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Imido−Titanium/Molybdenum Heterobimetallic Systems. Switching from η^6-Arene to Fischer-Type Aminocarbene Complexes by Tuning Reactivity Conditions

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Two types of bimetallic titanium/molybdenum systems are described: the first possesses unprecedented η^6-arene-imido groups, while the second has Fischer-type aminocarbene ligands bridging the two metals. The (η^6-arene)−Mo imido−Ti complex $Ti[{=}N(\eta^6\text{-}Ar)Mo(CO)_3]Cl_2(NHMe_2)_2$ (**2**; Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$) has been prepared through the reaction of (η^6-ArNH$_2$)Mo(CO)$_3$ (**3**) and TiCl$_2$(NMe$_2$)$_2$. The alternative route from **2** and Ti(NMe$_2$)$_4$/Me$_3$SiCl also afforded **1**, but it was contaminated with a small amount of Ti(=NAr)Cl$_2$(NHMe$_2$)$_2$ (**1**). The reaction between the dimeric complexes {Ti(μ-NAr)(NMe$_2$)$_2$}$_2$ and Mo(CO)$_6$ gave complex mixtures of products, among which the Fischer-type aminocarbene complex [(CO)$_5$Mo{=C(NMeCH$_2$NMe$_2$)O}Ti(=N-2,6-Pr$^i_2$-C$_6$H$_3$)(NMe$_2$)(NHMe$_2$)] (**4**) could be characterized. The formation of **4** resulted from the nucleophilic attack of the amido −NMe$_2$ to the carbonyl that afforded the titanoxy aminocarbene linker between the Mo and the Ti centers, followed by a subsequent C−H activation of a methyl group of the aminocarbene and C,N coupling with an amido ligand on titanium. Treatment of Ti(NMe$_2$)$_4$ with 1 equiv of Mo(CO)$_6$ produced the titanoxy aminocarbene [(CO)$_5$Mo{=C(NMe$_2$)O}Ti(NMe$_2$)$_3$] (**5**), while in the presence of 1 equiv of ArNH$_2$ the imido complex [(CO)$_5$Mo{=C(NMe$_2$)O}Ti(=N-2,6-Pr$^i_2$-C$_6$H$_3$)(NMe$_2$)(NHMe$_2$)$_2$] (**6**) is formed. The molecular structures of **1**−**6** have been determined by X-ray diffraction.

Introduction

The metal-catalyzed carbonylation of amines has been intensively studied, as it gives access to important molecules containing carbonyl−nitrogen bonds, such as ureas, urethanes, oxamides, formamides, and oxazolidinones. It also represents a more environmentally friendly alternative to the traditional and stoichiometric synthesis of ureas from amines and toxic and/or corrosive phosgene or isocyanate derivatives. A great number of mid- and late-transition-metal complexes have been reported to catalyze the mono- or dicarbonylation of amines.[1] With the exception of tungsten,[2] studies of early-transition-metal-catalyzed carbonylation of amines are unknown. One reason for that may arise from the difficulty of insertion of CO into an early-metal−amide bond,[3] whereas such insertion is a known reaction for late-transition-metal complexes[4] and, to a lesser extent, for some actinide compounds.[5,6] It is worth noting that alkali-metal salts of strongly basic nitrogen are known to attack CO.[7,8]

As there is still a need for new catalysts, in particular those that could operate under milder conditions, we have embarked on the study of bimetallic systems combining an early transition metal (that could form M−NR bonds) with a carbonyl complex (that could effect the carbonylation). Herein we report our first results concerning the synthesis

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(1) For a recent review on transition-metal-catalyzed oxidative carbonylation of amines, see: Diaz, D. J.; Darko, A. K.; McElwee-White, L. *Eur. J. Org. Chem.* **2007**, 4453–4465and references cited therein.

(2) For tungsten-catalyzed carbonylations, see: (a) Jetz, W.; Angelici, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 3799–3802. (b) Doxsee, K. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7696–7698. (c) McCusker, J. D.; Abboud, K. A.; McElwee-White, L. *Organometallics* **1997**, *16*, 3863–3866. (d) McCusker, J. D.; Logan, J.; McElwee-White, L. *Organometallics* **1998**, *17*, 4037–4041. (e) McCusker, J. D.; Main, A. D.; Johnson, K. S.; Grasso, C. A.; McElwee-White, L. *J. Org. Chem.* **2000**, *65*, 5216–5222. (f) McCusker, J. D.; Grasso, C. A.; Main, A. D.; McElwee-White, L. *Org. Lett.* **1999**, *1*, 961–964.

(3) For a rare CO insertion into a metal−amide bond in molybdenum chemistry, see: Chisholm, M. H.; Hammond, C. E.; Huffman, J. C. *Organometallics* **1987**, *6*, 210–211.

(4) For examples of CO insertion into late-metal−amide bonds, see: (a) Holland, P. L.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 1092–1104. (b) Belli Dell'Amico, D.; Calderazzo, F.; Pelizzi, G. *Inorg. Chem.* **1979**, *18*, 1165–1168. (c) Bryndza, H. E.; Fultz, W. C.; Tam, W. *Organometallics* **1985**, *4*, 939–940. (d) Beers, O. C. P.; Delis, J. G. P.; Mul, W. P.; Vrieze, K.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **2002**, *32*, 3640–3647. (e) Cowan, R. L.; Trogler, W. C. *Organometallics* **2002**, *6*, 2451–2453.

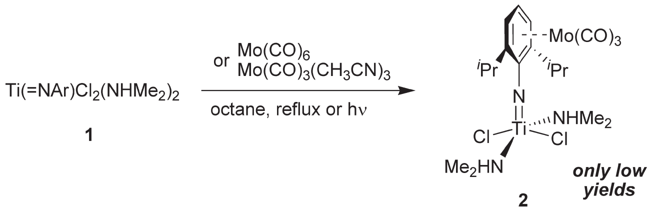
(5) Boisson, C.; Berthet, J. C.; Lance, M.; Nierlich, M.; Ephritikhine, M. *J. Organomet. Chem.* **1997**, *548*, 9–16.

(6) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J . Am. Chem. Soc.* **1981**, *103*, 2206–2220.

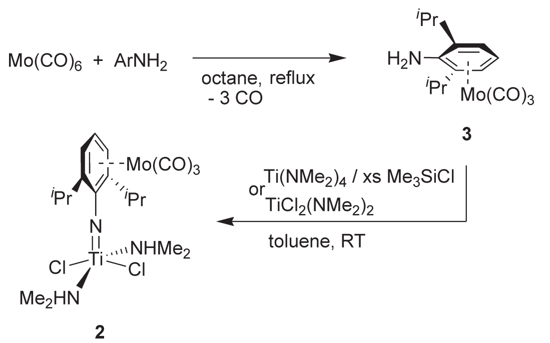
(7) Rautenstrauch, V.; Joyeux, M. *Angew. Chem., Int. Ed.* **1979**, *18*, 85–86.

(8) Rautenstrauch, V.; Joyeux, M. *Angew. Chem., Int. Ed.* **1979**, *18*, 83–85.

Scheme 1. Attempted Synthesis of 2 Starting from 1 and $Mo(CO)_6$ or $Mo(CO)_3(CH_3CN)_3$



Scheme 2. Two-Step Synthesis of 2 Starting via Formation of 3



and structure of Ti/Mo heterobimetallic systems that led us to characterize the first "Mo/η^6-*arene-imido*/Ti" complex as well as "Mo/*aminocarbene*/Ti" complexes.

Results and Discussion

The synthesis and proposed structures of the new complexes are summarized in Schemes 1−6. Structures of six complexes are set out in Figures 1−6 or are given in the Supporting Information. Selected metric data are collected in Tables 1 and 2.

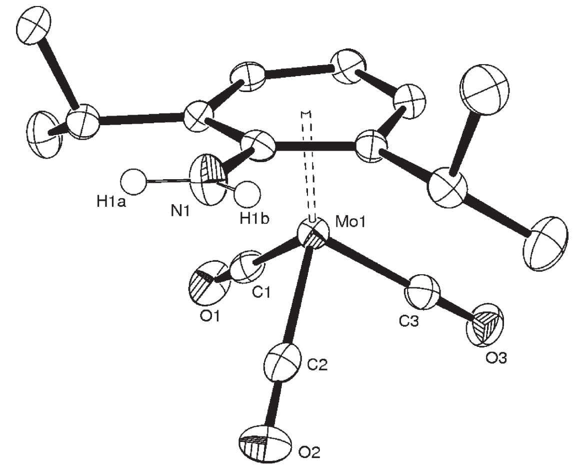


Figure 1. Molecular structure of **3**, showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity (except for NH_2).

