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Nitrosoarene and nitrosoalkane insertion reactions of titanacyclobutenes

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Abstract

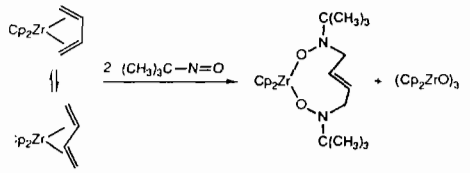
Titanacyclobutenes react with 2-methyl-2-nitrosopropane and nitrosoarenes to afford products of insertion into the Ti–CH_2 bond of the metallacycle. Structural confirmation was obtained through single crystal X-ray diffraction analysis of the insertion product of the diphenyltitanacyclobutene and 2-methyl-2-nitrosopropane: $C_{29}H_{31}NOTi$, monoclinic, $P2_1/n$, $a=7.984(2)$, $b=20.383(8)$, $c=15.005(4)$ Å, $\beta=100.55(2)°$, $V=2400(2)$ Å^3, $Z=4$. The insertion products display dynamic NMR behavior consistent with pyramidal inversion at nitrogen, with activation barriers of *c.* 14 kcal mol^{-1}. Hydrolysis of the insertion products affords the corresponding hydroxylamines, while treatment of them or of the titanacyclobutenes with excess nitrosoarene results in metallacycle degradation and formation of azoxyarene.

Key words: Crystal structures; Insertion reactions; Titanium complexes; Titanacyclobutene complexes; Nitrosoarene complexes; Nitrosoalkane complexes

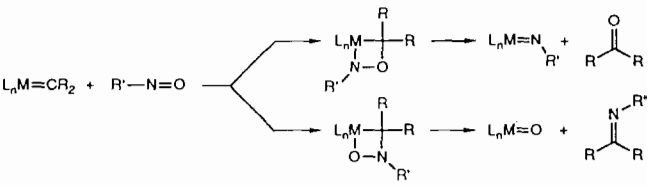
Introduction

Insertion of unsaturated substrates into metal–carbon bonds, creating new carbon–carbon and/or carbon–heteroatom bonds, represents one of the central themes in transition-metal mediated organic synthesis [1]. Through the years, countless examples of insertion reactions of carbon monoxide, alkenes, alkynes, nitriles, isocyanides, isocyanates, aldehydes, ketones and a number of other organic functionalities have been reported. Perhaps surprisingly, although nitroso compounds are isoelectronic with ketones and aldehydes, there have been comparatively few reports of their insertion reactions. Our long-standing interest in the chemistry of metallacyclobutenes [2], together with the potential for facile syntheses of interesting products from simple precursors, prompted us to examine the reactions of titanacyclobutenes with nitroso compounds.

Other reports of early metal insertion reactions with nitroso compounds are rare. Erker and Humphrey [3] reported the reactivity of 2-methyl-2-nitrosopropane with zirconocene– and hafnocene–butadiene complexes. These complexes, which were earlier [4] shown to react with ketones as if they were metallacyclopentenes, readily insert the nitroso compound into each metal–carbon bond, affording large-ring metallacyclic products. Some metallocene oxide is also formed in these reactions.



Metathesis-like reactions of nitroso compounds with Fischer-type carbene complexes have also been reported [5]. Formal [2+2] cycloaddition can afford two isomeric heterometallacyclobutanes, which upon fragmentation can form either an oxo complex or a nitrene (imido) complex.



Our earlier studies of the insertion reactions of titanacyclobutenes with ketones and aldehydes revealed two competing reaction paths, one involving insertion into the titanium–alkyl bond of the metallacycle, the

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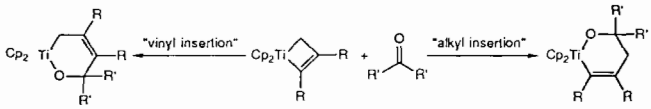
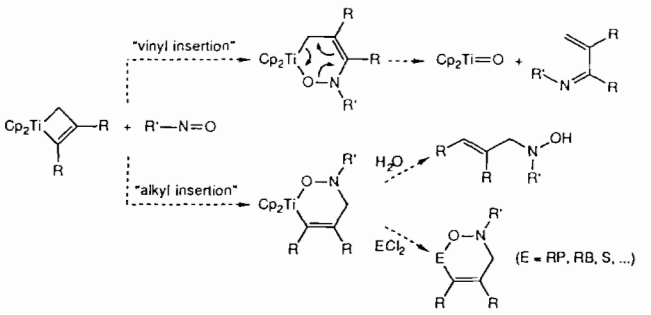
other insertion into the titanium–vinyl bond [6]. The latter insertion, although originally unanticipated, appears to be the favored mode of reaction, with alkyl insertion dominant only in cases which present high steric hindrance to insertion into the more crowded titanium–vinyl bond.



Either insertion mode for nitroso compounds would present unique opportunities in titanium-mediated syntheses of organic functionalities. Vinyl insertion would offer promise for the facile preparation of synthetically useful 1-azadienes [7] (by analogy with the formation of dienes from the thermal decomposition of the ketone and aldehyde vinyl insertion products), while alkyl insertion would afford intermediate metallacyclic complexes which could in turn be converted into a number of other products, including *N*-allylhydroxylamines (through hydrolytic cleavage), and N,O-heterocyclic compounds (through ligand transfer [8] from titanium to main-group electrophiles).



As we report herein, the insertion reactions of nitroso compounds with titanacyclobutenes are all highly regioselective, with exclusive insertion into the titanium–alkyl bond. No products arising from insertion into the titanium–vinyl bond appear to be formed, even for systems displaying less steric hindrance for this insertion than is present in several aldehyde reactions which afford exclusive vinyl-side insertion. This selectivity has potentially important implications regarding the insertion mechanism, as we discuss below. The resulting metallacycles display temperature-dependent spectral properties consistent with pyramidal inversion at the ring nitrogen; the barrier to this inversion process has been determined for several of the metallacycles. Finally, hydrolysis of the metallacycles affords the anticipated *N*-allylhydroxylamines.

Experimental

General considerations

All manipulations were carried out under an atmosphere of purified argon or nitrogen, using standard Schlenk and glove box techniques [9]. Argon and nitrogen were purified by passage first through activated BASF catalyst, then through activated molecular sieves. After purification and drying, all solids and solvents were stored under nitrogen in a Vacuum Atmospheres glove box equipped with a Dri-Train MO 40-1 inert gas purifier unit, RGF-1 regeneration flow unit, Pedatrol pressure control unit, DK-3E Dri-Kool refrigeration unit and Dri-Cold freezer.

Materials

2-Methyl-2-nitrosopropane dimer, nitrosobenzene and 2-nitrosotoluene were obtained from Aldrich Chemical Co. and used as received. Benzene, benzene-d_6, toluene-d_8 and tetrahydrofuran (THF) were distilled or vacuum transferred from Na/K alloy and benzophenone under a pre-purified nitrogen atmosphere. Pentane was stirred over concentrated H_2SO_4, then washed with aqueous $NaHCO_3$, dried over calcium hydride, and distilled from Na/K alloy and benzophenone under a pre-purified nitrogen atmosphere. Dimethyltitanacyclobutene [10], diphenyltitanacyclobutene [11] and benzotitanacyclobutene [12] were prepared as described.

