Reactions of Nitrogen Mono-oxide with Dicyclopentadienyltitanium Complexes, including the Formation of Isocyanate from Nitrogen Mono-oxide and Carbon Mono-oxide

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Nitrogen mono-oxide (NO) rapidly oxidises $Ti^{III}(cp)_2$ complexes (cp = η-C_5H_5) according to the equations (i)—(iii) where '$Ti(cp)_2O$' refers to a polymeric oxide of Ti^{IV}. The oxidation (iii) is complicated by the formation of small amounts of an NCO complex. Excess of $[Ti(cp)_2(CO)_2]$ and NO react in toluene at 20 (70) or 65 °C (16 h)

$$[\{Ti(cp)_2Cl\}_2] + 2NO \longrightarrow [\{Ti(cp)_2Cl\}_2O] + N_2O \qquad (i)$$

$$2[Ti(cp)_2(NCO)] + 2NO \longrightarrow [\{Ti(cp)_2(NCO)\}_2O] + N_2O \qquad (ii)$$

$$[\{Ti(cp)_2\}_4(CO_3)_2] + 4NO \longrightarrow 4\text{ '}Ti(cp)_2O\text{' } + 2N_2O + 2CO_2 \qquad (iii)$$

to give CO, $[Ti(cp)_2(NCO)]$, and '$Ti(cp)_2O$,' along with traces of $Ti^{III}(cp)_2$ products. The NO(reacted) : CO(produced) ratio is between 1 : 2.5 and 1 : 3.0. From e.s.r. and i.r. spectral data and product analyses it is suggested that $[Ti(cp)_2(CO)_2]$ and NO initially give an equilibrium between $[Ti(cp)_2(CO)(NO)]$ and $[Ti(cp)_2(NO)]$, and that subsequent oxygen abstraction from $[Ti(cp)_2(NO)]$ {by CO or $[Ti(cp)_2(CO)_2]$} or from the coupled intermediate $[\overline{Ti(cp)_2\{N(=O)-C}(=O)\}]$ {by $[Ti(cp)_2(CO)_2]$} gives the $[Ti(cp)_2(NCO)]$ product. The compound $[Ti(cp)_2]$ reacts with excess of NO to give a complex of empirical formula $[Ti(cp)_2(NO)]$, which appears to contain Ti^{IV} and bridging N_2O_2 and cp ligands. The properties of $[Ti(cp)_2(NCO)]$ are reported.

ALTHOUGH complexes containing nitrogen mono-oxide (NO) and reactions of NO with various transition-metal compounds have been investigated extensively, most investigations have concentrated on transition metals to the right of the Periodic Table, particularly those of Group 8.[1-6] Apart from $[V(CN)_6(NO)]^{4-}$,[7] $[V(CN)_5(NO)]^{3-}$,[8] and $[V(cp)(CO)(NO)_2]$ (cp = η-cyclopentadienyl, η-C_5H_5),[9,10] three reports on insertion of NO into Ti–C,[11] Zr–C,[12,13] or Nb–C and Ta–C [14] bonds, and a brief report on the reaction of NO with a reduced $Ti(cp)_2$ derivative,[15] nothing is known of nitrosyls of, or reactions of NO with, complexes of the Group 4 and 5 metals. We are making a comprehensive investigation of this area, and have begun with the reactions between NO and $Ti(cp)_2$ derivatives, because of the remarkable reactivity of these complexes towards small molecules.[16] A brief report of part of this work has appeared.[17]