Table 1. Comparison of Average Interatomic Distances (Å) and Angles (deg) in Complexes 1−3

	1	2	3
$Ti-N_{imido}$	1.7108(8)	1.7091(16)	
$C_{ipso}-N$	1.3838(11)	1.380(2)	
Ti−Cl	2.3169(3) (Cl1)	2.3014(6) (Cl1)	
	2.3532(3) (Cl2)	2.3359(7) (Cl2)	
$Ti-N_{NHMe_2}$	2.2053(9) (N2)	2.1967(16) (N2)	
	2.2235(9) (N3)	2.2130(17) (N3)	
$Mo-C_{ipso}$		2.4528(18)	2.518(3)
$Mo-C_{ortho}$		2.4142(19) (C4)	2.429(3) (C4)
		2.4310(19) (C8)	2.415(3) (C6)
$Mo-C_{meta}$		2.375(2) (C5)	2.375(3) (C7)
		2.352(2) (C7)	2.354(3) (C9)
$Mo-C_{para}$		2.349(2)	2.373(3)
$Mo-C_{centroid}$		1.950	1.931
Mo−CO		1.950(2) (C1)	1.935(3) (C1)
		1.952(3) (C2)	1.944(3) (C2)
		1.953(2) (C3)	1.946(4) (C3)
C−O		1.159(3) (C1)	1.169(4) (C1)
		1.160(3) (C2)	1.164(4) (C2)
		1.153(3) (C3)	1.155(4) (C3)
$Ti-N_{imido}-C_{ipso}$	179.49(7)	175.39(14)	
Cl−Ti−Cl	132.745(13)	133.64(3)	
$N_{NHMe_2}-Ti-N_{NHMe_2}$	166.34(3)	165.26(6)	
Mo−C−O		177.8(3) (C1)	178.3(3) (C1)
		179.5(3) (C2)	177.7(3) (C2)
		178.2(2) (C3)	179.0(3) (C3)

1. Arene Complexes. The imide functionality is ubiquitous in transition-metal chemistry[9,10] and has found practical use in multiple areas of research.[11−15] In the past few years, our group has developed new synthetic routes to early-transition-metal titanium−, zirconium−, and vanadium−imido complexes, including those bearing functional, chiral, and electron-deficient imido groups.[16−23] As an extension of this imido chemistry, we first examined the possibility of forming bimetallic complexes via an η^6-arene-type coordination of a metal carbonyl complex to the aryl substituent of an arylimido−titanium synthon.

Our first attempts consisted of conducting the direct reaction of $[Ti({=}NAr)Cl_2(NHMe_2)_2]$ (**1**; Ar = 2,6-Pr^i_2-C_6H_3) with $Mo(CO)_6$ or $Mo(CO)_3(CH_3CN)_3$, as illustrated in Scheme 1. However, this route met with limited success: despite many attempts and varying the experimental conditions (solvent, time, temperature), the reactions were sluggish and the conversions into the desired η^6-arene-imido complex Ti $[({=}N\text{-}\eta^6\text{-}Ar)Mo(CO)_3]Cl_2(NHMe_2)_2$ (**2**) were always very low (< 10%). One reason for that might be the instability of **2** in solution under the thermal conditions (refluxing octane) required to generate the η^6-arene coordination to the Mo center (as shown later). Moreover, assisting CO ligand release via UV irradiation of an octane solution of **1** and $Mo(CO)_6$ did not lead to improved formation of the expected **2**. The extreme difficulty in synthesizing this com-

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(9) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175.

(10) Nugent, W. A.; Mayer, J. M. In *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1998.

(11) Wigley, D. E. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Interscience: New York, 1994; Vol. *42*, pp 239−482.

(12) Mountford, P. *Chem. Commun.* **1997**, 2127–2134.

(13) Duncan, A. P.; Bergman, R. G. *Chem. Rec.* **2002**, *2*, 431–445.

(14) Hazari, N.; Mountford, P. *Acc. Chem. Res.* **2005**, *38*, 839–849.

(15) Odom, A. L. *Dalton Trans.* **2005**, 225–233.

(16) Lorber, C.; Donnadieu, B.; Choukroun, R. *Dalton Trans.* **2000**, 4497–4498.

(17) Lorber, C.; Choukroun, R.; Donnadieu, B. *Inorg. Chem.* **2002**, *41*, 4217–4226.

(18) Lorber, C.; Choukroun, R.; Donnadieu, B. *Inorg. Chem.* **2003**, *42*, 673–675.

(19) Lorber, C.; Choukroun, R.; Vendier, L. *Organometallics* **2004**, *23*, 1845–1850.

(20) Lorber, C.; Choukroun, R.; Vendier, L. *Eur. J. Inorg. Chem.* **2006**, 4503–4518.

(21) Lorber, C.; Choukroun, R.; Vendier, L. *Inorg. Chem.* **2007**, *46*, 3192–3202.

(22) Lorber, C.; Vendier, L. *Organometallics* **2008**, *27*, 2774–2783.

(23) Lorber, C.; Vendier, L. *Dalton Trans.* **2009**, 6972–6984.

pound may also simply result from the presence of a strong π-accepting substituent (the imido function, vide infra) that is known to render the formation of $M(CO)_3$(arene) more difficult.[24,25]

We then decided to use a different synthetic route, depicted in Scheme 2. In a first step, we prepared the molybdenum η^6-aniline tricarbonyl complex [$Mo(CO)_3(\eta^6\text{-}ArNH_2)$] (**3**) by the thermal replacement of three carbonyls in $Mo(CO)_6$ by $ArNH_2$.[26] In order to achieve higher conversions and to limit the purification required, the reaction was conducted in refluxing octane under a stream of argon,[27] in the presence of a small amount of THF; it was also necessary to use a slight excess of the aniline (1.2−1.4 equiv/$Mo(CO)_6$). Furthermore, the reaction and workup procedure were conducted in the dark, as we noticed that the aniline complex was light sensitive while in solution. Under these conditions, **3** was obtained in 52% yield as pale yellow crystals.[28]

Spectroscopic studies (IR, NMR), elemental analyses, and X-ray studies confirmed these pale yellow crystals to be complex **3**. The IR spectrum displays the expected pairs of strong carbonyl stretching frequencies of the $Mo(CO)_3$ unit (1930 and 1835 cm^{-1}), while the ^1H and ^{13}C NMR data reveal that the diastereotopic methyl signals of the isopropyl substituents and the aromatic protons of the η^6-aniline are shielded upfield. In the ^{13}C NMR, the measure of the difference between the chemical shifts of the para and the meta aromatic carbon atoms is in agreement with the π-donor character of the aniline ligand.[24]

The pale yellow crystals of **3** were suitable for an X-ray structure determination. A thermal ellipsoid plot of the molecular structure of **3** is presented in Figure 1, and Table 1 gives a comparison of its structural parameters. The overall geometry around the molybdenum center is identical with that of previously structurally characterized group 6 $M(CO)_3(\eta^6$-arene) complexes. The complex exhibits the expected three-legged piano-stool structure having η^6-bonded arene rings. The relative (arene)$Mo(CO)_3$ conformation is syn-eclipsed (torsion angle N1C2Mo1C5 6.1(2)°), in agreement with theoretical calculations for donor-substituted arene.[29,30] The bond distances are in the expected range (Mo−CO(av) = 1.942(4) Å, $Mo-C_{centroid}$ = 1.950 Å, C−O(av) = 1.163(4) Å).

The $-NH_2$ in **3** is bent away from the $Mo(CO)_3$ fragment (see other views in the Supporting Information), which induces a distortion of the arene planarity with an angle between the least-squares plane defined by the ipso and ortho carbon atoms of the aniline, and the least-squares plane defined by the ortho, meta, and para carbon atoms of the aniline is 9.4° away from $Mo(CO)_3$. Such distortion *away* from the metal center is a common feature for arenes having strong π-donor substituents, whereas π-acceptors are found in the plane or present a small bend *toward* the metal center.[31−33]

In a second step, **3** was treated with an equimolar amount of $Ti(NMe_2)_4$ in the presence of an excess of Me_3SiCl (6 equiv) (see Scheme 2). We have previously established this one-pot synthesis as a very convenient and general way to prepare a number of $M({=}NR)Cl_2(NHMe_2)_2$ complexes with various terminal imido $[NR]^{2-}$ groups (M = Ti,[20] V[17]). Nevertheless, in the present study, when using the $Ti(NMe_2)_4$/Me_3SiCl route, the expected η^6-arene-imido complex **2** was repeatedly obtained contaminated with ca. 10% of unreacted molybdenum precursor and ca. 10% of $Ti({=}NAr)Cl_2(NHMe_2)_2$. Apparently in this reaction, Me_3SiCl has a detrimental effect on the η^6 coordination of the arene to the Mo center by inducing decoordination of the arene moiety from the Mo center. Indeed, using a larger amount of Me_3SiCl (8 equiv) induced a higher degree of decoordination (**2**:**1** ratio ~2).[34]

To prevent decoordination of the $Mo(CO)_3$ moiety induced by the presence of the chlorosilane during the formation of the arene-imido function, we turned instead to $TiCl_2(NMe_2)_2$ as a starting material. The transamination reaction of $TiCl_2(NMe_2)_2$ with complex **3** proceeded smoothly at room temperature and afforded compound **2** in almost quantitative yields (92%) as red-orange crystals (Scheme 2).

The IR spectrum of **2** exhibits two strong absorption bands in the carbonyl region at 1947 and 1841 cm^{-1} characteristic of coordinated CO in *fac*-$M(CO)_3L_3$ complexes, as well as a band at 3239 cm^{-1} for the $NHMe_2$ ligands (ν_{NH}). The increase of CO frequency in **2** vs **3** (with ν_{CO} 1930 and 1835 cm^{-1} in **3**) reflects the lower electron-donating capability of the arene-imido fragment. As already seen in precursor compound **3,** the coordination of the Mo center to the arene ring of the aryl-imido function is clearly visible in the ^1H and ^{13}C NMR data of **2**. This coordination renders the two methyl groups inequivalent ($-CHMe^aMe^b$), as they are in very different chemical environments. The aromatic protons are also shifted considerably upfield and consist of a doublet at 4.93 ppm and a triplet at 4.71 ppm (the two signals are found at 6.99 and 6.85 ppm in the parent $Ti(NAr)Cl_2(NHMe_2)_2$ compound).

