Preparation and X-ray Structures of Alkyl−Titanium(IV) Complexes Stabilized by Indenyl Ligands with a Pendant Ether or Amine Substituent and Their Use in the Catalytic Hydroamination of Alkynes

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Complexes Ind^XTiCl_3 (**1**, **2**) react with 1.0, 2.0, and 3.0 equiv of MeMgCl to give $Ind^XTiMeCl_2$ (**3**, **4**), Ind^XTiMe_2Cl (**5**, **6**), and Ind^XTiMe_3 (**7**, **8**), respectively (X = CH_2CH_2OMe (**1**, **3**, **5**, **7**), $CH_2CH_2NMe_2$ (**2**, **4**, **6**, **8**)). Complexes **3**, **6**, and **8** have been characterized by X-ray diffraction analysis. The structures prove that in the solid state the pendant substituents of the indenyl ligands are coordinated to the metal center (d(Ti−O) = 2.296(3) Å (**3**); d(Ti−N) = 2.4006(19) (**6**), 2.4214(17) Å (**8**)) disposed transoid to a methyl ligand. In solution the pendant donor groups are involved in coordination−dissociation equilibria ($\Delta H°$ = 4.2 ± 0.6 kcal mol^{-1} and $\Delta S°$ = 15.5 ± 3 eu for **3**; $\Delta H°$ = 3.4 ± 0.2 kcal mol^{-1} and $\Delta S°$ = 11.6 ± 0.3 eu for **4**; $\Delta H°$ = 3.5 ± 1.1 kcal mol^{-1} and $\Delta S°$ = 15.2 ± 4.4 eu for **5**; $\Delta H°$ = 4.3 ± 1.3 kcal mol^{-1} and $\Delta S°$ = 16.0 ± 2.8 eu for **6**; $\Delta H°$ = 2.2 ± 0.5 kcal mol^{-1} and $\Delta S°$ = 11.0 ± 2.2 eu for **7**; $\Delta H°$ = 4.9 ± 0.5 kcal mol^{-1} and $\Delta S°$ = 20.8 ± 2.2 eu for **8**). Complexes **7**, **8**, $IndTiMe_3$ (**9**), and $H_4IndTiMe_3$ (**10**; H_4Ind = 4,5,6,7-tetrahydroindenyl) are efficient catalyst precursors for the regioselective hydroamination of 1-octyne, phenylacetylene, and 1-phenylpropyne with aromatic (2,6-dimethylaniline and 2,6-diisopropylaniline) and aliphatic (*tert*-butylamine, dodecylamine, and cyclohexylamine) amines. The reactions give imine or imine−enamine mixtures, which are reduced to the corresponding secondary amines. The Markovnikov or anti-Markovnikov nature of the obtained products depends on the aliphatic or aromatic character of both the alkyne and the amine. Markovnikov products with regioselectivities of 100% are formed from the reactions between 1-octyne and aromatic amines, while anti-Markovnikov derivatives with regioselectivities of 100% are obtained from the reactions of aromatic alkynes with all the studied amines and from the reactions of 1-octyne with *tert*-butylamine and dodecylamine. The reactions of 1-octyne with cyclohexylamine give mixtures of both types of products. A comparative study between the catalytic efficiencies of **7**−**10** and those of their cyclopentadienyl counterparts is also included (Table 4).

Introduction

Half-sandwich titanium complexes with a two-electron-donor substituent on the η^5 ligand constitute an area of great interest.[1] In addition to the hemilabile properties, the pendant group exerts a significant influence on the thermodynamic stability of the titanium−coligand bonds.[2] However, the chemistry of this type of compounds is underrepresented in comparison with that of related derivatives of constrained geometry.[3] The indenyl compounds are particularly rare; those previously reported are restricted to a few trichloro and trialkoxide derivatives.[4]

As part of our work on half-sandwich transition-metal compounds,[5] we have recently reported that the complexes Cp^XTiCl_3 (X = $CH_2CH_2NMe_2$ (N),[6] CH_2CH_2OMe (O),[7] $CH_2CH_2PPh_2$ (P))[8] react with 1.0, 2.0, and 3.0 equiv of MeMgCl to afford selectively the mono-, di-, and trimethyl derivatives Cp^X-

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$TiMeCl_2$, Cp^XTiMe_2Cl, and Cp^XTiMe_3. The trimethyl compounds are efficient catalyst precursors for the regioselective hydroamination of aliphatic and aromatic alkynes with aliphatic and aromatic amines. In this context, it should be mentioned that this catalytic reaction is an attractive route to numerous classes of nitrogen-containing compounds.[9] With titanium, important progress has been also reported by the groups of Beller,[10] Bergman,[11] Doye,[12] Odom,[13] and others.[14]

In solution the pendant X substituents of the coordinated cyclopentadienyl ligands of the precursors are involved in coordination−dissociation processes, and equilibria between six- and seven-coordinate species are reached. The catalytic efficiency increases as the affinity of the donor pendant group toward the titanium atom decreases, suggesting that during the catalysis X is not coordinated to the metal center. In contrast to the metallocene systems, amido−imido intermediates do not work for the reactions.[6−8]

A substantial increase in the rates of substitution reactions has been observed for indenyl derivatives in comparison to the rates for their cyclopentadienyl analogues. This so-called "indenyl effect" has been invoked in numerous reports to account for the greater reactivity of indenyl complexes both in catalysis and in stoichiometric reactions.[15] For instance, several studies have demonstrated that replacing the cyclopentadienyl ligand with an indenyl group increases the catalytic activity, stereospecificity, and thermal stability of the polymerization half-sandwich titanium catalysts.[16] For the alkyne hydroamination Doye and co-workers have reported that Ind_2TiMe_2 is a more general precursor than Cp_2TiMe_2.[12k]

With the aim of evaluating the effect of the replacement of cyclopentadienyl groups by indenyl ligands on the intermolecular alkyne hydroamination catalyzed by half-sandwich titanium complexes, and as a part of our effort to develop effective methods of C−N bond formation,[6−8,17] we have recently studied the catalytic behavior of the precursors $IndTiMe_3$ and Ind^XTiMe_3 (X = $CH_2CH_2NMe_2$ (N), CH_2CH_2OMe (O)). Because the "indenyl effect" spans associative[18] and dissociative[19] pathways, and both of these pathways might arise from the presence of carbon−carbon double bonds at positions 4 and 6 of the six-membered ring, we have also included the complex $H_4IndTiMe_3$ (H_4Ind = 4,5,6,7-tetrahydroindenyl) within the study.

This paper reports (i) the preparation and characterization of complexes $Ind^XTiMeCl_2$, Ind^XTiMe_2Cl, Ind^XTiMe_3, including the behavior of X in the solid state and in solution, (ii) the hydroamination of 1-octyne with aliphatic and aromatic amines in the presence of Ind^XTiMe_3, $IndTiMe_3$, and $H_4IndTiMe_3$, (iii) the hydroamination of unsymmetrical aromatic alkynes with the aforementioned amines and in the presence of the aforemen-

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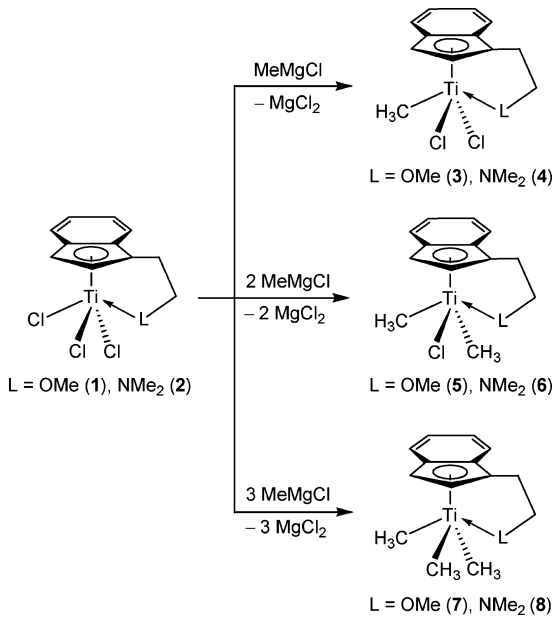
Scheme 1



tioned precursors, and (iv) a comparison of the catalytic behavior of the indenyl and the previously reported cyclopentadienyl precursors.

Results and Discussion

1. Synthesis and Characterization of Ind^{O}TiMe$_x$Cl$_{3-x}$ and Ind^{N}TiMe$_x$Cl$_{3-x}$ Complexes (x = 1−3). The addition of 1.0 equiv of MeMgCl in tetrahydrofuran to suspensions of the trichloro complexes Ind^{O}TiCl$_3$ (**1**) and Ind^{N}TiCl$_3$ (**2**) in diethyl ether results in the selective substitution of one of the chloride ligands of the starting compounds by a methyl group and the formation of the monomethyl derivatives Ind^{O}TiMeCl$_2$ (**3**) and Ind^{N}TiMeCl$_2$ (**4**), which are isolated as red (**3**) and orange (**4**) solids, in about 40% yields, according to Scheme 1.

Complexes **3** and **4** were characterized by elemental analysis and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. Complex **3** was further characterized by an X-ray crystallographic study. A view of the molecular geometry is shown in Figure 1.

