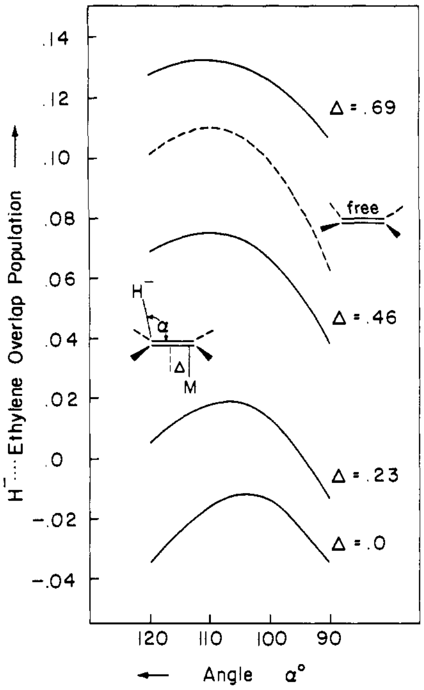
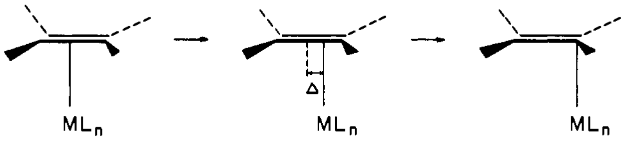


Figure 1. The H^-–ethylene overlap population in the model complex $(CO)_5Fe(C_2H_4)^{2+}\cdots H^-$ as a function of the approach angle (α) and the slipping of the ethylene (Δ).

that we presented above, implying *de*activation upon coordination, was supported.

A certain deformation of the complexed olefin, one which has no equivalent in the free molecule, supplies the anticipated but missed activation. This is a slipping of the ML_n fragment along the ethylene, idealized by a simple displacement from the center, Δ in structure b. Δ = 0 is the symmetrically bonded η^2 π complex while Δ = 0.69 is in our geometry for a model for an η^1 σ complex. The dramatic effect of this motion on the H^-–olefin overlap population is shown in Figure 1 for the model d^6 complex $(CO)_5Fe(C_2H_4)^{2+}\cdots H^-$. When the ethylene is π bonded, the overlap population with H^- is much lower than that in the free ethylene. As Δ is increased, the overlap population rises and eventually surpasses that of the free olefin.[12] There is a d-electron count and coordination number dependence of this activation mode. It takes place in our calculations for d^6 ML_5, d^8 ML_4, and d^8 ML_3, but not for the d^{10} ML_2.



a **b** **c**

Let us probe the possible origins of the activation through slipping. If one examines the orbitals of the complexed ethylene as a function of Δ, one does observe a lowering in energy of the lowest unoccupied molecular orbital (LUMO) as Δ increases. However, this stabilizing feature[10] is never large enough to compensate for the dispersion of the LUMO over the various ethylene and ML_n orbitals. What does increase substantially is the localization of the LUMO of the $L_nM(C_2H_4)$ complex on the far carbon, as illustrated in Figure 2. This localization is primarily responsible for the superior H^-–C_2H_4 bonding at large Δ.

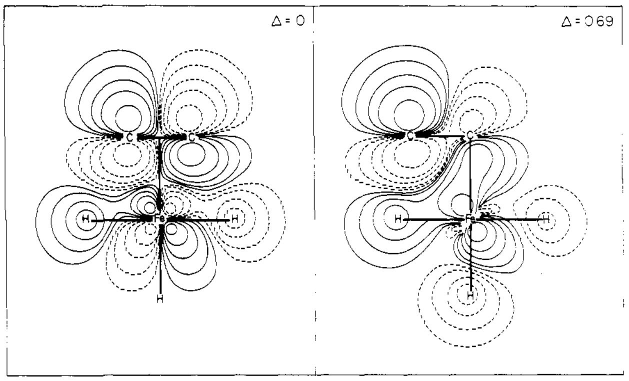
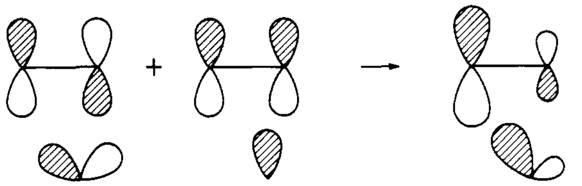


Figure 2. A plot of the $\pi^*-\lambda b_2$ MO in the $\eta^2\pi$ complex $H_5Fe(C_2H_4)^{3-}$ (Δ = 0) and of the LUMO of the $\eta^1\pi$ complex $H_5Fe(C_2H_4)^{3-}$ (Δ = 0.69). The contour values of Ψ are ± 0.2, 0.1, 0.055, 0.025, and 0.01.