X-ray-quality crystals were obtained for **2** and were studied by diffraction analysis. As it was interesting to compare directly the solid-state structure of **2** with that of its parent complex **1**, we have also determined the structure of **1** by X-ray crystallography. Thermal ellipsoid plots or **1** and **2** are presented in Figures 2 and 3 along with selected bond lengths and angles, and Table 1 gives a comparison of their structural parameters. The two studies showed **2** to have a structural arrangement around the titanium center analo-

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(24) Hunter, A. D.; Mozol, V.; Tsai, S. D. *Organometallics* **1992**, *11*, 2251–2262.

(25) Tamm, M.; Baker, R. J., Molybdenum compounds with CO or isocyanides. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H. M., Ed.; Elsevier: Oxford, U.K., 2007; Vol. *5*, pp 391−512.

(26) $Mo(CO)_3(CH_3CN)_3$ worked well too for this reaction but was somewhat more difficult to separate from complex **3** during the purification step.

(27) It is important to conduct the reaction under a stream of argon to remove the liberated carbon monoxide (in a closed vial the yields remained low).

(28) For a related $Cr(CO)_3(\eta^6$-aniline) complex, see: Mahaffy, C. A. L. *J. Organomet. Chem.* **1984**, *262*, 33–37.

(29) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546–7557.

(30) Chinn, J. W.; Hall, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 4930–4941.

(31) Hunter, A. D.; Shilliday, L.; Furey, W. S.; Zaworotko, M. J. *Organometallics* **1992**, *11*, 1550–1560.

(32) Djukic, J.-P.; Rose-Munch, F.; Rose, J.; Vaisserman, J. *Eur. J. Inorg. Chem.* **2000**, 1295–1306.

(33) Meyer, R.; Schindehutte, M.; van Rooyen, P. H.; Lotz, S. *Inorg. Chem.* **1994**, *33*, 3605–3608.

(34) In theory, only 2 equiv of Me_3SiCl is needed for this reaction. However, the synthesis of $M(NR)Cl_2(NHMe_2)_2$ complexes (M = Ti, V) requires the use of at least 3−4 equiv of Me_3SiCl in order to achieve complete transformation, and in practice a larger excess (8−10 equiv) is often used to speed up the reactions.[17,20] In the present study, we did not try to decrease the Me_3SiCl concentration below 6 equiv.

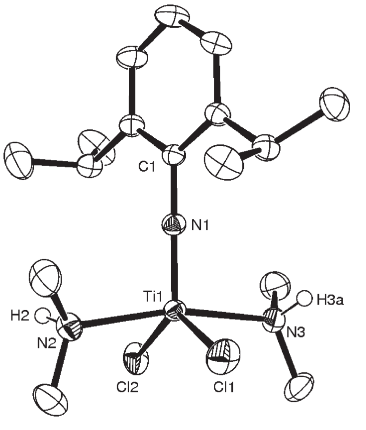

Figure 2. Molecular structure of **1**, showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity (except for N*H*Me_2).

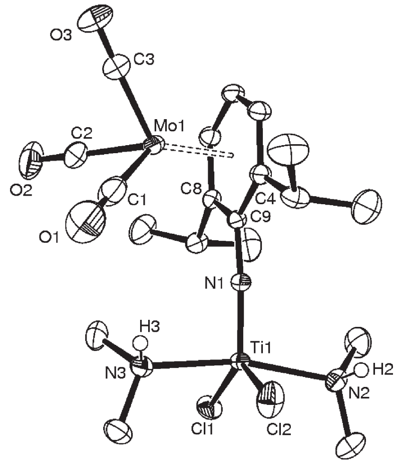

Figure 3. Molecular structure of **2**, showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity (except for N*H*Me_2).

gous to that of the parent *Mo-free* precursor **1**, i.e., between a square pyramid and a trigonal bipyramid (τ = 0.56 (**1**), 0.53 (**2**)),[35] containing an almost linear imido ligand in the apical position, two trans chloride ligands, and two $NHMe_2$ ligands. The $Ti-N_{imido}$ bond distance in the bimetallic complex **2** ($Ti-N_{imido}$ = 1.7091(16) Å) is identical within error to that in the Mo-free complex **1** ($Ti-N_{imido}$ = 1.7108(8) Å). However, all other bonds around the Ti center (Ti−Cl, $Ti-NHMe_2$) are shorter in **2** (vs **1**), which reflects the decreased donor capability of the aryl-imido function as a consequence of the η^6 coordination of the Mo center. In both imido compounds **1** and **2**, the supramolecular structure is dominated by similar $Me_2N-H\cdots Cl$ hydrogen bonding that associate pairs of molecules via intermolecular hydrogen bonds involving atoms N2, H2, and Cl2 ($N-H\cdots Cl$ bond lengths of 2.525 Å in **1** and 2.485 Å in **2**; associated $N-H\cdots Cl$ angles of 151.8° in **1** and 152.5° in **2**), features that they share with other related Ti and V compounds.[17,20,36] Furthermore, this may explain the unexpected longer bonds observed for Ti−Cl2 (vs Ti−Cl1) and shorter Ti−N2 (vs Ti−N3). The $Mo(CO)_3$ group in **2** lies directly below the center of the arene ring plane and shows the well-known piano-stool conformation found in half-sandwich tricarbonyl complexes, with comparable bond distances and angles (Mo−CO(av) = 1.952(3) Å, $Mo-C_{centroid}$ = 1.931 Å, C−O(av) = 1.157(4) Å, $C_{CO}-Mo-C_{CO}$(av) = 178.3(3)°). In contrast to the case for **3** (that has a syn-eclipsed conformation for the relative (arene)$Mo(CO)_3$ fragment due to the donor $-NH_2$ on the arene), the relative (arene-imido)$Mo(CO)_3$ conformation in **2** is now staggered with the torsion angle N1C9Mo1C1 = 22.1(2)°, again reflecting the π-accepting properties of the imido linkage (although we cannot exclude that it could be due to crystal packing). Consistently, the imido group in **2** is almost in the plane of the arene ring with an angle between the least-squares plane defined by the ipso and ortho carbon atoms of the aniline and the least-squares plane defined by ortho, meta, and para carbon atoms of the aniline only 1.5° away from $Mo(CO)_3$ (see the Supporting Information for other Ortep views of **2**).

In addition, compound **2** was shown not to be stable in solution for extended periods of time. For example, in benzene-d_6 solutions at 80 °C, we noticed after 4 h only 20% of the initial product (**2**) remained, and considerable decoordination of the $Mo(CO)_3$ unit with formation of 80% of **1**. In contrast, in octane solutions, we observed only 15% of the decoordination after 12 h at 80 °C.[37] Thermal displacement of the arene ligand in (η^6-arene)metal species has been reported.[38−40] This observation will be crucial for future comparative activity studies of **2** vs **1** in selected transformations.

2. Fischer-Type Aminocarbene Complexes. In the course of our investigations on the preparation of the η^6-arene-imido complex **2** described above, and under certain experimental conditions that quite obviously did not favor the formation of the η^6-arene complex (vide infra), we noticed the formation of complex mixtures of products. Intrigued by this observation, we decided to study in more detail the reactions between the different components but now with the aim of avoiding the formation of the η^6-arene complex (room-temperature reactions, closed vials to retain CO, no exclusion of light).

As a first example, the reaction between the imido-bridged dimer complex $\{Ti(\mu-NAr)(NMe_2)_2\}_2$ and $Mo(CO)_6$ or $Mo(CO)_3(CH_3CN)_3$ afforded a complex mixture containing several compounds (Scheme 3). Importantly, the reaction proved to be time- and solvent-dependent (mixtures of different products and compositions were obtained in toluene and octane), and we also have indications that some of the species involved may not be stable for long periods in solution (see below). Therefore, this explains our extreme difficulty in reproducing this synthesis and isolating pure compounds.

However, from these mixtures, when conducting the above reaction in octane, we have been very fortunate to

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(35) τ is the angular parameter commonly used to describe the geometry around the metal center in pentacoordinate complexes and is defined as $\tau = (\alpha - \beta)/60$ (α and β are the two largest L−M−L bond angles, with $\alpha \geq \beta$): Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J. V. *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.

(36) Adams, N.; Bigmore, H. R.; Blundell, T. L.; Boyd, C. L.; Dubberley, S. R.; Sealey, A. J.; Cowley, A. R.; Skinner, M. E. G.; Mountford, P. *Inorg. Chem.* **2005**, *44*, 2882–2894.

(37) The fate of the decoordinated $Mo(CO)_3$ fragment from **2** was not determined, but we can theorize the concomitant formation of $Mo(CO)_6$ or $Mo(CO)_3(C_6D_6)$.

(38) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1987; Vol. *3*, Chapter 26.2, pp 953−1076.

(39) Kündig, E. P.; Fabritius, C.-H.; Grossheimann, G.; Romanens, P. *Organometallics* **2004**, *23*, 3741–3744.

(40) Choukroun, R.; Lorber, C.; Vendier, L. *Organometallics* **2007**, *26*, 3604–3606.

