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Synthesis and reactivity of molybdenum imido alkylidene bis-pyrazolide complexes†

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Reaction of Li(3,5-R₂-pyrazolide) (R = *t*Bu or Ph, dXpz) with Mo(NAr)(CHCMe₂Ph)(OTf)₂(DME) yields Mo(NAr)(CHCMe₂Ph)(dXpz)₂ in good yield. These complexes react with alcohols or the surface silanols of silica, to yield bis-alkoxy and surface mono-siloxy alkene metathesis catalysts, respectively.

1 Introduction

Molybdenum imido alkylidene diphenylamido¹ and pyrrolyl² complexes have served as precursors to prepare highly active homogeneous³ and heterogeneous⁴ alkene metathesis Mo-based catalysts. The key to high reactivity is the formation of (Y)(X)Mo(NAr)(=CHR) with an asymmetric metal center (X ≠ Y in terms of σ-donating ability).⁵ Considering the unprecedented high performances of monoaryloxide monopyrrolyl (MAP)³ catalysts as well as the large influence of the pendant X ligand for silica supported systems, (≡SiO)(X)Mo(NAr)(=CHR),⁴ we decided to explore the formation of the corresponding pyrazolide family because these ligands can assume a variety of binding modes: η⁵, η², η¹, or μ², which could affect the overall performance of the catalyst.⁶

2 Experimental

General procedure

General. All manipulations were performed in oven-dried (150 °C) glassware under an atmosphere of nitrogen on a Schlenk line or in a Vacuum Atmospheres HE-492 drybox. For synthesis and treatment of the surface species, reactions were carried out using high vacuum lines (1.34 Pa) and glovebox techniques (Argon).

Materials. HPLC grade organic solvents were sparged with nitrogen, passed through activated alumina, and stored over 4 Å Linde-type molecular sieves prior to use. Benzene-*d*₆ was dried over sodium/benzophenone ketyl and distilled *in vacuo* prior to use. Mo(NAr)(CHCMe₂Ph)(OTf)₂(DME),⁷ Li(3,5-di-*t*-butylpyrazolide) {Li(dtpz)},⁸ and Li(3,5-diphenylpyrazolide) {Li(dppz)}⁹ were prepared according to literature procedures. All

other materials were prepared according to published procedures cited in the text or obtained from commercial sources and purified by standard procedures. Silica (Aerosil Degussa, 200 m² g⁻¹) was compacted with distilled water, dried, calcined at 500 °C under air for 2 h and treated under vacuum (1.34 Pa) at 500 °C for 12 h and then at 700 °C for 4 h (support referred to as SiO₂(700)). Pentane and toluene were distilled from NaK and sodium benzophenone ketyl under N₂, respectively. Propene (Scott, 99.95%) was purified over R3-11 BASF catalyst/MS 4 Å prior to use.

Measurements. NMR spectra were recorded at 298 K on Varian INOVA spectrometers operating at 500 MHz (¹H). Chemical shifts for ¹H and ¹³C spectra were referenced to the residual ¹H/¹³C resonances of the deuterated solvent and are reported as parts per million relative to tetramethylsilane. Elemental analyses were performed by Midwest Microlabs, Indianapolis, IN. Elemental analyses for surface complexes were performed at the Mikroanalytisches Labor Pascher. Infrared spectra were recorded on a Nicolet 550-FT by using an infrared cell equipped with CaF₂ windows, allowing *in situ* studies. Typically, 16 scans were accumulated for each spectrum (resolution, 2 cm⁻¹). Liquid phase analyses were performed on a Hewlett Packard 5890 series II GC apparatus equipped with a FID detector and a Fame column (50 m X 0.25 mm). Products were identified by GC-MS. All solid state NMR spectra were recorded under MAS on a Bruker Avance 500 spectrometer with a conventional double resonance 4 mm CP-MAS probe. The MAS frequency was set to 10 kHz for the experiments reported here. The samples were introduced in a 4 mm zirconia rotor in the glove box and tightly closed. Proton and carbon chemical shifts are reported in ppm downfield from liquid SiMe₄ (0 ppm).