The new LUMO of the "slipped" L_nM-C_2H_4 complex can be thought of as a mixture of the unfilled orbitals of the symmetrical species, $a_1-\lambda'\pi$ and $\pi^*-\lambda b_2$. We can write it as $c_1a_1 + c_2b_2 + c_3\pi + c_4\pi^*$, the signs of admixture given below. The LUMO is dominated by π^*, but the ethylene π contribution in it is important. By itself, the H^-–π^* component of the H^-–ethylene overlap population never surpasses the free ethylene value, at any Δ. It is aided, to a variable degree, by the π admixture. The latter is of the correct phase to give a bonding H^-–π contribution.



A detailed analysis of the system shows that the mixing of π into the LUMO in the slipped form depends on the energy of the ML_n fragment a_1 orbital. The higher the a_1, the less π mixing into the LUMO. In $(PH_3)_2Ni(C_2H_4)$, the vacant ML_n a_1 orbital is very high in energy.[8] Consequently, there is little admixture of π into the slipped ethylene LUMO and therefore insufficient activation of the olefin toward the nucleophile.

The detailed analysis, to be published, explores the differences between the various ML_n fragments. Substituent effects are predictable, e.g., that σ and π acceptors on the metal will increase the activation. But it will take some cleverly designed, conformationally constrained complexes to test our contention that ethylene slipping plays the dominant role in the activation of complexed olefins.[13]

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Received April 25, 1980

Titanacyclobutenes

Sir:

The isolation and structure of titanacyclobutenes of the type $Cp_2\overline{TiCH_2CR{=}C}R$ (**1a**,[1] R = Ph; **1b**, R = $SiMe_3$; Cp = η^5-C_5H_5) are reported. These compounds are prepared by reactions of $RC{\equiv}CR$ with $Cp_2TiCH_2AlClMe_2$ (**2**).[2,3] The acetylenic

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[12] The passage to activation occurs only when the slipping is substantial, nearer to a fully formed σ complex. Other geometrical changes in the olefin, not studied by us, certainly take place as the reaction proceeds, so that the activation may in fact occur earlier.

[13] Our work was generously supported by the National Science Foundation through Research Grant CHE 7828048. The permanent affiliation of O.E. is with the Laboratoire de Chimie Theorique, Orsay, France, and her stay at Cornell was made possible by grants from CNRS and NATO.

[1] Isolation of **1a** was briefly reported: Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074-5075.

[2] Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611-3613.

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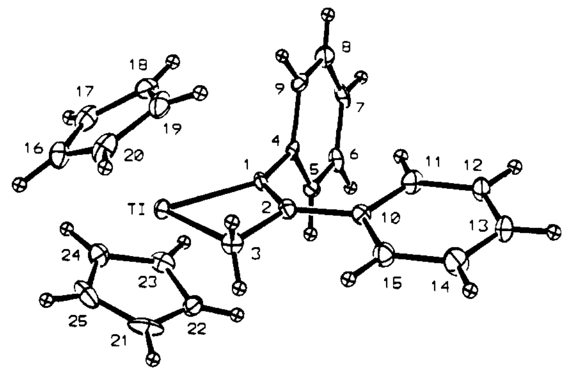


Figure 1. Structure of $Cp_2\overline{TiCH_2CPh{=}CPh}$ (**1a**).