Table 2. Comparison of Average Interatomic Distances (Å) and Angles (deg) in Complexes **4**−**6**

	4	**5**	**6**
$Ti{-}N_{imido}$	1.7343(14)		1.7363(16)
$C_{ipso}{-}N_{imido}$	1.388(2)		1.385(2)
$Ti{-}N_{NMe_2}$	1.8965(15)	1.8622(15) (N2), 1.8757(15) (N3), 1.8792(15) (N4)	1.9050(17)
$Ti{-}N_{NHMe_2}$	2.2302(15)		2.2438(16) (N4), 2.2406(16) (N5)
$Ti{-}N_{NMe_2CH_2}$	2.2844(15)		
Ti−O	2.0020(12)	1.8975(12)	2.0045(13)
$C{-}O_{Ti}$	1.295(2)	1.3125(19)	1.288(2)
$Mo{-}C_{carbene}$	2.2616(18)	2.2655(16)	2.293(2)
Mo−CO	2.047(2) (C1), 2.046(2) (C2), 2.031(2) (C3), 2.040(2) (C4), 2.001(2) (C5)	2.0477(19) (C4), 1.9947(19) (C5), 2.0270(19) (C6), 2.051(2) (C7), 2.0313(2) (C8)	2.040(3) (C4), 2.035(3) (C5), 2.018(3) (C6), 2.016(2) (C7), 1.984(3) (C26)
$C{-}O_{carbonyl}$	1.131(2) (C1), 1.135(2) (C2), 1.143(2) (C3), 1.140(3) (C4), 1.149(2) (C5)	1.134(2) (C4), 1.145(2) (C5), 1.138(2) (C6), 1.131(3) (C7), 1.139(2) (C8)	1.138(3) (C4), 1.144(3) (C5), 1.135(3) (C6), 1.147(3) (C7), 1.151(3) (C26)
$C{-}NMe_2/NMe$	1.345(2)	1.329(2)	1.344(3)
$Ti{-}N_{imido}{-}C_{ipso}$	169.89(13)		175.53(14)
$Mo{-}C{-}O_{carbonyl}$	177.03(18), 177.40(17), 174.56(19), 179.04(19), 178.64(17)	172.32(15), 178.10(18), 174.81(17), 178.49(19), 178.74(16)	177.12(19), 174.9(2), 175.7(3), 175.6(2), 176.9(2)
$Mo{-}C_{carbene}{-}O$	117.27(12)	117.79(11)	119.38(14)
$Mo{-}C_{carbene}{-}N$	129.20(12)	129.64(12)	127.09(14)
N−C−O	113.39(15)	112.32(15)	113.47(18)
Ti−O−C	141.74(11)	153.38(12)	164.88(13)

be able to obtain a few crystals of the new compound **4**. The yellow crystals were suitable for an X-ray structure determination. Salient structural features for complex **4** are depicted in Figure 4, along with selected bond lengths and angles in Table 2 for a comparison of its structural parameters.

4 is a bimetallic titanium−molybdenum complex composed of one $Ti({=}NAr)Cl_2(NHMe_2)_2$ and one $Mo(CO)_5$ subunit linked by an unprecedented Fischer-type aminocarbene ligand. This ligand coordinates the Mo center via the carbon atom of the carbene function, whereas the ligand coordinates to the Ti center by both the oxygen atom coming from the carbonyl and a dimethylamino group, the Ti atom being part of a six-membered titanoxy ring.

The coordination geometry of the pentacoordinated titanium center is between square pyramidal and trigonal bipyramidal (τ = 0.56), with the Ti atom surrounded by the nitrogen atom of the arylimido group ($Ti{-}N_{imido}$ = 1.7343(14) Å, Ti−N−C = 169.89(3)°) in an apical position. One nitrogen atom of the amido ligand $-NMe_2$ ($Ti{-}N_{amido}$ = 1.8665(15) Å), the oxygen atom of the metalloxy aminocarbene ligand (Ti−O = 2.0020(12) Å), and the two respectively trans-located nitrogen atoms of one $NHMe_2$ ligand (Ti−N = 2.2302(15) Å) and the dimethylamino group (Ti−N = 2.2844(15) Å) of the Fischer carbene ligand form the base of the pyramid. The molybdenum center has a distorted-octahedral geometry, with five carbonyl ligands with Mo−CO bond distances in the normal range ($Mo{-}C_{CO}$(av) = 2.033(3) Å, C−O(av) = 1.140(3) Å) and a carbon atom of the Fischer carbene at 2.2616(18) Å. The presence of a shorter than normal value for the C−O bond distance of the titanoxy-carbene ligand ($C{-}O_{Ti}$ = 1.295(2) Å) is indicative of some π-delocalization through the titanoxy-carbene bridging ligand. However, the Ti−O−C bond angle (141.74(11)°) is not as large as in other alkoxycarbene[41] or aminocarbene[42] compounds (also see below a comparison with the examples of **5** and **6**) in order to accommodate the coordination of the dimethylamino nitrogen atom to the Ti center. This unusual coordination mode forms a six-membered metallacycle ring with a distorted-boat conformation.

The formation of the Fischer aminocarbene function is explained by the nucleophilic attack of one of the dimethylamido group (on titanium) at the carbon atom of a coordinated carbon monoxide ligand of $Mo(CO)_6$ (path A in Scheme 4). This would generate the titanoxy-aminocarbene molybdenum pentacarbonyl intermediate species **A** with a Ti center that functions as the electrophile.[43] The next step consists of a C−H bond activation at the α-position to an amino group of the dimethylaminocarbene ligand (probably via loss of a proton assisted by an amido ligand), and intramolecular C,N coupling with a neighboring N atom of a $Ti{-}NMe_2$ ligand that transforms this group into a neutral amino ligand. However, one cannot exclude a second path (path B) in which the bidentate $-N(Me)CH_2NMe_2$ ligand is formed first by the coupling of two dimethylamido ligands on titanium followed by the nucleophilic attack of the new amido ligand at the coordinated CO on molybdenum. Such a coupling reaction, which might operate via the intermediacy of azametallacyclopropane or η^2-imine species, can be viewed as a hydroaminoalkylation of an amido group. As strong support for the involvement of $-NMe_2$ ligands in the formation of the fragment $-N(Me)CH_2NMe_2$, a similar coupling reaction of two dimethylamido ligands, resulting in the formation of a bidentate (dimethylamino)methylamide ligand ($-N(Me)CH_2NMe_2$), was recently observed by Xue in the reaction of $TaX(NMe_2)_4$ (X = NMe_2, $SiBu^tPh_2$) with O_2[44,45] and of MCl_5 with $LiNMe_2$.[46]

The NMR studies for **4** were conducted on the same crystalline sample as that used for the X-ray study (see the

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[41] Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178–5186.

[42] Galakhov, M.; Martin, A.; Mena, M.; Palacios, F.; Yelamos, C.; Raithby, P. R. *Organometallics* **2002**, *14*, 131–136.

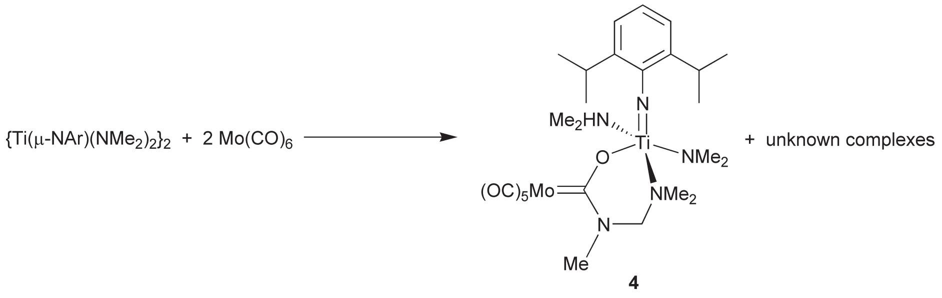
[43] For reviews on metalloxy Fischer carbene complexes, see: (a) Erker, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397–412. (b) Barluenga, J.; Fañanas, F. J. *Tetrahedron* **2000**, *56*, 4597–4628.

[44] Qiu, H.; Chen, S.-J.; Wang, C.-S.; Wu, Y.-D.; Guzei, I. A.; Chen, X.-T.; Xue, Z.-L. *Inorg. Chem.* **2009**, *48*, 3073–3079.

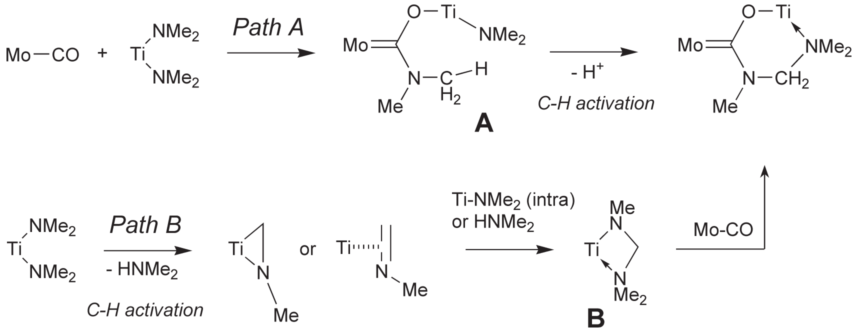
[45] Chen, S.-J.; Zhang, X.-H.; Yu, X.; Qiu, H.; Yap, G. P. A.; Guzei, I. A.; Lin, Z.; Wu, Y.-D.; Xue, Z.-L. *J. Am. Chem. Soc.* **2007**, *129*, 14408–14421.