Instrumentation

Nuclear magnetic resonance (NMR) spectra of all samples were obtained on a GE QE-300 (300.152 MHz, ^1H; 75.481 MHz, ^{13}C), with the sample at ambient temperature unless otherwise indicated. The following notation is used in reporting NMR data: (1) chemical shift in parts per million (ppm); (2) multiplicity of signal (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad); (3) coupling constant in hertz (Hz). Chemical shifts are referenced to residual solvent signals in C_6D_6 (δ 7.150, ^1H; δ 128.00, ^{13}C) or $CDCl_3$ (δ 7.26, ^1H; δ 128.0, ^{13}C). High resolution mass spectroscopy was performed on a VG Masslab VG12-250 instrument.

*3-t-Butyl-5,6-diphenyl-1,1-bis(cyclopentadienyl)-3-aza-2-oxa-1-titanacyclohex-5-ene (**4a**)*

To a dark-red solution of 0.700 g of diphenyltitanacyclobutene (1.89 mmol) in 10 ml of THF in a Schlenk flask was added a solution of 2-methyl-2-nitrosopropane dimer (0.164 g, 0.941 mmol) in 1 ml of THF. The solution was stirred at room temperature for 1 h, then the solvent was removed *in vacuo*, affording the product as a red solid, m.p. 185–200 °C (0.646 g, 75%). ^1H NMR (C_6D_6): δ 6.9–7.2 (m, 8H, ArH), 6.86 (t, 1H,

J = 7.5 Hz, ArH), 6.72 (m, 1H, ArH), 5.91 (s, 10H, Cp), 3.88 (s, 2H, CH_2), 0.96 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 188.7 (Ti–C), 152.2 (Ar), 144.7 (Ti–C=*C*), 136.4 (Ar), 130.0 (Ar), 128.3 (Ar), 127.8 (Ar), 127.5 (Ar), 125.2 (Ar), 123.2 (Ar), 114.0 (Cp), 66.2 (CH_2), 59.7 ($C(CH_3)_3$), 25.4 ($C(CH_3)_3$). ^{13}C NMR (C_6D_6): δ 188.7 (s, Ti–C), 152.2 (s, Ar), 144.7 (s, Ti–C=*C*), 136.3 (m, Ar), 130.0 (d, $^1J(CH)$ = 158 Hz, Ar), 128.3 (d, $^1J(CH)$ = 158 Hz, Ar), 127.8 (d, $^1J(CH)$ = 158 Hz, Ar), 127.5 (d, $^1J(CH)$ = 159 Hz, Ar), 125.2 (d, $^1J(CH)$ = 159 Hz, Ar), 123.2 (d, $^1J(CH)$ = 160 Hz, Ar), 114.0 (d of quintets, $^1J(CH)$ = 174 Hz, J_{app} = 6.5 Hz, Cp), 66.2 (t, $^1J(CH)$ = 131 Hz, CH_2), 59.7 (s, $C(CH_3)_3$), 25.4 (q, $^1J(CH)$ = 125 Hz, $C(CH_3)_3$). HRMS: Calc. for $C_{29}H_{31}NOTi$: 457.1885. Found: 457.1877. *Anal.* Calc. for $C_{29}H_{31}NOTi$: C, 76.14; H, 6.83; N, 3.06. Found: C, 76.01; H, 6.89; N, 2.98%.

*3,5,6-Triphenyl-1,1-bis(cyclopentadienyl)-3-aza-2-oxa-1-titanacyclohex-5-ene (**4b**)*

An analogous procedure, using 0.700 g of diphenyltitanacyclobutene (1.89 mmol) and 0.202 g of nitrosobenzene (1.89 mmol), afforded the product as an orange–red solid, m.p. 95–110 °C (0.635 g, 70%). ^1H NMR (C_6D_6): δ 7.41 (d, 2H, J = 7.8 Hz, ArH), 6.8–7.2 (m, 13H, ArH), 5.68 (s, 10H, Cp), 4.47 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 191.9 (Ti–C), 154.4 (Ar), 140.9 (Ti–C=*C*), 136.8 (Ar), 132.5 (Ar), 130.8 (Ar), 130.4 (Ar), 129.4 (Ar), 128.9 (Ar), 127.2 (Ar), 125.8 (Ar), 123.7 (Ar), 117.4 (Ar), 112.2 (Cp), 77.6 (CH_2). One aromatic resonance was not located. HRMS: Calc. for $C_{31}H_{27}NOTi$: 477.1572. Found: 477.1562.

*3-(2-Tolyl)-5,6-diphenyl-1,1-bis(cyclopentadienyl)-3-aza-2-oxa-1-titanacyclohex-5-ene (**4c**)*

An analogous procedure, using 0.700 g of diphenyltitanacyclobutene (1.89 mmol) and 0.228 g of 2-nitrosotoluene (1.89 mmol), afforded the product as an orange–red solid, m.p. 95–110 °C (0.698 g, 75%). ^1H NMR (C_6D_6): δ 7.55 (d, 1H, J = 8.1 Hz, ArH), 6.7–7.2 (m, 13H, ArH), 5.79 (s, 10H, Cp), 4.08 (s, 2H, CH_2), 2.48 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 192.4 (Ti–C), 152.7 (Ar), 141.2 (Ti–C=*C*), 137.4 (Ar), 131.4 (Ar), 129.0 (Ar), 127.8 (Ar), 126.6 (Ar), 125.6 (Ar), 124.4 (Ar), 123.6 (Ar), 120.3 (Ar), 119.5 (Ar), 115.3 (Ar), 113.2 (Cp), 76.0 (CH_2), 18.9 (CH_3). Two aromatic resonances were not located. HRMS: Calc. for $C_{32}H_{29}NOTi$: 491.1728. Found: 491.1710.

*3-t-Butyl-5,6-dimethyl-1,1-bis(cyclopentadienyl)-3-aza-2-oxa-1-titanacyclohex-5-ene (**4d**)*

An analogous procedure, using 0.500 g of dimethyltitanacyclobutene (2.03 mmol) and 0.177 g of 2-methyl-2-nitrosopropane dimer (1.02 mmol), afforded the product as a slightly oily red solid (0.460 g, 68%). ^1H NMR (C_6D_6): δ 5.83 (br s, 10H, Cp), 3.41 (br d, 1H, half of AB quartet for CH_2), 3.23 (br d, 1H, half of AB quartet for CH_2), 1.61 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 0.98 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 179.7 (Ti–C), 126.0 (Ti–C=*C*), 112.7 (Cp), 66.2 (CH_2), 59.1 ($C(CH_3)_3$), 25.4 ($C(CH_3)_3$), 23.3 (CH_3), 17.0 (CH_3). ^{13}C NMR (C_6D_6): δ 179.7 (s, Ti–C), 126.0 (m, J = 5.6 Hz, Ti–C=*C*), 112.7 (d, $^1J(CH)$ = 172 Hz, Cp), 66.2 (t, $^1J(CH)$ = 129 Hz, CH_2), 59.1 (m, $^3J(CH)$ = 4 Hz, $C(CH_3)_3$), 25.4 (q, $^1J(CH)$ = 125 Hz, $C(CH_3)_3$), 23.3 (q, $^1J(CH)$ = 124 Hz, CH_3), 17.0 (q, $^1J(CH)$ = 125 Hz, CH_3). HRMS: Calc. for $C_{19}H_{27}NOTi$: 333.1572. Found: 333.1577. *Anal.* Calc. for $C_{19}H_{27}NOTi$: C, 68.46; H, 8.16; N, 4.20. Found: C, 68.37; H, 8.17; N, 4.10%.

