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ANSA-METALLOCENE DERIVATIVES

III *. INFLUENCE OF AN INTERANNULAR ETHYLENE BRIDGE ON THE REACTIVITY OF TITANOCENE DERIVATIVES

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Summary

Titanocene derivatives with an interannular ethylene bridge, while resembling their unbridged counterparts in many transformations involving Ti^{IV} or Ti^{III} oxidation stages, do not follow reaction paths previously observed for unbridged titanocene in a number of reactions, such as formation of a Ti^{II} dinitrogen complex, isotope exchange of the cyclopentadienyl ring ligands with D_2, or formation of a Ti^{III} hydride compound. These reactions are considered to be blocked by the unavailability of a "free" titanocene species, $[(CH_2)_2(C_5H_4)_2Ti^{II}]_n$, as an intermediate in such systems.

Introduction

In a previous paper, we discussed the crystal structures and NMR spectral characteristics of methylene- and ethylene-bridged titanocene derivatives [1]. Considerable distortion of the titanocene framework was observed for the methylene-bridged compound Ia, $(CH_2)(C_5H_4)_2TiCl_2$, whereas the geometry of the ethylene-bridged analogue IIa, $(CH_2)_2(C_5H_4)_2TiCl_2$, was found to be quite similar to that of its unbridged counterpart 0a, $(C_5H_5)_2TiCl_2$. In a comparative study of the reactions of unbridged and ethylene-bridged titanocenes, we have now observed a number of rather pronounced differences in reactivity.

Results

1. *Reduction of the titanium center*

The ansa-[2]-titanocene dichloride IIa is easily reduced, in close analogy to

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its unbridged analogue $(C_5H_5)_2TiCl_2$ (0a), to the Ti^{III}-monochloro derivative $[(CH_2)_2(C_5H_4)_2TiCl]_2$ (IIb), e.g. by reaction with sodium sand in toluene. Alternatively, IIb can be obtained directly by reaction of the ethylene-bridged dicyclopentadienyl-dianion $(CH_2)_2(C_5H_4^-)_2$ in tetrahydrofuran (THF), with $TiCl_3 \cdot 3$ THF. Compound IIb shows the expected sensitivity towards oxygen, but is thermally quite stable. It can be purified by sublimation at 130°C and 10^{-3} Torr without substantial decomposition. In contrast to its green titanocene counterpart $[(C_5H_5)_2TiCl]_2$ (0b), the ansa derivative IIb has an orange-brown color, as crystals and in solution in hydrocarbon or ethers. Possibly related to this is the observation that the ansa-Ti^{III} derivative IIb gives rise to a half-field EPR signal at $g = 4.26$ in its toluene or ether solutions at —78°C, whereas the EPR signal at $g = 1.98$, normally associated with mononuclear $(C_5H_5)_2Ti^{III}$ species [3], is quite small. These observations indicate that an increased Ti—Ti bond strength in $[(CH_2)_2(C_5H_4)_2TiCl]_2$ diminishes its tendency to dissociate even in ethereal solvents.

In contrast to its unbridged Ti^{III} counterpart, 0b, which undergoes further reduction by alkali metals either to various dinuclear titanocene species free of chlorine [4—7] or, in the presence of N_2, to a number of N_2 complexes [7—9], the ethylene-bridged monochloro derivative IIb is recovered unchanged from its toluene or ether solutions even after prolonged reaction with sodium sand in vacuo or under N_2 at temperatures between 60 and 90°C. Under forcing conditions (refluxing toluene and molten Na), IIb is reduced to a black residue, from which no materials containing a $(CH_2)_2(C_5H_4)_2Ti$ moiety could be isolated.

If reduction of IIa or IIb with an alkali metal is carried out in toluene under CO, however, the ethylene-bridged titanocene dicarbonyl complex $(CH_2)_2(C_5H_4)_2Ti(CO)_2$ (IIc) is formed in low yield.

This dicarbonyl compound, IIc, can also be obtained, in almost quantitative yield, by treatment of the ethylene-bridged titanocene dimethyl derivative $(CH_2)_2(C_5H_4)_2Ti(CH_3)_2$, IId, with CO gas, acetone being formed. However, compound IIc is most conveniently obtained from the dichloride IIa by reaction with 2 equivalents of methyl-, ethyl- or butyl-lithium under CO.