Table I. Selected Bond Distances (Å) with Estimated Standard Deviations[a]

Ti-C(1)	2.104 (4)	C(2)-C(3)	1.537 (6)
Ti-C(2)	2.533 (5)	C(2)-C(10)	1.489 (6)
Ti-C(3)	2.122 (5)	C(3)-H(3)A	0.96 (4)
C(1)-C(2)	1.344 (6)	C(3)-H(3)B	0.88 (4)
C(1)-C(4)	1.475 (6)	C(1)-C(3)	2.403 (7)

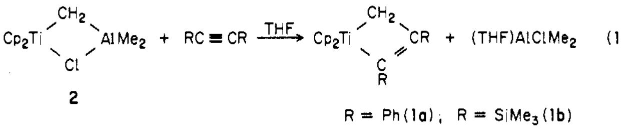
[a] The Ti-C(16-25) bonds range from 2.379 (6) to 2.408 (5) Å with an average value of 2.389 Å. The C-C bonds of the two Cp rings range from 1.378 (7) to 1.413 (7) Å with an average value of 1.392 Å.

Table II. Selected Bond Angles (deg) with Estimated Standard Deviations

C(1)-Ti-C(3)	69.3 (2)	Ti-C(3)-C(2)	86.0 (3)
Ti-C(1)-C(2)	91.8 (3)	Ti-C(3)-H(3)A	120 (2)
Ti-C(1)-C(4)	136.8 (3)	Ti-C(3)-H(3)B	119 (3)
C(2)-C(1)-C(4)	131.2 (4)	C(2)-C(3)-H(3)A	111 (2)
C(1)-C(2)-C(3)	112.8 (4)	C(2)-C(3)-H(3)B	112 (2)
C(1)-C(2)-C(10)	128.5 (4)	H(3)A-C(3)-H(3)B	108 (3)
C(3)-C(2)-C(10)	118.6 (4)		

$Me_3SiCCSiMe_3$ group in titanacyclobutene **1b** may be substituted by another acetylene ($PhC{\equiv}CPh$), by an olefin ($^{13}CH_2{=}CMe_2$), or by $ClAlMe_2$. At this stage, it is useful to attempt to draw comparisons between titanacyclobutenes and titanacyclobutanes, which may be transient intermediates in olefin metathesis reactions catalyzed by **2**.[1] Conditions which were found to favor synthesis of titanacyclobutenes also significantly enhance rates of olefin metathesis catalyzed by **2**.

Compound **2** reacts with diphenylacetylene or bis(trimethylsilyl)acetylene, in tetrahydrofuran (THF) solvent, to produce titanacyclobutenes **1a** and **1b** (eq 1).[9] With toluene as solvent, reactions are sluggish, or significant byproduct is formed. Tetrahydrofuran appears to assist the synthesis of **1** by complexing with aluminum, freeing the Cp_2TiCH_2 group for addition to acetylene. The effect of basic reagents on the chemistry of **2** is further discussed below.



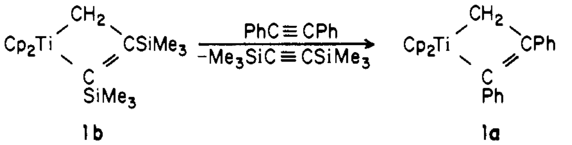
(1)

2

R = Ph(1a); R = SiMe3(1b)

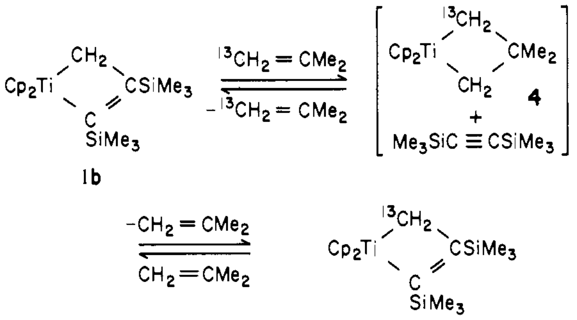
An X-ray crystal structure (Figure 1) (Tables I and II) shows **1a** to be a planar titanacyclobutene.[10] The C(1)-C(2) and C(2)-C(3) distances are within the ranges expected for C-C double and single bonds, respectively. The behavior of **1a** in solution is consistent with this structure. In *p*-xylene, **1a** is monomeric. It reacts with water to produce α-methyl-*cis*-stilbene (**3**), or with D_2O to produce **3**-d_2.