*3-Phenyl-5,6-dimethyl-1,1-bis(cyclopentadienyl)-3-aza-2-oxa-1-titanacyclohex-5-ene (**4e**)*

An analogous procedure, using 0.500 g of dimethyltitanacyclobutene (2.03 mmol) and 0.217 g of nitrosobenzene (2.03 mmol), afforded the product as a slightly oily red solid (0.464 g, 65%). ^1H NMR (C_6D_6): δ 7.19 (d, 2H, $^3J(HH)$ = 7.8 Hz, ArH), 7.02 (d, 2H, $^3J(HH)$ = 7.8 Hz, ArH), 6.86 (t, 1H, $^3J(HH)$ = 7.8 Hz, ArH), 5.69 (s, 10H, Cp), 3.92 (s, 2H, CH_2), 1.63 (s, 3H, CH_3), 1.53 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 182.5 (Ti–C), 152.9 (Ar), 131.2 (Ar), 122.6 (Ti–C=*C*), 121.7 (Ar), 116.5 (Ar), 111.9 (Cp), 74.0 (CH_2), 23.6 (CH_3), 15.1 (CH_3). HRMS: Calc. for $C_{21}H_{23}NOTi$: 353.1259. Found: 353.1229. *Anal.* Calc. for $C_{21}H_{23}NOTi$: C, 71.39; H, 6.56; N, 3.96. Found: C, 71.43; H, 6.68; N, 3.90%.

*3-(2-Tolyl)-5,6-dimethyl-1,1-bis(cyclopentadienyl)-3-aza-2-oxa-1-titanacyclohex-5-ene (**4f**)*

An analogous procedure, using 0.500 g of dimethyltitanacyclobutene (2.03 mmol) and 0.246 g of 2-nitrosotoluene (2.03 mmol), afforded the product as a slightly oily red solid (0.566 g, 76%). ^1H NMR (C_6D_6): δ 7.51 (d, 1H, $^3J(HH)$ = 8.1 Hz, ArH), 7.15 (m, 1H, ArH), 7.03 (d, 1H, $^3J(HH)$ = 7.5 Hz, ArH), 6.94 (t, 1H, $^3J(HH)$ = 7.5 Hz, ArH), 5.73 (s, 10H, Cp), 3.54 (s, 2H, CH_2), 2.31 (s, 3H, Ar–CH_3), 1.61 (s, 3H, CH_3), 1.49 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 192.9 (Ti–C), 152.9 (Ar), 131.2 (Ar), 128.1 (Ar), 127.3 (Ar), 126.7 (Ar), 123.9 (Ti–C=*C*), 119.6 (Ar), 112.2 (Cp), 75.1 (CH_2), 23.4 (Ar–CH_3), 18.5 (CH_3), 15.5 (CH_3). HRMS: Calc. for $C_{22}H_{25}NOTi$: 367.1415. Found: 367.1422. *Anal.* Calc. for $C_{22}H_{25}NOTi$: C, 71.93; H, 6.86; N, 3.81. Found: C, 71.86; H, 6.88; N, 3.75%.

*3-t-Butyl-1,1-bis(cyclopentadienyl)-3-aza-2-oxa-1-titana-5,6-benzocyclohexene (**4g**)*

A solution of benzotitanacyclobutene (38.3 mg, 0.143 mmol) in 0.5 ml of C_6D_6 was added to 12.4 mg of 2-methyl-2-nitrosopropane dimer (0.071 mmol) in a small

vial. The resulting solution was transferred to an NMR tube which was then flame sealed. ^{1}H NMR spectroscopy showed the reaction to be complete within 10 min at room temperature. The product was not isolated. ^{1}H NMR (C_6D_6): δ 7.12 (br s, 1H, ArH), 7.02 (m, 2H, ArH), 6.56 (dd, 1H, J(HH) = 6.9, 1.5 Hz, ArH), 5.79 (s, 10H, Cp), 3.87 (br s, 2H, CH_2), 0.99 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 184.5 (Ti–C), 143.5 (Ti–C=*C*), 137.8 (Ar), 127.2 (Ar), 123.8 (Ar), 123.5 (Ar), 114.0 (Cp), 64.0 (CH_2), 59.1 ($C(CH_3)_3$), 25.5 ($C(CH_3)_3$).

*3-Phenyl-1,1-bis(cyclopentadienyl)-3-aza-2-oxa-1-titana-5,6-benzocyclohexene (**4h**)*

To 18.3 mg of nitrosobenzene (0.171 mmol) and 0.25 ml of C_6D_6 in an NMR tube was added a solution of benzotitanacyclobutene (45.8 mg, 0.171 mmol) in 0.25 ml of C_6D_6. ^{1}H NMR spectroscopy showed the reaction to be complete within 10 min at room temperature. The product was not isolated. ^{1}H NMR (C_6D_6): δ 7.15–7.0 (m, 7H, ArH), 6.86 (t, 2H, ^3J(HH) = 7.5 Hz, ArH), 5.65 (s, 10H, Cp), 4.43 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 186.0 (Ti–C), 153.3 (Ar), 145.1 (Ti–C=*C*), 138.4 (Ar), 128.9 (Ar), 124.8 (Ar), 124.7 (Ar), 123.7 (Ar), 122.3 (Ar), 117.0 (Ar), 112.9 (Cp), 73.2 (CH_2). ^{13}C NMR (C_6D_6): δ 186.0 (s, Ti–C), 153.3 (s, Ar), 145.1 (s, Ti–C=*C*), 138.4 (d, ^1J(CH) = 157 Hz, Ar), 128.9 (d, ^1J(CH) = 160 Hz, Ar), 124.8 (d, ^1J(CH) = 170 Hz, Ar), 124.7 (d, ^1J(CH) = 170 Hz, Ar), 123.7 (d, ^1J(CH) = 158 Hz, Ar), 122.3 (d, ^1J(CH) = 160 Hz, Ar), 117.0 (d, ^1J(CH) = 161 Hz, Ar), 112.9 (d, ^1J(CH) = 174 Hz, Cp), 73.2 (t, ^1J(CH) = 135 Hz, CH_3).

*3-(2-Tolyl)-1,1-bis(cyclopentadienyl)-3-aza-2-oxa-1-titana-5,6-benzocyclohexene (**4i**)*

To 23.0 mg of 2-nitrosotoluene (0.190 mmol) and 0.25 ml of C_6D_6 in an NMR tube was added a solution of benzotitanacyclobutene (50.7 mg, 0.189 mmol) in 0.25 ml of C_6D_6. ^{1}H NMR spectroscopy showed the reaction to be complete within 10 min at room temperature. The resulting solution was passed through a 1.5 cm column of silica gel in a small pipette, eluting with 3 ml of pentane. Removal of solvent *in vacuo* afforded the product as a red solid (30 mg, 41%). ^{1}H NMR (C_6D_6): δ 7.43 (d, 1H, ^1J(HH) = 8.1 Hz, ArH), 7.18 (t, 1H, ^1J(HH) = 7.2 Hz, ArH), 7.05–6.9 (m, 5H, ArH), 6.62 (dd, 1H, J(HH) = 4.5, 3.3 Hz, ArH), 5.72 (s, 10H, Cp), 4.08 (s, 2H, CH_2), 2.21 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 185.6 (Ti–C), 156.7 (Ar), 143.9 (Ti–C=*C*), 137.8 (Ar), 131.0 (Ar), 128.3 (Ar), 126.7 (Ar), 126.0 (Ar), 124.4 (Ar), 123.9 (Ar), 123.7 (Ar), 119.4 (Ar), 115.7 (Cp), 72.6 (CH_2), 18.8 (CH_3). ^{13}C NMR (C_6D_6): δ 185.6 (s, Ti–C), 156.7 (s, Ar), 143.9 (s, Ti–C=*C*), 137.8 (d, ^1J(CH) = 155 Hz, Ar), 131.0 (d, ^1J(CH) = 155 Hz, Ar), 128.3 (?, obscured by solvent resonances), 126.7 (d, ^1J(CH) = 160 Hz, Ar), 126.0 (d, ^1J(CH) = 147 Hz, Ar), 124.4 (d, ^1J(CH) = 150 Hz, Ar), 123.9 (d, ^1J(CH) = 166 Hz, Ar), 123.7 (d, ^1J(CH) = 163 Hz, Ar), 119.4 (d, ^1J(CH) = 164 Hz, Ar), 113.7 (d, ^1J(CH) = 176 Hz, Cp), 72.6 (t, ^1J(CH) = 135 Hz, CH_2), 18.8 (q, ^1J(CH) = 130 Hz, CH_3). *Anal.* Calc. for $C_{24}H_{23}NOTi$: C, 74.04; H, 5.95; N, 3.60. Found: C, 73.87; H, 6.04; N, 3.54%.