Attempts to obtain either a Ti^{II} species or a Ti^{III}-hydride derivative by reaction of the dimethyl compound IId with H_2 were unsuccessful. The ethylene-bridged dimethyl compound IId is quite inert under conditions under which its unbridged counterpart is completely decomposed [10—12]. After prolonged treatment of a solution of $(CH_2)_2(C_5H_4)_2Ti(CH_3)_2$ with H_2 we could not obtain any indication of the presence of a Ti^{III} hydride, such as release of H_2 from the product solution or formation of an allyl complex upon addition of a diolefin. Admission of N_2 to the product solution at —78°C generates a blue N_2 complex, but only about 0.03 mmol of N_2 is taken up per mmol of Ti present. This miniscule N_2-uptake reaction may very well be due to some unbridged titanocene impurity.

Thermolysis of the dimethyl compound IId before reaction with H_2, or in the presence of H_2 yielded ca. 1 mmol of CH_4 per mmol of Ti; however, even under these conditions no hydride compound could be isolated or trapped by reaction with a diolefin to give a stable Ti^{III}-containing allyl product.

On the other hand, Ti^{III}-allyl derivatives, such as $(CH_2)_2(C_5H_4)_2Ti(C_3H_5)$, (IIe), are readily available by reaction of the Ti^{III} monochloro compound IIb with an allyl lithium or magnesium compound. $(C_5H_5)_2Ti(C_3H_5)$ (0e), and other titanocene allyl compounds have been found by Martin et al. [13] to undergo hydrogenolysis to release C_3H_8 and give the Ti^{II} and Ti^{III}-hydride species $[(C_5H_5)_2Ti]_n$ and $[(C_5H_5)_2TiH]_n$. The ansa-(2)-titanocene allyl compound IIe, however, proved quite unreactive toward H_2, and was recovered unchanged in quantitative yield when its solution in toluene stirred under H_2 for four days.

2. *Olefin hydrogenation catalysis and ring hydrogen exchange*

In order to ascertain whether an activation of H_2, which is a characteristic reaction of reduced titanocene derivatives, is also brought about by their ansa-titanocene analogues, we undertook a comparative study of catalytic hydrogenation of cyclohexene in the presence of $(C_5H_5)_2TiCl_2$ (0a), $(CH_2)(C_5H_4)_2$-$TiCl_2$ (Ia), $(CH_2)_2(C_5H_4)_2TiCl_2$ (IIa) and $(CH_2)_3(C_5H_4)_2TiCl_2$ (IIIa), in about 10^{-3} molar toluene solutions, after activation with a five- to tenfold excess of LiC_2H_5. After a more or less pronounced induction period, there is a period of rather rapid H_2 uptake; thereafter, the activity of the catalyst falls and after about 20—50 min H_2 uptake ceases, although some olefin still remains. At this stage, the reaction mixtures have become almost colorless; after reoxidation with HCl, neither the original titanocene dichloro derivatives nor any other titanocene derivatives can be recovered from these solutions.

The duration of each of these reaction phases depends on the concentration of LiC_2H_5 present: higher LiC_2H_5 concentrations cause an extension of the induction period as well as of the total duration of the catalytic reaction. If the LiC_2H_5 concentration exceeds a value of about 10^{-2} *M*, corresponding to a LiC_2H_5 : Ti ratio of about 10 : 1, induction periods extend up to an hour, but if the LiC_2H_5 : Ti ratio is below 5—6 : 1, the total catalytic H_2 uptake is drastically reduced. A maximum total uptake of about 10^3 mmol of H_2 per mmol of titanocene is obtained, at titanocene concentrations of about 10^{-3} mol/l, in the presence of a tenfold excess of LiC_2H_5. From the data given in Table 1 it is apparent that under these conditions all three of the ansa-titanocene derivatives investigated yield more active hydrogenation catalysts than their unbridged counterparts, in terms of maximal specific reaction rate as well as total H_2 uptake. The highest activity is obtained with the reaction system based on the

TABLE 1

CATALYTIC ACTIVITY OF ANSA-TITANOCENE DERIVATIVES IN CYCLOHEXENE HYDROGENATION [a]

