

# **CHEMISTRY** A European Journal



# **Accepted Article** Title: Influence of a Metallic Substrate on the Small Molecule Activation Mediated by a Surface Adsorbed Complex Authors: Alexander Schlimm, Nadja Stucke, Benedikt Maria Flöser, Talina Rusch, Jan Krahmer, Thomas Strunskus, Christian Näther, Olaf Magnussen, and Felix Tuczek This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article. To be cited as: Chem. Eur. J. 10.1002/chem.201800911 Link to VoR: http://dx.doi.org/10.1002/chem.201800911 **Supported by** ACES



WILEY-VCH

# Influence of a Metallic Substrate on the Small Molecule Activation Mediated by a Surface Adsorbed Complex

Alexander Schlimm<sup>#[a]</sup>, Nadja Stucke<sup>#[a]</sup>, Benedikt M. Flöser<sup>[a]</sup>, Talina Rusch<sup>[b]</sup>, Jan Krahmer<sup>[a]</sup>, Christian Näther<sup>[a]</sup>, Thomas Strunskus<sup>[c]</sup>, Olaf M. Magnussen<sup>[b]</sup>, Felix Tuczek<sup>\*[a]</sup>

Dedicated to Professor Bernt Krebs on the occasion of his 80th anniversary

Abstract: Activating small molecules with transition metal complexes adsorbed on metallic surfaces is a novel approach combining aspects of homogeneous and heterogeneous catalysis. In order to study the influence of an Au(111) substrate on the activation of the small molecule ligand carbon monoxide a molybdenum triscarbonyl complex containing a PN<sup>3</sup>P pincer ligand is synthesized and investigated in the bulk, in solution and adsorbed on an Au(111) surface. Via a platform approach a perpendicular orientation of the molybdenum complex is achieved and confirmed by IRRAS and NEXAFS. Using vibrational spectroscopy (IR, Raman, IRRAS) coupled to DFT calculations the influence of the metallic substrate on the activation of the CO ligands bound to the molybdenum complex is determined. The electron withdrawing behavior of gold causes an overall shift of the CO stretching vibrations to higher frequencies, which is partly compensated by a dynamic charge transfer from the substrate to the molybdenum center, increasing its (dynamic) polarizability.

#### Introduction

Many important reactions in industry, biology or energy conversion are based on the activation of small molecules by transition metal complexes.<sup>[1–8]</sup> Often these processes also



Figure 1: Different deposition methods of transition metal complexes on surfaces: a) physisorption (direct deposition), b) chemisorption via a functional group (e.g. thiols).

# The authors contributed equally to this paper.

[a]	A. Schlimm, N. Stucke, B. M. Flöser, J. Krahmer, Prof. Dr. C.	
	Näther, Prof. Dr. F. Tuczek*	
	Institute of Inorganic Chemistry	
	Christian Albrechts University Kiel	
	Max-Eyth-Str. 2, 24118 Kiel	
	E-mail: ftuczek@ac.uni-kiel.de	
[b]	T. Rusch, Prof. Dr. O. M. Magnussen	
	Institute of Experimental and Applied Physics	
	Christian Albrechts University Kiel	
	Leibnizstr. 19, 24118 Kiel	
[c]	Dr. T. Strunskus	
	Institute for Materials Science – Multicomponent Materials	
	Christian Albrochta University Kiel	

Christian Albrechts University K Kaiserstr. 2, 24143 Kiel

Supporting information for this article is given via a link at the end of the document.



Figure 2: Design of the new  $[Mo(CO)_3(Me-PN^3P_{TATA})]$  (1) complex and formation of a monolayer of 1 on Au(111).

involve the simultaneous transfer of electrons and protons to or from the activated substrate. Important examples for such reactions are hydrogen evolution (HER), oxygen evolution during water splitting (OER), oxygen reduction (ORR) or reduction of CO<sub>2</sub>. A particular challenging case is nitrogen fixation as it involves protonation and reduction of the most inert molecule of the universe, N<sub>2</sub>.<sup>[9]</sup> Inspired by the biological process of nitrogen fixation,<sup>[10]</sup> a number of molybdenum, iron and other transition metal complexes have been synthesized which catalyze the conversion of N<sub>2</sub> to NH<sub>3</sub> in homogeneous solution.<sup>[2,3,5,11–20]</sup> Besides proton donors like HBArF<sub>4</sub> (BArF<sub>4</sub>= tetrakis[3,5bis(trifluoromethyl)-phenyl]borate) or lutidinium salts these processes require the addition of reducing agents; e.g., decamethylchromocene or KC<sub>8</sub>.<sup>[2,11,12,15]</sup>

In the past years, significant effort has been directed towards the attachment of catalysts active in HER, OER or ORR to metallic or semiconducting electrodes with the goal of performing the processes in an electrocatalytic fashion.[21] Moreover, the functionalized electrodes were studied with electrochemistry and surface spectroscopy in order to obtain mechanistic information on the investigated reactions. Regarding nitrogen fixation, attachment of the FeMoco of nitrogenase to a cathode with the goal of electrocatalytically synthesizing NH<sub>3</sub> from N<sub>2</sub> has been reported.<sup>[22]</sup> Similar studies with synthetic transition metal complexes binding and activating N2 are, however, scarce.[23-25] Nevertheless, attachment of dinitrogen complexes to metallic surfaces could provide significant advantages; i.e., it may lower the activation energy required for the conversion of N<sub>2</sub> to ammonia in a sequence of protonation and reduction steps. Moreover, it might enable alternative pathways, e.g., the reaction of N<sub>2</sub> with H<sub>2</sub> under ambient conditions.<sup>[26,27]</sup>

In the literature a number of strategies to fix transition metal complexes (often porphyrins or related systems) to surfaces have been described (fig. 1).<sup>[28]</sup> In the most direct fashion, the molecule is physisorbed to the surface by deposition from solution or, after evaporation of the bulk material, from the gas phase (fig. 1a).<sup>[29,30]</sup> This approach potentially entails some problems. Firstly, due to the direct contact between the metal complex and the surface some complexes may decompose.<sup>[31]</sup> Depending on the nature of

### WILEY-VCH



Scheme 1: Synthesis of the tridentate pincer ligand Me-PN<sup>3</sup>P<sub>TMS</sub> (2).

the complex, the interaction between the surface and the metal complex may be weak or sensitive to changes in its electronic and geometric structure.<sup>[32–34]</sup> In the case of porphyrins, e.g., the interaction of the complex with the surface is reduced upon binding of a ligand *trans* to the surface.<sup>[33]</sup> This is avoided if the molecules are covalently attached to the surface, e.g. by a thiol function to Au(111) (fig. 1b).<sup>[35,36]</sup> In this case, however, the orientation of the complex with respect to the surface is less defined. The complex may also be "clicked" to a self-assembled monolayer (SAM) which has been deposited first onto the metal surface.<sup>[24,37–40]</sup> The aliphatic spacer groups thereby lead a large separation between the surface and the head group. Consequently, the electronic influence of the metallic substrate is distinctly decreased compared to the direct deposition.<sup>[40]</sup>

Another useful and elegant approach to surface attachment molecules.[41-48] is based on platform The TATA (triazatriangulenium) platform, developed by LAURSEN et al.[49], allows the fixation and orientation of functional molecules on a metallic substrate. The adsorbed molecules thereby form highly ordered monolayers.<sup>[41]</sup> The advantage of the TATA platform compared to the thiol concept is the increased lateral distance between the surface-adsorbed molecules, suppressing intermolecular interactions which may affect the functionality of the molecule.<sup>[50]</sup> Furthermore, the coupling unit between the platform and the metal complex can be modified in order to tune the interaction between the metallic substrate and the complex.<sup>[42,51]</sup> Finally, the molecule attached to the platform is strictly perpendicular to the surface, rendering this concept amenable to the application of Infrared-Reflection-Absorption-Spectroscopy (IRRAS) in order to obtain electronic and structural information.[52,53]

In order to elucidate the influence of a metallic substrate on the electronic structure of surface-adsorbed transition metal complexes activating small-molecule ligands like  $N_2$  or CO, we herein investigate a molybdenum(0) triscarbonyl complex supported by a tridentate PN<sup>3</sup>P pincer ligand which is linked via an alkyne spacer to a TATA platform, allowing its deposition to metallic surfaces (fig. 2). Compared to complexes of the isoelectronic dinitrogen ligand, carbonyl complexes are more stable. Furthermore, C-O stretches exhibit high IR-activities and are therefore well suited for investigations using surface vibrational spectroscopy. The new TATA-functionalized  $[Mo(CO)_3(Me-PN^3P_{TATA})]$  complex (1) is investigated in the solid state, in solution and adsorbed on a gold(111) surface using a range of spectroscopic and analytical methods. The electronic effect of the metallic substrate on the molybdenum carbonyl complex is evaluated, and the implications on the reactivity of small-molecule ligands bound to surface-adsorbed transition metal complexes are considered.

### **Results and Discussion**

#### Synthesis and characterization of [Mo(CO)<sub>3</sub>Me-PN<sup>3</sup>P<sub>TATA</sub>] (1) in solution and the bulk

#### Synthesis of the PN<sup>3</sup>P ligand and [Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TMS</sub>)] (3)

It has been shown in previous studies by HAUPT *et al.*<sup>[54]</sup> and KIRCHNER *et al.*<sup>[55]</sup> that PN<sup>3</sup>P ligands can coordinate in a meridional fashion to metal centers *via* two phosphine donors and the pyridine unit. In order to couple the PN<sup>3</sup>P ligand to the TATA platform the central pyridine ring has been functionalized in 4-position with a trimethylsilyl-protected acetylene moiety. The corresponding Me-PN<sup>3</sup>P<sub>TMS</sub> ligand (2) was obtained by the synthetic route shown in Scheme 1. Metalation of 2 afforded the Mo(0) carbonyl complex [Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TMS</sub>)] (3), which in turn was connected with the TATA platform, leading to the target complex 1 (see below, Scheme 2).



Scheme 2: Synthesis of  $[Mo(CO)_3(Me-PN^3P_{TMS})]$  (3) and  $[Mo(CO)_3(Me-PN^3P_{TATA})]$  (1).

For the synthesis of ligand **2** the hydroxyl group in 4-position of chelidamic acid was first substituted by bromide using PBr<sub>5</sub> (Scheme 1). In the course of this reaction the carboxylic acid groups were esterified yielding the diethyl ester **4**.<sup>[56]</sup> Employing

### **FULL PAPER**

hydrazine hydrate the dihydrazide **5** was generated which was subsequently converted into the diazide.<sup>[56]</sup> *Via* a CURTIUS rearrangement and the addition of *tert*-butanol the dicarbamate **6** was obtained.<sup>[56]</sup> As a next step the dicarbamate **6** were deprotonated by sodium hydride and methylated using iodomethane. The TMS-protected ethynyl group was introduced by a Sonogashira cross coupling. Due to the lability of the TMS unit towards acids the Boc protecting group was cleaved by ZnBr<sub>2</sub> in dichloromethane.<sup>[57]</sup> Finally, the diphenylphosphine groups were introduced with chlorodiphenyl-phosphine in the presence of *n*-BuLi.<sup>[58]</sup>

#### Crystal structure of [Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TMS</sub>)] (3)

Reaction of ligand **2** with the precursor  $[Mo(CO)_3(CH_3CN)_3]$ afforded the Mo(0) carbonyl complex  $[Mo(CO)_3(Me-PN^3P_{TMS})]$  (**3**). Crystals of **3**·2 CH<sub>3</sub>CN suitable for single crystal X-ray determination were obtained by slow evaporation of the solvent (acetonitrile). The structure of **3** is shown in figure 3.