RESULTS AND DISCUSSION

Reactions in which NO *oxidised* $Ti^{III}(cp)_2$ *Derivatives.*—A variety of $Ti^{III}(cp)_2$ complexes were readily oxidised by NO, with concomitant production of N_2O. It will become apparent later in the discussion why the particular compounds discussed were investigated. Two complexes, $[\{Ti(cp)_2Cl\}_2]$ and $[Ti(cp)_2(NCO)]$, were simply oxidised according to equations (1) and (2). Complete

$$[\{Ti(cp)_2Cl\}_2] + 2NO \longrightarrow [\{Ti(cp)_2Cl\}_2O] + N_2O \qquad (1)$$

$$2[Ti(cp)_2(NCO)] + 2NO \longrightarrow [\{Ti(cp)_2(NCO)\}_2O] + N_2O \qquad (2)$$

determination of reaction stoicheiometry was achieved by the methods outlined in the Experimental section. Reactions (1) and (2) were rapid, millimolar quantities requiring a few minutes for completion. Although the major products of the reactions were $[\{Ti(cp)_2X\}_2O]$ (X = Cl [18] or NCO), there was also evidence for more highly polymerised titanium(IV) species, in which some cp ring loss had occurred. Since two titanium(III) centres are involved in the reactions we assume the reduction of NO proceeds *via* formation of NO^- and/or $N_2O_2^{2-}$ intermediates, as has been suggested for other reductions of NO,[19] and in fact it was possible to isolate a small quantity of a brown nitrogen-containing solid which may be a reaction intermediate.

The oxidation of $[\{Ti(cp)_2\}_4(CO_3)_2]$ [20] was rather more complicated than those of reactions (1) and (2), gas-phase analysis indicating that loss of CO_2 occurred on oxidation [equation (3)].† We have previously observed

$$[\{Ti(cp)_2\}_4(CO_3)_2] + 4NO \longrightarrow 4\text{ '}Ti(cp)_2O\text{' } + 2N_2O + 2CO_2 \qquad (3)$$

loss of CO_2 on oxidation of $[\{Ti(cp)_2\}_4(CO_3)_2]$ by N_2O or O_2.[21] The stoicheiometry shown in equation (3) cannot however be a complete description of the reaction since the i.r. spectrum of the '$Ti(cp)_2O$' product clearly showed a weak sharp absorption at 2 202 cm^{-1}, assignable to co-ordinated NCO^- (see below).

Reaction of NO *with* $[Ti(cp)_2(CO)_2]$.—When NO was

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† The nature of the yellow product obtained on oxidation of $Ti(cp)_2$ derivatives has been the subject of some discussion.[15,18] It is agreed that the product is a polymer containing Ti^{IV}. In the present work the gas-phase stoicheiometry indicated the formula $Ti(cp)_2O$. The actual solid polymer which could be isolated had a lower cp content than implied by this formula, as found also by Giddings.[18]

allowed to react with a large excess of $[Ti(cp)_2(CO)_2]$ for 70 (25) or 16 h (65 °C) in toluene the gaseous products were CO and traces (<1 mole percent) of N_2 and CO_2. The ratio NO(reacted) : CO(produced) was somewhat variable with respect to temperature, concentration of reactants, and time of reaction, but always lay between 1 : 2.5 and 1 : 3. At 25 °C, a green solid was isolated from the reaction mixture by the addition of hexane. This product showed a strong absorption band in the i.r. spectrum at 2 202 cm^{-1}, was paramagnetic ($g = 1.979$ in the e.s.r. spectrum), and had a microanalysis corresponding to the formula $[Ti(cp)_2(NCO)]$. Its physical and chemical properties are discussed in more detail below.

Attempts to separate the other titanium-containing products of the reaction were not completely successful. The toluene solution obtained after removal of $[Ti(cp)_2(NCO)]$ showed e.s.r. signals at $g = 1.979$ {due to residual $[Ti(cp)_2(NCO)]$} and at $g = 1.976$. Evaporation of toluene from the solution gave mainly the yellow titanium(IV) polymer ' $Ti(cp)_2O$ ', which would no longer redissolve after isolation. Washing the polymer with hexane gave a solution which showed i.r. evidence for residual NCO [ν(NCO) at 2 202 cm^{-1}], $[Ti(cp)_2(CO)_2]$ [ν(CO) at 1 980 and 1 885 cm^{-1}], and a CO_2 complex [ν(CO_2) at 1 440 and 1 360 cm^{-1}].[21] In some experiments it was also possible to isolate and purify a very small quantity of $[\{Ti(cp)_2\}_4(CO_3)_2]$. We have shown previously that $[\{Ti(cp)_2\}_2O]$ shows an e.s.r. signal at $g = 1.975$, and can be obtained from $[\{Ti(cp)_2\}_2(CO_2)]$ ($g = 1.978$). However, the nature of the minor products of the reaction, and of the e.s.r. signals, remains obscure. Note that despite the wealth and variable proportions of the titanium-containing products only CO was observed in the gas phase.