	Concentration (mol/l)	Max. turnover rate (mmol H_2/min mmol Ti)	Total H_2 consumption (mmol H_2/mmol Ti)
$(C_5H_5)_2TiCl_2$	8.9×10^{-4}	25	740
$(CH_2)(C_5H_4)_2TiCl_2$	8.6×10^{-4}	33	1140
$(CH_2)_2(C_5H_4)_2TiCl_2$	8.8×10^{-4}	74	1490
$(CH_2)_3(C_5H_4)_2TiCl_2$	8.0×10^{-4}	62	1180

[a] Solutions of the appropriate dichloride and of 30 mmol of cyclohexene in 10 ml of toluene were activated, at 20°C under 1 atm of H_2, with a tenfold excess of C_2H_5Li (1.0 *M* in heptane solution). The reaction was followed by the rate of H_2 uptake.

ethylene-bridged compound IIa, which reaches at about three times the maximum specific reaction rate and about twice the total H_2 uptake observed for the analogous $(C_5H_5)_2TiCl_2$-based reaction system.

A reactive species capable of catalytic olefin hydrogenation can also be obtained by reaction of the ansa-2-titanocene monochloride, IIb, with benzyl lithium in toluene at —78°C. The resulting red solution probably contains the ansa-titanocene monobenzyl complex $(CH_2)_2(C_5H_4)_2Ti^{III}CH_2C_6H_5$; this species, which we could not isolate as a solid, catalyzes the reaction $C_3C_6 + H_2 \rightarrow C_3H_8$, at a rate of about 40 mmol C_3H_8 per mmol Ti per hour.

A rather remarkable reaction of reduced $(C_5H_5)_2Ti$ derivatives is the isotope exchange between deuterium gas and all ten ring hydrogen positions. This H—D isotope exchange is normally observed in all titanocene reaction systems which activate dihydrogen for hydrogenation or hydride transfer reactions [13,14]. Since the ansa-titanocene dimethyl and allyl derivatives had proved rather unreactive towards H_2, we choose as a reaction system of known reactivity to H_2 the mixture of $(CH_2)_2(C_5H_4)_2TiCl_2$ with LiC_2H_5. In order to avoid degradation of the titanocene framework, these reactions were carried out with only a two-fold excess of LiC_2H_5 in the following manner.

A suspension of 1.0 mmol of solid $(C_5H_5)_2TiCl_2$ in 10 ml of toluene was cooled to —78°C, a heptane solution of 2 mmol LiC_2H_5 was added. The mixture was allowed to warm to room temperature with stirring under 1 atm of D_2 gas; after about 5—10 min the solution became dark brown-violet in colour. Subsequently, 1.6 mmol of monodeuterated ethane were released in 10 hours. The gas atmosphere was exchanged for fresh D_2 every 12—16 hours. After four days the mixture was reoxidized with an excess of HCl dissolved in THF. The titanocene dichloride, which was removed in about 80% yield, was found, by mass spectral analysis to consist of a statistical mixture of d^1-to d^{10}-deuterated $(C_5H_5)_2TiCl_2$ molecules, corresponding to an average content of about 5 D atoms per titanocene.