Figure 3: Crystal structure of [Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TMS</sub>)] (3) (left: side view) right: top view).

Selected bond distances and angles are collected in table 1. The complex **3** is located on a 2-fold rotation axis. The molybdenum center is coordinated in a distorted octahedral fashion by the Me-PN<sup>3</sup>P<sub>TMS</sub> pincer ligand (**2**) and the three carbonyl groups. The P1-Mo-P1A angle amounts to 156.4 ° and is distinctly smaller than 180 °. Conversely, the t wo equatorial CO ligands are inclined towards the axial carbonyl ligand; i.e., the C31-Mo-C31A angle (169.1 °) is also reduced from 180 °. The experimental bond lengths reflect the bonding properties of the donor atoms obtained from DFT (SI, fig. S 14). The Mo-N bond (2.240 Å) between the metal center and the pyridine N is elongated compared to related Mo-PNP compounds in the literature (2.182 Å).<sup>[2]</sup> This goes along with a loss of  $\pi$ -

Table 1. Selected bond lengths [Å] and angles [] of [Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TMS</sub>)] (3)

Mo(1)-C(32)	1.968(3)	C(32)-Mo(1)-P(1)	101.809(12)
Mo(1)-C(31)	2.023(2)	C(32)-Mo(1)-P(1A)	101.809(12)
Mo(1)-C(31A)	2.023(2)	C(C31A)-Mo(1)-P(1)	93.71(6)
Mo(1)-N(1)	2.2400(19)	C(31A)-Mo(1)-P(1A)	88.52(6)
Mo(1)-P(1)	2.3750(5)	C(31)-Mo(1)-P(1)	88.52(6)
Mo(1)-P(1A)	2.3750(5)	C(31)-Mo(1)-P(1A)	93.71(6)
O(1)-C(31)	1.145(3)	C(32)-Mo(1)-N(1)	180.0
O(1A)-C(31A)	1.145(3)	C(31)-Mo(1)-N(1)	95.44(6)
O(2)-C(32)	1.144(4)	C(31A)-Mo(1)-N(1)	95.44(6)
		N(1)-Mo(1)-P(1)	78.191(12)
C(32)-Mo(1)-C(31)	84.56(6)	N(1)-Mo(1)-P(1A)	78.191(12)
C(32)-Mo(1)-C(31A)	84.56(6)	P(1)-Mo(1)-P(1A)	156.38(2)
C(31)-Mo(1)-C(31A)	169.11(12)		

backbonding. As a consequence  $\pi$  backbonding between molybdenum and the axial carbonyl ligand (C32) is increased, causing a shortening of the Mo-C32 bond (1.968 Å) compared to the bond lengths between molybdenum and the equatorial carbonyl ligands ( $\approx 2.023$  Å). In spite of these electronic differences the C-O distances within the carbonyl ligands differ only slightly: whereas the C<sub>eq</sub>-O<sub>eq</sub> bond lengths are 1.145 Å (C31-O1) and the C<sub>ax</sub>-O<sub>ax</sub> bond length is 1.144 Å. Due to the methyl residues at the amine N atoms the rotation of the phenyl rings is sterically restricted. As a result the Mo(CO)<sub>3</sub>(PPh<sub>2</sub>) fragment (fig. 3, right) exhibits C<sub>2</sub> symmetry (*vide supra*).

#### Synthesis of [Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TATA</sub>)] (1)

The key step in the synthesis of the target molecule was the coupling between the alkyne function and TATA platform. A common strategy to functionalize the TATA unit is the reaction of an unprotected, anionic ethynyl residue with the cationic platform.<sup>[59]</sup> The alkyne functionality serves as linker between the TATA molecule and the desired functional unit (in our case the metal complex). We started our investigation using the related ligand H-PN<sup>3</sup>P<sub>TMS</sub> which has protons instead of methyl residues at the amine units. First attempts to couple this ligand to "octyl-TATA" (i.e., a TATA platform with octyl substituents)[41] were unsuccessful. This negative result most probably is due to the protons at the secondary amine units. In the presence of an excess of KOH (which is necessary to eliminate the TMS protecting group) the secondary amine groups may become deprotonated. To prevent this side reaction we introduced methyl groups into the PN<sup>3</sup>P<sub>TMS</sub> ligand.<sup>[58]</sup> However, attempts to couple this ligand to the TATA platform using KOH failed as well. Using NMR spectroscopy we determined that potassium hydroxide cleaves the N-P bond instead of exclusively eliminating the protecting group. To ensure that the ligand remains intact during the reaction we decided to coordinate the ligand first to the molybdenum carbonyl precursor and connect the complex to the octyl-TATA platform afterwards. In this way, the phosphine units are protected by coordination to the molybdenum center.<sup>[60]</sup> An additional advantage of this approach is the fact that it avoids a metalation of surface-deposited ligands which may be associated with further problems. Following this strategy, the TMS protecting





group could easily be removed *in situ* within one hour using KOH without a decomposition of the complex or ligand, respectively. After the addition of octyl-TATA\*BF<sub>4</sub> the reaction mixture was stirred for another 75 min. The target compound could be obtained after purification via column chromatography using basic alumina under air. The same reaction using the complex [Mo(CO)<sub>3</sub>(H-PN<sup>3</sup>P<sub>TMS</sub>)] (crystal structure is shown in fig. S 13) and the octyl-TATA platform failed. This result underscores the necessity of the methyl substituents at the amine groups.

The new complex [Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TATA</sub>)] (1) was first investigated in the bulk and in solution. The <sup>13</sup>C-NMR spectrum of 1 is shown in figure 4. Using DEPT-135 and 2D correlation NMR techniques all resonances could be located and assigned to the respective carbon atoms. In particular, the meridional coordination geometry around the Mo(0) center is supported by <sup>13</sup>C-NMR spectroscopy. The axial CO (red, fig. 4) exhibits a signal at 226.2 ppm and gives rise to a triplet with a coupling constant of 5 Hz due to a coupling to the equivalent <sup>31</sup>P nuclei. The signal of the equatorial COs is located at 211.0 ppm and is split as well into a triplet with a coupling constant of 9.9 Hz. The molybdenum mediated coupling between the equatorial <sup>13</sup>COs and the <sup>31</sup>P nuclei is twice as large as the coupling between the axial <sup>13</sup>CO and the phosphorus atoms because of a better overlap of the Mod-orbitals and the orbitals of the CO and PPh<sub>2</sub> units in the equatorial plane.<sup>[61]</sup> In contrast, the <sup>13</sup>C-<sup>31</sup>P coupling could not be observed in the <sup>31</sup>P-NMR spectrum. Consequently, the two phosphorus nuclei give rise to a singlet at 133.0 ppm.

Complex 1 was further investigated by infrared and Raman spectroscopy. Vibrational spectroscopy is particularly useful to monitor the activation of small molecules coordinated to transition metal centers. The IR (top) and Raman (bottom) spectra of 1 are shown in figure 5. The first coordination sphere of the molybdenum center comprises the three CO ligands, two phosphorus atoms and one pyridine nitrogen. The phenyl rings of the phosphine units can rotate freely at room temperature; therefore, the complex exhibits effective  $C_{2v}$  symmetry. As expected for this point group, three carbonyl bands are observed in the IR spectrum. The totally symmetric A<sub>1</sub>(1) vibration, in which all three carbonyl ligands oscillate in phase, is located at 1964 cm<sup>-1</sup> (fig. 5, blue) in the IR and Raman spectrum. A second A<sub>1</sub> vibration (A<sub>1</sub>(2)), located at 1840 cm<sup>-1</sup>, (fig. 5, green), is the outof-phase combination of a symmetric stretch of the equatorial CO ligands and the stretch of the axial CO ligand. The intensity in the Raman spectrum is weak compared to the signal of the  $A_1(1)$ vibration. Furthermore, this signal is broadened due to overlap with the B1 vibration. The two vibration bands can be resolved in the IR with the A1(2) and the B1 modes being located at 1840 and 1862 cm<sup>-1</sup>, respectively (fig. 5, green and red). The latter vibration is characterized by the antisymmetric stretching motion of the equatorial CO ligands. Although the A1(2) and B1 vibrations are group-theoretically Raman-allowed, their Raman intensity is weak since, due to their antisymmetric character, there is no change in polarizability along the respective vibrational coordinate. Taken together, the results of vibrational spectroscopy indicate an activation of the carbonyl ligands compared to free carbon monoxide (2143 cm<sup>-1</sup>).<sup>[62]</sup> The intense peak in the Raman spectrum at 1589 cm<sup>-1</sup> is assigned to a symmetric C-C stretching vibration of the pyridine ring whereas the peak at 2205 cm<sup>-1</sup> is

associated with the stretching vibration of the alkyne group that is IR-inactive.



Figure 5: Left: IR und Raman spectra of [Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TATA</sub>)] (1). Right: Illustration of the observed CO vibrations. The Raman data were multiplied with the factor 15.

# Deposition and characterization of monolayers of $[Mo(CO)_3Me-N^3P_{TATA}]$ @ Au(111)

After synthesizing the novel molybdenum(0) complex containing the Me-PN<sup>3</sup>P ligand (2), connecting the [Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TMS</sub>)] complex (3) to the octyl-TATA platform and characterizing the resulting complex 1 in solution and the bulk, 1 was deposited on Au(111). The resulting monolayer was investigated using a range of surface-spectroscopic and -analytical methods.

#### STM measurements of [Mo(CO)<sub>3</sub>Me-PN<sup>3</sup>P<sub>TATA</sub>]@Au(111)

Scanning Tunneling Microscopy (STM) was employed to image the in-plane arrangement of the molecular adsorbates on Au(111) surfaces. In particular, the long-range order and intermolecular distances within monolayers of surface-adsorbed molecules were determined.<sup>[50,63]</sup> Previous studies revealed that inert gold substrates are well suited for the deposition of TATA derivatives.<sup>[42,43]</sup> Following the procedures in these studies, monolayers of [Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TATA</sub>)] (1) were prepared by immersing an Au(111) substrate in a toluene solution of 1 for 5-10 minutes.



Figure 6: STM image (35 x 35) nm<sup>2</sup> of  $[Mo(CO)_3(Me-PN^3P_{TATA})]$  (1) adlayer on Au(111). The pink spheres (right) represent the octyl chains of the TATA platform.