The structure proves the coordination of the ether pendant group to the titanium atom, in the solid state. Thus, the distribution of ligands around the metal center can be described as a four-legged piano-stool geometry. The oxygen atom of the pendant group lies in the four-membered face disposed transoid to the methyl ligand (C(1)−Ti−O = 152.28(16)°). The Ti−O bond length of 2.296(3) Å compares well with those found in the complexes Cp^{O}TiMeCl$_2$ (2.3373(18) Å),[7] {η^5(C_5),$\kappa'O$-[C$_5$H$_4$-CH$_2$CHCH$_2$CH$_2$CH$_2$O]}TiCl$_3$ (2.165(4) Å),[20] Cp^{O}TiCl$_3$ (about 2.214 Å),[21] {η^5(C_5),$\kappa'O$-[C$_5$Me$_4$CH$_2$CH$_2$OMe]}TiCl$_3$ (2.295(2) Å),[22] and {η^5(C_5),$\kappa'O$-[C$_5$H$_4$CH(CH$_3$)CH$_2$OMe]}TiCl$_3$ (2.26(2) and 2.22(3) Å).[23] The coordination of the indenyl ligand is the common one in η^5-indenyl complexes, which should be more accurately called η^3 + η^2, as recently suggested.[18,24] A small distortion of this ligand is found. The two hinge carbon atoms

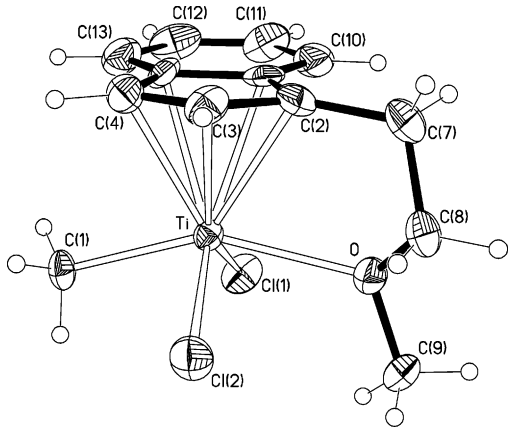
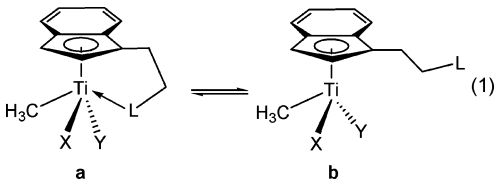


Figure 1. Molecular diagram of Ind^{O}TiMeCl$_2$ (**3**). Selected bond distances (Å) and angles (deg): Ti−Cl(1) = 2.2888(14), Ti−Cl(2) = 2.2963(14), Ti−C(1) = 2.165(4), Ti−O = 2.296(3), Ti−C(2) = 2.330(5), Ti−C(3) = 2.330(4), Ti−C(4) = 2.337(5), Ti−C(5) = 2.427(4), Ti−C(6) = 2.414(5), O−C(8) = 1.442(5), O−C(9) = 1.433(5); C(1)−Ti−Cl(1) = 87.06(12), C(1)−Ti−Cl(2) = 84.90(13), C(1)−Ti−O = 152.28(16), Cl(1)−Ti−Cl(2) = 121.75(6), Cl(1)−Ti−O = 79.92(9), Cl(2)−Ti−O = 81.43(9), Ti−O−C(8) = 112.2(3), Ti−O−C(9) = 121.1(3), C(8)−O−C(9) = 110.9(4).

have Ti−C bond lengths of 2.427(4) (C(5)) and 2.414(5) Å (C(6)), which are slightly longer than those of the three allylic carbon atoms: 2.330(5) (C(2)), 2.330(4) (C(3)), and 2.337(5) Å (C(4)). The folding angle Ω between the plane C(2), C(3), and C(4) and the mean plane of C(2), C(4), C(5), and C(6) is 5.0(8)°. The separation between the titanium atom and the ring centroid (Ti−D$_1$) of 2.040 Å is longer than that found in the complex IndTiCl$_3$ (2.0312(7) Å).[16h] However, the distance between the perpendicular projection of the titanium atom on the plane of the five-membered cycle and the ring centroid (ring slippage) is shorter for **3** (0.106 Å) than for IndTiCl$_3$ (0.12 Å).

In solution, the pendant substituents of the indenyl ligands of **3** and **4** are involved in a coordination−dissociation process (eq 1). This is strongly supported by the ^{1}H NMR spectra of



	3	4	5	6	7	8
X	Cl	Cl	Cl	Cl	CH_3	CH_3
Y	Cl	Cl	CH_3	CH_3	CH_3	CH_3
L	OMe	NMe_2	OMe	NMe_2	OMe	NMe_2

these compounds in toluene-d_8, which are temperature-dependent. Figure 2 shows the ^{1}H NMR spectrum of **3** as a function of the temperature. Due to the rigidity of the pendant group in the seven-coordinate species **a**, at 203 K, the spectrum contains

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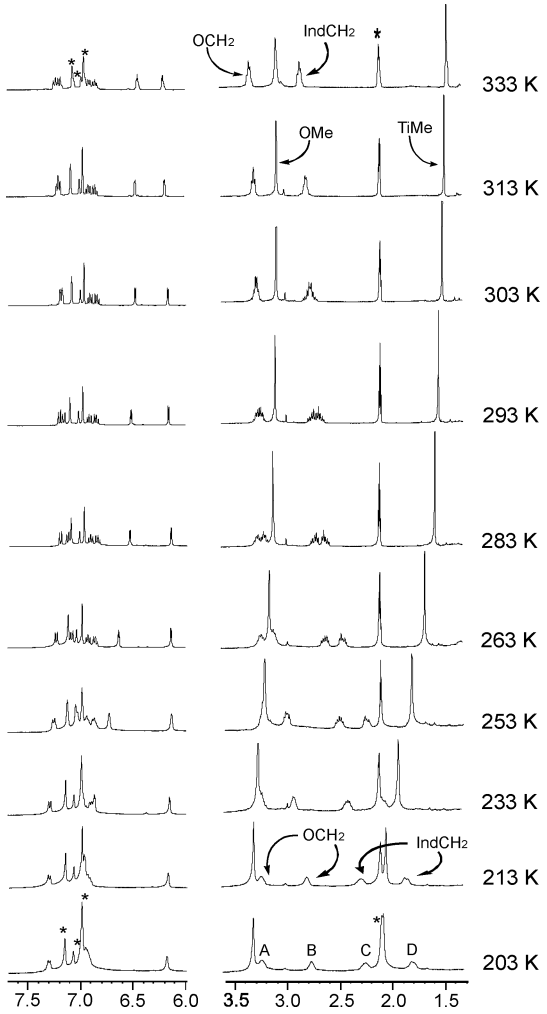

Figure 2. Variable-temperature ^{1}H NMR spectra for the complex Ind^{O}TiMeCl$_2$ (**3**) (toluene-d_8). Asterisks denote residual solvent peaks.

an ABCD spin system for the methylene protons at δ_A 3.23 and δ_B 2.75 (CH_2O) and at δ_C 2.24 and δ_D 1.80 (CH_2Ind). The resonances corresponding to the protons of the five-membered ring of the indenyl ligand (C_5H_2) appear at 6.97 and 6.19 ppm, whereas methyl resonances are observed at 3.31 (OMe) and 2.08 ppm (TiMe). Raising the sample temperature produces an approach between δ_A and δ_B, and between δ_C and δ_D, to afford two complex signals at temperatures higher than 303 K. At 333 K, they appear centered at 3.32 (CH_2O) and 2.85 (CH_2Ind) ppm. Between 183 and 363 K, the C_5H_2 resonances of the indenyl group also undergo an approach process. However, as expected, they do not give rise to only one signal. The behavior of the ^{1}H NMR spectra of **4** with temperature is similar to that mentioned above for **3**.

In the $^{13}C\{^1H\}$ NMR spectra, the most noticeable resonances are those due to the ring junction carbon atoms that, at room temperature, appear at 129.4 and 129.3 ppm (**3**) and 130.6 and 127.0 ppm (**4**). In agreement with the structure shown in Figure 1, the values of the $\Delta\delta$ ^{13}C parameters, −0.5 for **3** and −0.9 for **4**, are as expected for a distorted η^5 hapticity of the indenyl ligand.[25]

For the process shown in eq 1, the equilibrium constants between 363 and 183 K were determined according to eq 2.[26]

$$K=\frac{[\mathbf{b}]}{[\mathbf{a}]}=\frac{\left(\frac{\delta_A+\delta_B}{2}\right)^{CH_2L}_{min}-\left(\frac{\delta_A+\delta_B}{2}\right)^{CH_2L}}{\left(\frac{\delta_A+\delta_B}{2}\right)^{CH_2L}-\left(\frac{\delta_A+\delta_B}{2}\right)^{CH_2L}_{max}}=\frac{\left(\frac{\delta_C+\delta_D}{2}\right)^{IndCH_2}_{min}-\left(\frac{\delta_C+\delta_D}{2}\right)^{IndCH_2}}{\left(\frac{\delta_C+\delta_D}{2}\right)^{IndCH_2}-\left(\frac{\delta_C+\delta_D}{2}\right)^{IndCH_2}_{max}} \quad (2)$$

The temperature dependence of the equilibria gives the values $\Delta H° = 4.2 \pm 0.6$ kcal mol^{-1} and $\Delta S° = 15.5 \pm 3$ eu for **3** and $\Delta H° = 3.4 \pm 0.2$ kcal mol^{-1} and $\Delta S° = 11.6 \pm 0.3$ eu for **4**. The positive values of $\Delta S°$ are in agreement with the free character of the pendant groups in **b**, whereas the low values of $\Delta H°$ indicate weak Ti−O and Ti−N bonds in **3** and **4**, respectively.