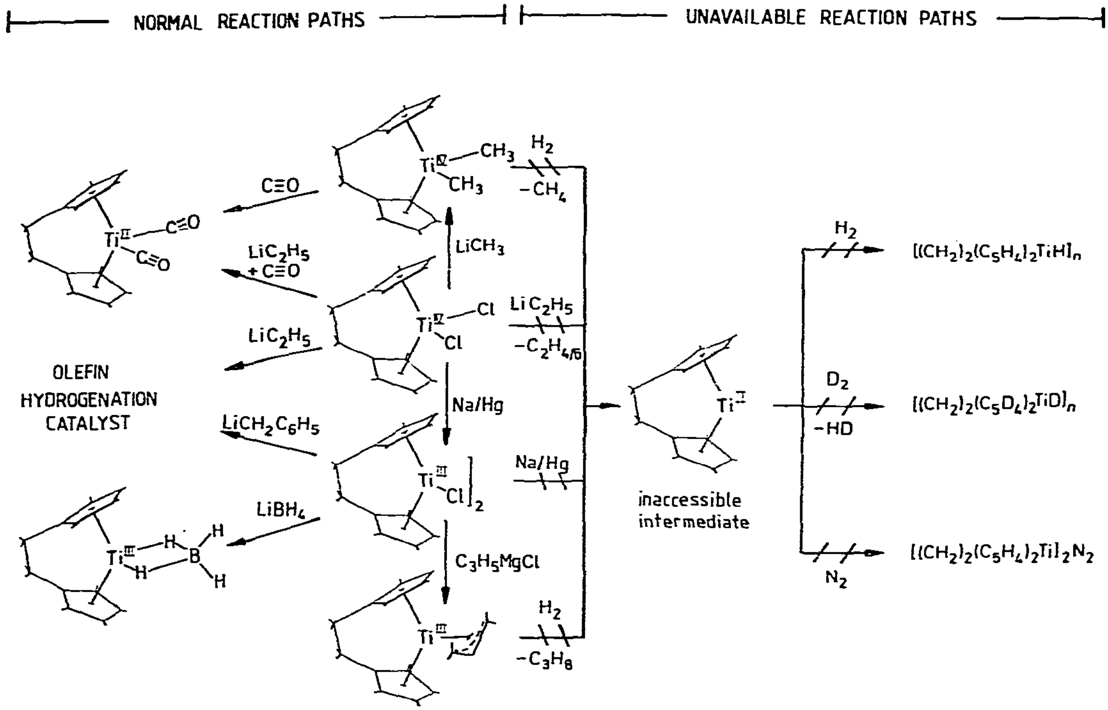
When the reaction with LiC_2H_5 and D_2 was carried out with $(CH_2)_2(C_5H_4)_2TiCl_2$ instead of $(C_5H_5)_2TiCl_2$, a largely analogous sequence of events was observed. Upon warming to room temperature, the mixture turned dark, after 6 hours the color of the reaction mixture had changed to yellow-orange and 1.0 mmol C_2H_5D per mmol Ti had been released. Subsequent treatment with HCl/THF regenerated the dichloride, the mass spectrum of which was completely identical with that of a sample of pure, undeuterated $(CH_2)_2(C_5H_4)_2TiCl_2$, thus excluding any significant degree of deuteration under the conditions employed.

Discussion

The observations on normal reaction paths as well as on reaction paths unavailable for ethylene-bridged titanocene derivatives are summarized in Scheme 1.

Interconversions between ansa-titanocene derivatives containing a Ti^{IV} or a Ti^{III} centre follow closely the patterns established for the unbridged $(C_5H_5)_2Ti$ derivatives. The products which cannot be formed from the ethylene-bridged titanocene reaction systems all appear to be blocked by the unavailability of $[(CH_2)_2(C_5H_4)_2Ti]_n$ as an intermediate. Formation of the N_2 complex $[(CH_2)_2$-

SCHEME 1



$(C_5H_4)_2Ti]_2N_2$, of the hydride $[(CH_2)_2(C_5H_4)_2TiH]_n$ as well as the ring-to-metal hydrogen shift involved in deuteration of the ring ligands depend on the presence of a Ti^{II} centre in $[(CH_2)_2(C_5H_4)_2Ti]_n$. This species however, does not appear to form by any of the routes which normally lead to its unbridged congener $[(C_5H_5)_2Ti]_n$. Neither reduction of the monochloro derivative IIb with an alkali metal nor alkane elimination from any of the $(CH_2)_2(C_5H_4)_2Ti(H)R$ species arising in the other reaction systems investigated appears to afford this crucial intermediate. If this assumption is correct, then the formation of $(CH_2)_2(C_5H_4)_2Ti(CO)_2$ must circumvent the intermediacy of an uncomplexed $[(CH_2)_2(C_5H_4)_2Ti]_n$ intermediate. It is known [15] that $(C_5H_5)_2Ti(CO)_2$ is formed by a CO-induced disproportionation of $[(C_5H_5)_2TiCl]_2$. Here, and presumably also in the reaction between $(CH_2)_2(C_5H_4)_2Ti(CH_3)_2$ and CO, the Ti^{II} center is probably formed while in contact with one or two stabilizing CO π-acceptor ligands. For the olefin-hydrogenation catalysis, our results suggest that the catalytic cycle operates exclusively via Ti^{III}- and/or Ti^{IV}-containing titanocene species.