Investigation of the adsorbed  $[Mo(CO)_3(Me-PN^3P_{TATA})]$  (1) revealed highly ordered hexagonal monolayers on the Au(111) surface (fig. 6). The measured lattice constant of 1.25 (±0.05) nm

and the angles between the rotational domains are in good agreement with previous STM results of different octyl-TATA derivatives and correspond to a commensurate ( $\sqrt{19} \times \sqrt{19}$ ) *R*23.4° superstructure.<sup>[50]</sup> The intermolecular distance of 1.25 ± 0.05 nm and hexagonal superstructure thus indicate that the octyl side chains dominate the organization process on surface. Thus, in contrast to other TATA derivatives with sterically demanding central substituents, the phenyl units of the attached molybdenum complex have no influence on the lateral organization of the functionalized TATA molecules on the surface.<sup>[59]</sup>

#### XPS measurements of [Mo(CO)<sub>3</sub>Me-PN<sup>3</sup>P<sub>TATA</sub>]@Au(111)

In order to check whether the  $[Mo(CO)_3(Me-PN^3P_{TATA})]$  complex (1) was deposited intactly and without contaminations on Au(111) X-ray photoelectron spectroscopy (XPS) was employed. The resulting XP spectra are given in figure 7. The major signals shown in the survey spectrum (fig. 7a) are the Au 4f lines at 84.0 eV and 87.5 eV. Furthermore, the Au 3d signals at 335.0 eV and 352.5 eV are clearly visible as well as the C 1s peak at 284.5 eV. Based on the survey spectrum the N 1s signal is identified at 399 eV.

To determine the binding energies of the different species located in the N 1s, P 2p and Mo 3d signals, high resolution spectra of the different regions with acquisition times up to one hour were measured. The C 1s spectrum (fig 7b) contains three signals. The most prominent signal at 284.7 eV (blue trace) reflects the aliphatic and aromatic carbon atoms connected among each other. A smaller signal at 285.5 eV (red trace) can be assigned to the carbon atoms which are bonded either to nitrogen or phosphorus atoms. The third species (green trace) corresponds to the C atoms of the C-O ligands.<sup>[64]</sup> Importantly, the ratio of the relative intensities (74:23:3) fits to the values derived from the molecular composition (74:22:4). Considering the high resolution N 1s spectrum (fig 7c) three species can be located in the main signal. The one with the highest intensity (blue trace) at 399.6 eV can be assigned to nitrogen atoms directly connected to carbon atoms representing the nitrogen atoms of the TATA platform. The signal at 400.4 eV (green trace) refers to the



Figure 7:Survey (a), C 1s (b), N 1s (c), Mo 3d (d) and P 2p (e) XP spectra of a monolayer of  $[Mo(CO)_3(Me-PN^3P_{TATA})]$  (1) on Au(111).

nitrogen atom of the pyridine. At lower energy, 398.7 eV (red trace), a signal of the amine nitrogen atoms of the Me-PN<sup>3</sup>P ligand moiety can be observed. Again, the ratio of the relative intensities (50:33:17) conforms to the values (50:33:17) calculated from the elemental composition.

The Mo 3d spectrum (fig. 7d) contains only one doublet at 227.4 eV and 230.5 eV with a characteristic splitting of 3.1 eV (38:62). Such binding energies are typical for Mo(0) complexes with phosphine ligands.<sup>[65]</sup> Another doublet is found in the P 2p spectrum (fig. 7e) at 132.8 eV and 131.5 eV with the typical splitting of 1.3 eV (65:35). This signal corresponds to the phosphine species of the Me-PN<sup>3</sup>P-pincer ligand. In conclusion, the XP-spectra confirm the presence of a monolayer of the [Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TATA</sub>)] complex (1) in high purity and without any oxidized species.

#### NEXAFS measurements of [Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TATA</sub>)]@ Au-(111)

NEXAFS spectra were measured at the carbon and nitrogen Kedges for monolayers of [Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TATA</sub>)] (1) on Au(111) single crystals. The C K-edge spectrum, shown in figure 8a, exhibits two π\* resonances which can be found in the spectrum derived from DFT (fig. 8, bottom) as well. Using this calculation the first resonance at 285.4 eV is assigned to a C 1s to  $\pi^*$ transition of the phenyl groups and the pyridine moiety of the Me-PN<sup>3</sup>P ligand backbone. It is literature-known that pyridine (285.6 eV) and alkyne (286.0 eV) carbons give rise to a resonance at these energies.<sup>[66,67]</sup> The contribution of the pyridine and alkyne unit to this resonance is distinctly smaller than the contribution of the PPh<sub>2</sub> carbons. Consequently, the small shoulder at 285.9 eV is assigned to the pyridine and alkyne carbons. This also accounts for the missing angular dependence, as the phenyl groups of the ligand are freely rotatable and show no preferred orientation. The calculations show that the CO ligands also have a small contribution to this resonance at 285.4 eV. The second  $\pi^*$ resonance located at 289.1 eV contains transitions of the Me-PN<sup>3</sup>P ligand and the TATA platform. At higher binding energies (293.6 eV) the C 1s-to-σ\* transitions can be observed. The N Kedge NEXAFS spectrum (fig. 8b) shows three resonances. Based on the DFT calculations and former studies on TATA systems the  $\pi^*$  resonance at 402.4 eV are assigned to the N 1s-to-LUMO transition of the TATA nitrogen atoms.[68] Importantly, this resonance exhibits a significant angular dependence with



**Figure 8**: Normalized NEXAFS spectra of a monolayer of  $[Mo(CO)_3(Me-PN^3P_{TATA})]$  (1) on Au(111) at different angles (30°, 55°, 70°, 90°) and the calculated NEXAFS data (shifted by +10.7 eV (C) and +12.6 eV (N)) with the contributions of the different subunits summarized over all angles: a) C K-edge spectrum; b) N K-edge spectrum.

10.1002/chem.201800911

# FULL PAPER

vanishing intensity at 90°. This result confirms the parallel orientation of the TATA platform to the surface and has also been observed in previous investigations.<sup>[50]</sup> The  $\pi^*$  resonance at 401.2 eV is of low intensity and corresponds to the amines of the ligand backbone. The intense  $\pi^*$  resonance at 399.1 eV corresponds to the pyridine nitrogen atom. Suprisingly, it only exhibits a a very weak angular dependence. This transition was therefore investigated in more detail using DFT. As can be seen in figure 9 the target orbitals of the dominant transitions involving this atom are close in energy and strongly delocalized over the molybdenum center and the ligands. The angular dependence of the pyridine  $\pi^*$  resonance thus almost disappears. In conclusion, the measured NEXAFS spectra can be well understood with the help of DFT calculations.



Figure 9: Contour plots of the LUMO, LUMO+1, LUMO+3, LUMO+6 of  $[Mo(CO)_3(Me-PN^3P_{TATA})]$  (1) with orbital energies given as differences to the LUMO.

#### IRRAS measurements of [Mo(CO)3Me-PN3PTATA]@Au(111)

Besides the commonly applied surface spectroscopic methods STM, XPS and NEXAFS, IRRA spectroscopy was employed to investigate [Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TATA</sub>)] adsorbed on aold (1@Au(111)). Intensities of around 10<sup>-3</sup> absorbance units reflect the formation of a monolayer on Au(111) (fig. 10).<sup>[52]</sup> To determine the influence of the gold substrate on the activation of the carbonyl ligands the measured IRRA spectrum was compared to bulk and computed IR spectra. The calculated bulk and IRRA spectra look very similar to the measured IR spectra (fig. 10). Consequently, the bands appearing in the measured spectra could be assigned to specific vibrational modes. Note that differences in relative intensities of the bands in the bulk IR and IRRA spectra are caused by the surface-selection-rule of IRRAS.<sup>[53]</sup> In this way, precise information about the orientation of molecules to the surface are accessible. Thereby it is of great advantage that the carbonyl ligands of 1 exhibit intense IR bands. Because of the



Figure 10: Computed and measured vibrational spectra of  $[Mo(CO)_3(Me-PN^3P_{TATA})]$  (1) in bulk material and adsorbed on Au(111).

better signal-to-noise ratio the surface IR spectrum of 1@Au(111) was measured using PM-IRRAS. Thus the signals in the fingerprint region are also better resolved. The absorption band at 1087 cm<sup>-1</sup> in the IRRA spectrum is associated with C-H deformation vibrations of the octyl side chains. In the IRRA spectrum, this vibrational mode shows a higher relative intensity than in the bulk IR spectrum because of the free mobility of the side chains although the molecule is adsorbed on the surface. In the region between 1400 cm<sup>-1</sup> and 1530 cm<sup>-1</sup> different aromatic (TATA platform), aliphatic C-H rocking and bending vibrations are located. These vibrations are of low intensity in the IRRA spectrum as the transition dipole moments are mostly parallel to the surface. The aromatic deformation vibrations of the phosphine phenyl groups correspond to the band at 1587 cm<sup>-1</sup> in the IRRA spectrum. This absorption band shows a high relative intensity due to the fact that the phenyl units can rotate freely. For this reason there are different conformers with transition dipole moments of the respective vibration perpendicular to the surface.

In the region of the carbonyl stretching vibrations three bands of the CO ligands of 1 can be detected in the bulk IR spectrum (vide supra). The A<sub>1</sub>(1) mode at 1964 cm<sup>-1</sup> shows a higher relative intensity in the IRRA spectrum than in the bulk IR as the transition dipole moment of this vibration is exactly perpendicular to the surface. This behavior is also shown in the calculated IR and IRRA spectra. The B1 vibration is located at 1862 cm<sup>-1</sup> in the bulk IR spectrum. The transition dipole moment of this vibration mode is nearly parallel to the surface. Therefore, the relative intensity of this mode in the IRRA spectrum (1893 cm<sup>-1</sup>) is drastically decreased in comparison to the bulk IR. The  $A_1(2)$  vibration, finally, is observed at 1876 cm<sup>-1</sup> in the IRRA spectrum. The obtained relative intensity in the IRRA spectrum is higher than in the bulk IR spectrum. Thus, the transition dipole moment of this mode is perpendicular to the surface. Consequently, the perpendicular orientation of the metal complex 1 with respect to the surface is proven. However, the frequency difference of the B<sub>1</sub>/A<sub>1</sub>(2)-CO stretches is significantly smaller in the IR spectrum calculated for 1. Consequently, only one band appears in the simulation (fig. 10). Nevertheless, the detailed vibrational analysis (Table S 7.) reveals that both vibrational modes are present in the calculated spectra. The frequencies of

the carbonyl stretching vibrations in the free and the surfaceadsorbed complex **1** are collected in table 2.

Table 2. Comparison of the CO absorption bands in IRRAS and Bulk IR.

Band	Bulk IR/cm <sup>-1</sup>	IRRAS/cm <sup>-1</sup>	Shift cm <sup>-1</sup>
A <sub>1</sub> (1)	1964	1972	8
B <sub>1</sub>	1862	1893	31
A <sub>1</sub> (2)	1840	1876	36

In order to account for the observed frequency shifts of the CO vibrations a possible transfer of electronic charge between the gold substrate and adsorbed metal complex has to be considered. A few examples in literature reveal an electron donating behavior from the gold towards the deposited transition metal complex.<sup>[32,33,69]</sup> The opposite effect, corresponding to an electron withdrawing behavior of the gold substrate, would lead to a decreased electron density at the adsorbed molecules. The results of the vibrational spectroscopic investigations in the present study in fact indicate an electron withdrawing behavior of the gold as the CO stretching frequencies of the adsorbed complex shift to higher energies.

