Hz), 6.61 (s, cp, 10 H), 6.92 (s, Ar, 2 H). ¹³C NMR (CD₂Cl₂): $\delta$ 20.8 and 21.5 (2s, Me), 27.7 (s, Me), 107.1 (s, CF₃), 120.4 (s, cp), 129.5, 134.9, 135.6, and 139.8 (4s, Ar), 175.4 and 180.8 (2s, ketone).

**Synthesis of 15.** To a CH₂Cl₂ (30 mL) solution of 2 (0.50 g, 1.33 mmol) was added silver triflate (0.35 g, 1.36 mmol), and then, after 15 min, benzonitrile (0.50 mL, 4.8 mmol). A red solution was obtained, which was stirred for 2 days and turned violet. AgCl was filtered off and the solvent evaporated to 10 mL. Ether (50 mL) was added dropwise and a blue-violet crystalline solid suddenly formed (61%). IR (Nujol): $\nu$(NH) 3243 (m) cm⁻¹. Anal. Calcd for $C_{29}H_{28}F_3NO_4STi$: C, 58.89; H,

**Table VII. Selected Bond Distances (Å) and Angles (deg) for Complex 14**

| | | | |
|---|---|---|---|
| Ti1–Cp1 | 2.053(14) | C11–C20 | 1.498(13) |
| Ti1–Cp2 | 2.044(12) | C12–C17 | 1.518(19) |
| Ti1–O1 | 1.915(8) | C14–C19 | 1.527(15) |
| Ti1–N1 | 2.096(9) | C16–C18 | 1.494(18) |
| O1–C20 | 1.266(13) | C20–C21 | 1.342(17) |
| N1–C22 | 1.271(15) | C21–C22 | 1.431(18) |
| C22–C23 | 1.506(18) | | |
| | | | |
| O1–Ti1–N1 | 84.7(4) | C12–C11–C20 | 121.6(8) |
| Cp2–Ti1–N1 | 105.5(5) | C12–C11–C16 | 120.0(7) |
| Cp2–Ti1–O1 | 110.7(5) | O1–C20–C11 | 114.7(9) |
| Cp1–Ti1–N1 | 106.5(4) | C11–C20–C21 | 122.7(10) |
| Cp1–Ti1–O1 | 106.3(4) | O1–C20–C21 | 122.6(10) |
| Cp1–Ti1–Cp2 | 132.5(4) | C20–C21–C22 | 125.5(12) |
| Ti1–O1–C20 | 135.4(7) | N1–C22–C21 | 122.4(12) |
| Ti1–N1–C22 | 128.0(8) | C21–C22–C23 | 116.8(11) |
| C16–C11–C20 | 118.4(8) | N1–C22–C23 | 120.7(11) |

4.77; N, 2.37. Found: C, 59.50; H, 5.54; N, 2.66. ¹H NMR (CD₂Cl₂): $\delta$ 2.31 and 2.40 (2s, Me, 9 H), 6.12 (d, =CH, 1 H), 6.70 (s, cp, 10 H), 6.96 (s, Ar, 2 H), 7.55 and 7.80 (m, Ar, 5 H).

**X-ray Crystallography.** The crystals of 1, 3, and 14 were mounted in glass capillaries and sealed under nitrogen. Crystal data and details associated with data collection are given in Table I. The reduced cells quoted were obtained using TRACER.[10] Data were collected at room temperature (295 K) on a single-crystal four circle diffractometer. For intensities and background individual reflection profiles were analyzed.[11] The structure amplitudes were obtained after the usual Lorentz and polarization corrections, and the absolute scale was established by the Wilson method.[12] The crystal quality was tested by $\psi$ scans, showing that crystal absorption effects could not be neglected. Data were corrected for absorption using a semiempirical method[13] for complexes 1 and 14 and ABSORB[14] for complex 3. The function minimized during the full-matrix least-squares refinement was $\sum w|\Delta F|^2$. A weighting scheme $\{w = k/[\sigma^2(F_o) + g|F_o|^2]$, based on counting statistics, was applied.[15] For complex 14 unit weights were used. Anomalous scattering corrections were included in all structure factor calculations.[16b] Scattering factors for neutral atoms were taken from ref 16a for non-hydrogen atoms and from ref 17 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary. All calculations were carried out on a IBM-AT personal computer equipped with an INMOS T800 Transputer using SHELX-76.[15] Solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map.

**Complex 1.** Refinement was first done isotropically and then anisotropically for all the non-H atoms. All the hydrogen atoms were located from a difference Fourier map and introduced in the final refinement as fixed atom contributions (isotropic $U$'s fixed at 0.08 Å²). The crystal chirality was tested by inverting all the coordinates $(x,y,z \rightarrow -x,-y,-z)$ and refining to convergence once again. The resulting $R$ values ($R$ = 0.038, $R_G$ = 0.050 vs $R$ = 0.034, $R_G$ = 0.046) indicated the original choice should be the correct one. The final difference map showed no unusual features, with no significant peak above the general background.

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(16) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99. (b) *Ibid.*, p 149.

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**Complex 3.** Refinement was first done isotropically and then anisotropically by full-matrix least squares for all the non-H atoms. All the hydrogen atoms were located from a difference Fourier map and introduced in the final refinement as fixed atom contributions (isotropic $U$'s fixed at 0.08 $Å^2$). The crystal chirality was tested by inverting all the coordinates $(x, y, z \rightarrow -x, -y, -z)$ and refining to convergence once again. The resulting $R$ values $(R = 0.073, R_G = 0.099$ vs $R = 0.045, R_G = 0.058)$ indicated the original choice should be the correct one. The final difference map showed no unusual features, with no significant peak above the general background.

**Complex 14.** Refinement was first done isotropically and then anisotropically by full-matrix least squares for all the non-H atoms. The $CF_3SO_3^-$ anion was found to be affected by high thermal motion (or disorder). Attempts to solve the disorder in terms of "partial" atoms were unsuccessful. The best fit was found allowing the atoms to vary anisotropically. As a consequence the $U_{ij}$ temperature factors reached rather high values. This, as well as the poor quality of the crystals available, could be taken into account to justify the rather low accuracy of the analysis. The hydrogen atoms were located in a difference Fourier map and introduced as fixed contributors in the final refinement $(U_{iso} = 0.12 Å^2)$. During the refinement the Cp and Ph rings were constrained to be regular pentagons (C–C = 1.420 Å) and hexagons

(C–C = 1.395 Å), respectively. The final difference map showed no unusual features, with no significant peak above the general background, except for a peak of 0.8 e $Å^{-3}$ in the region of the $CF_3SO_3^-$ anion.

Final atomic coordinates are listed in Tables II–IV for non-H atoms and in Tables SII–SIV (supplementary material) for hydrogens. Thermal parameters are given in Tables SV–SVII; selected bond distances and angles, in Tables V–VII.[18]

**Supplementary Material Available:** Tables of experimental details associated with data collection and structure refinement (Table SI), hydrogen atom coordinates (Tables SII–SIV), thermal parameters (Tables SV–SVII), and bond distances and angles (Tables SVIII–SX) for complexes 1, 3, and 14 (13 pages). Ordering information is given on any current masthead page.

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(18) See paragraph at the end regarding supplementary material.