Acetylene or olefin substitution of the $Me_3SiCCSiMe_3$ group in **1b** occurs at elevated temperatures. Diphenylacetylene converts **1b** to **1a** in 36% yield at 85 °C over 6 h (eq 2).[11] The reverse of eq 2 does not occur significantly, even with prolonged heating. 2-Methylpropene-*1*-^{13}C and **1b** react to yield **1b**-^{13}C with enrichment in the methylene [C(3)] position. Methylene equilibration between titanacycle and olefin occurs during 30-40 h at 85 °C.[12] A portion of the mechanism suggested for this exchange reaction (eq 3) consists of substitution of acetylene in **1b** by olefin



(2)

1b 1a



1b

(3)

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(3) Titanacyclobutenes apparently differ from the products obtained by reacting acetylenes ($RC{\equiv}CR'$) with mixtures of titanocene dichloride and methylaluminum compounds. These systems are thought to produce species of the type $RMeC{=}CR'M$ (M = Ti or Al).[4] The complexes $(CO)_5W{=}CHPh$[5] and $CpTaCl_2({=}CHCMe_3)$[6] react with substituted acetylenes to yield ring-opened products, where an acetylene is inserted between the metal and ═CHR fragments.[5,6] A titanacyclobutene structure is found in the compound $[(CH_3C_5H_4)_2TiC_2(C_6H_5)]_2$[7] and is thought[7] to occur in the $[(C_5H_5)_2TiC_2(C_6H_5)]_2$[8] derivative.

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(8) Teuben, J. H.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1969**, *17*, 87-93.

(9) Compound **1a** and its precursor, **2**, are highly sensitive to air and water. Synthesis and reactions of **1** and **2**[2] were conducted under a good nitrogen atmosphere or under vacuum. **CAUTION**: Compound **2** should be treated with precautions appropriate to aluminum alkyls. The byproduct of synthesis of **2** and **1** is $ClAlMe_2$ or its THF adduct, respectively, and should be treated accordingly. For **1a**, a solution of 5.2 g (29 mmol) of diphenylacetylene in 25 mL of THF was added to a freshly prepared solution of 8.3 g (29 mmol) of **2** in 25 mL of THF. After 2 days, solvent was evaporated and the residue crystallized from toluene to yield 5.6 g (52%) of reddish brown crystals. Repeated crystallization from toluene produced bright reddish purple crystals. Anal. Calcd for $C_{25}H_{22}Ti$ (M_w 370): C, 81.1; H, 6.0; Ti, 12.9. Found: .C, 80.6; H, 6.2; Ti, 13.4; M_w 360 (cryoscopic in *p*-xylene). ^1H NMR (toluene-d_8, Me_4Si): τ 3.01 (m, 5 H, C_6H_5), 4.36 (s, 5 H, C_5H_5), 6.63 (s, 1 H, CH_2). For the single-crystal X-ray-diffraction study, crystals were grown from a THF solution. Compound **1b** was prepared by a similar procedure and was purified by passage of a hexane solution of the product mixture through neutral alumina (Woelm, activity grade 1) and by crystallization from pentane. Calcd for $C_{19}H_{30}Si_2$,Ti: M_w 362.1364. Found: 362.1389 (mass spectrum); ^1H NMR (toluene-d_8, Me_4Si) τ 4.81 (s, 10 H, C_5H_5), 5.36 (s, 2 H, CH_2), 9.68 (s, 9 H, CH_3), 9.80 (s, 9 H, CH_3); ^{13}C NMR (toluene-d_8, reference is the C_1 peak of toluene, assigned a shift of δ 137.0) δ 108.3 (CH_2), 107.12 (C_5H_5), 2.34 (CH_3), 1.02 (CH_3).

(10) *Crystal data*: orthorhombic, space group *Pbca*; at −80 °C, $a = 21.339$ (5), $b = 8.142$ (2), $c = 21.230$ (5) Å; $V = 3689$ Å^3; $Z = 8$. *Intensity data*: Syntex P3 diffractometer, graphite monochromator, Mo Kα radiation, $\lambda = 0.71069$ Å; omega scans of 1.0°, $4° < 2\theta < 48°$, 2892 reflections. *Structure solution and refinement*: structure solved by direct methods (MULTAN); hydrogen-atom positions were calculated; all atoms refined by full-matrix least-squares techniques, 1542 reflections with $F^2 > \sigma(F^2)$, 323 variables, $R = 0.048$, $R_w = 0.038$; largest peak in final difference Fourier was less than 0.20 e Å^{-3}.