The postulate that $[(CH_2)_2(C_5H_4)_2Ti]_n$ is significantly less stable, i.e. energetically much less accessible, than its unbridged counterpart $[(C_5H_5)_2Ti]_n$ appears hard to reconcile at first sight with the close similarity in bonding geometries observed for the corresponding dichlorides 0a and IIa. We can offer the following rationale for such a disparity, however. The structures of Ti^{IV}-containing species such as 0a or IIa reveal a strong interannular approach of the two C_5H_5 π-systems. In the region of closest approach, i.e. between the bridgehead C atoms of IIa, nonbonding C—C distances are only 268 ppm, considerably shorter than the normal Van der Waals distance of about 330 ppm between two carbocyclic π-systems. The charge build-up in this region results in a shift of electron density towards the β ring positions, thus leading to the characteristic high-field shifts of the ^1H and ^{13}C signals in these positions [1]. Undoubtedly, however, part of the excess electron density is transferred to an electron-deficient Ti^{III} or Ti^{IV} metal centre. If the metal centre is reduced to the Ti^{II} stage, its electron acceptor capacity is significantly diminished. Such a reduced metal centre would act as an electron source rather than as an electron sink. This is turn should result in an increased π-electron density on both ring ligands and, hence, in a larger interannular contact distance. An effect of this kind is apparent from a comparison of the molecular structure of the Ti^{IV} derivative $(C_5H_5)_2Ti(NCO)_2$ [16] with that of the Ti^{II} derivative $(C_5H_5)_2Ti(CO)_2$ [17]. The spatial requirements of the CO and NCO^- ligands are practically identical in these two compounds and could not cause any significant structural interference. Yet the Cp—Ti—Cp bond angle increases from 133° in $(C_5H_5)_2Ti(NCO)_2$ (a value representative of many Ti^{IV}- and Ti^{III}-titanocene derivatives [17—21,22—25]) to one of 139° in $(C_5H_5)_2Ti(CO)_2$. The interannular ring contact distance of 307 pm in $(C_5H_5)_2Ti(CO)_2$ is considerably larger than that of 268 pm between the bridgehead C atoms in $(CH_2)_2(C_5H_4)_2TiCl_2$, and suggests that even the ansa-dicarbonyl $(CH_2)_2(C_5H_4)_2Ti(CO)_2$, while still a stable molecule, must be significantly strained.

In accord with this view, we find that its methylene-bridged congener, $(CH_2)(C_5H_4)_2Ti(CO)_2$, while formed under appropriate conditions in solution, is thermally unstable and decomposes completely when subjected to sublimation conditions ($P = 10^{-3}$ Torr, $T = 30°C$).

Of all the Ti^{II}-containing titanocene derivatives, however, the dicarbonyl still contains the most strongly electron accepting metal center. Structural data for other Ti^{II} species are available only for permethyl titanocene derivatives, in which the interannular contact distances are undoubtedly controlled to some degree by the spatial requirements of the methyl substituents. Nevertheless, there is an increase of the Cp—Ti—Cp bond angle from 137° in the Ti^{IV} derivative $(C_5(CH_3)_5)_2TiCl_2$ [26] to values of 144° and 146° in the Ti^{II} derivatives $(C_5(CH_3)_5)_2Ti(C_2H_4)$ [27] and $[(C_5(CH_3)_5)_2Ti]_2N_2$ [28], respectively. In these cases, the closest C—C contact distance between the aromatic ring ligands is increased to 330—340 pm, which is typical of normal carbocyclic π-systems. This leaves so little room on the "open" side of the molecule, however, that only one N_2 or C_2H_4 ligand can be coordinated to the Ti^{II} center. The increased repulsion between ring ligands in these compounds as well as in the unsubstituted analogue, $[(C_5H_5)_2Ti]_2N_2$, explains their departure from a normal pseudotetrahedral ligand arrangement and their adaption of a quite unusual pseudotrigonal coordination geometry around the Ti center. Since an interannular distance of anywhere close to 330 pm is impossible for an ethylene-bridged titanocene molecule, it would appear plausible that not even an N_2- or C_2H_4-stabilized $(CH_2)_2(C_5H_4)_2Ti$ unit, much less an uncomplexed one, would be accessible in ansa-titanocene-based reaction systems.

This finding, if corroborated by further observations, might be of help as a test for the participation of Ti^{II} intermediates in studies of the mechanisms of catalytic reactions. In addition, the resistance of the ansa-titanocene framework towards isotope exchange of its ring hydrogen positions might be useful in isotope labelling studies on interligand hydrogen transfer reactions, which otherwise are frequently obscured by the exchangeability of the cyclopentadienyl hydrogen atoms.