[46] Zhang, X.-H.; Chen, S.-J.; Cai, H.; Im, H.-J.; Chen, T.; Yu, X.; Chen, X.; Lin, Z.; Wu, Y.-D.; Xue, Z.-L. *Organometallics* **2008**, *27*, 1338–1341.

Scheme 3. Synthesis Leading to the Unexpected Compound 4



Scheme 4. Proposed Mechanism for the Formation of 4



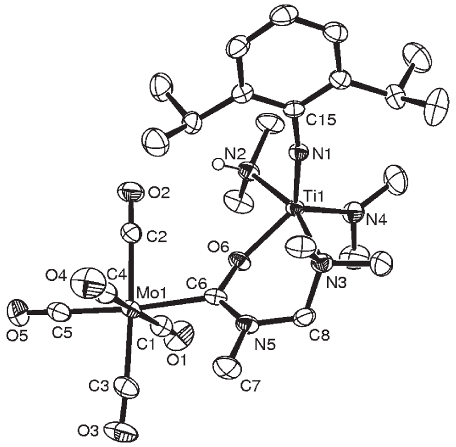


Figure 4. Molecular structure of **4**, showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity (except for N*H*Me$_2$).

Supporting Information). However, the assignment was very difficult due to the presence of two slightly different compounds (complex **4** and a second compound that might be [(CO)$_5$Mo{=C(NMeCH$_2$NMe$_2$)O}Ti(=N-2,6-Pr$^i_2$-C$_6$H$_3$)(*NHAr*)(NHMe$_2$)] with a −NHAr amido group) that are probably both present as two conformers (chair or boat conformation of the metallacyclic bridging ligand) and further complicated by dynamic equilibrium phenomena. In any case, the data for the bridging aminocarbene fragment compares particularly well with Xue's data for the related (dimethylamino)methylamide ligand on tantalum.[44] The two hydrogen atoms in the −CH$_2$− group are diasterotopic, giving rise to two broad signals at room temperature (4.52 and 2.21 ppm) in the ^{1}H NMR spectrum and one signal at 71.5 ppm in the ^{13}C NMR spectrum. The carbene function is observed at 243.5 ppm in the ^{13}C NMR spectrum, and carbonyl ligands appear at 213.6 and 208.6 ppm.

Although the synthesis of **4** is fortuitous and very difficult to reproduce, the observation of an unusual reactivity leading to the formation of compound **4**, which also presents very interesting features in relation to hydroaminoalkylation and also potentially to aminocarbonylation, was a stimulating factor that led us to investigate further the reaction between similar components.

In the first instance, we came back to former studies, initially reported by Bradley,[47,48] on reactions between M(NMe$_2$)$_4$ (M = group 4 metals) or CpTi(NMe$_2$)$_3$ and M′(CO)$_n$ (M′ = Fe, Mo, W). Apparently, at that time, the authors did not see the formation of the aminocarbene complexes,[49] but instead they reported adduct type compounds with bridging dimethylamido ligands. Later, Petz gave the correct interpretation of the formulation of the species that are formed in the reaction of Ti(NMe$_2$)$_4$ and metal carbonyls and characterized the aminocarbene function by IR and ^{1}H NMR.[50,51] To complete these studies, in 1995 Mena et al. reported an X-ray structure of the heterobimetallic compound formed between Cp*Ti(NMe$_2$)$_3$ and W(CO)$_6$.[42]

In order to characterize without ambiguity the species that might form in the reaction, we reproduced the reaction between equimolar amounts of Ti(NMe$_2$)$_4$ and Mo(CO)$_6$. As shown in Scheme 5, the reaction proceeded smoothly in toluene at room temperature to afford an orange solution from which, after suitable workup, yellow-orange crystals of **5** were obtained in 79% yield. It is worth noting that, in the solid state, **5** slowly decomposed into Mo(CO)$_6$ (that sublimed as colorless crystals) and unknown Ti species. Mena et

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(47) Bradley, D. C.; Charalamboud, J.; Jain, S. *Chem. Ind.* **1965**, 1730–1730.

(48) Bradley, D. C.; Kasenally, A. S. *Chem. Comm.* **1968**, 1430–1430.

(49) For a review on carbamoyl (aminocarbene) complexes, see: Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335–341.

(50) Petz, W. *J. Organomet. Chem.* **1974**, *72*, 369–375.

(51) Petz, W. *J. Organomet. Chem.* **1993**, *456*, 85–88.

Scheme 5. Synthesis of 5

$$Mo(CO)_6 + Ti(NMe_2)_4 \xrightarrow[\text{toluene, RT}]{} (Me_2N)_3Ti\text{-}OC(NMe_2){=}Mo(CO)_5$$

5

al. have also observed some decomposition in their related Ti/W compounds.[42]

The spectral data (IR, NMR) and elemental analysis are in agreement with the formulation $[(CO)_5Mo({=}C(NMe_2)O)\text{-}Ti(NMe_2)_3]$ for **5**, as suggested by Petz. In particular, the IR spectrum shows three bands in the carbonyl region that are characteristic of $M(CO)_5L$ complexes with pseudo-C_{4v} symmetry.[52] The ^1H NMR presents a signal for three equivalent $-NMe_2$ groups at 2.96 ppm, and two signals for the two diastereotopic methyl groups of the aminocarbene NMe_2 group due to restricted rotation around the $OC-NMe_2$ bond (arising from a significant CN double-bond character typical of aminocarbenes). The ^{13}C NMR spectrum presents characteristic signals of Mo=C at 238.8 ppm, as well as signals for CO being located cis (207.9 ppm) and trans (213.2 ppm) to the carbene ligand.

This formulation was unambiguously confirmed by a X-ray diffraction study. Thermal ellipsoid plots are presented in Figure 5 along with selected bond lengths and angles, and Table 2 gives a comparison of their structural parameters. As anticipated, **5** is a monomer in the solid state; the bulky $Mo(CO)_5$ unit apparently prevents the dimerization of $Ti(NMe_2)_3$. The Ti center has a tetrahedral geometry and is coordinated by three dimethylamido (Ti−N(av) = 1.872(2) Å) and an oxygen atom of the titanoxy aminocarbene ligand (Ti−O = 1.8975(12) Å). This Ti−O bond is significantly shorter than in **4** (and **6**, vide infra). The six-coordinated Mo center is bonded to five CO (C−O(av) = 1.137(2) Å, Mo−C(av) = 2.030(2) Å) and a carbenic carbon atom (Mo−C = 2.2655(16) Å). As previously noted in **4**, the short C−O bond distance (1.3125(19) Å) and the wide Ti−O−C bond angle (153.38(12)°) are indicative of π-delocalization.

Next we examined the reaction of **5** with $ArNH_2$ as a possible route to **4** (or to **6**). Such transamination reactions between a primary amine and a group 4 and 5 metal precursor with dialkylamido ligands is a well-known route to imido complexes.[14,17,19,21,22,36,53] However, the treatment of a C_6D_6 solution of **5** with 1 equiv of $ArNH_2$ proved to be more difficult. In general, generation of an imido function by transamination with an aniline is over within 1−2 h, whereas in the case of **5** we observed a very slow reaction with formation after 6 h of less than 5% of an intermediate complex (namely **6**). As this complex **6** is unstable in solution (see later), we were unable to obtain this compound by this route, and instead we noted after 2 weeks of reaction the total conversion of **5** into a new compound, which separates from the C_6D_6 solution as a brown insoluble oil. When separated from the C_6D_6 supernatant solution, this oil eventually solidified and was shown to contain $Mo(CO)_6$,[54] which suggests that the decomposition observed in the C_6D_6 reaction involves the loss of the $Mo(CO)_5$ fragment with formation of $Mo(CO)_6$ and a titanium-only unidentified compound.

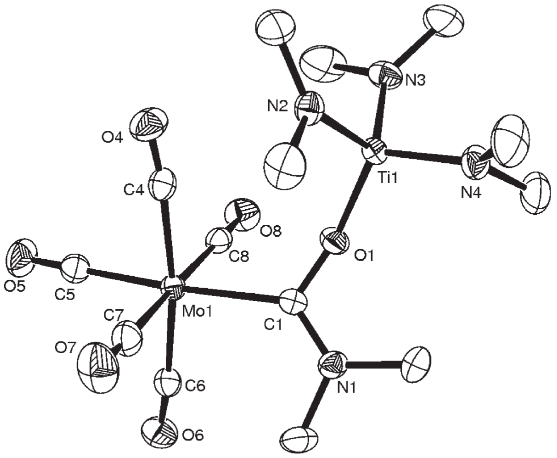

Figure 5. Molecular structure of **5**, showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

In contrast, when the same reaction of **5** with 1 equiv of $ArNH_2$ was performed in cyclohexane-d_{12} and followed by ^1H NMR, we observed a slow but complete transformation of **5** in about 3 days (Scheme 6), leading to the imido complex **6**, together with a second unidentified species **X**. In order to isolate complex **6**, we reproduced this experiment in a larger scale and in pentane, but unfortunately we could not obtain **6** in a pure form due to similar solubility.[55]

We then turned our attention to the one-pot reaction between equimolar amounts of $Ti(NMe_2)_4$ and $Mo(CO)_6$, now in the presence of 1 equiv of $ArNH_2$ (Scheme 6). It was difficult to obtain reproducible results from this reaction (depending on the reaction time and the workup procedure), which prompted us to followed the reaction by ^1H NMR. The ^1H NMR studies showed the formation of a single product within the first hours, which after 6−12 h further evolved to afford a complex mixture of unidentified products. Consequently, in order to get the compound in a pure form, we reproduced the reaction in a larger scale and stopped the reaction after 6 h of stirring by removing the solvent or precipitation with pentane (as for the preparation of **4**). In this manner, we could produce the new complex **6** in pure form, albeit in low yields (20%). Again, we attribute this problem to instability in solution, as we noted that allowing a benzene-d_6 solution of **6** to stand at room temperature showed slow decomposition (after 1 day) with almost complete disappearance of the initial signals within 1 week and formation of unidentified species. The decomposition product of **6** seems identical with that obtained through the reaction of **5** with $ArNH_2$ when a C_6D_6 solution was left over 2 weeks (vide supra). Although uncharacterized, the product(s) of decomposition is (are) apparently not complex **4**, and further studies will be necessary to clarify its (their) exact nature.[56]

Compound **6** reveals a diagnostic carbene resonance in the ^{13}C NMR spectrum centered at 233.9 ppm. The ^1H NMR

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(52) Cotton, F. A.; Darensbourg, D. J.; Fang, A.; Kolthammer, B. W. S.; Reed, D.; Thompson, J. L. *Inorg. Chem.* **1981**, *20*, 4090–4096.