Treatment of **1** and **2** with 2.0 equiv of MeMgCl produces the substitution of two chloride ligands of the starting compounds by methyl groups and the formation of the dimethyl derivatives Ind^{O}TiMe$_2$Cl (**5**) and Ind^{N}TiMe$_2$Cl (**6**), which are isolated as dark orange (**5**) and red (**6**) solids in 51% and 32% yields, respectively, according to Scheme 1.

Like **3** and **4**, complexes **5** and **6** were characterized by elemental analysis and ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. Complex **6** was further characterized by an X-ray crystallographic study. A view of the molecular geometry is shown in Figure 3.

The distribution of ligands around the titanium is like that of **3**, with the methyl groups disposed mutually cisoid (C(14)−Ti−C(15) = 81.62(12)°) and the pendant dimethylamino group disposed transoid to C(14) (C(14)−Ti−N = 149.46(10)°). The Ti−N bond length of 2.4006(19) Å compares well with the Ti−N distance found in the related cyclopentadienyl derivative Cp^{N}TiMe$_2$Cl (2.433(4) Å)[6] and other complexes containing dative nitrogen−titanium bonds.[27] The coordination of the indenyl ligand is η^5 with a small distortion similar to that of **3**. The hinge carbon atoms have Ti−C distances of 2.472(2) (C(4)) and 2.483(2) Å (C(5)), which are about 0.1 Å longer than those of the allylic carbon atoms: 2.368(2) (C(3)), 2.363(2) (C(6)), and 2.332(2) Å (C(7)). In agreement with the case for **3**, the values of the folding angle Ω, the Ti−D_1 distance, and the ring slippage are 3.7(3)°, 2.079 Å, and 0.167 Å, respectively.

The distorted η^5 coordination of the indenyl ligand in **5** and **6** is also supported by the $^{13}C\{^1H\}$ NMR spectra of these compounds, which show resonances due to the ring junction carbon atoms at 127.9 and 125.4 ppm (**5**) and at 127.2 and 126.1 ppm (**6**). According to these chemical shifts the $\Delta\delta(^{13}C)$ parameters are −3.2 for **5** and −3.1 for **6**, in good agreement with those of **3** and **4**.

In solution, the pendant substituents of the indenyl ligands of **5** and **6** are also involved in a coordination−dissociation process like that shown in eq 1. Thus, the behavior of the ^{1}H NMR spectra of these compounds with the temperature is similar to that described for **3**. In this case, the temperature dependence of the equilibria gives the values $\Delta H° = 3.5 \pm 1.1$ kcal mol^{-1}

(25) (a) $\Delta\delta(^{13}C) = \{\delta(C_{3a,7a})$ of $L_nMInd^L\} - \{\delta(C_{3a,7a})$ of $LiInd^L\}$;[15] $\delta(C_{3a,7a})$ for $LiInd^O$ is 129.8 ppm and for $LiInd^N$ is 129.7 ppm. (b) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839.

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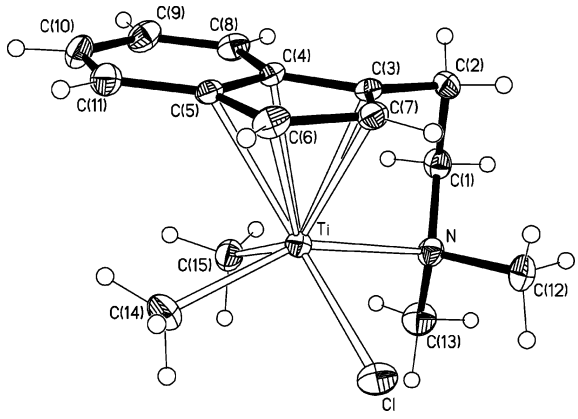


Figure 3. Molecular diagram of Ind^NTiMe_2Cl (**6**). Selected bond distances (Å) and angles (deg): Ti−Cl = 2.3260(7), Ti−C(14) = 2.150(2), Ti−C(15) = 2.126(3), Ti−N = 2.4006(19), Ti−C(3) = 2.368(2), Ti−C(4) = 2.472(2), Ti−C(5) = 2.483(2), Ti−C(6) = 2.363(2), Ti−C(7) = 2.332(2), N−C(1) = 1.489(3), N−C(12) = 1.480(3), N−C(13) = 1.482(3); C(14)−Ti−Cl = 83.78(8), C(14)−Ti−C(15) = 81.62(12), C(14)−Ti−N = 149.46(10), Cl−Ti−C(15) = 124.50(7), Cl−Ti−N = 82.68(5), C(15)−Ti−N = 83.74(9), Ti−N−C(1) = 107.24(13), Ti−N−C(12) = 113.13(15), Ti−N−C(13) = 113.28(15), C(1)−N−C(12) = 108.06(19), C(1)−N−C(13) = 108.7(2), C(12)−N−C(13) = 106.27(19).

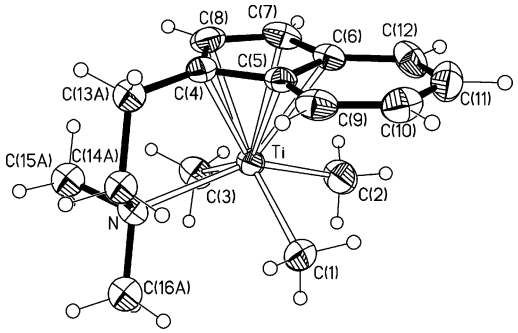


Figure 4. Molecular diagram of Ind^NTiMe_3 (**8**). Selected bond distances (Å) and angles (deg): Ti−C(1) = 2.142(2), Ti−C(2) = 2.143(2), Ti−C(3) = 2.152(2), Ti−N = 2.4214(17), Ti−C(4) = 2.394(2), Ti−C(5) = 2.492(2), Ti−C(6) = 2.498(2), Ti−C(7) = 2.377(2), Ti−C(8) = 2.343(2), N−C(14A) = 1.472(3), N−C(15A) = 1.497(3), N−C(16A) = 1.477(3); C(1)−Ti−C(2) = 83.07(11), C(1)−Ti−C(3) = 125.03(10), C(1)−Ti−N = 83.40(7), C(2)−Ti−C(3) = 83.04(10), C(2)−Ti−N = 149.46(8), C(3)−Ti−N = 82.56(8), Ti−N−C(14A) = 107.78(15), Ti−N−C(15A) = 113.76(15), Ti−N−C(16A) = 114.40(15), C(14A)−N−C(15A) = 106.7(2), C(14A)−N−C(16A) = 109.1(2), C(15A)−N−C(16A) = 104.8(2).

and $\Delta S° = 15.2 \pm 4.4$ eu for **5** and $\Delta H° = 4.3 \pm 1.3$ kcal mol^{-1} and $\Delta S° = 16.0 \pm 2.8$ eu for **6**.

The addition of 3.0 equiv of MeMgCl to a diethyl ether suspension of **1** and **2** produces the substitution of the three chloride ligands of the starting compounds by methyl groups, and the formation of the trimethyl derivatives Ind^OTiMe_3 (**7**) and Ind^NTiMe_3 (**8**), which are isolated as an orange oil (**7**) and an orange solid (**8**) in 63% and 55% yields, respectively, according to Scheme 1.

Like the mono- and dimethyl derivatives, complexes **7** and **8** were characterized by elemental analysis and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. Complex **8** was further characterized by an X-ray crystallographic study. A view of the molecular geometry is given in Figure 4.

The structure proves that also in the trimethyl derivatives the pendant substituent of the indenyl ligand is coordinated to the titanium atom. Thus, the distribution of ligands around the metal center can be described as a four-legged piano-stool geometry, with the nitrogen atom of the amine substituent disposed transoid to C(2) (C(2)−Ti−N = 149.46(8)°). The Ti−N bond length of 2.4214(17) Å is about 0.02 Å longer than the Ti−N distance in **6**, suggesting that in the latter the titanium−pendant bond is slightly stronger than in **8**. The coordination of the indenyl ligand is η^5 with a small distortion similar to those of **3** and **6**. The hinge carbon atoms have Ti−C distances of 2.492(2) (C(5)) and 2.498(2) Å (C(6)), which are between 0.10 and 0.15 Å longer than those of the allylic carbon atoms: 2.394(2) (C(4)), 2.377(2) (C(7)), and 2.343(2) Å (C(8)). In this case, the values of the folding angle Ω, the Ti−D_1 distance, and the ring slippage are 3.5(3)°, 2.100 Å, and 0.172 Å, respectively.

The ^{13}C{^{1}H} NMR spectra of **7** and **8** are consistent with those of **3**−**6** and with the structure shown in Figure 4. Thus, the resonances due to the ring junction carbon atoms are observed at 127.3 and 125.1 ppm, for both **7** and **8**. In agreement with a distorted η^5 coordination of the indenyl ligand, the $\Delta\delta$(^{13}C) parameter is −3.6.