Crystallography. Low temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo-Kα radiation (λ 0.71073 Å), performing φ- and ω-scans. All structures were solved by direct methods using SHELXS¹⁰ and refined against F² on all data by full-matrix least squares with SHELXL-97.¹¹ All non-hydrogen atoms were refined anisotropically. Unless described otherwise, all hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

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Synthesis of molecular complexes

Mo(NAr)(CHCMe₂Ph)(dppz)₂ (1-dppz-Ph). The complex Mo(NAr)(CHCMe₂Ph)(OTf)₂(DME) (1.00 g, 1.28 ol) was weighed and dissolved in 10 mL of Et₂O. Li(dppz) (0.586 g, 2.65 mmol, 2.05 equiv.) was added as a solid to the rapidly stirring solution kept at -30 °C over the course of 5 min. The reaction mixture was then allowed to warm to room temperature and was stirred for 90 min during which time it became translucent yellow and a pale yellow precipitate formed. All volatile components were removed *in vacuo* and the resulting yellow powder was extracted with 20 mL of toluene which was filtered through medium porosity sintered glass frit. The toluene was removed *in vacuo* then the resulting solid was triturated in 20 mL of pentane. Mo(NAr)(CHCMe₂Ph)(dppz)₂ (0.975 g, 1.15 mmol, 90%) was isolated by filtration as a pale yellow microcrystalline solid. X-Ray quality crystals were grown from a mixture of pentane and toluene at -30 °C. The ¹³C labelled analog, Mo(NAr)(¹³CHCMe₃)(dppz)₂ was prepared similarly utilizing Mo(NAr)(¹³CHCMe₃)(OTf)₂(DME). ¹H NMR (C₆D₆): δ 13.10 (s, 1 H, J_{CH} 124 Hz, Mo=CH), 7.71 (d, 8 H, dppz *ortho*), 7.28 (d, 2 H), 7.14 (app. t, 8 H, dppz *meta*), 7.06 (t, 4 H, *para*), 7.03 (s, 2 H, dppz), 6.93 (m, 6 H, NAr + CMe₂Ph), 3.74 (septet, 2 H, CHMe₂), 1.47 (s, 6 H, CMe₂Ph), 0.98 (d, 12 H, CHMe₂). ¹³C{¹H} NMR (C₆D₆): δ 305.4(Mo=C), 153.1, 152.3, 149.2, 148.0, 133.8, 129.2, 129.0, 128.6, 128.4, 127.5, 126.7, 126.6, 123.6, 107.6, 55.7, 30.9, 28.8, 24.0. Anal. calcd for MoC₅₃H₅₁N₅Mo: C 74.18, H 6.11, N 8.32; found: C 74.20, H 6.18, N 8.31.

Mo(NAr)(CHCMe₂Ph)(dtpz)₂ (1-dtpz-Ph). The complex Mo(NAr)(CHCMe₂Ph)(OTf)₂(DME) (1.00 g, 1.28 ol) was weighed and dissolved in 10 mL of Et₂O. Li(dtpz) (0.482 g, 2.65 mmol, 2.05 equiv.) was added as a solid to the rapidly stirring solution kept at -30 °C over the course of 5 min. The solution was then allowed to warm to room temperature and was stirred for 90 min during which time the color of the solution became dark yellow. All volatile components were removed *in vacuo* and the resulting powder was extracted with 20 mL of pentane, which was filtered through a medium porosity sintered glass frit. The solution was then concentrated *in vacuo* and then left for 18 h at -30 °C. Mo(NAr)(CHCMe₂Ph)(dtpz)₂ (0.717 g, 0.94 mmol, 73%) was isolated as yellow crystalline solid. ¹H NMR (C₆D₆): δ 13.35 (s, 1 H, J_{CH} 124 Hz, Mo=CH), 7.76 (d, 2 H, J_{CH} 8.2 H, ind), 7.31 (d, 2 H, NAr), 7.09 (t, 2 H, CMe₂Ph), 7.02 (m, 4 H, NAr + CMe₂Ph), 6.19 (s, 2 H, dtpz), 4.08 (septet, 2 H, CHMe₂), 1.81 (s, 6 H, CMe₂Ph), 1.31 (s, 36 H, *t*-Bu), 1.12 (d, 12 H, CHMe₂). ¹³C{¹H} NMR (C₆D₆): δ 303.5 (Mo=C), 159.3, 152.8, 150.8, 148.3, 128.7, 126.8, 123.8, 104.1, 55.8, 32.5, 31.3, 28.7, 24.8. Anal. calcd for MoC₄₄H₆₇N₅: C 69.36, H 8.86, N 9.19; found: C 69.27, H 8.88, N 9.14.