The i.r. spectrum of the reaction solution showed a decrease in the intensity of both absorption bands (1 980 and 1 885 cm^{-1}) assignable to ν(CO) of $[Ti(cp)_2(CO)_2]$ as reaction proceeded. A weak band at 1 700 cm^{-1}, assignable to a nitrosyl complex, appeared during this time, but no additional bands in the carbonyl region were observed. The course of the reaction was unaffected by visible light.

The e.s.r. spectrum of the solution during reaction of excess of $[Ti(cp)_2(CO)_2]$ with NO at 20 °C in toluene showed very rapid appearance of two signals at $g = 1.984$ and 1.979, of which the former was much more intense. On changing the conditions of the experiment (temperature, concentration, agitation of the solution) the relative intensity of these two signals varied in a manner which clearly indicated that the complexes responsible for the signals were in equilibrium with one another. After a few minutes a new signal at $g = 1.978$ appeared and slowly increased in intensity, with no equilibrium evident. After several hours the increase in the signal having $g = 1.978$ began to be complicated by the appearance of several other signals including that of $[Ti(cp)_2(NCO)]$ ($g = 1.979$) and a signal at $g = 1.976$.

When NO was passed rapidly through a toluene solution of $[Ti(cp)_2(CO)_2]$ an insoluble brown-yellow solid was obtained. This showed a very weak i.r. absorption at 2 202 cm^{-1}, indicating only traces of NCO, and no strong i.r. bands other than those due to cp. The product, which could not be further purified, analysed as ' $Ti_3(cp)_3N_2O_2$ ' and was stable in air. Reaction of $[Ti(cp)_2(CO)_2]$ with excess of NO in a static system gave a complicated mixture of titanium-containing products and CO, N_2, CO_2, and N_2O in the gas phase.

The e.s.r. spectrum of the reaction at 20 °C indicates rapid formation of two paramagnetic species which are in equilibrium with one another. The most reasonable explanation of this is the reaction sequence (4) and (5).

$$[Ti(cp)_2(CO)_2] + NO \longrightarrow [Ti(cp)_2(CO)(NO)] + CO \quad (4)$$

$$[Ti(cp)_2(CO)(NO)] \rightleftharpoons [Ti(cp)_2(NO)] + CO \quad (5)$$

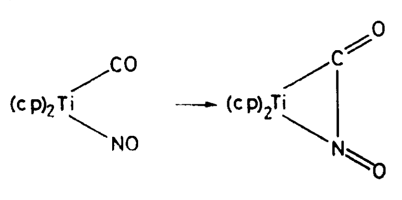
In reaction (4) we regard NO as an electrophile and the $[Ti(cp)_2(CO)(NO)]$ and $[Ti(cp)_2(NO)]$ complexes as being formally of Ti^{III} and NO^-. The e.s.r. signals at $g = 1.979$ and 1.984 are assigned to $[Ti(cp)_2(CO)(NO)]$ and $[Ti(cp)_2(NO)]$ respectively, the i.r. studies indicating that the equilibrium favours the latter.

The formation of small quantities of an isocyanate complex from $[\{Ti(cp)_2(NH)\}_2H]$ and CO by an unknown mechanism has been reported,[22] as have two photochemical reactions in which co-ordinated NCO was obtained from co-ordinated NO and CO [equations (6) [23] and (7) [24]]. It was suggested that both reactions (6) and (7) proceeded *via* metal–nitrene intermediates. Such an intermediate is however not possible in the present case, since titanium cannot provide sufficient electrons for a Ti≡N moiety. The presence of only traces of CO_2 in the gas phase and $[\{Ti(cp)_2\}_4(CO_3)_2]$ in the solid product, together with the absence of N_2O, also indicate that a nitrene is not being formed.