In solution, the behavior of the pendant substituents of the indenyl ligands of **7** and **8** is like that of **3**−**6**. In accordance with this, the ^{1}H NMR spectra are also temperature dependent, and completely analogous to those of **3**−**6**. The values of the parameters $\Delta H°$ and $\Delta S°$, obtained from the temperature dependence of the equilibria, are 2.2 ± 0.5 kcal mol^{-1} and 11.0 ± 2.2 eu for **7** and 4.9 ± 0.5 kcal mol^{-1} and 20.8 ± 2.2 eu for **8**.

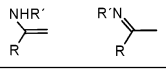
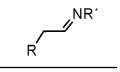
According to the values of $\Delta H°$ and $\Delta S°$ calculated for **3**, **5**, and **7** and for **4**, **6**, and **8**, the molar fractions of hexacoordinate form **b** at 20 °C in toluene-d_8 increase in the sequences **3** (0.6) < **5** (0.8) < **7** (0.9) and **4** (0.5) < **6** (0.7) < **8** (0.9): i.e., as the chloride ligands at the titanium atom are replaced by methyl groups. This, which has been also observed for the cyclopentadienyl counterparts,[6,7] appears to be a consequence of the steric hindrance experienced by the donor groups of the pendant substituents and the methyl ligands, when they are disposed mutually cisoid. In addition, it should be also noted that, in agreement with the cyclopentadienyl systems, the NMe_2 donor group has a higher affinity for the titanium atom than the OMe donor group in these indenyl compounds. Thus, for each pair of methyl derivatives, it is observed that the molar fraction of hexacoordinate form **b** is higher for OMe than for NMe_2; i.e. **3** > **4**, **5** > **6**, and **7** ≈ **8**.

2. Hydroamination of 1-Octyne. Complexes **7** and **8** and the related compounds $IndTiMe_3$ (**9**) and $H_4IndTiMe_3$ (**10**) are very efficient catalyst precursors for the addition of one of the N−H bonds of aromatic and aliphatic primary amines to the carbon−carbon triple bond of 1-octyne. The reactions were performed in toluene at 100 °C, using 5 mol % of catalyst precursor and stoichiometric amounts of alkyne. In contrast to metallocene precursors[10f,12k] but in agreement with half-sandwich cyclopentadienyl systems,[8] under the conditions used, the loss of alkyne as a consequence of dimerization or polymerization side reactions is not observed.

As can be seen in Table 1, 1-octyne reacts with aromatic amines, such as 2,6-dimethylaniline and 2,6-diisopropylaniline, to give enamine−imine mixtures resulting from regioselective Markovnikov couplings. The mixtures were transformed in quantitative yield into the corresponding secondary amines, by reduction with $NaCNBH_3$/*p*-TsOH in tetrahydrofuran at room temperature (Scheme 2).

For the reactions shown in Scheme 2, the pendant substituents of the indenyl ligands have certainly a marked influence on the

Table 1. Hydroamination of 1-Octyne[a]

Entry	Catalyst	Amine	*t* (h)	Conv.[b] (%)	Markovnikov[c] 	Anti-Markovnikov[c] 
1	$Ind^{O}TiMe_3$ (**7**)		0.25	100	0	100	0
2	$Ind^{O}TiMe_3$ (**7**)		0.25	100	75	25	0
3	$Ind^{O}TiMe_3$ (**7**)		0.25	100	0	0	100
4	$Ind^{O}TiMe_3$ (**7**)	$CH_3(CH_2)_{11}NH_2$	8 24	34 40	0	0	100
5	$Ind^{O}TiMe_3$ (**7**)		8 24	94 100	0	30	70
6	$Ind^{N}TiMe_3$ (**8**)		8 24	75 100	40	60	0
7	$Ind^{N}TiMe_3$ (**8**)		8 24	52 70	56	44	0
8	$Ind^{N}TiMe_3$ (**8**)		8 24	90 100	0	0	100
9	$Ind^{N}TiMe_3$ (**8**)	$CH_3(CH_2)_{11}NH_2$	8 24	20 30	0	0	100
10	$Ind^{N}TiMe_3$ (**8**)		8 24	83 100	0	23	77
11	$IndTiMe_3$ (**9**)		1.5	100	0	100	0
12	$IndTiMe_3$ (**9**)		6	100	70	30	0
13	$IndTiMe_3$ (**9**)		0.25	100	0	0	100
14	$IndTiMe_3$ (**9**)	$CH_3(CH_2)_{11}NH_2$	8 24	19 50	0	0	100
15	$IndTiMe_3$ (**9**)		8 24	60 100	0	18	82
16	$H_4IndTiMe_3$ (**10**)		7	100	0	100	0
17	$H_4IndTiMe_3$ (**10**)		8 24	56 100	56	44	0
18	$H_4IndTiMe_3$ (**10**)		0.25	100	0	0	100
19	$H_4IndTiMe_3$ (**10**)	$CH_3(CH_2)_{11}NH_2$	8 24	32 56	0	0	100
20	$H_4IndTiMe_3$ (**10**)		1	100	0	25	75

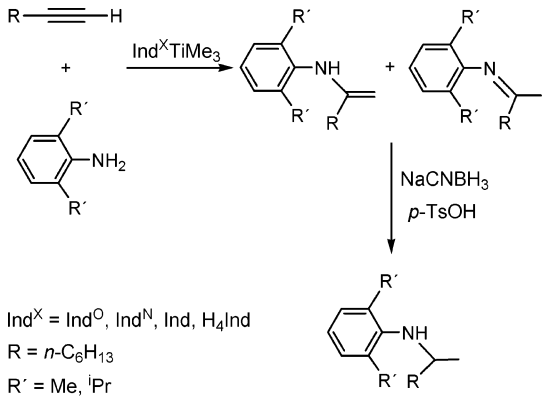
[a] Reaction conditions: 1-octyne (2.40 mmol), amine (2.64 mmol), *n*-octane (2.40 mmol), catalyst (0.12 mmol, 5 mol %), toluene (2.0 mL), 100 °C. [b] Determined by GC. [c] Determined by ^{1}H NMR spectroscopy at the end of the reaction.

efficiency of the catalytic systems. This is clearly evident when the results for the hydroamination reactions in the presence of **7**−**9** are compared. Complex **7**, containing an ether pendant substituent, is extremely efficient (entries 1 and 2); thus, the quantitative conversion of the alkyne into the hydroamination products occurs within a very short time (15 min). Complex **9**, which contains an unsubstituted indenyl ligand, is also efficient, but the quantitative transformation of the alkyne occurs after hours (entries 11 and 12), while with the amine derivative **8**, the quantitative conversion of the alkyne needs 1 day or more. The tetrahydroindenyl derivative shows an efficiency intermediate between those of **9** and **8**.

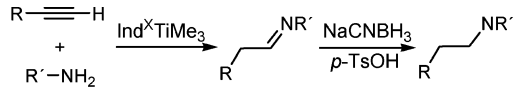
These results indicate that the efficiency of the substituted-indenyl half-sandwich precursors, with a donor group in the pendant substituent, increases as the affinity of the donor group toward the titanium atom decreases: i.e., NMe_2 < OMe. This is in agreement with previously observations for related substituted cyclopentadienyl half-sandwich systems, for which it has been suggested that during the catalysis the pendant donor group is not coordinated to the titanium atom.

The quantitative formation of Markovnikov products according to Scheme 2 is remarkable. This is the main advantage of the half-sandwich catalytic systems with regard to the metallocene precursors. In contrast to the case for the anilines, *tert*-butylamine and dodecylamine selectively give the imines resulting from regioselective anti-Markovnikov couplings (Scheme 3). The change of regioselectivity by changing the nature of the substituent of the amine has been also observed by Beller

Scheme 2

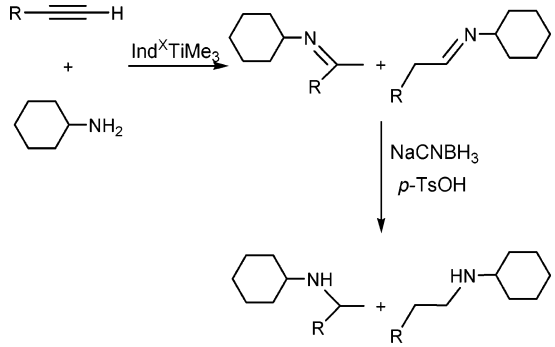


Scheme 3



Ind^X = Ind^O, Ind^N, Ind, H_4Ind; R = *n*-C_6H_{13}; R´ = *tert*-butyl, dodecyl

Scheme 4



Ind^X = Ind^O, Ind^N, Ind, H_4Ind

R = *n*-C_6H_{13}

using $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$,[10f] by Doye using Ind_2TiMe_2,[12k] and by us using Cp^PTiMe_3 (P = $CH_2CH_2PPh_2$).[8] However, again it should be noted that regioselectivities of 100% are only achieved with half-sandwich precursors. Like the enamine−imine mixtures shown in Scheme 2, the imines resulting from aliphatic amines were transformed in quantitative yield into the corresponding secondary amines, by treatment with $NaCNBH_3$/*p*-TsOH in tetrahydrofuran at room temperature.