The electron withdrawing character of the gold substrate with respect to a Mo(0) carbonyl complex can be reproduced by DFT considering Löwdin partial charges; the results are collected in table 3. As evident from the bottom line of table 3, 1.64 charge units are transferred from  $[Mo(CO)_3(Me-PN^3P_{TATA})]$  (1) to the gold surface.

Table 3. Löwdin partial charges of  $[Mo(CO)_3(Me-PN^3P_{TATA})]$  (1) and  $[Mo(CO)_3(Me-PN^3P_{TATA})]$  @Au(111).

	1	1@Au(111)	Δ
Мо	-1.76	-1.67	0.09
СО	0.45	0.53	0.08
Me-PN <sup>3</sup> P	1.25	1.44	0.19
ΤΑΤΑ	0.06	1.35	1.29
sum	0	1.64	1.64

To further investigate the changes in electronic structure upon surface adsorption we performed an energy decomposition analysis (EDA)<sup>[70]</sup> for the binding between the two fragments complex **1** and Au surface. To this end total binding energy  $\Delta E$  between the fragments (about -40 kcal/mol, i.e., between typical bond dissociation energies and H-bonding) is decomposed according to:

$$\Delta E = \Delta E_{prep} + \Delta E_{steric} + \Delta E_{orb}$$

 $\Delta E_{prep}$  consists of the energy necessary to promote the fragments from their relaxed state to their geometry and electronic state in the complex and  $\Delta E_{steric}$  corresponds to a so-called steric repulsion term consisting of classical electrostatic interactions and nonclassical Pauli repulsion. The orbital interaction energy  $\Delta E_{orb}$ , finally, is recognized to reflect covalent bonding. It can be decomposed into contributions from natural orbitals for chemical valence (NOCV).<sup>[70]</sup> These are made up by donor-acceptor pairs of eigenvectors associated with an eigenvalue reflecting the energy contribution of each pair. Note, however, that these

eigenvalues suffer from basis set superposition errors (BSSE). For  $\Delta E$  this was corrected with a counterpoise correction which unfortunately was not possible for the  $\Delta E_{orb}$  contribution. Nonetheless, the leading pair of eigenvectors can be depicted as deformation density as in figure 11 and showcases the regions of electron accumulation and depletion upon interaction of the fragments. It can be seen that the net electron density on (1) is decreased notably on the Mo center and its vicinity whereas the electron density on the gold surface increases in a delocalized fashion. The majority of the deformation density, however, mostly shows electron depletion on the TATA platform (not shown here). This is consistent with the computed partial charges listed in table 3 which indicate that charge transfer predominantly occurs between the platform and the surface. Nonetheless it should be noted that a non-negligible amount of charge is taken from the Mo atom under participation of metal d-orbitals as is shown by the NOCV analysis. This indicates electronic coupling between the gold surface and the Mo central atom and accounts for the electronic and vibrational structure changes observed upon surface adsorption of complex 1.



### WILEY-VCH

Figure 11: Leading term of EDA-NOCV of 1@Au(111) depicted as deformation density. Regions of electron depletion and accumulation are shown in blue and red, respectively.

Looking closer at the bulk IR and IRRAS data of complex 1, it becomes apparent that the three carbonyl stretching modes exhibit distinctly different frequency shifts if 1 is deposited on the surface; i.e., whereas the antisymmetric B1 and A1(2) modes shift by 31 - 36 cm<sup>-1</sup> to higher energies, the totally symmetric  $A_1(1)$ stretch only exhibits a shift of 8 cm<sup>-1</sup> (Table 2). Obviously the net flow of charge from the Mo(0) center to the Au substrate affects the three vibrations differently. figure 12 describes a possible explanation for this observation: charge depletion on the metal center leads to an overall shift of all three bands to higher energy, leading to an overall shortening of C-O bond distances and, thus, to a global positive frequency shift. We associate this shift with a change in "static" activation upon deposition of the metal complex on the Au(111) surface (fig. 12, top and middle). A second effect modulating vibrational frequencies derives from a charge flow from the metal into the ligand  $\pi^*$  orbitals when the C-O bonds are elongated. This (dynamic) effect flattens the potential curve, reduces the corresponding force constant and thus acts to lower the CO-stretching frequency ("dynamic" activation). Importantly, it only comes into play if the vibrational coordinate is associated with a net flow of charge between the metal and the ligands. This, however, only applies to the totally symmetric  $A_1(1)$  vibration. For the other two vibrations, only a redistribution of charge density occurs along the corresponding nuclear coordinate; i.e., between the two equatorial ligands (B1) or between the equatorial ligands

#### 10.1002/chem.201800911

### WILEY-VCH

### **FULL PAPER**



Figure 12: Influence of static and dynamic activation on the carbonyl stretching modes of  $[Mo(CO)_3(Me-PN^3P_{TATA})]$  (1) (@Au(111)).

and the axial ligand ( $A_1(2)$ ). Thus, only the  $A_1(1)$  mode is susceptible to a change in dynamic activation. From the reduced positive frequency shift of the  $A_1(1)$  mode we assume that the dynamic activation in the surface-deposited complex **1** is higher than in the free complex and thus acts against the global positive shift due to the change in static activation (fig. 12, bottom). The increase in dynamic activation can in turn be explained by the fact that the metal complex is coupled to a metallic substrate; i.e., although this substrate statically withdraws electron density from the complex, it can dynamically back-donate electron density to this complex *via* the linker unit if the ligands are elongated.

Figure 13 shows the C-H region of the computed and measured IR spectra. The aliphatic C-H stretching vibrations are located at 2960 cm<sup>-1</sup>, 2929 cm<sup>-1</sup> and 2856 cm<sup>-1</sup> in the IRRA spectrum. Because of the free mobility of the octyl side chains on the surface (*vide supra*), the shape of the aliphatic C-H region is similar to that of the bulk IR. The bands at 3076 cm<sup>-1</sup> and 3066 cm<sup>-1</sup> can be assigned to aromatic C-H stretches of the phosphine phenyl rings. In conclusion the results of vibrational spectroscopy support the STM, XPS and NEXAFS measurements.





#### Conclusion

Establishing a new approach to small molecule activation, a molybdenum(0) triscarbonyl complex supported by a Me-PN<sup>3</sup>P ligand was synthesized, connected to a TATA platform, and characterized in solution, bulk material as well as adsorbed on Au(111). Applying different surface-spectroscopic methods (XPS, NEXAFS, IRRAS) the zerovalent oxidation state of the molybdenum center and the perpendicular orientation of the complex with respect to the surface were demonstrated. Importantly, the IRRAS measurements revealed a distinct influence of the gold substrate on the activation of the carbonyl ligands. Even though the static activation was found to be smaller on the surface than in bulk material due to the electronwithdrawing character of the Au substrate, a dynamic backtransfer of electronic charge from the substrate to the Mo complex could be evidenced, enhancing the (dynamic) polarizability of the metal center. The latter effect could become important in the case of chemical transformations (e.g., protonation reactions) involving ligands bound to surface-adsorbed complexes, lowering the activation energies associated with these processes.

### **Experimental Section**

#### General synthetic procedures

Commercially available starting materials and solvents were used as received. Water and oxygen sensitive reagents were handled in an M. Braun Labmaster 130 Glovebox under N<sub>2</sub>. Moisture and air sensitive reactions were carried out in dried solvents under N<sub>2</sub> atmosphere using Schlenk techniques. Dimethylacetamide was dried over molecular sieve (3 Å) under N<sub>2</sub>. NEt<sub>3</sub>, toluene, DCM and *n*-hexane were dried over CaH<sub>2</sub>, THF over LiAlH<sub>4</sub> under Ar and were distilled prior to use.

#### Column chromatography

Purification of crude products was performed using a flash chromatography Isolera One Spektra System (Co. Biotage). SNAP Ultra cartridges (spherical silica gel, HP-Sphere; 10 g, 25 g, 50 g) were used according to the amount of crude product (Co. Biotage). Depending in the  $R_f$  value of the product the flash chromatography was performed with a solvent gradient.

#### IR and Raman spectroscopy

IR spectra were recorded on a Bruker Alpha-P ATR-IR Spectrometer. Raman spectra were measured on a Bruker IFS 66 RA 106.

#### NMR spectroscopy

The <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded in deuterated solvents on a Bruker Avance 400 Puls Fourier Transform spectrometer at 300 K and are referenced to the solvent. <sup>31</sup>P NMR spectra were referenced to H<sub>3</sub>PO<sub>4</sub> 85% ( $\delta$ (<sup>31</sup>P)=0 ppm) as substitutive standard.

#### Single crystal structure analysis

Data collections were performed at 170 K using an imaging plate diffraction system (IPDS-2 from STOE & CIE) using Mo-K  $\alpha$ 

radiation. Structure solutions were performed with SHELXT and structure refinements were done against F<sup>2</sup> using SHELXL-2014.<sup>[71,72]</sup> A numerical absorption correction was applied using programs X-RED and X-SHAPE of the program package X-Area.<sup>[73]</sup> All non-hydrogen atoms were refined anisotropically. The C-H hydrogen atoms were positioned with idealized geometry and were refined isotropic with  $U_{iso}(H) = 1.2 U_{eq}(C)$  (1.5 for methyl H atoms) using a riding model. The complex is located on a 2-fold rotation axis and therefore, the trimethylsilyl group is disordered in two positions because of symmetry. The asymmetric unit also contain two acetonitrile solvate molecules. For the figures the CYLview software was used.<sup>[74]</sup> CCDC-1824953 (3) and CCDC-1824954 ([Mo(CO)<sub>3</sub>(H-PN<sup>3</sup>P<sub>TMS</sub>)]·NCCH<sub>3</sub>) the contain supplementary crystallographic data for this paper. These data can be obtained free charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data\_request/cif.

#### Elemental analyses

Elemental analyses were performed using a Euro Vector CHNS-O-element analyzer (Euro EA 3000) or a vario MICRO cube (Co. Elementar Analysensysteme).

#### Gold Substrates

Glass substrates with a 50 Å titanium adlayer and a 200 nm evaporated gold film from EMF corporation (Ithaca, NY) were used for IRRAS measurements. STM, XPS and NEXAFS measurements were made with sputtered Au(111) single crystals.

#### Preparation of Monolayers

Monolayers of  $[Mo(CO)_3(Me-PN^3P_{TATA})]$  were prepared by immersing Au(111) substrates in 0.5 mM solutions of the respective compound in toluene (Uvasol, Merck) at room temperature. After 5-10 mins of immersion the sample was removed from the solution, rinsed with toluene and dried in a stream of nitrogen gas.

#### <u>STM</u>

STM measurements were performed with a PicoPlus STM (Agilent, Inc., Santa Clara, USA) at room temperature with mechanically cut Pt/Ir (70:30) tips.