Experimental

All manipulations of air-sensitive compounds were carried out in an inert gas atmosphere, using high-vacuum line and Schlenk tube techniques. Solvents were dried and freed of oxygen with lithium alkyl compounds, stored under N_2 and distilled in vacuo on a high-vacuum line.

$(CH_2)_2(C_5H_4)_2TiCl_2$ *(IIa)*

To a suspension of 21.1 g (137 mmol) of $(C_5H_5)_2Mg$ and 16.6 g (274 mmol) of ethylene diamine in 180 ml of diethyl ether, stirred at −78°C, 25.7 g (137 mmol) of 1,2-dibromoethane were added. The mixture was allowed to warm to 5°C during 2 hours, and stirred for an additional 1.5 hours at this temperature. After cooling again to −70°C, a mixture of 150 ml of diethyl ether and 100 ml of 7 *M* aqueous HCl was added. After warming to room temperature, the organic layer was separated, washed to neutrality with water, and dried with $CaCl_2$, and the solvent evaporated off at about 0°C. The crude $(CH_2)_2(C_5H_5)_2$ product, which was obtained as a yellow oil, was immediately poured onto a short column containing 25 g of silica gel, from which it was eluted, at room temperature, with about 300—400 ml of petroleum ether. To the eluent solution, cooled to −70°C, was added 150 ml of a 2 *M* solution of ethyllithium in petroleum ether, and the mixture was allowed to warm to room temperature, whereupon the dilithium salt $(CH_2)_2(C_5H_4Li)_2$ began to separate as a white powder. After 2 hours, the salt was filtered off, washed with petroleum ether, dried in vacuo, and stored under N_2. Yield 12.8 g (55%).

To a suspension of 11.6 g $TiCl_3 \cdot 3$ THF (31.2 mmol) stirred in 150 ml THF at −40°C was added 5.3 g (31.2 mmol) solid $(CH_2)_2(C_5H_4Li)_2$. The mixture was allowed to warm up and subsequently kept under reflux for 4 hours. After cooling to −40°C, 3.1 ml of 12 *M* aqueous HCl were added, and the mixture was stirred for 2 hours without cooling. Addition of 150 ml of CH_2Cl_2, filtration through kieselgur, and removal of solvent in vacuo, gave dark red crystals of $(CH_2)_2(C_5H_4)_2TiCl_2$ (yield 7.8 g, 91%). The product could be purified by recrystallization from toluene, by chromatography on silanated silica gel at 8—10°C with toluene as eluent or by sublimation at 130—140°C in vacuo. Elemental analysis, Found: C, 52.51; H, 4.32; Cl, 26.08. $C_{12}H_{12}Cl_2Ti$ calc.: C, 52.40; H, 4.40; Cl, 25.82%. ^1H NMR data (chemical shifts δ in ppm relative to $\delta(CHCl_3) = 7.24$ ppm): 6.91t(4); 6.09t(4); 3.26s(4). Crystal structure data for this compound have been reported previously [1].

$[(CH_2)_2(C_5H_4)_2TiCl]_2$ *(IIb)*

A suspension of 0.95 g (3.5 mmol) $(CH_2)_2(C_5H_4)_2TiCl_2$ and 0.088 g (3.8 mmol) of sodium sand in 50 ml dry toluene was stirred for 40 hours at 80°C. During this time the solution turned gold-brown and NaCl separated. Dark brown crystals formed on cooling the solution to room temperature. The solution was filtered under Ar and the residue washed with two 15 ml portions of toluene. The brown residue obtained by evaporation of the filtrate and washing solutions in vacuo was sublimed at 130—140°C/10^{-3} Torr to yield 0.82 g (ca. 75%) of dark brown $[(CH_2)_2(C_5H_4)_2TiCl]_2$. The compound proved to be too air-sensitive for complete elemental analysis. However, its Cl content of 15.5% is in reasonable agreement with the value of 14.82% expected for IIb, and distinguishes it clearly from IIa, which has a very similar mass spectrum.