The pendant substituent of the indenyl ligands has also a marked influence on the efficiency of the catalytic precursors, for the reaction with *tert*-butylamine. With **7** the quantitative formation of the imine occurs after 15 min, while with **8** high conversions are achieved only after hours (entries 3 and 8). Complexes **9** and **10** are also extremely active. As for **7**, with both compounds, the quantitative formation of the imine is observed after 15 min. The four compounds are much more efficient for the reactions with *tert*-butylamine than for those with dodecylamine. For the latter, in the four cases, conversions between 30% and 56% are observed after 24 h.

The regioselectivity of the addition of cyclohexylamine to the triple bond of 1-octyne is much lower than in the previous cases. Although the formation of the anti-Markovnikov product is favored, mixtures of Markovnikov and anti-Markovnikov imines are obtained, which were also converted into the corresponding secondary amines by reduction with $NaCNBH_3$/*p*-TsOH (Scheme 4). For this reaction the tetrahydroindenyl precursor **10** is the most efficient.

Table 2. Hydroamination of Phenylacetylene[a]

Entry	Catalyst	Amine	*t* (h)	Conv.[b] (%)	Enamine : Imine[c]
1	Ind^{O}TiMe$_3$ (**7**)		4	100	70 : 30
2	Ind^{O}TiMe$_3$ (**7**)		2	100	70 : 30
3	Ind^{O}TiMe$_3$ (**7**)		0.25	100	40 : 60
4	Ind^{O}TiMe$_3$ (**7**)	$CH_3(CH_2)_{11}NH_2$	8 24	55 70	40 : 60
5	Ind^{O}TiMe$_3$ (**7**)		6	100	35 : 65
6	Ind^{N}TiMe$_3$ (**8**)		8 24	76 95	52 : 48
7	Ind^{N}TiMe$_3$ (**8**)		8 24	70 90	60 : 40
8	Ind^{N}TiMe$_3$ (**8**)		3	100	40 : 60
9	Ind^{N}TiMe$_3$ (**8**)	$CH_3(CH_2)_{11}NH_2$	8 24	18 35	30 : 70
10	Ind^{N}TiMe$_3$ (**8**)		8 24	90 100	25 : 75
11	IndTiMe$_3$ (**9**)		6.5	100	40 : 60
12	IndTiMe$_3$ (**9**)		6	100	0 : 100
13	IndTiMe$_3$ (**9**)		0.16	100	55 : 45
14	IndTiMe$_3$ (**9**)	$CH_3(CH_2)_{11}NH_2$	8 24	18 39	35: 65
15	IndTiMe$_3$ (**9**)		5	100	50 : 50
16	H_4IndTiMe$_3$ (**10**)		8 24	80 100	55 : 45
17	H_4IndTiMe$_3$ (**10**)		8 24	58 85	62 : 38
18	H_4IndTiMe$_3$ (**10**)		0.16	100	60 : 40
19	H_4IndTiMe$_3$ (**10**)	$CH_3(CH_2)_{11}NH_2$	8 24	20 40	30 : 70
20	H_4IndTiMe$_3$ (**10**)		2	100	40 : 60

[a] Reaction conditions: phenylacetylene (2.40 mmol), amine (2.64 mmol), *n*-octane (2.40 mmol), catalyst (0.12 mmol, 5 mol %), toluene (2.0 mL), 100 °C. [b] Determined by GC. [c] Determined by ^{1}H NMR spectroscopy at the end of the reaction.

3. Hydroamination of Aromatic Alkynes. Complexes **7**−**10** are also efficient catalyst precursors for the addition of one of the N−H bonds of 2,6-dimethylaniline, 2,6-diisopropylaniline, *tert*-butylamine, dodecylamine, and cyclohexylamine to the carbon−carbon triple bond of phenylacetylene (Table 2) and 1-phenylpropyne (Table 3). In all of the cases the reactions lead to enamine−imine mixtures resulting from the regioselective anti-Markovnikov couplings. The mixtures were transformed

Table 3. Hydroamination of 1-Phenylpropyne[a]

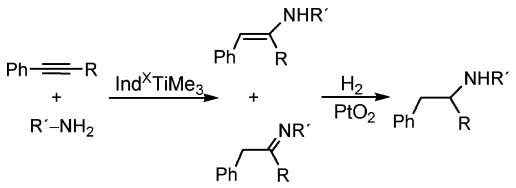
Entry	Catalyst	Amine	*t* (h)	Conv.[b] (%)	Enamine : Imine[c]
1	$Ind^{O}TiMe_3$ (**7**)		1	100	0 : 100
2	$Ind^{O}TiMe_3$ (**7**)		8 24	45 100	90 : 10
3	$Ind^{O}TiMe_3$ (**7**)		8 24	70 100	70 : 30
4	$Ind^{O}TiMe_3$ (**7**)	$CH_3(CH_2)_{11}NH_2$	8 24	0 5	-
5	$Ind^{O}TiMe_3$ (**7**)		8 24	30 55	0 : 100
6	$Ind^{N}TiMe_3$ (**8**)		8 24	24 50	20 : 80
7	$Ind^{N}TiMe_3$ (**8**)		8 24	15 40	60 : 40
8	$Ind^{N}TiMe_3$ (**8**)		8 24	8 15	-
9	$Ind^{N}TiMe_3$ (**8**)	$CH_3(CH_2)_{11}NH_2$	8 24	0 5	-
10	$Ind^{N}TiMe_3$ (**8**)		8 24	25 36	0 : 100
11	$IndTiMe_3$ (**9**)		3	100	0 : 100
12	$IndTiMe_3$ (**9**)		0.5	100	90 : 10
13	$IndTiMe_3$ (**9**)		1.5	100	25 : 75
14	$IndTiMe_3$ (**9**)	$CH_3(CH_2)_{11}NH_2$	8 24	7 14	35 : 65
15	$IndTiMe_3$ (**9**)		8 24	40 100	30 : 70
16	$H_4IndTiMe_3$ (**10**)		6	100	10 : 90
17	$H_4IndTiMe_3$ (**10**)		0.25	100	55 : 45
18	$H_4IndTiMe_3$ (**10**)		1	100	70 : 30
19	$H_4IndTiMe_3$ (**10**)	$CH_3(CH_2)_{11}NH_2$	8 24	8 13	-
20	$H_4IndTiMe_3$ (**10**)		1	100	0 : 100

[a] Reaction conditions: 1-phenylpropyne (2.40 mmol), amine (2.64 mmol), *n*-octane (2.40 mmol), catalyst (0.12 mmol, 5 mol %), toluene (2.0 mL), 100 °C. [b] Determined by GC. [c] Determined by ^{1}H NMR spectroscopy at the end of the reaction.

in quantitative yield into the corresponding secondary amines, by reduction with molecular hydrogen in the presence of PtO_2 (Scheme 5).

It should be noted that also for the formation of the anti-Markovnikov products the regioselectivity is 100%. The behavior of these half-sandwich indenyl systems agrees well with the behavior previously observed for the related half-sandwich cyclopentadienyl precursors.[6−8] However, this behavior is in contrast to that observed by Doye and co-workers using the bis(indenyl) derivative Ind_2TiMe_2 as catalyst precursor. Doye's group has found that the regioselectivity of the reactions is

Scheme 5



Ind^X = Ind^O, Ind^N, Ind, H_4Ind

R = H, Me

R´ = 2,6-$Me_2C_6H_3$, 2,6-$^iPr_2C_6H_3$, *tert*-butyl, dodecyl, Cy

influenced by the nature of the substituent of the aromatic alkyne and the bulkiness of the primary amine.[12k]

The pendant substituents of the indenyl ligands have also a marked influence on the yield of the reactions shown in Scheme 5. Thus, for all of the reactions, complex **7** is more efficient than **8**. Complex **7** is the most efficient precursor in the addition of a NH bond of 2,6-dimethylaniline, 2,6-diisopropylaniline, and dodecylamine to phenylacetylene and in the hydroamination of 1-phenylpropyne with 2,6-dimethylaniline.

In general, the bulkier aliphatic amines give rise to higher conversions. Thus, for both alkynes, the conversions decrease in the sequence *tert*-butylamine > cyclohexylamine > dodecylamine. The influence of the bulkiness of the aromatic amines in the hydroamination is less significant than that of the aliphatic amines, in particular for phenylacetylene. For 1-phenylpropyne, the influence depends on the catalytic precursor. In the presence of **7** and **8**, the reactions are faster for 2,6-dimethylaniline than for 2,6-diisopropylaniline, while in the presence of **9** and **10** an inverse relationship is observed.

4. Ind^XTiMe_3 versus Cp^XTiMe_3. The first clear fact from the results shown in Tables 1−3 and those previously reported for Cp^XTiMe_3[6−8] (X = $CH_2CH_2PPh_2$ (P), $CH_2CH_2NMe_2$ (N), CH_2CH_2OMe (O)) is that the pendant substituents X have a marked influence on the efficiency of the half-sandwich precursors for the hydroamination reactions of alkynes. The efficiency increases as the affinity of the donor groups of the pendant substituents toward the titanium atom decreases. This is in agreement with mechanistic studies indicating that the catalytically active species are six-coordinate complexes with a free pendant donor group.[8] The role of the pendant substituents appears to be to prevent the formation of side inactive species (probably dimeric compounds), due to their demand of space.[12l]

Because the indenyl group has a demand of space greater than that of the cyclopentadienyl ligand and the electronic differences between both groups are not very significant, one should expect that the catalytic precursors reported here would be more efficient than the corresponding cyclopentadienyl counterparts. Table 4 shows that this is correct for the hydroamination of 1-octyne. Complex **7** is the most efficient precursor with the sterically more demanding amines 2,6-diisopropylaniline, 2,6-dimethylaniline, and *tert*-butylamine, whereas for the reaction with cyclohexylamine and dodecylamine the tetrahydroindenyl complex **10** is the best precursor.