*Single-crystal X-ray diffraction analysis of **4a***

Red crystals of **4a** suitable for X-ray diffraction analysis were obtained by slow evaporation under an inert atmosphere of a solution of **4a** in benzene. A dark red block of **4a** was mounted in a dab of silicone grease in a glass capillary, which was then sealed with wax. The cell dimensions and orientation matrix were obtained from the setting angles of a CAD-4 goniometer for 25 centered reflections in the range $13 < \theta < 15°$. A summary of crystal data, details of data collection and refinement, and residuals is given in Table 1. Scattering by the capillary and residual silicone grease resulted in a somewhat elevated background for all reflections; however, 60% of reflections up to the limit $\theta = 25°$ had intensities greater than $3\sigma(I)$. No significant crystal decay was observed during 80 h of data collection at 22 °C.

The position of the titanium atom was obtained from the Patterson function. A cycle of DIRDIF [13] gave the positions of all other heavy atoms and confirmed the expected connectivity. Peaks were apparent near the expected positions for all hydrogen atoms in a difference synthesis following anisotropic refinement. The hydrogen atoms were included at 'riding' positions in the last cycles of the refinement, with B(H) set at $1.2B_{eq}$(C). A secondary extinction parameter was also refined. No solvent of crystallization was present, and the final difference map was featureless. The TEXSAN program suite [14], incorporating complex atomic scattering factors [15], was used in all calculations. An empirical absorption correction [16] based on the isotropic model led to no decrease in residuals or standard deviations, and the results presented herein are derived from the data without absorption correction. Atomic coordinates and equivalent isotropic thermal parameters for all non-hydrogen atoms are provided in Table 2, and selected bond lengths and angles are provided in Tables 3 and 4. See also 'Supplementary material'.

*Hydrolysis of **4a***

To a solution of 0.50 g of **4a** (1.1 mmol) in THF was added 39.3 μl of water (2 equiv.). The solution was stirred for 1 h at room temperature, then the solvent was removed *in vacuo*. The pasty residue was extracted with chloroform and filtered through a 2.5 cm column of silica gel, eluting with chloroform. Removal of the solvent *in vacuo* afforded the hydroxylamine

TABLE 1. Details of data collection and structural analysis of complex **4a**

Crystal data	
Chemical formula	$C_{29}H_{31}NOTi$
Formula weight	457.47
Crystal size (mm)	$0.20\times0.30\times0.55$
Appearance	dark red block
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	7.984(2)
b (Å)	20.383(8)
c (Å)	15.005(4)
α (°)	90
β (°)	100.55(2)
γ (°)	90
V (Å^3)	2400(2)
Z	4
ρ_{calc} (g cm^{-3})	1.266
μ (cm^{-1})	3.7
$F(000)$	968
Data collection	
Temperature (K)	295
Radiation	Mo Kα (graphite monochromator)
Wavelength (Å)	0.71073
Scan mode	ω–2θ
2θ max. (°)	50
Data collected	$0\leqslant h\leqslant 9,\ 0\leqslant k\leqslant 24,\ -17\leqslant l\leqslant 17$
Scan width (°)	$(1.00+0.344\ \tan\theta)$
Scan rate (° min^{-1})	1.6–5.5
Reference reflections	3, every 1 h exposure
No. unique reflections	4221
R_{int} (based on F^2)	0.047
Refinement	
Absorption correction	none
Secondary parameter (g)	$9.5(7)\times10^{-7}$
No. observed reflections ($I>3\sigma(I)$)[a]	2579
No. parameters refined	290
Function minimized	$\Sigma w(\|F_o\|-\|F_c\|)^2$
Weighting factor (w)	$1/\sigma^2(F)$
$R(F)$[b], $R_w(F)$[c]	0.041, 0.043
Goodness-of-fit index (S)[d]	1.78
Max. Δ/σ, last cycle	0.074
Max., min. in final difference map (e Å^{-3})	+0.34 (near Ti), −0.35

[a] $I_{obs}(\text{corr})=I_{obs}(1+2gI_{calc})$. [b] $R(F)=\Sigma|(|F_o|-|F_c|)|/\Sigma|F_o|$. [c] $R_w(F)=[\Sigma w(|F_o|-|F_c|)^2/\Sigma|F_o|^2]^{1/2}$. [d] $S=[\Sigma w(|F_o|-|F_c|)^2/(N-V)]^{1/2}$.

7a as a yellow–orange oil. ^{1}H NMR ($CDCl_3$): δ 7.3–6.8 (m, 10H, ArH), 6.47 (s, 1H, OH), 6.30 (s, 1H, =CH), 3.65 (s, 2H, CH_2), 1.31 (s, 9H, $C(CH_3)_3$).

*Hydrolysis of **4b***

To a solution of 0.50 g of **4b** (1.0 mmol) in THF was added 37.8 μl of water (2 equiv.). The solution was stirred for 1 h at room temperature, then the solvent was removed *in vacuo*. The pasty residue was extracted with benzene and filtered through a 2.5 cm column of silica gel, eluting with benzene. Removal of the solvent *in vacuo* afforded the hydroxylamine **7b** as a pale-yellow oil (0.19 g, 60%). MS (70 eV): 299 ($M-2H$, 28%), 298 (12%), 285 ($M-O$, 5%), 282 (21%), 271 ($M-NO$, 5%), 268 (31%), 267 (12%), 222 ($M-2H-C_6H_5$, 7%), 218 (16%), 208 (27%), 207 (17%), 195 (14%), 194 ($M-NO-C_6H_5$, 76%), 193 ($M-C_6H_5-NOH$, 25%), 191 (16%), 189 (10%), 167 (10%), 165 (32%), 152 (17%), 142 (10%), 116 (12%), 115 (38%), 105 ($C_6H_5NCH_2$, 33%), 103 (13%), 102 (14%), 91 (C_6H_5N, 33%), 89 (20%), 78 (22%), 77 (C_6H_5, 100%), 76 (13%), 75 (10%), 74 (13%), 65(19%), 63 (22%), 51 (54%), 50 (21%), 39 (26%).

*Hydrolysis of **4c***

An analogous hydrolysis of 0.30 g of **4c** (0.61 mmol) afforded the hydroxylamine **7c** as a pale-yellow oil (0.12 g, 63%). ^{1}H NMR ($CDCl_3$): δ 7.79 (d, 1H, $^3J(HH)=8.1$ Hz, ArH), 7.2–6.9 (m, 13H), 6.85 (s, 1H, =CH), 4.85 (s, 1H, OH), 3.79 (s, 2H, CH_2), 2.06 (s, 3H, CH_3).