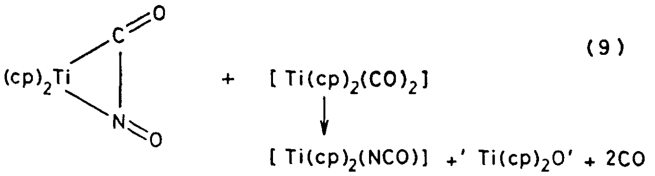
$$[Mo(cp)(CO)_2(NO)] + 3PPh_3 \xrightarrow{h\nu} [Mo(cp)(CO)(NCO)(PPh_3)_2] + PPh_3O \quad (6)$$

$$[Ir(CO)(NO)(PPh_3)_2] + 2PPh_3 \xrightarrow{h\nu} [Ir(NCO)(PPh_3)_3] + PPh_3O \quad (7)$$

An alternative route to NCO is NO–CO coupling [equation (8)] followed by oxygen-atom abstraction (from the oxygen atom attached to N) by $[Ti(cp)_2(CO)_2]$ and rearrangement [equation (9)]. The e.s.r. signal at $g = 1.978$ can be assigned to the coupled intermediate. The overall equation for this mechanism is (10). We previously found that ' $Ti(cp)_2O$ ' was reduced by $[Ti(cp)_2(CO)_2]$, particularly when formed directly in the presence of the latter.[21] We ascribe the e.s.r. signals which appear after longer reaction times, *e.g.* that at $g = 1.976$, to the products of such reductions.



(8)



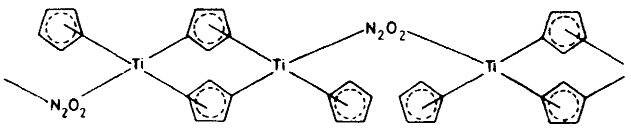
(9)

In the presence of excess of NO, oxidation of either of the Ti^{III}(cp)$_2$ products, [Ti(cp)$_2$(NCO)] and [{Ti(cp)$_2$}$_4$(CO$_3$)$_2$], would occur, and formation of [Ti(cp)$_2$(NO)] would be favoured. The presence of N$_2$O and CO$_2$, but not N$_2$, in the gas phase is therefore expected. However, the variety and variability of the products prevent us from suggesting a mechanism under these conditions.

$$2[\mathrm{Ti(cp)_2(CO)_2}] + \mathrm{NO} \longrightarrow [\mathrm{Ti(cp)_2(NCO)}] + \text{' Ti(cp)}_2\text{O '} + 3\mathrm{CO} \qquad (10)$$

Reaction of NO *with* [Ti(cp)$_2$].—Toluene solutions of [Ti(cp)$_2$] turned brown instantaneously on adding NO even at −70 °C. The reaction stoicheiometry was as in equation (11), there being no gaseous products. Precipitation of a brown solid began almost immediately and continued for several hours. It was insoluble in toluene, diamagnetic, analysed excellently (C, H, Ti, and N) as ' Ti(cp)$_2$(NO) ', and showed, in addition to broad cp absorptions, only a very weak broad band at 1 620 cm^{-1} and another similar band at 1 040 cm^{-1} in the i.r. spectrum. The complex was stable to air and did not react with CO. Salzmann[15] reported that a form of [Ti(cp)$_2$] {prepared by sodium–naphthalene reduction of [Ti(cp)$_2$Cl$_2$]} reacted with NO to give a weakly paramagnetic complex which he suggested as being a derivative of N$_2$O$_2$$^{2-}$. Although a species such as [{Ti(cp)$_2$}$_2$(N$_2$O$_2$)] could be suggested for the complex obtained here, such a formula is only compatible with the diamagnetism of the complex if Ti^{III}–Ti^{III} coupling occurs, and is not compatible with the air stability and insolubility of the product. The only formula which is not inconsistent with the observed properties is that below involving alternate N$_2$O$_2$$^{2-}$ and cp bridges. The insolubility and unreactivity of the complex have prevented further characterisation.