The indenyl precursors are also more efficient than their cyclopentadienyl counterparts in the hydroamination of phenylacetylene with the sterically less demanding amines cyclohexylamine and dodecylamine. For the hydroamination reactions with *tert*-butylamine, 2,6-diisopropylaniline, and 2,6-dimethylaniline, the differences are not significant and the trend is not clear. For the hydroamination of 1-phenylpropyne, the sterically most demanding alkyne, the cyclopentadienyl precursors Cp^P-

Table 4. Comparative Catalytic Efficiencies of the Half-Sandwich Titanium Precursors

Alkyne	Amine	Catalytic Precursors							
n-C_6H_{13}—≡—H		Ind^OTiMe_3 >	Cp^PTiMe_3 >	$IndTiMe_3$ >	$CpTiMe_3$ ≈	$H_4IndTiMe_3$ >	Ind^NTiMe_3	-	-
n-C_6H_{13}—≡—H		Ind^OTiMe_3 >	Cp^PTiMe_3 >	$IndTiMe_3$ >	$H_4IndTiMe_3$ >	$CpTiMe_3$ ≈	Ind^NTiMe_3	-	-
n-C_6H_{13}—≡—H		Ind^OTiMe_3 ≈	$IndTiMe_3$ ≈	$H_4IndTiMe_3$ ≈	$CpTiMe_3$ >	Cp^PTiMe_3 >	Ind^NTiMe_3	-	-
n-C_6H_{13}—≡—H	$CH_3(CH_2)_{11}NH_2$	$H_4IndTiMe_3$ >	$IndTiMe_3$ ≈	Ind^OTiMe_3 ≈	Ind^NTiMe_3 ≈	$CpTiMe_3$ >	Cp^PTiMe_3	-	-
n-C_6H_{13}—≡—H		$H_4IndTiMe_3$ >	Ind^OTiMe_3 ≈	Ind^NTiMe_3 ≈	Cp^PTiMe_3 >	$IndTiMe_3$ ≈	$CpTiMe_3$	-	-
Ph—≡—H		Cp^PTiMe_3 >	Cp^OTiMe_3 >	Ind^OTiMe_3 >	$IndTiMe_3$ >	$H_4IndTiMe_3$ ≈	Ind^NTiMe_3 ≈	$CpTiMe_3$ ≈	Cp^NTiMe_3
Ph—≡—H		Ind^OTiMe_3 ≈	Cp^PTiMe_3 >	Cp^OTiMe_3 ≈	$CpTiMe_3$ >	$IndTiMe_3$ >	Ind^NTiMe_3 >	$H_4IndTiMe_3$ >	Cp^NTiMe_3
Ph—≡—H		$H_4IndTiMe_3$ ≈	$IndTiMe_3$ ≈	Cp^OTiMe_3 ≈	$CpTiMe_3$ ≈	Ind^OTiMe_3 >	Cp^PTiMe_3 >	Cp^NTiMe_3 >	Ind^NTiMe_3
Ph—≡—H	$CH_3(CH_2)_{11}NH_2$	Ind^OTiMe_3 >	$H_4IndTiMe_3$ ≈	$IndTiMe_3$ ≈	Ind^NTiMe_3 >	Cp^PTiMe_3	-	-	-
Ph—≡—H		$H_4IndTiMe_3$ >	$IndTiMe_3$ >	Ind^OTiMe_3 >	Ind^NTiMe_3 >	Cp^OTiMe_3 >	$CpTiMe_3$ ≈	Cp^PTiMe_3 ≈	Cp^NTiMe_3
Ph—≡—Me		Cp^OTiMe_3 >	Ind^OTiMe_3 ≈	$CpTiMe_3$ >	Cp^PTiMe_3 >	$IndTiMe_3$ >	Cp^NTiMe_3 ≈	$H_4IndTiMe_3$ >	Ind^NTiMe_3
Ph—≡—Me		$CpTiMe_3$ ≈	$H_4IndTiMe_3$ >	$IndTiMe_3$ >	Cp^OTiMe_3 >	Cp^PTiMe_3 >	Cp^NTiMe_3>	Ind^OTiMe_3 >	Ind^NTiMe_3
Ph—≡—Me		$CpTiMe_3$ >	Cp^PTiMe_3 >	Cp^OTiMe_3 >	$H_4IndTiMe_3$ >	$IndTiMe_3$ >	Cp^NTiMe_3 ≈	Ind^OTiMe_3 >	Ind^NTiMe_3
Ph—≡—Me	$CH_3(CH_2)_{11}NH_2$	$IndTiMe_3$ ≈	$H_4IndTiMe_3$ >	Cp^PTiMe_3 ≈	Ind^OTiMe_3 ≈	Ind^NTiMe_3	-	-	-
Ph—≡—Me		Cp^OTiMe_3 ≈	$H_4IndTiMe_3$ >	Cp^PTiMe_3 >	Cp^NTiMe_3 ≈	$IndTiMe_3$ ≈	$CpTiMe_3$ >	Ind^OTiMe_3 >	Ind^NTiMe_3

$TiMe_3$ and Cp^OTiMe_3 are, in general, more efficient precursors than those reported here.

In summary, the half-sandwich indenyl−titanium precursors keep the same level of regioselectivity as the half-sandwich cyclopentadienyl counterparts for the intermolecular hydroamination of alkynes. In terms of reaction yields, the indenyl precursors are more efficient than the cyclopentadienyl species for the reactions involving the sterically less demanding substrates, while the cyclopentadienyl complexes should be the chosen precursors for the reactions involving the sterically more demanding substrates.

Concluding Remarks

The previously reported complexes Ind^OTiCl_3 and Ind^NTiCl_3 react with 1.0, 2.0, and 3.0 equiv of MeMgCl to afford the mono-, di-, and trimethyl derivatives $Ind^OTiMeCl_2$ and $Ind^NTiMeCl_2$, Ind^OTiMe_2Cl and Ind^NTiMe_2Cl, and Ind^OTiMe_3 and Ind^NTiMe_3, respectively. In the solid state, the donor pendant groups of the indenyl ligands are weakly bonded to the metal center, disposed transoid to a methyl ligand. In solution they dissociate and equilibria between seven-coordinate and six-coordinate species are reached. The molar fraction of six-coordinate species increases as the number of methyl ligands at the titanium atom also increases and as the affinity of the donor group of the pendant substituent toward the metal center decreases (NMe_2 > OMe).

The trimethyl derivatives Ind^OTiMe_3, Ind^NTiMe_3, $H_4IndTiMe_3$, and $IndTiMe_3$ are efficient catalyst precursors for the regioselective hydroamination of aliphatic and aromatic alkynes with aliphatic and aromatic amines. The Markovnikov or anti-Markovnikov nature of the obtained products depends on the aliphatic or aromatic character of both the alkyne and the amine.

The pendant substituents of the indenyl ligands have a marked influence on the efficiency of the catalytic systems, which increases as the affinity of the donor groups toward the titanium atom decreases. This suggests that during the catalysis the pendant donor groups are not coordinated to the metal center. Thus, due to their demand of space, they can protect the active species from side reactions. In agreement with this, the precursors reported here are more efficient than the previously described half-sandwich cyclopentadienyl derivatives, for the reactions involving the sterically less demanding substrates.

In conclusion, we have increased the family of half-sandwich titanium catalyst precursors for the intermolecular hydroamination of alkynes with new indenyl derivatives, which are more efficient than their cyclopentadienyl counterparts for the reactions involving sterically less demanding substrates.

Experimental Section

General Methods and Instrumentation. All reactions were carried out under argon with rigorous exclusion of air using Schlenk-line or drybox techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials Ind^OTiCl_3 (**1**),[4a] Ind^NTiCl_3 (**2**),[4b] $IndTiMe_3$ (**9**),[16f] and $H_4IndTiCl_3$[16c] were prepared by the published methods. Phenylacetylene, 1-phenylpropyne, and 1-octyne were distilled, and amines were distilled from CaH_2 and stored in the drybox. All other reagents were purchased from commercial sources and were used without further purification. The course of the catalytic reactions was followed using a Hewlett-Packard 5890 series gas chromatograph with a flame ionization detector, using a 100% cross-linked methyl silicone gum column (30 m × 0.25 mm, with 0.25 μm film thickness) and *n*-octane as the internal standard. The oven conditions used are as follows: 35 °C (hold 6 min) to 280 °C at 25 °C/min

(hold 5 min). GC-MS experiments were run on an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system. Samples were injected into a 30 m × 250 μm HP-5MS 5% phenyl methyl siloxane column with a film thickness of 0.25 μm (Agilent). The GC oven temperature was programmed as follows: 35 °C for 6 min to 280 °C at 25 °C/min for 5 min. The carrier gas was helium at a flow of 1 mL/min.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian UNITY 300, a Varian Gemini 2000, a Bruker ARX 300, or a Bruker Avance 300 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks. Coupling constants, *J*, are given in hertz. C and H analyses were carried out on a Perkin-Elmer 2400 CHNS/O analyzer.