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2$) for complex **4a**

Atom	x	y	z	B_{eq}[a]
Ti	6047.7(8)	2231.1(3)	2138.5(4)	2.64(2)
O(1)	5833(3)	1780(1)	3197(1)	2.9(1)
N(1)	4197(3)	1777(1)	3475(2)	2.9(1)
C(1)	5046(4)	3093(2)	2722(2)	2.5(1)
C(2)	4328(4)	3022(2)	3462(2)	2.7(1)
C(3)	4107(5)	2391(2)	3962(2)	3.3(2)
C(4)	4545(5)	2429(2)	628(2)	4.4(2)
C(5)	3304(5)	2383(2)	1184(2)	3.9(2)
C(6)	3329(5)	1754(2)	1503(2)	4.1(2)
C(7)	4555(6)	1398(2)	1165(3)	4.9(2)
C(8)	5287(5)	1817(2)	612(3)	5.0(2)
C(9)	8838(5)	1826(2)	2099(3)	4.5(2)
C(10)	8898(5)	2073(2)	2972(3)	4.5(2)
C(11)	8637(4)	2735(2)	2919(3)	4.4(2)
C(12)	8445(5)	2927(2)	2007(3)	4.4(2)
C(13)	8604(5)	2366(2)	1513(3)	4.7(2)
C(14)	5326(4)	3764(2)	2396(2)	2.8(1)
C(15)	6457(5)	4195(2)	2921(2)	3.6(2)
C(16)	6810(5)	4806(2)	2604(3)	4.4(2)
C(17)	6053(5)	5011(2)	1751(3)	4.8(2)
C(18)	4924(5)	4596(2)	1228(3)	4.7(2)
C(19)	4561(5)	3992(2)	1538(2)	3.5(2)
C(20)	3653(4)	3592(2)	3910(2)	2.7(1)
C(21)	2198(5)	3921(2)	3504(2)	3.7(2)
C(22)	1571(5)	4448(2)	3914(3)	5.0(2)
C(23)	2397(6)	4664(2)	4749(3)	5.1(2)
C(24)	3828(6)	4346(2)	5172(3)	4.3(2)
C(25)	4468(5)	3815(2)	4765(2)	3.4(2)
C(26)	4184(4)	1177(2)	4043(2)	3.1(2)
C(27)	4163(5)	588(2)	3414(3)	4.6(2)
C(28)	5732(5)	1132(2)	4811(3)	4.9(2)
C(29)	2556(5)	1176(2)	4437(3)	4.5(2)

[a] $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$, defined by Hamilton [41]. Units of each e.s.d., in parentheses, are those of the least significant digit of the corresponding parameter.

TABLE 3. Selected bond lengths (Å) for complex **4a**

Ti–O(1)	1.870(2)
Ti–C(1)	2.179(3)
Ti–Cp(1)[a]	2.097(3)
Ti–Cp(2)[a]	2.098(3)
O(1)–N(1)	1.442(3)
N(1)–C(3)	1.459(4)
N–C(26)	1.491(4)
C(1)–C(2)	1.347(4)
C(1)–C(14)	1.483(4)
C(2)–C(3)	1.516(4)
C(2)–C(20)	1.490(4)

[a] Cp(1) and Cp(2) denote the centroids of cyclopentadienyl rings C(4–8) and C(9–13).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.6 (Ar), 140.7 (Ar), 139.1 (ArHC=C), 137.3 (Ar), 130.3 (Ar), 129.7 (ArHC=*C*), 129.3 (Ar), 128.2 (Ar), 127.3 (Ar), 127.0 (Ar), 126.8 (Ar), 125.1 (Ar), 120.0 (Ar), 69.0 (CH_2), 17.8 (CH_3). Three aromatic resonances were not resolved. MS (70 eV): 315 (M^+, 16%), 314 (26%), 313 ($M-2H$, 100%), 312 (62%), 300 (37%), 299 ($M-O$, 100%), 298 (15%), 297 (47%), 296 (85%), 285 ($M-NO$, 26%), 268 (16%), 267 (23%), 265 (12%), 236 ($M-2H-C_6H_5$, 21%), 208 ($M-NO-C_6H_5$, 31%), 207 (26%), 196 (10%), 194 (21%), 193 ($M-CH_3-C_6H_4-NOH$, 66%), 192 (21%), 191 (23%), 152 (12%), 120 (28%), 118 (18%), 115 (39%), 105 ($CH_3C_6H_4N$, 20%), 91 ($CH_3C_6H_4$, 39%), 77 (C_6H_5, 16%).

TABLE 4. Selected bond angles (°) for complex **4a**

O(1)–Ti–C(1)	87.6(1)
O(1)–Ti–Cp(1)[a]	112.9(1)
O(1)–Ti–Cp(2)[a]	102.7(1)
C(1)–Ti–Cp(1)	106.4(1)
C(1)–Ti–Cp(2)	105.5(1)
Cp(1)–Ti–Cp(2)	132.5(1)
Ti–O(1)–N(1)	118.5(2)
O(1)–N(1)–C(3)	105.8(2)
O(1)–N(1)–C(26)	105.7(2)
C(3)–N(1)–C(26)	114.3(2)
Ti–C(1)–C(2)	119.2(2)
Ti–C(1)–C(14)	121.5(2)
C(2)–C(1)–C(14)	118.9(3)
C(1)–C(2)–C(3)	127.2(3)
C(1)–C(2)–C(20)	122.2(3)
C(3)–C(2)–C(20)	110.6(3)
N(1)–C(3)–C(2)	117.3(3)

[a] Cp(1) and Cp(2) denote the centroids of cyclopentadienyl rings C(4–8) and C(9–13).

Hydrolysis of ***4d***

Hydrolysis of a solution of **4d** in C_6D_6 (prepared as described above) afforded the hydroxylamine **7d**. The product decomposed upon attempted isolation. ^1H NMR ($CDCl_3$): δ 5.48 (q, 1H, $^3J(HH) = 6.6$ Hz, =CH), 4.17 (br s, 1H, OH), 3.09 (s, 2H, CH_2), 1.68 (s, 3H, CH_3), 1.58 (d, 3H, $^3J(HH) = 6.6$ Hz, CH_3), 1.07 (s, 9H, $C(CH_3)_3$).

Hydrolysis of ***4e***

An analogous hydrolysis of 0.464 g of **4e** (1.31 mmol) afforded the hydroxylamine **7e** as a pale-yellow oil (0.188 g, 64%). ^1H NMR ($CDCl_3$): δ 7.5–7.0 (m, 5H, ArH), 5.67 (br q, 1H, $^3J(HH) = 7.0$ Hz, =CH), 5.32 (s, 1H, OH), 3.78 (s, 2H, CH_2), 1.77 (s, 3H, CH_3), 1.69 (d, 3H, $^3J(HH) = 7.0$ Hz, CH_3). MS (70 eV): 177 (M^+, 4%), 175 ($M-2H$, 9%), 173 (9%), 162 (11%), 161 ($M-O$, 24%), 160 ($M-OH$, 10%), 159 ($M-H_2O$, 12%), 148 (10%), 147 ($M-NO$, 23%), 146 ($M-NO-H$, 11%), 145 (17%), 135 (10%), 133 (16%), 132 ($M-NO-CH_3$, 16%), 131 (16%), 130 ($M-2CH_3-OH$, 18%), 121 (10%), 120 (17%), 119 (24%), 118 (23%), 117 (18%), 115 (10%), 109 (11%), 107 (C_6H_4NOH, 10%), 106 (17%), 105 ($C_6H_5NCH_2$, 18%), 104 (30%), 99 (11%), 97 (13%), 93 (44%), 92 (17%), 91 (C_6H_5N, 29%), 85

(28%), 83 (17%), 79 (10%), 78 (18%), 77 (C_6H_5, 100%), 71 (39%), 70 ($M-NO-C_6H_5$, 11%), 69 ($M-C_6H_5-NOH$, 42%), 67 (12%), 66 (13%), 65 (33%), 57 (61%), 56 (13%), 55 (30%), 53 (10%), 51 (35%), 50 (12%), 43 (50%), 41 (46%), 39 (28%).