#### **IRRAS**

The surface adsorbed molecules were investigated by using a Bruker VERTEX 70 FT-IR spectrometer equipped with a Polarization Modulation Accessory (PMA) 50 unit (Bruker Optik GmbH, Ettlingen, Germany). This instrument allows recording IRRAS and PM-IRRAS data with a spectral range from 4000 down to 800 cm<sup>-1</sup>. IRRAS data were collected with a liquid nitrogen cooled MCT detector in a horizontal reflection unit for grazing incidence (Bruker A518). The sample chamber was purged with dry nitrogen before and during measurements. A deuterated hexadecane-thiol SAM on Au(111) was used as a reference for the background spectrum for conventional IRRA spectra. Each spectrum contains 2048 averaged spectra. A p-polarized beam at an incident angle of 80° to the surface normal was used for measurements. All spectra were recorded with 4 cm<sup>-1</sup> resolution. PM-IRRAS data were collected with the PMA 50 accessory using a liquid nitrogen-cooled MCT detector. The PEM maximum efficiency was set for the half-wave at 3000 cm<sup>-1</sup> for analysis of the area from 2000 cm<sup>-1</sup> to 1000 cm<sup>-1</sup>. All spectra were recorded with 4 cm<sup>-1</sup> resolution.

Processing of IRRAS and PM-IRRAS data was carried out using the OPUS software Version 6.5 (Bruker, Germany). Baseline correction of the resulting IRRAS data was performed by the rubber band method in an interactive mode. PM-IRRAS data were processed by the implicit removal of the Bessel function through manual baseline correction.

#### XPS & NEXAFS

The XPS and NEXAFS measurements were performed at the BESSY II synchrotron radiation facility using the PREVAC endstation at the beamline HE-SGM. The experimental station is equipped with a hemispherical VG Scienta R3000 photoelectron analyzer. The energy resolution E/DE of the beamline with 150 mm slits is 800. XP survey spectra were secured at 700 eV photon energy using an analyzer pass energy of 100 eV, whereas for the C 1s, Mo 3d and P 2p spectra the photon energy used was 350 eV with pass energy of 50 eV. For N 1s spectra the photon energy was at 500 eV with pass energy of 50 eV.

All spectra were acquired at normal electron emission. For determination of the relative composition of the TATA adlayers, the XP spectra were energy-corrected using the Au  $4f_{7/2}$  line at a binding energy of 84.0 eV as reference. Background correction was performed using a combination of a Shirley and a linear background for all signals. Peak fitting was performed using the program CASA XPS. The fitting parameter are shown in table S 6.

To correct for the photon flux of the NEXAFS measurements, all spectra were divided by the spectrum obtained for a freshly sputtered clean gold substrate and then edge-step normalized (using the average intensities for the C K-edge between 275  $\pm$ 0.5 eV and 320  $\pm$  0.5 eV and for the N K-edge between 395  $\pm$ 0.5 eV and 420  $\pm$ 0.5 eV as pre- and post-edge).

#### Computational Details

Throughout the whole study a reduced model of **1** was used with propyl instead of octyl moieties on the TATA platform to reduce turnover times.

The geometry optimizations and frequency calculations necessary for the simulation of the IRRA spectra were obtained with Gaussian09 Rev.D01.<sup>[75]</sup> Therefor the PBE0 hybrid DFA<sup>[76]</sup> was used as recommended for second row transition metal complexes in conjunction with the Ahlrichs def2-SVP basis set<sup>[77]</sup> and Grimme's D3 dispersion correction with Becke-Johnson damping (D3BJ).<sup>[78,79]</sup> Furthermore all calculations used the appropriate def2 effective core potential on molybdenum.<sup>[80]</sup> No imaginary frequencies above 5 cm<sup>-1</sup> were obtained which indicates a minimum. The IRRA spectrum was then simulated by only taking those components of the transition dipole moment vectors into account that are collinear to the backbone axis of the ligand which is assumed to be perpendicular to the surface.

Since the computation of the NEXAFS data was assumed to be mostly invariant to conformational changes the molecule was optimized in the gas phase with DFT in ORCA 4.0.1.<sup>[81,82]</sup> This was also used for the calculation of the NEXAFS spectra. For the optimization the GGA DFA BP86<sup>[83,84]</sup> was used with a def2-SVP basis set with dispersion correction (D3BJ) and the resolution of

# **FULL PAPER**

identity for additional speed.<sup>[85,86]</sup> With the optimized structures C-1s and N-1s-core to valence electronic spectra were calculated. This was done in the framework of TDDFT with the hybrid DFA B3LYP<sup>[87]</sup>, the def2-TZVPP basis set<sup>[77]</sup>, the RIJCOSX approximation<sup>[88]</sup> and fine numerical integration grids (grid6 and gridX6 in ORCA nomenclature). The orbital window from which electrons were to be excited was restricted to the 1s orbital of the atom of interest. Where necessary the orbital was previously localized with the Pipek-Mezey localization scheme.<sup>[89]</sup> On this atom the integral accuracy was increased and 80 roots with electric quadrupole contributions computed. This was repeated for every unique C and N atom in the molecule. Local symmetry was exploited when appropriate so not every single atomic spectrum had to be calculated. The influence of the C atoms from the TATA-octyl moieties missing in this study was included by assuming that they show the same spectral features as the central C atom in the propyl moiety. Consequently the atomic spectra of this atom were included multiple times to make up for the deficiency of the model. All the resulting atomic spectra were collected, scaled according to symmetry and summed up to yield the spectrum of the whole molecule.

Electronic structure calculations on the surface-adsorbed molecule were also conducted with ORCA and used the RPBE DFA<sup>[90]</sup> which was parameterized to yield improved adsorption and noncovalent interaction energies in conjunction with dispersion correction, a def2-SVP basis set and the RI approximation as above. The model was built from a hexagonal cut from an Au(111) surface slab with one surface layer and the propyl-substituted variant of **(1)**. The geometry optimization was conducted with the semiempirical GFN-xTB tight binding code.<sup>[91]</sup>

#### Syntheses

#### N,N'-Dimethyl-4-bromopyridine-2,6-di-tert-butyl-dicarbamate

(7) The synthesis was performed under nitrogen atmosphere. To a suspension of NaH (571 mg, 23.8 mmol) in dimethylacetamide (30 mL) di-*tert*-butyl (4-bromopyridine-2,6-diyl) dicarbamate (6) (4.00 g, 10.3 mmol) in dimethylacetamide (25 mL) was added at 0 °C. After stirring for 5 min at 0 °C and 60 min a t rt methyliodide (1.71 mL, 27.5 mmol) was added to the suspension. The reaction mixture was stirred for 16 h at rt. Afterwards ethyl acetate (150 mL) was added and the organic layer was washed with aqueous 10percent citric acid (100 mL), a saturated NaHCO<sub>3</sub> solution (100 mL) and brine (100 mL). The organic layer was dried over sodium sulfate and the solvent was evaporated under reduced pressure. The crude product was purified by automated column chromatography (*n*-hexane/ethyl acetate, 8-66 % ethyl acetate, R<sub>f</sub> = 0.55). The product was obtained as a yellow oil (4.00 g, 9.64 mmol, 94 %), which crystallized over time.

**Anal.** calcd for C<sub>17</sub>H<sub>26</sub>BrN<sub>3</sub>O<sub>4</sub>: C, 49.1; H, 6.3; N, 10.1. Found: C, 49.5; H, 6.3; N, 9.7.

<sup>1</sup>**H NMR** (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.68 (s, 2H, py  $H^{3.5}$ ), 3.35 (s, 6H, N(C*H*<sub>3</sub>)), 1.53 (s, 18H, C(C*H*<sub>3</sub>)<sub>3</sub>) ppm.

<sup>13</sup>**C NMR** (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 154.1$  (s, *C=O*), 153.2 (s, py  $C^{2.6}$ ), 133.3 (s, py  $C^4$ ), 116.0 (s, py  $C^{3.5}$ ), 81.8 (s, *C*(CH<sub>3</sub>)<sub>3</sub>, 33.9 (s, N(*C*H<sub>3</sub>)), 28.4 (s, C(*C*H<sub>3</sub>)<sub>3</sub>) ppm.

**IR** (ATR):  $\tilde{v} = 3151$  (w), 3002 (w), 2981 (m), 2933 (w), 1705 (ss), 1668 (w), 1558 (m), 1477 (w), 1464 (w), 1451 (w), 1419 (w), 1385 (s), 1365 (s), 1334 (s), 1269 (sh), 1268 (w), 1253 (m), 1197 (w), 1139 (ss), 1117 (ss), 1094 (m), 1040 (w), 1026 (m), 970 (m), 924 (w), 886 (m), 850 (m), 837 (s), 803 (m), 768 (s), 761 (m), 740 (m), 693 (w), 660 (m), 599 (m), 562 (m), 517 (w), 467 (w), 459 (w), 426 (w) cm<sup>-1</sup>.

#### *N*,*N*'-Dimethyl-4-((trimethylsilyl)ethynyl)pyridine)-2,6-di-*tert*butyl-dicarbamate (8)

The synthesis was performed under nitrogen atmosphere. To ditert-butyl-(4-bromopyridine-2,6-diyl)bis(methylcarbamate) (7) (2.00 g, 4.80 mmol), copper(I) iodide (190 mg, 998 µmol) and tetrakis(triphenylphoshine)palladium(0) (382 mg, 331 µmol) was added triethylamine (50 mL). Trimethylsilylacetylene (992 µL, 6.65 mmol) was added dropwise and the reaction mixture was stirred for 3 d under reflux. Afterwards the suspension was filtered through Celite and the filter cake was washed with THF. The solvent was evaporated under reduced pressure and the crude product was purified *via* automated column chromatography (cyclohexane/ ethyl acetate + 1% TEA, 3-30 % ethyl acetate, R<sub>f</sub> = 0.52). The product was obtained as light brown solid (1.84 g, 4.24 mmol, 88 %).

**Anal.** calcd for  $C_{22}H_{35}N_3O_4Si$ : C, 60.9; H, 8.1; N, 9.7. Found: C, 61.7; H, 8.1; N, 9.1.

<sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\overline{o}$  = 7.51 (s, 2H, py H<sup>3,5</sup>), 3.34 (s, 6H, N(CH<sub>3</sub>)), 1.53 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.23 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\overline{o}$  = 154.4 (s, C=O), 152.9 (s, py C<sup>2.6</sup>), 133.3 (s, py C<sup>4</sup>), 115.7 (s, py C<sup>3.5</sup>), 103.0 (s, C=C(Si(CH<sub>3</sub>)<sub>3</sub>)), 98.0 (s, C=C(Si(CH<sub>3</sub>)<sub>3</sub>)), 81.4 (s, C(CH<sub>3</sub>)<sub>3</sub>), 34.0 (s, N(CH<sub>3</sub>)), 28.5 (s, C(CH<sub>3</sub>)<sub>3</sub>), -0.09 (s, Si(CH<sub>3</sub>)<sub>3</sub>)) ppm.