Preparation of Ind^{O}TiMeCl$_2$ (3). To a purple suspension of **1** (625 mg, 1.91 mmol) in 18 mL of diethyl ether at −40 °C was added dropwise 1.0 equiv of MeMgCl (0.63 mL, 1.91 mmol, 3 M in tetrahydrofuran). After addition, the mixture was warmed slowly to room temperature and stirred for 4 h. The volatiles were removed under reduced pressure, and the residue was extracted with pentane (5 × 40 mL). The resultant red solution was concentrated to ca. 3 mL, and a red solid appeared, which was separated by decantation, washed with pentane (2 × 3 mL), and dried in vacuo. Yield: 237 mg (41%). Anal. Calcd for $C_{13}H_{16}Cl_2OTi$: C, 50.83; H, 5.26. Found: C, 51.19; H, 5.36. ^{1}H NMR (300 MHz, C_7D_8, 363 K): δ 7.31−7.21, 7.01−6.86 (both m, each 2H, C_6H_4), 6.46, 6.27 (both d, ^3J = 2.4, each 1H, C_5H_2), 3.37 (m, 2H, CH_2O), 3.09 (s, 3H, OMe), 2.91 (m, 2H, $C_9H_6CH_2$), 1.42 (s, 3H, TiMe). ^{1}H NMR (300 MHz, C_7D_8, 183 K): δ 7.30−6.97 (m, 5H, 4H C_6H_4 + 1H C_5H_2), 6.22 (br, 1H, C_5H_2), 3.34 (s, 3H, OMe), 3.25, 2.64 (both m, each 1H, CH_2O), 2.14 (m, 4H, 3H TiMe + 1H $C_9H_6CH_2$), 1.64 (m, 1H, $C_9H_6CH_2$). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K, plus APT and HETCOR): δ 129.4, 129.3 (C_{ipso} C_9H_6), 128.3, 127.8 (C_6H_4), 127.6 (C_{ipso} C_9H_6), 127.0, 125.1 (C_6H_4), 121.0, 111.5 (C_5H_2), 81.9 (TiMe), 74.5 (CH_2O), 59.8 (OMe), 28.4 ($C_9H_6CH_2$).

Preparation of Ind^{N}TiMeCl$_2$ (4). The same procedure described for **3** was followed, except that **2** (400 mg, 1.18 mmol) and 1.0 equiv of MeMgCl (0.40 mL, 1.18 mmol, 3 M in tetrahydrofuran) were used. The product was obtained as an orange solid. Yield: 143 mg (38%). Anal. Calcd for $C_{14}H_{19}Cl_2NTi$: C, 52.51; H, 5.99; N, 4.37. Found: C, 52.37; H, 5.86; N, 4.30. ^{1}H NMR (300 MHz, C_7D_8, 293 K): δ 7.49 (m, 2H, C_6H_4), 7.00−6.89 (m, 3H, 2H C_6H_4 + 1H C_5H_2), 6.15 (d, ^3J = 3.6, 1H, C_5H_2), 2.34−2.29 (m, 4H, CH_2CH_2), 2.13 (s, 6H, NMe_2), 1.80 (s, 3H, TiMe). ^{1}H NMR (300 MHz, C_7D_8, 223 K): δ 7.52 (m, 2H, C_6H_4), 7.05−6.82 (m, 3H, 2H C_6H_4 + 1H C_5H_2), 6.20 (d, ^3J = 3.6, 1H, C_5H_2), 2.16 (m, 2H, $C_9H_6CH_2$), 2.10 (s, 6H, NMe_2), 2.05 (m, 2H, NCH_2), 2.00 (s, 3H, TiMe). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K, plus APT and HETCOR): δ 130.6 (C_{ipso} C_9H_6), 127.5 (C_6H_4), 127.0 (C_{ipso} C_9H_6), 126.9, 126.3 (C_6H_4), 126.2 (C_{ipso} C_9H_6), 123.4 (C_6H_4), 120.9, 111.7 (C_5H_2), 76.1 (TiMe), 63.6 (CH_2N), 49.2 (NMe_2), 24.3 ($C_9H_6CH_2$).

Preparation of Ind^{O}TiMe$_2$Cl (5). The same procedure described for **3** was followed, except that **1** (870 mg, 2.65 mmol) and 2.0 equiv of MeMgCl (2.65 mL, 7.97 mmol, 3 M in tetrahydrofuran) were used. The product was obtained as a dark orange solid. Yield: 385 mg (51%). Anal. Calcd for $C_{14}H_{19}ClOTi$: C, 58.64; H, 6.70. Found: C, 58.75; H, 6.30. ^{1}H NMR (300 MHz, C_7D_8, 323 K): δ 7.18−6.84 (m, 4H, C_6H_4), 6.35, 5.95 (both d, ^3J = 3.3, each 1H, C_5H_2), 3.31 (m, 2H, CH_2O), 3.10 (s, 3H, OMe), 2.71 (m, 2H, $C_9H_6CH_2$), 1.15, 0.87 (both s, each 3H, $TiMe_2$). ^{1}H NMR (300 MHz, C_7D_8, 183 K): δ 7.51 (m, 1H, C_6H_4), 6.98−6.80 (m, 3H, C_6H_4), 6.67, 5.79 (both br, each 1H, C_5H_2), 3.21 (s, 3H, OMe), 3.06, 2.59 (both m, each 1H, CH_2O), 2.09 (m, 1H, $C_9H_6CH_2$), 1.78 (s, 3H, $TiMe_2$), 1.67 (m, 1H, $C_9H_6CH_2$), 0.30 (s, 3H, $TiMe_2$). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K, plus APT and HETCOR): δ 127.9 (C_{ipso} C_9H_6), 126.4, 126.3, 125.7 (C_6H_4), 125.4 (C_{ipso} C_9H_6), 124.5 (C_6H_4), 122.9 (C_{ipso} C_9H_6), 118.7, 106.2 (C_5H_2), 74.2 (CH_2O), 73.6, 71.5 ($TiMe_2$), 59.3 (OMe), 28.1 ($C_9H_6CH_2$).

Preparation of Ind^{N}TiMe$_2$Cl (6). The same procedure described for **3** was followed, except that **2** (482 mg, 1.41 mmol) and 2.0 equiv of MeMgCl (0.94 mL, 2.83 mmol, 3 M in tetrahydrofuran) were used. The product was obtained as a red solid. Yield: 136 mg (32%). Anal. Calcd for $C_{15}H_{22}NClTi$: C, 60.10; H, 7.41; N, 4.67. Found: C, 60.18; H, 7.35; N, 4.50. ^{1}H NMR (300 MHz, C_7D_8, 293 K): δ 7.43 (m, 1H, C_6H_4), 7.09−6.85 (m, 3H, C_6H_4), 6.54, 5.82 (both d, ^3J = 3.0, each 1H, C_5H_2), 2.49−2.31 (m, 4H, CH_2-CH_2), 2.05 (s, 6H, NMe_2), 1.15, 0.69 (both s, each 3H, $TiMe_2$). ^{1}H NMR (300 MHz, C_7D_8, 223 K): δ 7.53 (m, 1H, C_6H_4), 6.94−6.76 (m, 3H, C_6H_4), 6.65, 5.67 (both br, each 1H, C_5H_2), 2.10 (m, 2H, $C_9H_6CH_2$), 1.92 (s, 6H, NMe_2), 1.71 (m, 2H, NCH_2), 1.22, 0.66 (both s, each 3H, $TiMe_2$). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K, plus APT): δ 127.2 (C_{ipso} C_9H_6), 126.6, 126.3 (C_6H_4), 126.1 (C_{ipso} C_9H_6), 125.6 (C_6H_4), 124.8 (C_{ipso} C_9H_6), 123.6 (C_6H_4), 118.0, 108.0 (C_5H_2), 71.9, 71.4 ($TiMe_2$), 63.5 (CH_2N), 48.6 (NMe_2), 24.7 ($C_9H_6CH_2$).

Preparation of Ind^{O}TiMe$_3$ (7). The same procedure described for **3** was followed, except that **1** (1.0 g, 3.07 mmol) and 3.0 equiv of MeMgCl (3.07 mL, 9.20 mmol, 3 M in tetrahydrofuran) were used. The product was obtained as an orange oil. Yield: 517 mg (63%). Anal. Calcd for $C_{15}H_{22}OTi$: C, 67.66; H, 8.34. Found: C, 68.11; H, 8.74. ^{1}H NMR (300 MHz, C_7D_8, 353 K): δ 7.23−7.16, 6.89−6.79 (both m, each 2H, C_6H_4), 6.25, 6.12 (both d, ^3J = 3.4, each 1H, C_5H_2), 3.51−3.40 (m, 2H, CH_2O), 3.10 (s, 3H, OMe), 2.90, 2.78 (both m, each 1H, $C_9H_6CH_2$), 0.94 (s, 9H, $TiMe_3$). ^{1}H NMR (300 MHz, C_7D_8, 203 K): δ 7.41 (m, 1H, C_6H_4), 7.07−6.90 (m, 3H, C_6H_4), 6.53, 5.91 (both br, each 1H, C_5H_2), 3.10 (m, 1H, CH_2O), 3.06 (s, 3H, OMe), 2.95 (m, 1H, CH_2O), 2.48, 2.35 (both m, each 1H, $C_9H_6CH_2$), 0.97 (s, 9H, $TiMe_3$). ^{13}C{^{1}H} NMR (75.42 MHz, C_7D_8, 293 K, plus APT and HETCOR): δ 127.3 (C_{ipso} C_9H_6), 125.6 (C_6H_4), 125.1 (C_{ipso} C_9H_6), 124.7, 124.2, 123.9 (C_6H_4), 118.6 (C_5H_2), 117.6 (C_{ipso} C_9H_6), 101.8 (C_5H_2), 73.2 (CH_2O), 66.4 ($TiMe_3$), 58.3 (OMe), 28.8 ($C_9H_6CH_2$).