Hydrolysis of ***4f***

An analogous hydrolysis of 0.566 g of **4f** (1.54 mmol) afforded hydroxylamine **7f** as a pale-yellow oil (0.20 g, 54%). ^{1}H NMR ($CDCl_3$): δ 7.5–7.0 (m, 4H, ArH), 5.74 (q, 1H, ^3J(HH) = 7.0 Hz, =CH), 5.09 (s, 1H, OH), 3.44 (s, 2H, CH_2), 2.34 (s, 3H, ArCH_3), 1.83 (s, 3H, CH_3), 1.70 (d, 3H, ^3J(HH) = 7.0 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.1, 132.4, 130.4, 129.0, 126.5, 124.8, 123.2, 119.4, 68.7 (CH_2), 17.8 (ArCH_3), 14.5 (CH_3), 13.3 (CH_3). MS (70 eV): 191 (M^+, 15%), 190 ($M-H$, 35%), 175 ($M-O$, 12%), 174 ($M-OH$, 44%), 158 ($M-CH_3-H_2O$, 12%), 147 (11%), 146 ($M-NO-CH_3$, 11%), 144 ($M-2CH_3-OH$, 12%), 134 (28%), 133 (10%), 132 (16%), 131 (13%), 130 (10%), 123 (11%), 120 (11%), 119 (14%), 118 ($CH_3C_6H_4NCH$, 40%), 117 (11%), 107 (C_6H_4NOH, 23%), 106 (24%), 105 ($CH_3C_6H_4N$, 12%), 104 ($C_6H_4NCH_2$, 16%), 92 (13%), 91 ($CH_3C_6H_4$, 100%), 89 (10%), 79 (16%), 78 (14%), 77 (24%), 69 ($M-CH_3C_6H_4NOH$, 26%), 65 (38%), 63 (11%), 51 (13%), 41 (29%), 39 (22%).

Dynamic NMR behaviour of ***4d***

A sample of **4d** was dissolved in toluene-d_8 and sealed in a 5 mm NMR tube. Limiting chemical shift values for the AB quartet arising from the methylene group (3.442, 3.392, 3.255, 3.205 ppm) and the two cyclopentadienyl resonances (5.810, 5.761 ppm) were obtained at −40 °C (233 K). The temperature was then incrementally increased, allowing the sample to equilibrate at each new temperature for 10 min before data acquisition. Coalescence of the cyclopentadienyl resonances was achieved at 15 °C (288 K) and of the methylene group AB quartet at 12 °C (285 K). Standard analysis of these data [17] afforded a value for $\Delta G^{\ddagger}$ of 15.0 kcal mol^{-1} from both observed coalescences.

Dynamic NMR behaviour of ***4g***

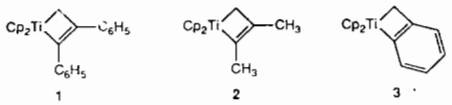
A sample of **4g** was dissolved in toluene-d_8 and sealed in a 5 mm NMR tube. Limiting chemical shift values for the AB quartet arising from the methylene group (4.022, 3.975, 3.716, 3.699 ppm) were obtained at −32 °C (241 K). The temperature was then incrementally increased, allowing the sample to equilibrate at each new temperature for 10 min before data acquisition. Coalescence was achieved at 12 °C (285 K). Standard analysis of these data, as above, afforded a value for $\Delta G^{\ddagger}$ of 13.7 kcal mol^{-1} at 285 K.

Formation of azoxybenzene

To a solution of 27.2 mg of diphenyltitanacyclobutene (0.073 mmol) in 0.5 ml C_6D_6 in a 5 mm NMR tube were added 81.6 mg of nitrosobenzene (0.762 mmol, 10 equiv.). Examination of the reaction mixture by ^{1}H NMR showed the reaction to be complete within 10 min at room temperature. The solution was passed through a *c.* 2.5 cm column of dry silica, eluting with benzene. The leading, pale-green band was collected and brought to dryness *in vacuo*, affording azoxybenzene as a pale yellow–green solid. NMR analysis before and after chromatography showed azoxybenzene and excess nitrosobenzene to be the only major components of the initial reaction mixture. ^{1}H NMR (C_6D_6): δ 8.36 (d, 2H, ^3J(HH) = 7.8 Hz, ArH), 8.24 (d, 2H, ^3J(HH) = 7.5 Hz, ArH), 7.18 (t, 2H, ^3J(HH) = 7.8 Hz, ArH), 7.03 (t, 1H, ^3J(HH) = 7.8 Hz, ArH), 6.9–7.0 (m, 3H, ArH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 149.0, 144.8, 131.4, 129.6, 128.9, 128.8, 125.9, 122.6. MS (70 eV): m/z = 198 (M^+, 23%), 169 (26%), 141 (14%), 105 ($C_6H_5N_2^+$, 23%), 91 ($C_6H_5N^+$, 33%), 78 (12%), 77 ($C_6H_5^+$, 100%), 65 (32%), 64 (26%), 63 (15%), 51 (60%), 50 (24%), 38 (28%), 37 (14%).

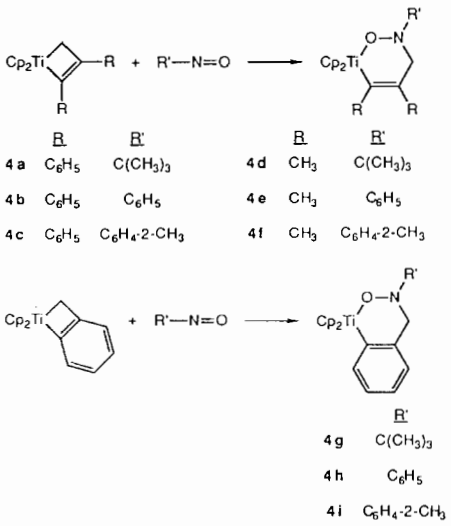
Results and discussion

Our earlier studies of ketone [6], aldehyde [6] and nitrile [18] insertion reactions showed diphenyltitanacyclobutene (**1**) to react predominantly via titanium–alkyl insertion, while the dimethyl metallacycle **2** afforded the products of titanium–vinyl insertion with all but the bulkiest substrates. Benzo metallacycle **3**, in contrast, does not react with ketones or aldehydes at all under analogous reaction conditions, but does react with nitriles, affording exclusively titanium–alkyl insertion products [19].