$$[\mathrm{Ti(cp)_2}] + \mathrm{NO} \longrightarrow [\mathrm{Ti(cp)_2(NO)}] \qquad (11)$$



Properties of [Ti(cp)$_2$(NCO)].—As part of the work on reactions of NO with Ti(cp)$_2$ derivatives it has been necessary to reinvestigate [Ti(cp)$_2$(NCO)]. This complex was obtained from the reaction between an excess of [Ti(cp)$_2$(CO)$_2$] and NO at room temperature, and could also be obtained by reaction of [Ti(cp)$_2$]$^+$ (generated by dissolving [{Ti(cp)$_2$Cl}$_2$][25] in water) with NCO$^-$. Coutts and Wailes[26] have briefly described [Ti(cp)$_2$(NCO)] obtained from ' Ti(cp)$_2$Cl ' by a similar route. The [Ti(cp)$_2$(NCO)] was extremely sensitive to traces of water, becoming blue on standing, probably due to the formation of blue hydrated [Ti(cp)$_2$]$^+$. This was particularly true of material obtained from aqueous solutions of [{Ti(cp)$_2$Cl}$_2$] because removal of the last traces of water was very difficult.

The nature of the bonding between [Ti(cp)$_2$]$^+$ and NCO$^-$ in [Ti(cp)$_2$(NCO)] is not clear. Coutts and Wailes[26] suggested their complex was monomeric and involved *N*-bonded NCO$^-$. The absence of a half-field line in the e.s.r. spectrum of our material is consistent with a monomer, although most other titanium(III) complexes of this type are dimeric. We are unable to write a reasonable mechanism for formation of *O*-bonded NCO$^-$ from NO and [Ti(cp)$_2$(CO)$_2$], and therefore also favour *N*-bonding for this material (although the [Ti(cp)$_2$(NCO)] observed as a product of the reaction between NO and [{Ti(cp)$_2$}$_4$(CO$_3$)$_2$] could be *O*-bonded). We note however that, although all other physical and chemical properties were the same, [Ti(cp)$_2$(NCO)] obtained from the reaction between NO and [Ti(cp)$_2$(CO)$_2$] had a slightly different green colour from that obtained from aqueous solutions of [{Ti(cp)$_2$Cl}$_2$] and NCO$^-$. While this colour difference may be attributable to residual traces of solvent, it is also possible that two modes of bonding do indeed occur. {Note that the mode of bonding of [Ti(cp)$_2$(NCO)$_2$] in solution is not yet settled.[27]} We are attempting to solve this problem crystallographically.

EXPERIMENTAL

Since all compounds described were air sensitive, standard vacuum-line, Schlenk-tube, and dry-box or glove-bag techniques were used in the reactions. Diethyl ether, tetrahydrofuran (thf), hexane, and toluene were stored over methyl-lithium under vacuum and distilled under vacuum. Dicyclopentadienyltitanium dichloride, [Ti(cp)$_2$Cl$_2$], was obtained from Strem Chemicals. Argon (99.996%) was used as blanketing gas. Nitric oxide (NO, 99.0%) was purified by passage through silica gel at −70 °C. Bis(chlorodicyclopentadienyltitanium), [{Ti(cp)$_2$Cl}$_2$],[25] dicarbonyldicyclopentadienyltitanium, [Ti(cp)$_2$(CO)$_2$],[28] di-μ-carbonato-tetrakis(dicyclopentadienyltitanium), [{Ti(cp)$_2$}$_4$(CO$_3$)$_2$],[21,29] and dicyclopentadienyltitanium isocyanate, [Ti(cp)$_2$(NCO)],[26] were prepared by the literature methods. Toluene solutions of dicyclopentadienyltitanium, [Ti(cp)$_2$], were obtained from [Ti(cp)$_2$Cl$_2$] *via* the intermediates [Ti(cp)$_2$(CH$_3$)$_2$] and [{Ti(cp)$_2$H}$_x$] as previously described.[16,30]