**IR** (ATR):  $\tilde{v} = 2999$  (w), 2975 (m), 2931 (w), 2161 (w), 1701 (ss), 1667 (w), 1594 (m), 1545 (m), 1474 (m), 1458 (sh), 1448 (sh), 1426 (w), 1397 (s), 1392 (s), 1365 (m), 1338 (s), 1314 (m), 1247 (m), 1141 (sh), 1135 (ss), 1107 (sh), 1040 (w), 1024 (m), 1012 (w), 929 (m), 915 (m), 888 (m), 854 (sh), 840 (s), 726 (s), 727 (m), 701 (w), 657 (m), 608 (m), 589 (m), 483 (w), 460 (w), 422 (sh), 413 (w) cm<sup>-1</sup>.

# *N*,*N*'-Dimethyl-4-((trimethylsilyl)ethynyl)pyridine-2,6-diamine (9)

The synthesis was performed under nitrogen atmosphere. To ditert-butyl-(4-bromopyridine-2,6-diyl)bis(methylcarbamate) (8) (2.15 g, 4.96 mmol) and dry ZnBr<sub>2</sub> (9.74 g, 43.3 mmol) was added dichloromethane (40 mL). The suspension was stirred for 7 h under reflux and overnight at rt. Afterwards distilled water (20 mL) was added and the mixture was stirred for 1 h. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 30 mL).The combined organic layer was dried over MgSO<sub>4</sub> and the solvent was evaporated under reduced pressure. The crude product was purified by automated column chromatography (cyclohexane/ethyl acetate, + 1% TEA, 18-100 % ethyl acetate, R<sub>f</sub> = 0.47). The product was obtained as light brown solid (758 mg, 3.25 mmol, 65 %).

**Anal.** calcd for C<sub>12</sub>H<sub>19</sub>N<sub>3</sub>Si: C, 61.8; H, 8.2; N, 18.0. Found: C, 62.1; H, 8.1; N, 17.7.

<sup>1</sup>**H NMR** (400.1 MHz, CDCl<sub>3</sub>): δ = 5.80 (s, 2H, py  $H^{3.5}$ ), 4.30 (br q, <sup>3</sup>*J*=4.7 Hz, 2H, N*H*), 2.84 (d, <sup>3</sup>*J*=5.3 Hz, 6H, N(C*H*<sub>3</sub>)), 0.24 (s, 9H, Si(C*H*<sub>3</sub>)<sub>3</sub>) ppm.

<sup>13</sup>**C** NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 159.1 (s, py  $C^{2,6}$ ), 133.3 (s, py  $C^4$ ), 104.5 (s,  $C \equiv C(Si(CH_3)_3)$ ), 96.9 (s, py  $C^{3,5}$ ), 95.5 (s,  $C \equiv C(Si(CH_3)_3)$ ), 29.3 (s, N(CH<sub>3</sub>)), 0.04 (s, Si(CH<sub>3</sub>)<sub>3</sub>)) ppm.

**IR** (ATR):  $\vec{v}$  = 3402 (br, m), 3376 (sh), 3271 (br, m), 3084 (br, w), 2957 (m), 2928 (m), 2901 (w), 2797 (w), 2163 (sh), 2152 (w), 1592 (m), 1555 (s), 1540 (s), 1481 (m), 1450 (m), 1400 (s), 1271 (w), 1246 (s), 1229 (sh), 1170 (m), 1094 (w), 1087 (w), 990 (m), 964

### **FULL PAPER**

(m), 836 (s), 803 (s), 754 (m), 720 (w), 697 (w), 674 (w), 637 (m), 609 (m), 567 (m), 517 (w), 489 (w), 455 (w), 409 (w) cm^{-1}.

#### *N*,*N*<sup>2</sup>-Bis(diphenylphosphino)-*N*,*N*<sup>2</sup>-dimethyl-4-((trimethylsilyl)ethynyl)pyridine-2,6-diamine (2)

The synthesis was performed according to KIRCHNER et al.[58] and N,N'-dimethyl-4atmosphere. under dinitrogen То ((trimethylsilyl)ethynyl)pyridine-2,6-diamine (9) (641 mg, 2.75 mmol) was added toluene (40 mL). After cooling to -20 °C n-BuLi (2.5 M in n-hexane, 1.16 mL, 2.90 mmol) was added dropwise and the solution was stirred for 2 h at rt. At - 60  $^\circ$ C chlorodiphenylphosphine (605 mg, 2.75 mmol) was added and the solution was first stirred for 2 h at rt and afterwards overnight at 80 °C. The following steps were performed under air. The reaction solution was allowed to cool down to rt and a saturated NaHCO<sub>3</sub> solution (8 mL) was added. The organic layer was separated and the aqueous layer was washed with toluene (15 mL). The combined organic layer was dried over sodium sulfate and the solvent was evaporated under reduced pressure. Under dinitrogen atmosphere, the yellow-brown intermediate product was dissolved in toluene (40 mL) and cooled to -20 °C. To the solution n-BuLi (2.5 M in n-hexane, 1.16 mL, 2.90 mmol) was added dropwise and the solution was stirred for 2 h at rt. Again the mixture was cooled to -60 °C and chlorodiphenylphosphine (605 mg, 2.75 mmol) was added. The reaction solution was stirred for 2 h at rt and afterwards overnight at 80 °C. As mentioned above, the following work-up was performed under air. A saturated NaHCO<sub>3</sub> solution (8 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was washed with toluene (15 mL). The combined organic layer was dried over sodium sulfate and the solvent was evaporated under reduced pressure. The crude product was recrystallized from acetonitrile. The solid was filtered, washed with acetonitrile and dried under vacuum. The product was obtained as colorless solid (1.22 g, 2.03 mmol, 74 %)

**Anal.** calcd for  $C_{36}H_{37}N_3P_2Si$ : C, 71.9; H, 6.2; N, 7.0. Found: C, 71.4; H, 6.3; N, 6.9.

<sup>1</sup>**H NMR** (400.1 MHz, CDCl<sub>3</sub>): δ = 7.42-7.43 (m, 20H, ph  $H^{all}$ ), 6.93 (d, <sup>4</sup>*J*=2.5 Hz, 2H, py  $H^{\beta,5}$ ), 2.83 (d, <sup>3</sup>*J*<sub>H-P</sub>=1.6 Hz, 6H, N(C*H*<sub>3</sub>)), 0.24 (s, 9H, Si(C*H*<sub>3</sub>)<sub>3</sub>) ppm.

<sup>13</sup>**C** NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 159.7 (dd, <sup>2</sup>*J*<sub>C-P</sub>=27.8, <sup>4</sup>*J*<sub>C</sub>. P=2.1, py *C*<sup>2,6</sup>), 137.3 (d, <sup>1</sup>*J*<sub>C-P</sub>=15.8 Hz, ph *C*<sup>pso</sup>), 132.8 (t, <sup>4</sup>*J*<sub>C</sub>. P=3.2 Hz, py *C*<sup>4</sup>), 132.2 (d, <sup>2</sup>*J*<sub>C-P</sub>=20.8 Hz, ph *C*<sup>otho</sup>), 129.0 (s, ph *C*<sup>para</sup>), 128.5 (d, <sup>3</sup>*J*<sub>C-P</sub>=5.9 Hz, ph *C*<sup>meta</sup>), 104.5 (s, *C*≡C(Si(CH<sub>3</sub>)<sub>3</sub>)), 102.5 (d, <sup>3</sup>*J*<sub>C-P</sub>=21.6 Hz, py *C*<sup>3,5</sup>), 95.9 (s, *C*≡*C*(Si(CH<sub>3</sub>)<sub>3</sub>)), 34.0 (d, <sup>2</sup>*J*<sub>C-P</sub>=8.8 Hz, N(CH<sub>3</sub>)), 0.05 (s, Si(CH<sub>3</sub>)<sub>3</sub>) ppm.

<sup>31</sup>**P NMR** (162.0 MHz, CDCl<sub>3</sub>): δ = 50.4 (s, 2P, *P*Ph<sub>2</sub>) ppm. **IR** (ATR):  $\tilde{v}$  = 3069 (w), 3056 (w), 3002 (w), 2961 (w), 2927 (w), 2901 (w), 2856 (w), 2163 (w), 1580 (m), 1536 (s), 1478 (w), 1433 (m), 1423 (m), 1379 (s), 1366 (s), 1304 (w), 1260 (w), 1246 (m), 1230 (s), 1185 (m), 1149 (m), 1118 (w), 1091 (m), 1081 (m), 1026 (w), 986 (s), 955 (m), 918 (w), 843 (s), 815 (m), 762 (m), 741 (ss), 693 (ss), 667 (m), 657 (m), 630 (m), 618 (w), 588 (s), 544 (m), 535 (m), 501 (s), 474 (s), 453 (m), 425 (w), 406 (w) cm<sup>-1</sup>.

**[Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TMS</sub>)] (3)** The synthesis was performed according to KIRCHNER *et al.*<sup>[55]</sup> and under nitrogen atmosphere. The precursor [Mo(CO)<sub>3</sub>(ACN)<sub>3</sub>] was obtained by stirring [Mo(CO)<sub>6</sub>] (132 mg, 499 µmol) in acetonitrile (5 mL) under reflux for 1.5 h. The solution was allowed to cool down to rt and the Me-PN<sup>3</sup>P<sub>TMS</sub> ligand (2) (300 mg, 499 µmol) in acetonitrile (5 mL) was added. Afterwards the reaction mixture was stirred at rt overnight. The suspension was filtered and the precipitate was washed with a small amount of acetonitrile. After drying under vacuum the product was obtained as orange powder (233 mg, 298 µmol, 60 %).

**Anal.** calcd for  $C_{39}H_{37}MoN_3O_3P_2Si$ : C, 59.9; H, 4.8; N, 5.4. Found: C, 59.7; H, 5.0; N, 5.5.

<sup>1</sup>**H NMR** (400.1 MHz, CDCl<sub>3</sub>): δ = 7.61-7.56 (m, 8H, ph *H*<sup>ortho</sup>), 7.44-7.35 (m, 12H, ph *H*<sup>meta,para</sup>), 6.32 (s, 2H, py *H*<sup>3.5</sup>), 2.97 (ps t,  $J_{4+P}$ =1.9 Hz, 6H, N(C*H*<sub>3</sub>)), 0.28 (s, 9H, Si(C*H*<sub>3</sub>)<sub>3</sub>) ppm.

<sup>13</sup>**C** NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 228.3 (t,  ${}^{2}J_{C,P}$ =5.0 Hz, *trans*-C=O), 211.6 (t,  ${}^{2}J_{C,P}$ =10.0 Hz, *cis*-C=O), 161.8 (ABX, py C<sup>2,6</sup>), 137.7 (ABX, C<sup>pso</sup>), 132.0 (s, py C<sup>4</sup>), 130.9 (ABX, ph C<sup>ortho</sup>), 129.5 (s, ph C<sup>para</sup>), 128.4 (ABX, ph C<sup>meta</sup>), 103.4 (s, C=C(Si(CH<sub>3</sub>)<sub>3</sub>)), 101.3 (ABX, py C<sup>3.5</sup>), 99.0 (s, C=C(Si(CH<sub>3</sub>)<sub>3</sub>)), 37.4 (s, N(CH<sub>3</sub>)), -0.06 (s, Si(CH<sub>3</sub>)<sub>3</sub>) ppm.