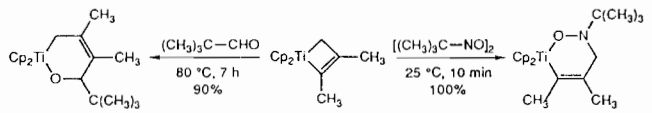


1 2 3

Reactions of the titanacycles **1–3** with 2-methyl-2-nitrosopropane (used in the form of its dimer), nitrosobenzene and 2-nitrosotoluene are all very rapid at room temperature, with essentially quantitative formation of insertion products **4a–i** upon time of mixing and transfer to a nuclear magnetic resonance (NMR) spectrometer for monitoring.



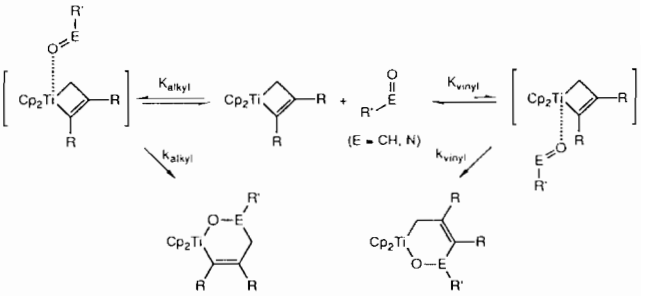
The speed of these reactions stands in contrast to the reactions of **1–3** with ketones, aldehydes and nitriles, which more commonly require a number of hours at 60–80 °C. Also significant is the high regioselectivity of these insertion reactions, with exclusive formation of the alkyl insertion products even with dimethyl metallacycle **2**. For example, the vinyl insertion product of 2,2-dimethylpropionaldehyde with **2** is obtained in *c.* 90% yield [6], while the isoelectronic and roughly isosteric 2-methyl-2-nitrosopropane gives quantitative formation of the alkyl insertion product with **2**.



Nuclear magnetic resonance spectroscopy provides the most convenient assay for the regiochemistry of titanacyclobutene insertion reactions. ^{1}H NMR spectra of the insertion products are suggestive with the methylene resonance appearing at fairly low field (3.4–4.5 ppm), more consistent with formulation as the alkyl insertion products than as the vinyl insertion products, which are expected to display this resonance at higher field. Most conclusive, however, are the ^{13}C NMR spectra of the insertion products. Our extensive studies of titanocene-based metallacycles have established that vinyl carbons attached to titanium in such complexes display ^{13}C resonances in the range of *c.* 180–220 ppm downfield from tetramethylsilane [20]*. Each of the insertion products displays such a resonance, supporting their formulation as alkyl insertion products and inconsistent with vinyl insertion products, which should display no resonances in this downfield window.

Mechanistic implications

Coordination of substrate to titanacyclobutene prior to insertion is apparent in the ketone, aldehyde and nitrile insertion reactions, as evidenced by exchange broadening of substrate resonances in ^{1}H NMR spectra taken at short reaction times. Consideration of steric effects leads one to anticipate preferential coordination on the less-encumbered alkyl 'side' of the titanacyclobutene (i.e. $K_{alkyl} > K_{vinyl}$). In order for vinyl insertion to occur, then, the alkyl insertion step (k_{alkyl}) must be rather slow relative to vinyl insertion (k_{vinyl}), allowing for equilibration between alkyl-side and vinyl-side coordination. The exclusive formation of alkyl insertion products with nitroso substrates and the high rate of these insertion reactions support this contention. Preferential alkyl-side coordination in this case is followed by rapid insertion, precluding loss of coordinated substrate and recapture on the vinyl side of the metallacycle.



Structural studies

In order to establish the structures of these insertion products unequivocally, a single crystal X-ray diffraction analysis was carried out for insertion product **4a**, arising from the insertion of 2-methyl-2-nitrosopropane into the diphenyl metallacycle **1**. This study confirmed the structure inferred from NMR spectral analysis (Fig. 1). Several features of the structure are noteworthy. The C–Ti–O bond angle, at 87°, is quite similar to that in other crystallographically characterized heteroatom-containing titanacycles [21] and, for that matter, in non-cyclic titanocene derivatives as well (e.g. Cp_2TiCl_2 displays a Cl–Ti–Cl angle of 95.2°) [22]. The relatively short Ti–O bond (1.87 Å) suggests partial multiple-bond character to this bond [23, 21]. The larger-than-tetrahedral Ti–O–N angle (118°) is consistent with this suggestion, although this angle is appreciably smaller than in an analogous complex (132.5°) bearing gross structural similarity [21]. As in the latter complex, the strain in the metallacyclic ring appears to be in part localized at the methylene carbon, which displays a

*The only exception found thus far is the titanacyclobutene derived from bis(trimethylsilyl)acetylene, which both solid-state structural studies and theory suggest is perhaps better represented as an alkyne complex rather than as a metallacyclobutene [10].

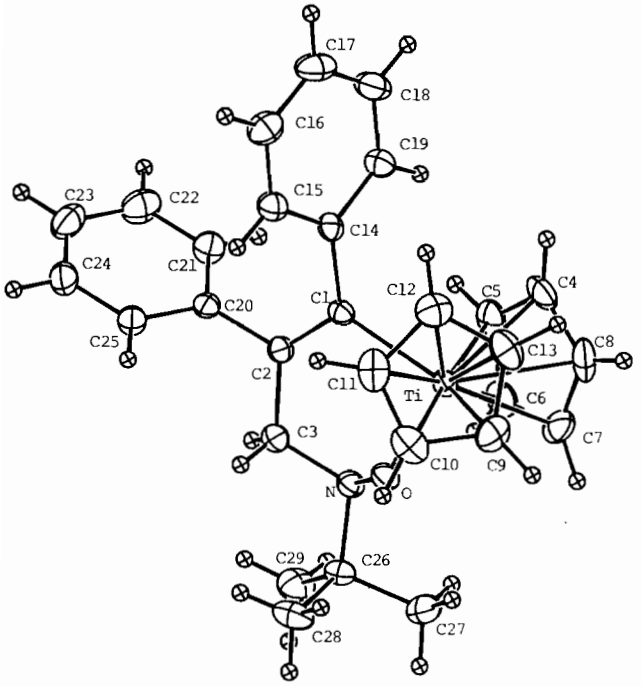


Fig. 1. Molecular structure and atom numbering scheme for complex **4a**.

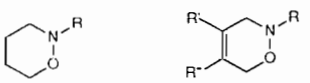
distorted C–C–N angle of 117°. Other bond lengths and angles appear unremarkable.

The orientation of the α-phenyl substituent, perpendicular to the metallacycle ring plane, is also noteworthy. Analogous orientations have been observed in a number of other Group 4 metallacyclic complexes, including diphenyltitanacyclobutene (**1**) [24], an azazirconacyclobutane [25] and an oxatitanacyclohexene [20, 26]. This orientation may allow the α-phenyl substituent to donate electron density to the electron-deficient metal center through interaction of the aromatic π electrons with the $1a_1$ LUMO of the 16-e$^-$ metal centers in these complexes [27].

Dynamic NMR studies

Four atoms of the metallacycle, O, Ti, C(1) and C(2), are roughly coplanar, while the nitrogen atom and the methylene carbon both are displaced toward one side of this plane. The nitroso compound insertion products display dynamic NMR behaviour consistent with maintenance of this geometry in solution. At lower temperatures, the methylene group appears in ^{1}H NMR spectra as an AB spin system, while at higher temperatures, coalescence to an A_2 system is observed. Similarly, inequivalent cyclopentadienyl rings are observed at low temperatures, while chemical equivalence is observed at higher temperatures. The energetics of this dynamic process were determined [28] for the insertion products of 2-methyl-2-nitrosopropane with dimethyltitanacyclobutene (**2**) and with benzotitanacyclobutene (**3**). For the dimethyl metallacycle, coalescence of both the methylene AB quartet ($T_c = 303$ K) and the cyclopentadienyl resonances ($T_c = 285$ K) was observed, providing two independent measures of the energetics of the process, for which an activation energy of 15.0 ± 0.2 kcal mol^{-1} was calculated. Coalescence of the methylene AB quartet for the benzo complex afforded an activation energy of 13.7 ± 0.2 kcal mol^{-1} for this complex; decoalescence of the cyclopentadienyl resonances was not reached for this complex even at the lowest temperatures studied (223 K).