(53) Thorn, D. L.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 357–363.

(54) The crystals were confirmed to be $Mo(CO)_6$ by determinatiion of the cell parameters by an X-ray diffraction analysis.

(55) Species **X** might be a coordination compound of the type $(ArNH_2)Mo(CO)_4(L)$ with a CO ligand that has been substituted by an $ArNH_2$ molecule. We believe the decomposition of our Ti/Mo compounds might be inherent to the presence of external donors such as the aniline that can further displace carbonyl ligands.

(56) Isolated compound **6** could be regarded as intermediate **A** in Scheme 4 for formation of **4**; however, attempted direct conversion of **6** into **4** has proved so far unsuccessful.

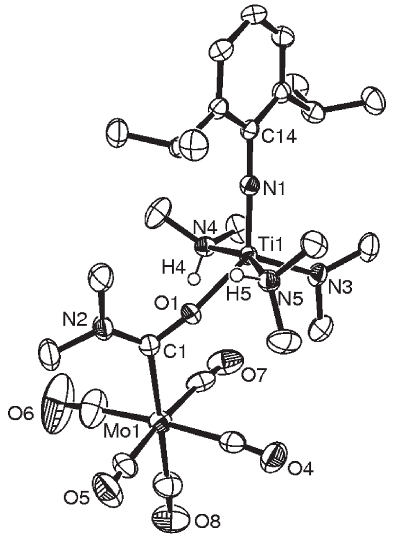
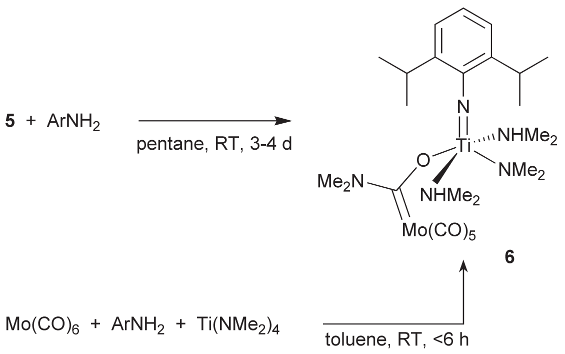


Figure 6. Molecular structure of **6**, showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity (except for N*H*Me$_2$).

Scheme 6. Synthesis of 6



data consists of sets of signals attributed to one arylimido group, two equivalent NHMe$_2$ ligands, and one −NMe$_2$ group, as well as two diastereotopic methyl groups of an aminocarbene ligand. Other spectroscopic features for **6** include the observation in the carbonyl region of the three characteristic bands for Mo(CO)$_5$L complexes at 1968, 1897, and 1876 cm^{-1}.

Altogether, the spectroscopic data, complemented by a combustion analysis, suggests compound **6** can be formulated as [(CO)$_5$Mo=C(NMe$_2$)O]Ti(=NAr)(NMe$_2$)(NHMe$_2$)$_2$ with (different from the case for compound **4**) a "simple" dimethylaminocarbene ligand bridging the two metals.

This formulation was consolidated by a X-ray diffraction analysis. The ORTEP diagram is shown in Figure 6 with selected bond lengths and angles provided in Table 2. The solid-state structure confirms the proposed connectivity and displays structural features resembling those of **4**. Complex **6** is a bimetallic system composed of a five-coordinate titanium(IV) center and an octahedral molybdenum center linked by a dimethylaminocarbene function. The Ti−N$_{\mathrm{imido}}$ bond distance of 1.7363(16) Å is comparable to that in **4** (1.7343(14) Å)], as is the Ti−N−C$_{\mathrm{ipso}}$ angle, which moderately deviates from 180°. The remaining structural features around the Ti atom are comparable to those in **4**, including the Ti−O (2.0045(13) Å) and O−C (1.288(2) Å) bond distances. As in complexes **4** and **5**, the molybdenum center in **6** has a distorted-octahedral geometry, with five carbonyl ligands with Mo−CO bond distances in the normal range (Mo−C$_{\mathrm{CO}}$(av) = 2.019(4) Å, C−O(av) = 1.143(4) Å) and a carbon atom of the Fischer carbene at 2.293(2) Å. Again, the presence of a shorter than normal value for the C−O bond distance of the titanoxycarbene ligand (C−O$_{\mathrm{Ti}}$ = 1.288(2) Å) is indicative of some π-delocalization through the titanoxycarbene bridging ligand. The Ti−O−C bond angle (164.88(13)°) is larger than in related aminocarbene compounds **4** and **5**.

Conclusions

We have prepared the first bimetallic (η^6-arene)molybdenum imido−titanium complex **2** from a transamination reaction between TiCl$_2$(NMe$_2$)$_2$ and the corresponding (η^6-aniline)Mo(CO)$_3$ precursor **3**. When it was treated with Mo(CO)$_6$, we reported that the dimer {Ti(μ-NAr)(NMe$_2$)$_2$}$_2$ afforded a complex mixture of products, from which complex **4** was characterized. Complex **4** was shown to contain an unprecedented aminocarbene ligand doubly bridging the Ti and the Mo centers, generated in part from the intramolecular CN coupling of a Ti−NMe$_2$ group with a Mo=CNMe$_2$ ligand. We have also reported other examples of bimetallic Ti/Mo complexes held together by a bridging dimethylaminocarbene function (namely compounds **5** and **6**).

As most of these species suffer from instability in solution and/or in the solid state, which may hamper their further use in catalytic processes, we are also examining other bimetallic systems composed of other pairs of complexes (group 4/5 metals and various metal carbonyl complexes). These studies are currently underway and will be reported in due course, as well as the reactivity studies toward carbonylation of amines, as some of the reported compounds can be viewed as the first step toward amine carbonylation.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon. Solvents were refluxed and dried over appropriate drying agents under an atmosphere of argon and collected by distillation. NMR spectra were recorded on Bruker ARX250, DPX300, and Avance500 spectrometers and referenced internally to residual protio-solvent (^{1}H) resonances and are reported relative to tetramethylsilane (δ 0 ppm). Chemical shifts are quoted in δ (ppm). Infrared spectra were prepared as KBr pellets under argon in a glovebox and were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrometer. Infrared data are quoted in wavenumbers (cm^{-1}). Elemental analyses were performed at the Laboratoire de Chimie de Coordination (Toulouse, France) or by the Service Central de Microanalyses du CNRS at Vernaison (France).

The Ti(NMe$_2$)$_4$ used in this study was prepared by a modification of a literature procedure[57] or purchased from commercial sources (Aldrich). TiCl$_2$(NMe$_2$)$_2$ was prepared from the reaction of equimolar amounts of TiCl$_4$ and Ti(NMe$_2$)$_4$.[22] The imido precursor Ti(=N-2,6-Pr$^i_2$-C$_6$H$_3$)Cl$_2$(NHMe$_2$)$_2$ (**1**) was prepared according to our published procedure.[20] The imido-bridged dimer {Ti(N-2,6-Pr$^i_2$-C$_6$H$_3$)(NMe$_2$)$_2$}$_2$ was prepared by a synthesis similar to that used for analogous vanadium compounds.[17,21] Mo(CO)$_3$(CH$_3$CN)$_3$ was prepared according to a literature procedure.[58]

Crystal Structure Determination. The structures of six compounds were determined. Crystal data collection and processing

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(57) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857–3861.
(58) King, R. B. *J. Organomet. Chem.* **1967**, *8*, 139–148.