(11) A toluene-d_8 solution, 0.3 M in both **1b** and $PhC{\equiv}CPh$, was heated and examined by ^1H NMR.

(12) Olefin isomerization ($^{13}CH_2{=}CMe_2 \rightarrow CH_2{=}C^{13}CH_3Me$) also occurs in this system by a process not accounted for in the scheme of eq 3. Small amounts of decomposition products are formed during the reaction. The reaction mixture consisted of 0.07 g (0.2 mmol) of **1b** and 0.2 mmol of $^{13}CH_2{=}CMe_2$ in 0.6 mL of toluene-d_8. The mixture was heated and examined periodically by ^1H NMR.

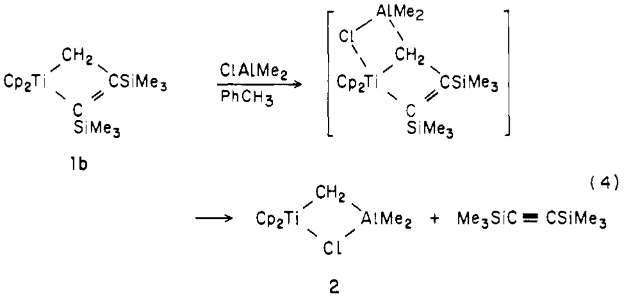
Table III. Promotion of CH_2 Exchange in the System[a] $Cp_2TiCH_2AlClMe_2 + {}^{13}CH_2{=}CMe_2 \rightleftharpoons Cp_2Ti^{13}CH_2AlClMe_2 + CH_2{=}CMe_2$

promoter[b]	CH_2 equilibration time at 25 °C
THF	<15 min
Et_2O	24 h
none	>18 days[c]

[a] Solutions containing 17 mg (0.060 mmol) of **2** in 0.15 mL of C_6D_6 were frozen and treated with 0.053 mmol of $^{13}CH_2{=}CMe_2$ and 0.053 mmol of the indicated ether. The mixtures were warmed to room temperature, and their ^1H NMR spectra were recorded immediately, and at intervals thereafter. Equilibration of methylene groups was judged to be complete when the concentrations of ^{13}C were the same in $CH_2{=}CMe_2$ and undecomposed $Cp_2TiCH_2AlClMe_2$. [b] Approximately two-thirds of the organometallic compound decomposed in the THF activated system. Decomposition in the diethyl ether system was ca. 12%. Decomposition was not detected in the ether-free system. We cannot eliminate the possibility that decomposition products are responsible for acceleration of the exchange rate. [c] The exchange was approximately 80% complete after 18 days.

to yield the metallacyclobutane **4**. Intermediate **4**, as yet not isolated or detected, is also used in a scheme describing CH_2 exchange between $Cp_2TiCH_2AlClMe_2$ (**2**) and $CH_2{=}CMe_2$.[1] This exchange reaction yields the information that titanacyclobutene **1b** is considerably more stable than titanacyclobutane **4**.

The acetylene in **1b** is also substituted by $ClAlMe_2$ when the aluminum reagent is supplied in the absence of THF (eq 4). Thus,

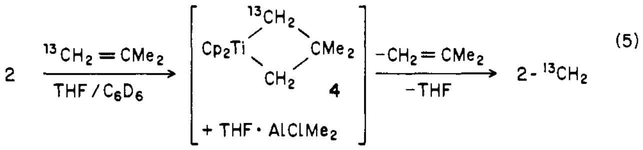


(4)

the synthesis reaction (eq 1) and its reverse (eq 4) are markedly dependent on the solvent. Uncomplexed $ClAlMe_2$ competes effectively with $Me_3SiCCSiMe_3$ for Cp_2TiCH_2, but $THF{\cdot}AlClMe_2$ is not competitive.