General procedure for *in situ* reactions with alcohols and phenol. The appropriate bispyrazolide complex was dissolved in C₆D₆ containing 1.1 mg ferrocene as internal standard. An alcohol or phenol was then added to the stirred mixture in one portion as a solid and the solution was stirred for 15 min. The entire reaction mixture was transferred to a J-Young tube and the ¹H NMR spectrum recorded.

Grafting molecular complexes onto silica

Grafting of [Mo(NAr)(=CHCMe₂Ph)(dppz)₂] (1-dppz-Ph) on SiO₂₋₍₇₀₀₎ monitored by *in situ* IR spectroscopy. Silica (30 mg) was pressed into a 18 mm self-supporting disk, put into a sealed glass high vacuum reactor equipped with CaF₂ windows. After calcination at 500 °C under air for 2 h, the silica disk was treated under vacuum (1.34 Pa) at 500 °C for 12 h and then at 700 °C for 4 h. The silica support thus obtained, referred to as SiO₂₋₍₇₀₀₎, (30 mg, 78 μmol SiOH), was then immersed into a solution of [Mo(NAr)(=CHCMe₂Ph)(dppz)₂] (7 mg, 86 μmol, 1.1 equiv.) in benzene (10 mL) at 25 °C. After 3 h, the disk was washed three times with benzene (3 × 10) and then dried under high vacuum (1.34 Pa) at 25 °C for 1 h. IR: 3745, 3618, 3068, 3032, 2965, 2930, 2872, 1566, 1495, 1469, 1445, 1425, 1388, 1364 cm⁻¹.

Grafting of [Mo(NAr)(=CHCMe₂Ph)(dppz)₂] (1-ddppz-Ph) on SiO₂₋₍₇₀₀₎ by impregnation (1-dppz-Ph/SiO₂). Preparation of [(≡SiO)Mo(NAr)(=CHCMe₂Ph)(dppz)] (2-dppz-Ph). A mixture of 1-dppz-Ph (84 mg, 0.1 ol) and SiO₂₋₍₇₀₀₎ (350 mg, 0.091 mmol SiOH) in benzene (8) was stirred at 25 °C for 3 h. After filtration, the yellow solid was washed three times with benzene (3 × ca. 5) and filtered. The resulting yellow powder was dried under high vacuum (1.34 Pa) at 25 °C for 1 h to yield a yellow solid. All the filtrate solutions were collected and distilled off. The resulting residue was analyzed by quantitative ¹H NMR spectroscopy (in C₆D₆) using Cp₂Fe (16 mg, 86 μmol, 10 H) as internal standard: 9.5 μmol of dppz (0.11 H for the NH proton) was formed during grafting, that is 0.2 equiv. of dppz/Mo_{surf}. ¹H MAS NMR: δ 12.7, 7.8, 4.4, 1.8 ppm. ¹³C CP MAS NMR: δ 152, 149, 128, 108, 54, 28, 22 ppm. Elemental analysis: 1.62 ± 0.05%_{wt} Mo.