Table 3. Crystallographic Data and Data Collection and Refinement Parameters for 1−6

	1	**2**	**3**[a]	**4**	**5**	**6**
chem formula	$C_{16}H_{31}Cl_2N_3Ti$	$C_{19}H_{31}Cl_2MoN_3O_3Ti$	$C_{15}H_{19}MoNO_3$	$C_{26}H_{41}MoN_5O_6Ti$	$C_{14}H_{24}MoN_4O_6Ti$	$C_{26}H_{43}MoN_5O_6Ti$
formula wt	384.24	564.21	357.25	663.48	488.21	665.49
cryst syst	monoclinic	triclinic	orthorhombic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a, Å	9.8809(6)	10.2058(3)	7.8652(11)	10.1513(8)	13.7140(4)	10.6408(5)
b, Å	22.4338(12)	11.2671(3)	13.455(2)	13.5008(11)	11.1816(3)	25.6907(10)
c, Å	10.2598(6)	12.2010(4)	14.318(2)	15.0634(13)	14.2280(4)	13.1933(7)
α, deg	90.0	92.430(2)	90.0	100.794(4)	90.0	90.0
β, deg	113.557(3)	108.6380(10)	90.0	108.827(4)	99.902(2)	113.001(6)
γ, deg	90.0	108.1860(10)	90.0	103.517(4)	90.0	90.0
V, Å^3	2084.7(2)	1247.16(6)	1515.2(4)	1820.8(3)	2149.28(10)	3319.9(3)
Z	4	2	4	2	4	4
D_{calcd}, g cm^{-3}	1.224	1.502	1.566	1.21	1.509	1.331
μ(Mo Kα), mm^{-1}	0.667	1.060	0.872	0.602	0.988	0.66
F(000)	816	576	728	688	992	1384
θ range (deg)	2.35−40.12	2.69−29.80	2.08−29.38	1.62−29.89	2.64−26.37	2.62−26.37
no. of measd rflns	66700	26446	17696	42720	16122	25658
no. of unique rflns/R_{int}	12 957/0.0351	7009/0.0337	4182/0.0474	10 352/0.0338	4383/0.0242	6789/0.0352
no. of params/restraints	207/0	270/0	191/2	363/0	243/0	363/0
final R indices ($I > \sigma^2(I)$)	R1 = 0.0397	R1 = 0.0314	R1 = 0.0348	R1 = 0.0346	R1 = 0.0212	R1 = 0.0292
	wR2 = 0.0658	wR2 = 0.0969	wR2 = 0.0651	wR2 = 0.0577	wR2 = 0.0862	wR2 = 0.0555
final R indices (all data)	R1 = 0.0653	R1 = 0.0475	R1 = 0.051	R1 = 0.0507	R1 = 0.0255	R1 = 0.0479
	wR2 = 0.0698	wR2 = 0.11	wR2 = 0.0705	wR2 = 0.0635	wR2 = 0.0901	wR2 = 0.0576
goodness of fit	1.013	1.025	1.027	1.029	1.079	1.031
$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.652, −0.441	0.462, −0.483	0.466, −0.625	0.406, −0.347	0.368, −0.431	0.431, −0.500

[a] Absolute structure parameter (Flack): −0.02(4).

parameters are given in Table 3. Crystals of **1** (orange blocks), **2** (orange blocks), **3** (colorless parallelepipeds), **4** (yellow plates), **5** (yellow blocks), and **6** (yellow parallelepipeds) were obtained. The selected crystals, sensitive to air and moisture, were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 180 K under a stream of cold N_2. For all the structures data collection was performed at low temperature (T = 180 K) on a Stoe Imaging Plate Diffraction System (IPDS), on an Oxford Diffraction Kappa CCD Excalibur diffractometer, or on a Bruker Kappa Apex II diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device. Final unit cell parameters were obtained by means of a least-squares refinement of a set of 8000 well-measured reflections, and the crystal decay was monitored during data collection by measuring 200 reflections by image; no significant fluctuation of intensities was observed. Structures were solved by means of direct methods using the program SIR92[59] and subsequent difference Fourier maps, models were refined by least-squares procedures on F^2 by using SHELXL-97[60] integrated in the package WINGX version 1.64,[61] and empirical absorption corrections were applied on data.[62] For **4**, it was not possible to solve diffuse electron-density residuals (enclosed solvent molecules). Treatment with the SQUEEZE facility from PLATON[63] resulted in a smooth refinement. Since a few low-order reflections are missing from the data set, the electron count was underestimated. Thus, the values given for D(calc), F(000), and the molecular weight are only valid for the ordered part of the structure. Details of the structure solutions and refinements are given in the Supporting Information. Full listings of atomic coordinates, bond lengths and angles, and displacement parameters for all structures have been deposited at the Cambridge Crystallographic Data Centre.

Synthesis of [Ti(=N-2,6-Pr$^i_2$-C_6H_3)Cl_2($NHMe_2$)$_2$][η^6-Mo(CO)$_3$] (2). Method 1 (from $TiCl_2(NMe_2)_2$ and Mo(CO)$_3$(η^6-2,6-^{i}Pr$_2$-$C_6H_3NH_2$). To a toluene solution (2 mL) of 58 mg of $TiCl_2(NMe_2)_2$ (0.2803 mmol) was added by portions 1 equiv of Mo(CO)$_3$(η^6-2,6-^{i}Pr$_2$-$C_6H_3NH_2$) (**3**; 100 mg, 0.2799 mmol) at room temperature. The resulting red solution was stirred for 2 h at room temperature. The volatiles were removed under vacuum, and the solid was washed with 2 mL of pentane. Yield: 145 mg (92%). ^{1}H NMR (300 MHz, C_6D_6): δ 4.93 (d, ^3J = 6.6 Hz, 2H, C_6H_3Pr$^i_2$), 4.71 (t, ^3J = 6.6 Hz, 1H, C_6H_3Pr$^i_2$), 4.25 (sept, ^3J = 6.8 Hz, 2H, $CHMe_2$), 3.05 (br sept, 2H, $HNMe_2$), 2.26 (d, ^3J = 6.6 Hz, 12H, NMe_2), 1.30 (d, ^3J = 6.6 Hz, 6H, CHMe^aMe^b), 1.18 (d, ^3J = 6.6 Hz, 6H, CHMe^aMe^b). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6): δ 224.3 (CO), 133.5 (*ipso*-C_6H_3), 122.8 (*o*-C_6H_3), 92.2 (*p*-C_6H_3), 91.1 (*m*-C_6H_3), 40.3 (NHMe_2), 27.7 ($CHMe_2$), 25.7 (CHMe^aMe^b), 22.2 (CHMe^aMe^b). IR: 3239 (w, NH), 2971 (m), 1947 (CO), 1841 (vs, CO), 1467 (m), 1396 (m), 1340 (m), 1019 (m), 895 (m), 622 (m), 501 (m), 442 (m). Anal. Calcd for $C_{19}H_{31}Cl_2MoN_3O_3Ti$ (564.18): C, 40.45; H, 5.54; N, 7.45. Found: C, 40.35; H, 5.59; N, 7.45.

Method 2 (from Ti(NMe_2)$_4$/Me_3SiCl and Mo(CO)$_3$(η^6-2,6-^{i}Pr$_2$-$C_6H_3NH_2$)). A 50 mg portion of Mo(CO)$_3$(η^6-2,6-^{i}Pr$_2$-$C_6H_3NH_2$) (0.1400 mmol) was added to a toluene (1 mL) solution of Ti(NMe_2)$_4$ (31.4 mg, 0.1401 mM), and the resulting solution was stirred for 5 min at room temperature. Me_3SiCl (92 mg, 0.8468 mmol) was added dropwise to the solution with stirring. After 3 h, the volatiles were pumped off and the red-orange solid was washed with pentane (2 × 2 mL) and dried under vacuum (67 mg). ^{1}H NMR spectroscopy showed this solid to be **2** contaminated by 10% of [Ti(=N-2,6-Pr$^i_2$-C_6H_3)Cl_2($NHMe_2$)$_2$].

Synthesis of [Mo(CO)$_3$(η^6-2,6-^{i}Pr$_2$-$C_6H_3NH_2$)] (3). Mo(CO)$_6$ (500 mg, 1.8939 mM), 2,6-^{i}Pr$_2$-$C_6H_3NH_2$ (470 mg, 2.6510 mM), 0.5 mL of THF, and 10 mL of octane were introduced into a Schlenk flask equipped with a magnetic stir bar and a reflux condenser connected to an oil bubbler and an argon inlet. The glassware was covered with aluminum foil during the time the compounds were in solution to prevent decomposition by light. The mixture was heated to reflux under a stream of argon for 7 h. Upon cooling to room temperature, pale yellow crystals

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(59) Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(60) Sheldrick, G. M. *SHELX97* [*Includes SHELXS97, SHELXL97, CIFTAB*]-*Programs for Crystal Structure Analysis* (*Release 97-2*); Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

(61) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

(62) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158–166.

(63) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C–34.

were formed. The crystals were collected by filtration (another crop of crystals; about 30 mg can be obtained by cooling the filtrate to −20 °C). Extraction with toluene (4 × 2 mL, to remove small amounts of unreacted $\mathrm{Mo(CO)_6}$) afforded a yellow solution that was filtered under a bed of Celite, and the volatiles were removed under vacuum to give 355 mg of pale yellow crystals of **3** (52%). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 5.25 (d, ^3J = 6.4 Hz, 2H, $\mathrm{C_6}\mathit{H}_3\mathrm{Pr}^i{}_2$), 4.43 (t, ^3J = 6.5 Hz, 1H, $\mathrm{C_6}\mathit{H}_3\mathrm{Pr}^i{}_2$), 2.96 (br s, 2H, $\mathrm{N}\mathit{H}_2$), 1.95 (sept, ^3J = 6.7 Hz, 2H, $\mathrm{C}\mathit{H}\mathrm{Me_2}$), 1.01 (d, ^3J = 6.6 Hz, 6H, $\mathrm{CH}\mathit{Me}^a\mathrm{Me}^b$), 0.71 (d, ^3J = 6.6 Hz, 6H, $\mathrm{CHMe}^a\mathit{Me}^b$). ^{13}C{^{1}H} NMR (75.47 MHz, $\mathrm{C_6D_6}$): δ 224.4 (CO), 130.6 (*ipso*-$\mathit{C}_6\mathrm{H_3}$), 105.5 (*o*-$\mathit{C}_6\mathrm{H_3}$), 95.6 (*m*-$\mathit{C}_6\mathrm{H_3}$), 85.4 (*p*-$\mathit{C}_6\mathrm{H_3}$), 27.9 ($\mathit{C}\mathrm{HMe_2}$), 22.5 ($\mathrm{CH}\mathit{Me}^a\mathrm{Me}^b$), 21.9 ($\mathrm{CHMe}^a\mathit{Me}^b$). IR 3509 (w, $\mathrm{NH_2}$), 3413 (w, $\mathrm{NH_2}$), 1930 (vs, CO), 1835 (vs, CO), 1629 (m), 1429 (m), 593 (m), 499 (m). Anal. Calcd for $\mathrm{C_{15}H_{19}MoNO_3}$ (357.26): C, 50.43; H, 5.36; N, 3.92. Found: C, 50.50; H, 5.38; N, 3.83.