Reactions of Nitrogen Mono-oxide.—(*a*) *With bis*(*chlorodicyclopentadienyltitanium*) *to give* μ-*oxo-bis*(*chlorodicyclopentadienyltitanium*). To a solution of [{Ti(cp)$_2$Cl}$_2$] (0.75 g, 1.75 mmol) in toluene (30 cm^3) under vacuum was added NO (3.5 mmol). The solution turned from green to brown-orange. It was stirred for 4 d, filtered [leaving a brown solid (0.15 g)], and the filtrate, on setting aside, slowly deposited bright orange crystals (0.2 g). The i.r. spectrum (Fluorolube) of the brown solid showed absorption bands at 1 438m and 1 360w cm^{-1} in addition to bands assignable to cp {Found: C, 51.9; H, 4.6; N, 1.2. Calc. for [Ti(cp)$_2$Cl(NO)]: C, 51.4; H, 4.3; N, 6.6%}.

The orange crystals showed absorption bands assignable to cp in the i.r. spectrum (but no other bands) and a single n.m.r. signal at τ 3.53 in [$^2H_6$]acetone (Found: C, 54.2; H, 4.7; Cl, 16.0. Calc. for $[\{Ti(cp)_2Cl\}_2O]$:[18] C, 54.2; H, 4.6; Cl, 16.0%).

(*b*) *With di-μ-carbonato-tetrakis(dicyclopentadienyltitanium).* A solution of $[\{Ti(cp)_2\}_4(CO_3)_2]$ (0.12 g, 0.15 mmol) in toluene (25 cm^3) was heated to 60 °C and incubated with NO (0.29 mmol) for 4 d. The gaseous products (N_2O and CO_2) were removed at a Toepler pump and the yellow solid (0.05 g) which had precipitated was filtered off. This diamagnetic insoluble solid could not be further purified. It showed a sharp weak absorption band at 2 200 cm^{-1} [ν(NCO)] in the i.r. spectrum, but otherwise only bands ascribable to cp. Its properties indicated it to be a mixture of a titanium(IV) polymer and a titanium(IV) NCO complex.

(*c*) *With dicyclopentadienyltitanium isocyanate to give μ-oxo-bis(dicyclopentadienylisocyanatotitanium).* A solution of $[Ti(cp)_2(NCO)]$ (0.75 g, 3.4 mmol) in toluene (40 cm^3) was incubated with NO (3.5 mmol) at room temperature for 1 d. The gaseous products [N_2O and NO, determined by i.r. spectroscopy, total 2.0 mmol; equation (2) requires a total N_2O + NO of 1.7 mmol] were removed at a Toepler pump. The orange-red $[\{Ti(cp)_2(NCO)\}_2O]$ which had precipitated was filtered off. Yield 0.57 mmol, 30% (Found: C, 57.4; H, 4.4; N, 6.0. $C_{22}H_{20}N_2O_3Ti$ requires C, 57.9; H, 4.4; N, 6.1%); ν(NCO) at 2 200m cm^{-1}.

(*d*) *With dicarbonyldicyclopentadienyltitanium at* 25 °C *to give dicyclopentadienyltitanium isocyanate.* A solution of $[Ti(cp)_2(CO)_2]$ (0.86 g, 3.67 mmol) in toluene (50 cm^3) was incubated with NO (1.18 mmol) at 25 °C for 72 h. Frothing was observed after 1 h, and the reaction solution slowly turned from purple to green-brown. Gas analysis (by pumping at the Toepler through liquid-nitrogen traps and passing over Cu–CuO at 310 °C)[21] showed that only CO (3.31 mmol) was produced. Pumping through traps at −78 or at 25 °C produced only toluene, no N_2O, CO_2, or other gas being observed. To the remaining solution was added hexane (100 cm^3), giving a bright green precipitate of $[Ti(cp)_2(NCO)]$ {0.12 g, 0.54 mmol; 46% based on a 1 : 1 relationship between NO (used) and $[Ti(cp)_2(NCO)]$ (obtained)}. The $[Ti(cp)_2(NCO)]$ product had similar chemical and physcal properties to a sample prepared by the literature method.[26]