Determination of the nature of the structural change giving rise to dynamic NMR behavior in nitrogen heterocycles can be problematic, as a number of distinct processes can give rise to the same net effect [29]. Thus, for example, in piperidine derivatives, chair–chair interconversion, pyramidal inversion at nitrogen [30], and rotation of the substituent on nitrogen [31] may all give rise to dynamic NMR behavior [32], and restriction of any of these processes in the insertion products might be expected to yield inequivalent cyclopentadienyl rings and methylene hydrogens. Free energies of activation for nitrogen pyramidal inversion in the range of 14 ± 1 kcal mol^{-1} have been reported for oxazine derivatives **5** [33]. However, some uncertainty appears to remain in these cases as to whether the dynamic process involved is exclusively due to pyramidal inversion or whether chair–chair interconversion is also involved [34]. Pyramidal inversion has been more conclusively assigned for dehydro oxazines **6** [35], in which no chair–chair interconversion is possible. Free energies of activation for nitrogen pyramidal inversion in the range of 13.5 ± 0.5 kcal mol^{-1} were measured for these compounds.



5 6

R = CH_3, CH_2CH_3, $CH_2CH_2CH_3$; R', R'' = H, CH_3

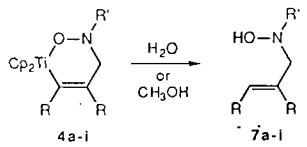
The metallacyclic products resulting from the insertion reactions of 2-methyl-2-nitrosopropane with the butadiene complexes of zirconocene and hafnocene, discussed above, display two different dynamic processes [3]. One process, displaying an activation energy of *c.* 19.5 ± 0.5 kcal mol^{-1}, was ascribed to ring conformational changes. The second process, with an activation energy of *c.* 8.2 ± 0.5 kcal mol^{-1}, was proposed to arise from restricted rotation about the N–t-butyl bond rather than from pyramidal inversion, primarily on the basis of its relatively low activation energy when compared to the typically higher barriers reported for pyramidal inversion processes. In support of this suggestion, acyclic *N*-t-butylhydroxylamines and related compounds display

compounds display barriers to rotation about the N–t-butyl bond of *c.* 8.3 ± 0.3 kcal mol^{-1} [36].

The similarity between the activation energies for the nitroso insertion products and the dehydro oxazines suggests that analogous dynamic processes are at play in each. The magnitude of the activation energy for the dynamic process suggests it is best ascribed to pyramidal inversion at nitrogen.

Protonolysis

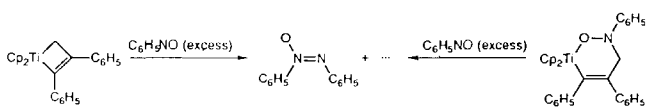
Attempted protonolysis of the insertion products with various proton donors (HCl, CF_3SO_3H, CH_3SO_3H, CH_3CO_2H) afforded intractable product mixtures. Simple hydrolysis or methanolysis, however, affords good yields of the anticipated *N*-allylhydroxylamines (**7**). NMR spectroscopy at intermediate reaction times suggested the initial formation of titanocene hydroxy complexes, with the final metal-containing product being the titanocene oxide oligomer. The hydroxylamines displayed characteristic vinyl and methylene proton resonances, shifted upfield from the corresponding resonances in their metallacyclic precursors.



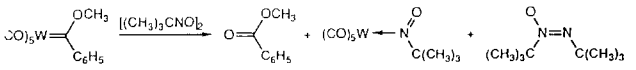
R = CH_3, C_6H_5; R' = $C(CH_3)_3$, C_6H_5, C_6H_4-2-CH_3

Reactions with excess nitroso compound

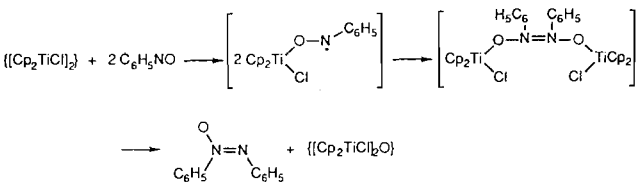
Treatment of dimethyltitanacyclobutene (**2**) with excess 2-methyl-2-nitrosopropane affords only the single insertion product discussed above. However, treatment of each of the titanacyclobutenes **1–3** with $\geqslant 3$ equiv. of nitrosobenzene or 2-nitrosotoluene, or of their nitroso compound insertion products with an additional 2 equiv. of nitrosoarene, results in metallacycle degradation. The major product of these reactions is the azoxyarene; the fate of the titanocene fragment has not been determined, but conversion to oligomeric titanocene oxide is probable.



Conversion of nitroso compounds to the corresponding azoxy derivatives has been reported to be mediated by triphenylphosphine [37] and by a number of organotransition-metal complexes. Thus, *N,N'*-ethylenebis(salicylideneiminato)iron(II) [Fe(salen)] converts nitrosobenzene to azoxybenzene [38]. Iron pentacarbonyl effects similar reactions, possibly via formation of intermediate nitrene complexes [39]. Variable amounts of azoxyarenes have also been obtained in metathesis reactions of tungsten carbene complexes with nitroso compounds [5]. For example, while 2,4,6-tri-t-butylnitrosobenzene did not produce any azoxy compound, 2-methyl-2-nitrosopropane dimer afforded the corresponding azoxy compound in *c.* 90% yield.



Deoxygenation of the dimer was proposed to account for azoxy formation. The fact that 2-methyl-2-nitrosopropane dimer does not yield an azoxy compound in the titanacyclobutene systems argues against such a pathway in these cases, however. Of particular relevance, deoxygenation of nitrosoarenes by titanocene derivatives such as $[Cp_2TiCl]_2$, affording primarily azoxyarenes and azoarenes, has also been reported [40]. In these cases, azoxyarenes were proposed to result from initial single electron transfer processes.



Conclusions

Titanacyclobutenes undergo very rapid insertion reactions with nitrosoarenes and 2-methyl-2-nitrosopropane, affording in all cases the product arising from insertion into the Ti–CH_2 bond of the metallacycle. The high regioselectivity for alkyl insertion of these insertion reactions stands in contrast to the insertion reactions of ketones, aldehydes and nitriles, which in many cases favor insertion into the Ti–vinyl bond of the titanacyclobutenes. The insertion products display dynamic NMR behavior consistent with pyramidal inversion at nitrogen, with activation barriers of *c.* 14 kcal mol^{-1}. Hydrolysis of the insertion products affords the corresponding hydroxylamines, while treatment of them or of the titanacyclobutenes with excess nitrosoarene results in metallacycle degradation and formation of azoxyarene.

Supplementary material

Unit cell and packing diagrams and tables of hydrogen atom atomic coordinates, anisotropic thermal parameters, bond lengths and angles, least-squares planes, intermolecular contacts, torsion angles, and observed and calculated structure factors have been deposited at the Cambridge Crystallographic Data Centre.

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