<sup>31</sup>**P NMR** (162.0 MHz, CDCl<sub>3</sub>): δ = 133.0 (s, 2P, *P*Ph<sub>2</sub>) ppm. **IR** (ATR):  $\tilde{v}$  = 3073 (w), 3057 (w), 3012 (w), 2985 (w), 2916 (w), 2865 (w),2160 (w), 2152 (w), 1969 (s), 1859 (s), 1837 (ss), 1584 (m), 1525 (m), 1470 (m), 1454 (sh), 1433 (m), 1402 (s), 1376 (m), 1329 (w), 1305 (w), 1263 (m), 1243 (s), 1193 (m), 1183 (m), 1166 (m), 1080 (m), 1024 (w), 1006 (s), 961 (m), 918 (w), 844 (s), 815 (m), 788 (m), 758 (w), 740 (w), 721 (m), 691 (s), 656 (m), 637 (m), 620 (w), 602 (m), 582 (m), 574 (m), 559 (m), 533 (m), 510 (s), 476 (s), 439 (m), 428 (w), 408 (w), 391 (m) cm<sup>-1</sup>.

**FT-Raman:**  $\tilde{v} = 3056$  (w), 2965 (w), 2903 (w), 2155 (s), 1968 (m), 1836 (w), 1587 (s), 1571 (m), 1192 (w), 1027 (m), 998 (s), 988 (s), 659 (m), 561 (m), 476 (m), 460 (m), 424 (m), 419 (sh) cm<sup>-1</sup>.

[Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>PTATA)] (1) The synthesis was performed under nitrogen atmosphere. First [Mo(CO)<sub>3</sub>(Me-PN<sup>3</sup>P<sub>TMS</sub>)] (3) (100 mg, 128 µmol) and water free KOH (44 mg, 782 µmol) was stirred at rt in THF (50 mL). The deprotection reaction was followed by thinlayer chromatography (neutral alox, cyclohexane/ethyl acetate: 6:1, R<sub>f</sub>-value: 0.42). The following steps were performed in the dark because of the instability of the TATA derivatives against UV light. 4,8,12-Tri-n-octyl-4,8,12-triazatriangulentetrafluoroborate (90 mg, 128 µmol) and THF (10 mL) was added and the reaction mixture was stirred at 50 °C for 75 min. The progress was followed by thin-layer chromatography (neutral alox. cyclohexane/ethyl acetate: 6:1, Rr-value: 0.64). The reaction mixture was filtered through basic alox in order to separate excess of TATA salt and KOH. The solvent was evaporated under reduced pressure. The following steps were performed under air. The crude product was purified via column chromatography (basic alox, cyclohexane/ ethyl acetate 95:5). The solvent was evaporated under reduced pressure. The yellow-orange product (111 mg, 83.6 µmol, 65 %) was dried in vacuum and stored in the dark under nitrogen at -18 °C.

**Anal.** calcd for  $C_{79}H_{88}MoN_6O_3P_2$ : C, 71.5; H, 6.7; N, 6.3. Found: C, 71.4; H, 7.0; N, 6.5.

<sup>1</sup>**H NMR** (400.1 MHz, toluene-d<sub>8</sub>):  $\delta$  = 7.53-7.48 (m, 8H, ph *H*<sup>ortho</sup>), 7.22 (t, <sup>3</sup>*J*=8.3 Hz, 3H, ph<sub>TATA</sub> *H*<sup>para</sup>) 7.09-7.05 (m, 8H, ph *H*<sup>meta</sup>), 7.01-6.99 (m, 4H, ph *H*<sup>para</sup>), 6.63 (d, <sup>3</sup>*J*=8.4 Hz, 6H, ph<sub>TATA</sub> *H*<sup>meta</sup>), 5.79 (s, 2H, py *H*<sup>3,5</sup>), 3.84 (ps t, 6H, N(CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>)), 2.11 (ps t, *J*<sub>H-P</sub>=1.7 Hz, 6H, N(CH<sub>3</sub>)), 1.82 (ps quint, 6H, N(CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>)), 1.29-1.18 (m, 30H, N(CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>)), 0.90 (t, <sup>3</sup>*J*=7.0 Hz, 9H, N(CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>)) ppm.

<sup>13</sup>C NMR (100.6 MHz, toluene-d<sub>8</sub>): δ = 227.2 (t,  ${}^{2}J_{C-P}$ =5.0 Hz, *trans*-C=O), 212.0 (t,  ${}^{2}J_{C-P}$ =9.9 Hz, *cis*-C=O), 161.4 (ABX, py C<sup>2,6</sup>), 141.1 (s, ph<sub>TATA</sub> C<sup>ortho</sup>), 138.4 (ABX, ph C<sup>pso</sup>), 132.8 (s, py C<sup>4</sup>), 131.1 (ABX, ph C<sup>ortho</sup>), 129.2 (s, ph C<sup>para</sup>), 128.9 (s, ph<sub>TATA</sub> C<sup>para</sup>), 128.3 (ABX, ph C<sup>meta</sup>), 110.1 (s, ph<sub>TATA</sub> C<sup>pso</sup>), 105.6 (s, ph<sub>TATA</sub> C<sup>meta</sup>), 101.7 (ABX, py C<sup>3,5</sup>), 97.9 (s, C=C(TATA)), 83.6 (s, C=C(TATA)), 46.8 (s, N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>)), 36.2 (s, N(CH<sub>3</sub>)), 32.3 (s, N((CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)), 29.8 (s, N((CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub> (CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>)), 29.4 (s, TATA C), 27.3 (s, N((CH<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>CH<sub>3</sub>)), 14.3 (s, N((CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>)) ppm.

<sup>31</sup>**P NMR** (162.0 MHz, toluene-d<sub>8</sub>):  $\delta$  = 133.0 (s, 2P, *P*Ph<sub>2</sub>) ppm.

**IR** (ATR):  $\tilde{v} = 3074$  (w), 3055 (w), 2948 (m), 2921 (m), 2850 (m), 1964 (m), 1861 (s), 1839 (s), 1613 (m), 1579 (m), 1532 (m), 1480 (m), 1454 (m), 1433 (m), 1393 (m), 1373 (m), 1305 (w), 1263 (m), 1243 (m), 1210 (w), 1166 (m), 1146 (sh), 1084 (m), 1047 (m), 1027 (w), 990 (w), 962 (w), 929 (w), 912 (w), 844 (w), 816 (w), 789 (m), 761 (w), 744 (w), 721 (m), 711 (m), 691 (m), 657 (w), 636 (m), 601 (m), 584 (m), 559 (m), 525 (w), 508 (m), 479 (m), 436 (w), 418 (w), 409 (w), 396 (w) cm<sup>-1</sup>.

**FT-Raman**:  $\tilde{v} = 3058$  (w), 2907 (br w), 2853 (w), 2205 (m), 1964 (m), 1850 (br, w), 1613 (sh), 1587 (s), 999 (m), 929 (w), 561 (w) cm<sup>-1</sup>.

#### Acknowledgements

The authors would like to thank the HZB for provision of beamtime at the BESSYII/HE-SGM and Christof Wöll for the provision of the Prevac endstation. Furthermore the authors would like to thank Kai Uwe Clausen and Imke Reuther for synthetic work performed during their bachelor's theses on project "Möwe".

**Keywords:** Small molecule activation • Carbonyl complexes • Surface chemistry • Surface spectroscopy • Vibrational spectroscopy

- B. Milani, G. Licini, E. Clot, M. Albrecht, *Dalton Trans.* 2016, 45, 14419–14420.
- [2] K. Arashiba, Y. Miyake, Y. Nishibayashi, Nat. Chem. 2011, 3, 120–125.
- [3] D. V. Yandulov, R. R. Schrock, Science 2003, 301, 76–78.
- [4] W. B. Tolman (Ed.) Small Molecule Activation, Wiley-VCH, Weinheim, 2006.
- [5] J. S. Anderson, J. Rittle, J. C. Peters, *Nature* 2013, 501, 84– 87.
- [6] M. Réglier, C. Jorand, B. Waegell, J. Chem. Soc., Chem. Commun. 1990, 107, 1752–1755.
- [7] M. Rolff, J. Schottenheim, G. Peters, F. Tuczek, Angew. Chem., Int. Ed. 2010, 49, 6438–6442.; Angew. Chem. 2010, 122, 6583–6587.
- [8] F. Ungváry, Coord. Chem. Rev. 1997, 167, 233–260.
- [9] B. A. MacKay, M. D. Fryzuk, Chem. Rev. 2004, 104, 385-401.
- [10] B. K. Burgess, D. J. Lowe, Chem. Rev. 1996, 96, 2983–3011.
- [11] K. Arashiba, E. Kinoshita, S. Kuriyama, A. Eizawa, K. Nakajima, H. Tanaka, K. Yoshizawa, Y. Nishibayashi, *J. Am. Chem. Soc.* 2015, 137, 5666–5669.
- [12] A. Eizawa, K. Arashiba, H. Tanaka, S. Kuriyama, Y. Matsuo, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Nat. Commun.* 2017, *8*, 14874.
- [13] K. Arashiba, A. Eizawa, H. Tanaka, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Bull. Chem. Soc. Jpn.* 2017, *90*, 1111–1118.
- [14] S. E. Creutz, J. C. Peters, J. Am. Chem. Soc. 2014, 136, 1105–1115.
- [15] T. J. Del Castillo, N. B. Thompson, J. C. Peters, J. Am. Chem. Soc. 2016, 138, 5341–5350.
- [16] J. Fajardo, J. C. Peters, J. Am. Chem. Soc. 2017, 139, 16105– 16108.
- [17] S. Kuriyama, K. Arashiba, K. Nakajima, Y. Matsuo, H. Tanaka, K. Ishii, K. Yoshizawa, Y. Nishibayashi, *Nat. Commun.* 2016, 7, 12181.
- [18] S. Kuriyama, K. Arashiba, H. Tanaka, Y. Matsuo, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Angew. Chem., Int. Ed.* 2016, 55, 14291–14295.; *Angew. Chem.*, 2016, 128, 14503-14507.