(*e*) *With* $[Ti(cp)_2(CO)_2]$ *at* 65 °C *to give* $[Ti(cp)_2(NCO)]$. A solution of $[Ti(cp)_2(CO)_2]$ (0.7 g, 3.0 mmol) in toluene (30 cm^3) was incubated under NO (0.7 mmol) at 65 °C for 20 h. Analysis showed that the only gas present after this time was CO (2.0 mmol). The remaining brown solution was filtered, leaving a brown solid. This was washed with toluene, then extracted with thf (15 cm^3) giving a brown solid and a green solution. Addition of hexane to the green solution gave a bright green precipitate of $[Ti(cp)_2(NCO)]$ (0.1 g, 0.45 mmol, 64%, based on NO) (Found: C, 59.7; H, 4.5; N, 6.1. Calc. for $C_{11}H_{10}NOTi$: C, 60.0; H, 4.6; N, 6.4%); ν(NCO) at 2 202s cm^{-1}, $g = 1.979$.

The brown thf-insoluble material (0.2 g) showed no i.r. absorptions other than those attributable to cp, was diamagnetic, and stable in air (Found: C, 61.4; H, 5.2. $C_{10}H_{10}OTi$ requires C, 61.9; H, 5.2%). In general, lower C analyses were found.

The initial toluene filtrate gave, on standing, a very small quantity of green crystalline $[\{Ti(cp)_2\}_4(CO_3)_2]$ [ν(CO_3) at 1 425 and 1 475 cm^{-1}]. Evaporation of the toluene from the remaining solution gave a khaki-brown residue which was paramagnetic ($g = 1.976$), showed weak i.r. absorptions at 1 360 and 1 440 cm^{-1}, had variable C and H analyses, and contained no nitrogen. The material appeared to be similar to the $[\{Ti(cp)_2\}_2O]$–$[\{Ti(cp)_2\}_2(CO_2)]$ mixture obtained previously.[21]

(*f*) *With* $[Ti(cp)_2(CO)_2]$ (*excess of* NO). A vigorous current of NO was passed through a solution of $[Ti(cp)_2(CO)_2]$ (0.27 g) in toluene (30 cm^3) for 10 min at room temperature. During this time an orange solid (0.2 g) precipitated. This showed, in addition to absorptions assignable to cp, only weak broad absorptions at 1 500 and 1 280 cm^{-1} and analysed as '$Ti_3(cp)_3N_2O_2$' (Found: C, 45.4; H, 4.0; N, 6.6. Calc. for $C_{15}H_{15}N_2O_2Ti_3$: C, 45.2; H, 3.8; N, 7.0%), but was stable in air and clearly far more oxidised than this formula implies.

(*g*) *With dicyclopentadienyltitanium.* To a toluene solution of $[Ti(cp)_2]$ (2.15 mmol, as determined by reaction with N_2)[16,30] was added NO (6.30 mmol). The green-black solution turned instantaneously brown and a precipitate began to form. The mixture was stirred for 18 h, the excess of NO (4.0 mmol) removed at the Toepler pump, and the solid [0.31 g, 1.5 mmol, 69%, based on reaction (11)] filtered off {Found: C, 57.4; H, 4.7; N, 6.5; Ti (as TiO_2), 22.9. Calc. for $[Ti(cp)_2(NO)]$: C, 57.7; H, 4.8; N, 6.7; Ti, 23.0%}. For other properties see text.

Instruments used in this work were: a Perkin-Elmer 457 i.r. spectrophotometer, spectra being measured as Nujol or Fluorolube mulls or in solution between KBr or CaF_2 plates; a Varian T60 n.m.r. spectrometer; a Hitachi–Perkin-Elmer RMU-60 mass spectrometer; and a locally modified version of the Varian E–4 e.s.r. spectrometer. The vacuum line used was a much modified version of that described by Shriver.[31] Microanalyses were by A. Bernhardt, West Germany.

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