Preparation of Ind^{N}TiMe$_3$ (8). The same procedure described for **3** was followed, except that **2** (809 mg, 2.37 mmol) and 3.0 equiv of MeMgCl (2.37 mL, 7.12 mmol, 3 M in tetrahydrofuran) were used. The product was obtained as an orange solid. Yield: 360 mg (55%). Anal. Calcd for $C_{16}H_{25}NTi$: C, 68.80; H, 9.04; N, 5.02. Found: C, 68.63; H, 8.98; N, 5.13. ^{1}H NMR (300 MHz, C_7D_8, 323 K): δ 7.20 (m, 2H, C_6H_4), 6.90−6.82 (m, 2H, C_6H_4), 6.28, 6.06 (both d, ^3J = 3.3, each 1H, C_5H_2), 2.79−2.68 (m, 2H, $C_9H_6CH_2$), 2.43−2.36 (m, 2H, CH_2N), 2.10 (s, 6H, NMe_2), 0.95 (s, 9H, $TiMe_3$). ^{1}H NMR (300 MHz, C_7D_8, 223 K): δ 7.65−7.55 (m, 2H, C_6H_4), 6.90−6.76 (m, 3H, 2H C_6H_4 + 1H C_5H_2), 5.76 (d, ^3J = 3.3, 1H, C_5H_2), 2.25 (m, 2H, $C_9H_6CH_2$), 1.84 (s, 6H, NMe_2), 1.76 (m, 2H, CH_2N), 0.80 (s, 9H, $TiMe_3$). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 127.3 (C_{ipso} C_9H_6), 125.8 (C_6H_4), 124.9 (C_{ipso} C_9H_6), 124.7, 124.1, 123.6 (C_6H_4), 119.5 (C_{ipso} C_9H_6), 118.0, 102.1 (C_5H_2), 66.3 ($TiMe_3$), 61.1 (CH_2N), 45.6 (NMe_2), 26.8 ($C_9H_6CH_2$).

Preparation of H$_4$IndTiMe$_3$ (10). The same procedure described for **3** was followed, except that $H_4IndTiCl_3$ (642 mg, 2.35 mmol) and 3.0 equiv of MeMgCl (2.35 mL, 7.04 mmol, 3 M in tetrahydrofuran) were used. The product was obtained as a green oil. Yield: 492 mg (98%). Anal. Calcd for $C_{12}H_{20}Ti$: C, 67.95; H, 9.52; N. Found: C, 68.13; H, 9.60. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 5.85 (t, ^3J = 3.3, 1 H, C_5H_3), 5.67 (d, ^3J = 3.3, 2H, C_5H_3), 2.42−2.15 (m, 4H, C_6H_8), 1.40−1.33 (m, 4H, C_6H_8), 1.21 (s, 9H, $TiMe_3$). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 126.6 (C_{ipso} C_9H_6), 112.3, 111.3 (C_5H_3), 62.6 ($TiMe_3$), 24.6, 22.9 (C_6H_8).

Determination of Constants and Thermodynamic Parameters for the Equilibria Shown in Eq 1. Variable-temperature ^{1}H NMR spectra of **3** (183−363 K), **4** (223−293 K), **5** (183−323 K), **6** (223−293 K), **7** (203−353 K), and **8** (223−323 K) were recorded in toluene-d_8. Equilibrium constants, *K*, were derived from the

Table 5. Crystal Data and Data Collection and Refinement Details for 3, 6, and 8

	3	6	8
Crystal Data			
formula	$C_{13}H_{16}ClOTi$	$C_{15}H_{22}ClNTi$	$C_{16}H_{25}NTi$
mol wt	307.06	299.69	279.27
color, habit	red, irregular block	red, needle	orange, irregular block
size, mm	0.12, 0.08, 0.06	0.46, 0.14, 0.14	0.24, 0.20, 0.10
symmetry, space group	orthorhombic, $P2_12_12_1$	orthorhombic, $P2_12_12_1$	orthorhombic, $P2_12_12_1$
a, Å	8.7267(10)	8.3491(14)	8.5922(10)
b, Å	9.9180(11)	8.6636(14)	11.9683(14)
c, Å	15.7027(18)	20.133(3)	14.5344(16)
V, Å^3	1359.1(3)	1456.3(4)	1494.6(3)
Z	4	4	4
D_{calcd}, g cm^{-3}	1.501	1.367	1.241
Data Collection and Refinement			
diffractometer		Bruker Smart APEX	
λ(Mo Kα), Å		0.710 73	
monochromator		graphite oriented	
scan type		ω scans	
μ, mm^{-1}	1.003	0.754	0.556
2θ range, deg	3, 57	3, 57	3, 57
temp, K	100.0(2)	100.0(2)	100.0(2)
no. of data collected	17 109	17 382	18 917
no. of unique data	3383 (R_{int} = 0.0695)	3620 (R_{int} = 0.0495)	3738 (R_{int} = 0.0474)
no. of params/restraints	157/0	230/0	171/10
Flack param	0.45(5)	0.00(3)	0.01(3)
R1[a] ($F^2 > 2\sigma(F^2)$)	0.0614	0.0343	0.0371
wR2[b] (all data)	0.1139	0.0584	0.0748
S[c] (all data)	1.007	0.904	0.888

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] GOF = $S = \{\sum[(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

temperature-dependent $\delta(^1H)$ signals of the methylene groups IndCH_2 and OCH_2 (**3**, **5**, and **7**) or IndCH_2 and NCH_2 (**4**, **6**, and **8**) using eq 2. Thermodynamic parameters were calculated from the equilibrium constants according to eq 3.

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (3)$$

Reasonable values for δ_{min} and δ_{max} were obtained by computer-assisted iteration: δ_{min} and δ_{max} were optimized in such a way that plotting of ln K versus $1/T$ gives the straightest line possible. Typical errors were obtained from the fitting program used (Microsoft Excel).

General Procedure for Hydroamination. A Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was charged with the alkyne (2.40 mmol), the amine (2.64 mmol), the catalyst (0.12 mmol, 5.0% mol), toluene (2 mL), and *n*-octane (2.40 mmol). The Schlenk tube was removed from the glovebox and heated at 100 °C. The reaction was monitored by periodic GC analysis of samples removed with a syringe. Either on completion of the reaction or after 24 h, the volatiles were removed under reduced pressure and the residue was analyzed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and by GC-MS. Imines and enamines were identified by comparison of their NMR spectra with their literature reported data.[6,8]

General Procedure for Hydrogenation. (a) Method for Enamines and Imines Resulting from Hydroamination of Aromatic Alkynes. In a Fischer−Porter bottle, PtO_2 (15 mg, 0.07 mmol) was stirred in tetrahydrofuran (3.0 mL) at 25 °C under 1 atm of H_2 for 10 min. A solution of the crude hydroamination product in tetrahydrofuran (3.0 mL) was then added. The resulting mixture was stirred under 3 atm of H_2 at 25 °C for 48 h. Filtration, concentration, and purification by flash chromatography on silica gel afforded the amines, whose purity was checked by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and by GC-MS.

(b) Method for Enamines and Imines Resulting from Hydroamination of Aliphatic Alkynes. The crude hydroamination product was dissolved in THF (2.0 mL). $NaCNBH_3$ (302 mg, 4.8 mmol) and *p*-toluenesulfonic acid hydrate (46 mg, 0.24 mmol) were added, and the mixture was stirred at room temperature. After 4 h, diethyl ether (4.0 mL) and 2 N HCl (4.0 mL) were added. The mixture was stirred for 1 h at room temperature. The organic layer was separated, and saturated $NaHCO_3$ solution was added to the water layer until pH 7 was reached. The water layer was extracted with diethyl ether (2 × 4 mL). The combined organic layers were dried with $MgSO_4$; filtration, concentration, and purification by flash chromatography on silica gel afforded the amines, whose purity was checked by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and by GC-MS. Amines were identified by comparison of their NMR spectra with their data reported in the literature.[6,8]

Structural Analysis of Complexes 3, 6, and 8. X-ray data were collected for all complexes at low temperature on a Bruker Smart APEX CCD diffractometer equipped with a normal-focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.710 73 Å) operating at 50 kV and 40 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 or 30 s covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[28] The structures for all compounds were solved by the Patterson method. Refinement, by full-matrix least squares on F^2 with SHELXL97,[29] was similar for all complexes, including isotropic and subsequent anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were observed or calculated and refined freely or using a restricted riding model, respectively.

For **8** the (dimethylamino)ethyl group is disordered over two positions and refined with two moieties with occupancies 0.75/0.25, respectively.

Crystal data and data collection and refinement details for **3**, **6**, and **8** are given in Table 5.

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Supporting Information Available: CIF files giving data for the crystal structure determinations, including bond lengths and angles of compounds **3**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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