Synthesis of [Ti(=N-2,6-Pr$^i{}_2$-$\mathrm{C_6H_3}$)($\mathrm{NMe_2}$)($\mathrm{NHMe_2}$)(OC-($\mathrm{NMeCH_2NMe_2}$)=Mo$\mathrm{(CO)_5}$)] (4). This compound was obtained using a slight modification of the procedure used for the synthesis of **6** (longer reaction time, solvent). $\{\mathrm{Ti(NAr)(NMe_2)_2}\}_2$ was prepared in situ by addition of 79 mg of $\mathrm{ArNH_2}$ (0.4456 mM) to a toluene solution (2 mL) of $\mathrm{Ti(NMe_2)_4}$ (100 mg, 0.4460 mM) and left overnight. The solvent was quickly removed under vacuum, and 10 mL of octane was added followed by the addition of 117 mg of $\mathrm{Mo(CO)_6}$ (0.4432 mM). The solution was stirred for 2 h and left for 3 days without stirring, during which time a few crystals of **4** were formed (although glued in an oily material) from a complex mixture of products. The crystals that were collected (about 40 mg) were of a sufficient amount for X-ray diffraction and NMR studies. Nevertheless, we were unable to fully assign the ^{1}H and ^{13}C NMR spectra (given in the Supporting Information) due to the presence of possible isomers or conformers of **4**, contaminated by another compound (see the text), further complicated by dynamic exchange phenomena.

Synthesis of [$\mathrm{(CO)_5}$Mo(=C($\mathrm{NMe_2}$)O)Ti$\mathrm{(NMe_2)_3}$] (5). To a toluene solution (5 mL) of $\mathrm{Ti(NMe_2)_4}$ (250 mg, 1.1151 mmol) was added by portions 1 equiv of $\mathrm{Mo(CO)_6}$ (293 mg, 1.1100 mmol) at room temperature. The resulting orange suspension was stirred overnight at room temperature, after which time the volatiles were removed under vacuum to give an orange oil. The oil was dissolved in the minimum amount of pentane (ca. 5−7 mL), and the solution was filtered through a bed of Celite and allowed to crystallize at −20 °C. Yellow crystals were collected, and a second crop of crystals could be obtained from cooling the concentrated filtrate. Yellow crystals were collected and dried under vacuum. Yield: 433 mg (79%). This compound slowly decomposed under argon in the solid state with sublimation of $\mathrm{Mo(CO)_6}$ and uncharacterized Ti species. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 2.99 (s, 3H, $=\mathrm{CN}\mathit{Me}^a\mathrm{Me}^b$), 2.96 (s, 18H, $\mathrm{N}\mathit{Me}_2$), 2.21 (s, 3H, $=\mathrm{CNMe}^a\mathit{Me}^b$). ^{13}C{^{1}H} NMR (75.47 MHz, $\mathrm{C_6D_6}$): δ 238.8 (Mo=C), 213.2 (CO) 1 $\mathrm{CO_{trans}}$, 207.9 ($\mathit{C}\mathrm{O_{cis}}$), 44.2 ($=\mathrm{CN}\mathit{Me}^a\mathrm{Me}^b$), 43.8 ($\mathrm{N}\mathit{Me}_2$), 32.9 ($=\mathrm{CNMe}^a\mathit{Me}^b$). IR: 2867 (m), 1975 (sh, CO), 1945 (vs, CO), 1904 (sh, CO), 1272 (m), 1229 (m), 942 (m), 729 (m), 591 (s). Anal. Calcd for $\mathrm{C_{14}H_{24}MoN_4O_6Ti}$ (488.17): C, 34.44; H, 4.96; N, 11.48. Found: C, 34.23; H, 5.00; N, 11.24.

Synthesis of [Ti(=N-2,6-Pr$^i{}_2$-$\mathrm{C_6H_3}$)($\mathrm{NMe_2}$)$\mathrm{(NHMe_2)_2}$(OC-($\mathrm{NMe_2}$)=Mo$\mathrm{(CO)_5}$)] (6). Method 1 (from the Reaction between 5 and $\mathrm{ArNH_2}$). A cyclohexane-d_{12} solution (0.5 mL) of 50 mg of **5** (0.102 42 mmol) and 18 mg of $\mathrm{ArNH_2}$ (0.101 53 mmol) was placed in an NMR tube, and the reaction was followed by ^{1}H NMR spectroscopy. The NMR studies showed the reaction to be complete after 3 days and to lead to complex **6** and an unidentified side product.

Method 2 (from $\mathrm{Ti(NMe_2)_4}$, $\mathrm{Mo(CO)_6}$, and $\mathrm{ArNH_2}$). $\mathrm{Ti(NMe_2)_4}$ (100 mg, 0.4460 mM) was added to a toluene (4 mL) suspension of $\mathrm{Mo(CO)_6}$ (117 mg, 0.4432 mM) and 2,6-$^i\mathrm{Pr_2}$-$\mathrm{C_6H_3NH_2}$ (79 mg, 0.4456 mM). The red solution was stirred for 6 h at room temperature. The solution was filtered, and the solvent was removed under vacuum to afford a red oily residue. Extraction of this oil with pentane (10 mL) afforded a red solution that upon cooling to −20 °C produced 60 mg of red-orange crystals of **6** (yield 20%) (note: the insoluble residue from the pentane extraction was also confirmed to be complex **6**, but in a less pure form, and we did not try to further purify it to optimize yields). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 7.03 (d, ^3J = 7.5 Hz, 2H, $\mathrm{C_6}\mathit{H}_3\mathrm{Pr}^i{}_2$), 6.88 (t, ^3J = 7.5 Hz, 1H, $\mathrm{C_6}\mathit{H}_3\mathrm{Pr}^i{}_2$), 4.19 (sept, ^3J = 6.9 Hz, 2H, $\mathrm{C}\mathit{H}\mathrm{Me_2}$), 3.28 (s, 6H, $\mathrm{N}\mathit{Me}_2$), 3.07 (s, 3H, $=\mathrm{CN}\mathit{Me}^a\mathrm{Me}^b$), 2.58 (s, 3H, $=\mathrm{CNMe}^a\mathit{Me}^b$), 2.14 (d, ^3J = 6.0 Hz, 12H, $\mathrm{NH}\mathit{Me}_2$), 1.23 (d, ^3J = 6.9 Hz, 12H, $\mathrm{CH}\mathit{Me}_2$) (note that (i) the peak at 2.14 ppm is a singlet at high concentration and (ii) the signal for $\mathrm{N}\mathit{H}\mathrm{Me_2}$ is too broad to be observed at room temperature). ^{13}C{^{1}H} NMR (75.47 MHz, $\mathrm{C_6D_6}$): δ 233.9 (Mo=C), 212.6 ($\mathit{C}\mathrm{O_{trans}}$), 208.7 ($\mathit{C}\mathrm{O_{cis}}$), 155.5 ($\mathit{C}_6\mathrm{H_3}$), 141.5 ($\mathit{C}_6\mathrm{H_3}$), 122.8 ($\mathit{C}_6\mathrm{H_3}$), 120.1 ($\mathit{C}_6\mathrm{H_3}$), 47.1 (br, $\mathrm{N}\mathit{Me}_2$), 44.1 ($=\mathrm{CN}\mathit{Me}^a\mathrm{Me}^b$), 40.2 ($\mathrm{NH}\mathit{Me}_2$), 32.8 ($=\mathrm{CNMe}^a\mathit{Me}^b$), 27.0 ($\mathit{C}\mathrm{HMe_2}$), 24.9 ($\mathrm{CH}\mathit{Me}_2$). IR 3296 (w, $\mathrm{NHMe_2}$), 2963 (m), 1968 (CO), 1897 (s, CO), 1876 (sh, CO), 1496 (m), 1420 (m), 1316 (m), 1277 (m), 983 (m), 950 (m), 896 (m), 755 (m), 613 (m), 594 (m). Anal. Calcd for $\mathrm{C_{26}H_{43}MoN_5O_6Ti}$ (665.46): C, 46.93; H, 6.51; N, 10.52. Found: C, 46.67; H, 6.54; N, 10.30.

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Supporting Information Available: Tables, figures, and CIF files giving data for the X-ray crystal structures of complexes **1**−**6**, other detailed Ortep views for **2** and **3**, and NMR data (^{1}H, ^{13}C) for complex **4**. This material is available free of charge via the Internet at http://pubs.acs.org.