$(CH_2)_2(C_5H_4)_2Ti(CH_3)_2$ (IId)

To a suspension of 1.2 g (4.4 mmol) $(CH_2)_2(C_5H_4)_2TiCl_2$ in 45 ml of dry diethyl ether at —78°C was added 5.1 ml of a 1.8 *M* solution of methyllithium in diethyl ether, and the mixture was allowed to warm to 0°C with stirring. The resulting yellow-orange solution was filtered from the precipitated LiCl and the solvent removed in vacuo. The crude product was purified by chromatography over a column of silylated silica gel cooled to —20°C, using a mixture of toluene/petroleum ether (1/9) as eluent. Cooling the eluent solution slowly, gave yellow-orange needles of $(CH_2)_2(C_5H_4)_2Ti(CH_3)_2$ (0.85 g; 81%). ^1H NMR data (chemical shifts δ in ppm relative to $\delta(C_6D_5H) = 7.15$ ppm; relative intensities in parentheses): 6.82t(4); 5.07t(4); 1.95s(4); 0.07s(6).

$(CH_2)_2(C_5H_4)_2Ti(CO)_2$ (IIc)

A. A solution of 0.32 g (1.35 mmol) $(CH_2)_2(C_5H_4)_2Ti(CH_3)_2$ in petroleum ether was stirred at room temperature in an atmosphere containing 7.3 mmol of CO. The originally yellow-orange solution turned brown in the course of 24 h. After an additional three days the red-brown solution was cooled to —90°C and the unreacted CO was removed at the Toepler pump; 3.7 mmol CO were recovered, indicating an uptake of 3.6 mmol. The solvent distilled from the reaction mixture contains acetone, as indicated by an IR absorption band at 1718 cm^{-1}. Complete formation of $(CH_2)_2(C_5H_4)_2Ti(CO)_2$ and acetone would require a total CO uptake of 4.05 mmol, thus indicating ca. 90% completion. The reddish-brown residue was sublimed at 65—75°C/10^{-3} Torr, giving 0.27 g (78%) of red-brown $(CH_2)_2(C_5H_4)_2Ti(CO)_2$. This material was identified by two $\nu(CO)$ absorption bands at 1980 and 1900 cm^{-1}, by ^1H NMR signals at 4.98t(4), 4.68t(4) and 1.88s(4) ppm (in C_6D_6), and by its mass spectrum with a parent ion at $m/e = 260$ as well as fragment ions corresponding to consecutive loss of two CO ligands.

B. To a stirred solution of 0.64 g (2.3 mmol) $(CH_2)_2(C_5H_4)_2TiCl_2$ in 50 ml toluene under Ar at —78°C, 34 ml of a petroleum ether solution of ethyl lithium (0.15 *M*) were added from a syringe. The argon was then replaced by CO and the mixture allowed to warm to room temperature. After 24 h, the toluene was removed in vacuo and the brown residue sublimed as described above, yielding 0.47 g (1.8 mmol, 78%) of $(CH_2)_2(C_5H_4)_2Ti(CO)_2$.

$(CH_2)_2(C_5H_4)_2TiC_3H_5$ (IIe)

A solution of 2 mmol of C_3H_5MgCl in THF was added from a syringe to a stirred solution of 0.225 g (0.94 mmol) $[(CH_2)_2(C_5H_4)_2TiCl]_2$ in 5 ml of dry toluene at room temperature. $MgCl_2$ separated immediately and the solution turned deep violet. The solution was filtered, the solvent removed in vacuo, and the residue sublimed at 130—135°C/10^{-3} Torr to yield 0.16 g (70%) of $(CH_2)_2(C_5H_4)_2TiC_3H_5$, identified by its mass spectrum, which had a parent ion at *m/e* = 245(31) $[(CH_2)_2(C_5H_4)_2TiC_3H_5]^+$ and fragment ions at *m/e* = 204(100) $[(CH_2)_2(C_5H_4)_2Ti]^+$ and 140(100) $[C_7H_8Ti]^+$.

$(CH_2)_2(C_5H_4)_2TiBH_4$ (IIf)

Diethyl ether (ca. 40 ml) was condensed onto 0.35 g (1.46 mmol) $(CH_2)_2(C_5H_4)_2TiCl$ and 0.034 g (1.6 mmol) $LiBH_4$. The stirred mixture was allowed to warm to room temperature, whereupon a blue-violet solution was formed and LiCl separated. The solution was filtered, the solvent removed in vacuo and the residue sublimed at 85—90°C/10^{-3} Torr to give 0.224 g (70%) of dark violet $(CH_2)_2(C_5H_4)_2TiBH_4$, characterized by its parent ion at *m/e* = 219(8) $[(CH_2)_2(C_5H_4)_2TiBH_4]^+$ and fragment ions corresponding to consecutive loss of four H atoms and a BH_4 unit.

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