In contrast to the elevated temperatures required for reactions of **1b** with unsaturated hydrocarbons, the reaction with $ClAlMe_2$ occurs easily at room temperature. The facility of the aluminum reaction may be related to the ease of coordination of $ClAlMe_2$ with the titanacycle, with the result that the complex is activated for acetylene release. Two of the potential sites of aluminum attack are illustrated in eq 4, where $ClAlMe_2$ adds across the $TiCH_2$ group. A similar effect of $ClAlMe_2$ on a titanacyclobutane (olefin + **2**) might limit its lifetime (see ref 1). In an early example of the effect of aluminum on a saturated titanacycle, Grubbs and Miyashita[13] found that $AlCl_3$ attacks $Cp_2\overline{TiCH_2(CH_2)_3CH_2}$ to produce butene and $Cp_2TiCH_2AlCl_3$.[2]

The $ClAlMe_2$ portion of **2** inhibits reactions of Cp_2TiCH_2 with acetylenes. One test for a similar $ClAlMe_2^-$ inhibition of olefin reactions is to examine the effect of bases on the rate of CH_2 exchange between **2** and an olefin. The olefin chosen for study is $^{13}CH_2{=}CMe_2$, which was found to exchange slowly with **2** in aromatic solvents.[1] We find that ethers markedly accelerate the rate of methylene exchange between **2** and $^{13}CH_2{=}CMe_2$ (Table III). With THF in the reaction mixture, the exchange (eq 5)[14] is faster by a factor of at least 10^3 compared with the rate for an unpromoted reaction. With **2** as an olefin metathesis catalyst[1] for methylene exchange between isobutene and methylenecyclohexane, rates of exchange are enhanced by THF.



(5)

The study of acetylene reactions of $Cp_2TiCH_2AlClMe_2$ (**2**) has assisted interpretation of the olefin chemistry of **2**. The aluminum in **2** inhibits the reactivity of the complex with acetylenes and, we presume, with olefins. The reaction of titanacyclobutene **1b** with $^{13}CH_2{=}CMe_2$ is a case of metal and olefin methylene exchange in an aluminum-free system. This information helps to refine the proposal that aluminum in $Cp_2TiCH_2AlClMe_2$ acts mainly to stabilize and deactivate the $TiCH_2$ group. It will be of interest to determine the effects of main-group alkyls on olefin metathesis catalysts generated from group 6 complexes.[15] Structures similar to **2** have been suggested for the catalyst made with WCl_6 and aluminum or zinc alkyls.[16]

The heterocycles $Cp_2\overline{TiCH_2CSiMe_3{=}CSiMe_3}$ and $Cp_2\overline{TiCH_2AlClMe_2}$ preserve the highly reactive (and quite unstable) Cp_2TiCH_2[17] group for controlled reactions with olefins. An analogous system has been considered by Grubbs, who discussed the potential of metallacyclobutanes for storage and controlled release of reactive metal carbenes.[15a]

Acknowledgment. We thank D. K. Babcock and L. F. Lardear for skilled experimental assistance, Drs. W. Mahler and P. L. Watson for helpful interpretative comments, and Professors R. H. Grubbs, C. P. Casey, and J. J. Eisch for a series of useful discussions.

Supplementary Material Available: Positional and thermal parameters, least-squares planes, and structure amplitudes (14 pages). Ordering information is given on any current masthead page.

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(14) The interpretation of the reaction expressed in eq 5 requires that Cp_2TiCH_2 or titanacyclobutane **4** displaces THF from $THF{\cdot}AlClMe_2$. Studies of this type could provide an approximate idea of the basicity of Cp_2TiCH_2, relative to other bases, toward the Lewis acid $ClAlMe_2$.

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Received November 26, 1979

Linkage Isomerism of a Bidentate Triphosphate Ligand Having Six- or Eight-Membered Chelate Rings

Sir:

The importance of metal binding to phosphates in biological systems has led us to study the different possible modes of binding in metal-phosphate complexes by using substitution-inert metal ions in order that the configuration of the complexes is the same in the crystalline state as in solution. We have previously reported[1,2] on the β,γ-bidentate[3] coordination of triphosphate ion

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