- [19] L. A. Wickramasinghe, T. Ogawa, R. R. Schrock, P. Müller, J. Am. Chem. Soc. 2017, 139, 9132–9135.
- [20] N. Stucke, B. Flöser, T. Weyrich, F. Tuczek, Eur. J. Inorg. Chem. 2018.; 10.1002/ejic.201701326.
- [21] W. Zhang, W. Lai, R. Cao, Chem. Rev. 2017, 117, 3717–3797.
- [22] R. D. Milton, R. Cai, S. Abdellaoui, D. Leech, A. L. de Lacey, M. Pita, S. D. Minteer, *Angew. Chem., Int. Ed.* 2017, *56*, 2680– 2683.; *Angew. Chem.* 2017, *129*, 2724–2727.
- [23] G. J. Leigh, C. J. Pickett, J. Chem. Soc., Dalton Trans. 1977, 1797–1800.
- [24] D. A. Offord, S. B. Sachs, M. S. Ennis, T. A. Eberspacher, J. H. Griffin, C. E. D. Chidsey, J. P. Collman, *J. Am. Chem. Soc.* 1998, 120, 4478–4487.
- [25] D. L. DuBois, Inorg. Chem. 1984, 23, 2047-2052.
- [26] M. P. Shaver, M. D. Fryzuk, Adv. Synth. Catal. 2003, 345, 1061–1076.
- [27] R. J. Burford, M. D. Fryzuk, Nat. Rev. Chem. 2017, 1, 26.
- [28] J. M. Gottfried, Surf. Sci. Rep. 2015, 70, 259–379.
- [29] E. Ludwig, H. Naggert, M. Kalläne, S. Rohlf, E. Kröger, A. Bannwarth, A. Quer, K. Rossnagel, L. Kipp, F. Tuczek, Angew. Chem., Int. Ed. 2014, 53, 3019–3023.; Angew. Chem. 2014, 126, 3063-3067.
- [30] H. Naggert, J. Rudnik, L. Kipgen, M. Bernien, F. Nickel, L. M. Arruda, W. Kuch, C. Näther, F. Tuczek, J. Mater. Chem. C 2015, 3, 7870–7877.
- [31] T. G. Gopakumar, M. Bernien, H. Naggert, F. Matino, C. F. Hermanns, A. Bannwarth, S. Mühlenberend, A. Krüger, D. Krüger, F. Nickel, W. Walter, R. Berndt, W. Kuch, F. Tuczek, *Chem. Eur. J.* 2013, *19*, 15702–15709.
- [32] K. Flechtner, A. Kretschmann, H.-P. Steinrück, J. M. Gottfried, J. Am. Chem. Soc. 2007, 129, 12110–12111.
- [33] W. Hieringer, K. Flechtner, A. Kretschmann, K. Seufert, W. Auwärter, J. V. Barth, A. Görling, H.-P. Steinrück, J. M. Gottfried, J. Am. Chem. Soc. 2011, 133, 6206–6222.
- [34] T. Miyamachi, M. Gruber, V. Davesne, M. Bowen, S. Boukari, L. Joly, F. Scheurer, G. Rogez, T. K. Yamada, P. Ohresser, E. Beaurepaire, W. Wulfhekel, *Nat. Commun.* **2012**, *3*, 938.
- [35] H. Jacob, K. Kathirvel, F. Petersen, T. Strunskus, A. Bannwarth, S. Meyer, F. Tuczek, *Langmuir* 2013, 29, 8534– 8543.
- [36] J. Liu, M. Kind, B. Schüpbach, D. Käfer, S. Winkler, W. Zhang, A. Terfort, C. Wöll, *Beilstein J. Nanotechnol.* 2017, *8*, 892–905.
- [37] W. Azzam, P. Cyganik, G. Witte, M. Buck, C. Wöll, *Langmuir* 2003, 19, 8262–8270.
- [38] B. Lüssem, L. Müller-Meskamp, S. Karthäuser, R. Waser, M. Homberger, U. Simon, *Langmuir* 2006, 22, 3021–3027.
- [39] U. Jung, O. Filinova, S. Kuhn, D. Zargarani, C. Bornholdt, R. Herges, O. Magnussen, *Langmuir* **2010**, *26*, 13913–13923.
- [40] J. P. Collman, N. K. Devaraj, C. E. D. Chidsey, *Langmuir* 2004, 20, 1051–1053.
- [41] B. Baisch, D. Raffa, U. Jung, O. M. Magnussen, C. Nicolas, J. Lacour, J. Kubitschke, R. Herges, J. Am. Chem. Soc. 2009, 131, 442–443.
- [42] U. Jung, S. Kuhn, U. Cornelissen, F. Tuczek, T. Strunskus, V. Zaporojtchenko, J. Kubitschke, R. Herges, O. Magnussen, *Langmuir* 2011, 27, 5899–5908.
- [43] S. Kuhn, B. Baisch, U. Jung, T. Johannsen, J. Kubitschke, R. Herges, O. Magnussen, *Phys. Chem. Chem. Phys.* 2010, 12, 4481–4487.
- [44] S. Katano, Y. Kim, H. Matsubara, T. Kitagawa, M. Kawai, J. Am. Chem. Soc. 2007, 129, 2511–2515.
- [45] T. Weidner, M. Zharnikov, J. Hoβbach, D. G. Castner, U. Siemeling, J. Phys. Chem. C 2010, 114, 14975–14982.
- [46] U. Glebe, J. E. Baio, L. Árnadóttir, U. Siemeling, T. Weidner, *ChemPhysChem* **2013**, *14*, 1155–1160.
- [47] K.-Y. Chen, O. Ivashenko, G. T. Carroll, J. Robertus, J. C. M. Kistemaker, G. London, W. R. Browne, P. Rudolf, B. L. Feringa, J. Am. Chem. Soc. 2014, 136, 3219–3224.
- [48] M. Valášek, M. Lindner, M. Mayor, *Beilstein J. Nanotechnol.* 2016, 7, 374–405.

WILEY-VCH

### **FULL PAPER**

- [49] B. W. Laursen, F. C. Krebs, Chem. Eur. J. 2001, 7, 1773– 1783.
- [50] S. Lemke, S. Ulrich, F. Claußen, A. Bloedorn, U. Jung, R. Herges, O. M. Magnussen, *Surface Science* 2015, 632, 71–76.
- [51] J. Kubitschke, C. Näther, R. Herges, Eur. J. Org. Chem. 2010, 2010, 5041–5055.
- [52] H. Jacob, S. Ulrich, U. Jung, S. Lemke, T. Rusch, C. Schütt, F. Petersen, T. Strunskus, O. Magnussen, R. Herges, F. Tuczek, *Phys. Chem. Chem. Phys.* **2014**, *16*, 22643–22650.
- [53] R. G. Greenler, J. Chem. Phys. **1966**, 44, 310–315.
  [54] W. Schirmer, U. Flörke, H.-J. Haupt, Z. anorg. allg. Chem.
- 1987, 545, 83–97. [55] D. Benito-Garagorri, E. Becker, J. Wiedermann, W. Lackner,
- M. Pollak, K. Mereiter, J. Kisala, K. Kirchner, Organometallics 2006, 25, 1900–1913.
- [56] M. Nettekoven, C. Jenny, Org. Process Res. Dev. 2003, 7, 38– 43.
- [57] R. Kaul, Y. Brouillette, Z. Sajjadi, K. A. Hansford, W. D. Lubell, J. Org. Chem. 2004, 69, 6131–6133.
- [58] S. R. M. M. de Aguiar, B. Stöger, E. Pittenauer, M. Puchberger, G. Allmaier, L. F. Veiros, K. Kirchner, J. Organomet. Chem. 2014, 760, 74–83.
- [59] F. L. Otte, S. Lemke, C. Schütt, N. R. Krekiehn, U. Jung, O. M. Magnussen, R. Herges, *J. Am. Chem. Soc.* **2014**, *136*, 11248– 11251.
- [60] P. Schober, R. Soltek, G. Huttner, L. Zsolnai, K. Heinze, Eur. J. Inorg. Chem. 1998, 1998, 1407–1415.
- [61] P. S. Pregosin, R. W. Kunz, <sup>31</sup>P and <sup>13</sup>C NMR of Transition Metal Phosphine Complexes, Springer, Heidelberg, 1979.
- [62] H. Vu, M. R. Atwood, B. Vodar, J. Chem. Phys. 1963, 38, 2671–2677.
- [63] G. Binnig, H. Rohrer, C. Gerber, E. Weibel, *Phys. Rev. Lett.* 1982, 49, 57–61.
- [64] M. K. Rajumon, M. S. Hegde, C. N. R. Rao, *Catal. Lett.* 1988, 1, 351–360.
- [65] S. O. Grim, L. J. Matienzo, Inorg. Chem. 1975, 14, 1014–1018.
- [66] C. Battocchio, I. Fratoddi, M. V. Russo, V. Carravetta, S. Monti, G. Iucci, F. Borgatti, G. Polzonetti, *Surface Science* 2007, 601, 3943–3947.
- [67] C. Silien, M. Buck, G. Goretzki, D. Lahaye, N. R. Champness, T. Weidner, M. Zharnikov, *Langmuir* 2009, 25, 959–967.
- [68] S. Ulrich, U. Jung, T. Strunskus, C. Schütt, A. Bloedorn, S. Lemke, E. Ludwig, L. Kipp, F. Faupel, O. Magnussen, R. Herges, *Phys. Chem. Chem. Phys.* **2015**, *17*, 17053–17062.
- [69] I. G. Hill, A. J. Mäkinen, Z. H. Kafafi, *J. Appl. Phys.* **2000**, *88*, 889–895.
- [70] M. P. Mitoraj, A. Michalak, T. Ziegler, J. Chem. Theory Comput. 2009, 5, 962–975.
- [71] G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Adv. 2015, 71, 3–8.

- [72] G. M. Sheldrick, Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3–8.
- [73] X-Area, Version 1.44. Program Package for Single Crystal Measurements, STOE & CIE GmbH, Darmstadt, Germany, 2008.
- [74] C. Y. Legault, CYLview, 1.0b, Université de Sherbrooke, 2009, http://www.cylview.org.
- Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. [75] Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox.; Gaussian Inc., Wallingford CT, 2013.
- [76] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158–6170.
- [77] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297–3305.
- [78] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
- [79] S. Grimme, S. Ehrlich, L. Goerigk, J. Comput. Chem. 2011, 32, 1456–1465.
- [80] D. Andrae, U. Huermann, M. Dolg, H. Stoll, H. Preu, *Theoret. Chim. Acta* **1990**, 77, 123–141.
- [81] F. Neese, WIREs Comput. Mol. Sci. 2012, 2, 73-78
- [82] F. Neese, WIREs Comput. Mol. Sci. 2018, 8, e1327.
- [83] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.
- [84] J. P. Perdew, *Phys. Rev. B* **1986**, 33, 8822–8824.
- [85] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, Chem. Phys. Lett. 1995, 240, 283–290.
- [86] F. Neese, J. Comput. Chem. 2003, 24, 1740-1747.
- [87] A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652
- [88] F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.* 2009, 356, 98–109.
- [89] J. Pipek, P. G. Mezey, J. Chem. Phys. 1989, 90, 4916-4926.
- [90] B. Hammer, L. B. Hansen, J. K. Nørskov, Phys. Rev. B 1999, 59, 7413–7421.
- [91] S. Grimme, C. Bannwarth, P. Shushkov, J. Chem. Theory Comput. 2017, 13, 1989–2009.

# **FULL PAPER**

#### Entry for the Table of Contents (Please choose one layout)

Layout 1:

### FULL PAPER

Text for Table of Contents



Title

Layout 2:

### FULL PAPER

((Insert TOC Graphic here; max. width: 11.5 cm; max. height: 2.5 cm))

Author(s), Corresponding Author(s)\*

Page No. – Page No. Title

Text for Table of Contents