Grafting of [Mo(NAr)(=CHCMe₃)(dppz)₂] (1*-dppz-Me) onto SiO₂₋₍₇₀₀₎ by impregnation. Preparation of [(≡SiO)Mo(NAr)(=CHCMe₃)(dppz)] (2*-dppz-Me). This reaction was carried out as described above by using 1*-dppz-Me in place of 1-dppz-Ph.

Grafting of [Mo(NAr)(=CHCMe₂Ph)(dtpz)₂] (1-dtpz-Ph) onto SiO₂₋₍₇₀₀₎ by impregnation (1b-Ph/SiO₂). Preparation of [(≡SiO)Mo(NAr)(=CHCMe₂Ph)(dtpz)] (2-dtpz-Ph). The complex 1-dtpz-Ph (115 mg, 0.14 ol) was grafted on SiO₂₋₍₇₀₀₎ (504 mg, 0.134 mmol SiOH) using the procedure described above for 1-dppz-Ph. Analysis of the filtrate showed the formation of 27.4 μmol of dtpz (0.3 H for the NH proton) during grafting, that is 0.3 equiv. of dtpz/Mo_{surf}. ¹H MAS NMR: δ 12.7, 6.9, 3.6, 2, 1 ppm. ¹³C CP MAS NMR: δ 162, 150, 128, 106, 50, 30, 23 ppm. DRIFT: 3608, 3064, 3030, 2967, 2932, 2910, 2874, 1601, 1560, 1521, 1495, 1486 cm⁻¹. Elemental analysis: 1.58 ± 0.05%_{wt} Mo.

Metathesis

General method employed for metathesis reactions in the solution phase. For metathesis reactions of diallyltosylamine or allyl ether, a 0.2 M solution of substrate in C₆D₆ and 10 μL of anisole (as internal standard) were placed in a Teflon capped NMR tube and the noted amount of catalyst was then added. The tube was capped and the solution was allowed to stand at room temperature. Conversion was determined *via* ¹H NMR spectroscopy.

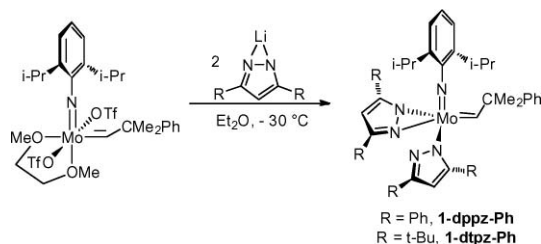
General method employed for the metathesis of propene in the gas phase catalyzed by 1-Ph/SiO₂ performed in a flow reactor.

Representative procedure. The solid **1-dppz-Ph/SiO₂** (105 mg, 17.5 μmol) was loaded in a flow reactor in the glove-box, the isolated reaction chamber was then connected to the propene line, the propene pressure was set to 1 bar, and the tubes were flushed with propene for 2 h. The flow rate was set to 400 $\text{mL} \times \text{min}^{-1}$ (16 (propene) $\times \text{mol}(\text{Mo})^{-1} \times \text{s}^{-1}$), the temperature was set to 30 $^{\circ}\text{C}$ and the opening of the valve corresponds to the beginning of the catalysis. The reaction was monitored by GC using an auto-sampler.

3 Results and discussions

Synthesis and structures of the molecular bis-pyrazolide complexes

The reaction of 2 equiv. of the bulky Li pyrazolides, Li(3,5-di-*t*-butylpyrazolide), Li(dtpz), or Li(3,5-diphenylpyrazolide), Li(dppz), with $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OTf})_2(\text{DME})$ at $-30\text{ }^{\circ}\text{C}$ in Et_2O gives the corresponding bis-pyrazolide Mo complexes $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{dppz})_2$ (**1-dppz-Ph**) and $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{dtpz})_2$ (**1-dtpz-Ph**) in 73 and 90% yield, respectively (Scheme 1). ^1H NMR spectra at 23 $^{\circ}\text{C}$ in C_6D_6 solution of both species reveal rapid rotation and rocking ($\eta^1\text{-N}_\alpha \rightarrow \eta^2 \rightarrow \eta^1\text{-N}_\beta$) of the pyrazolide ligands to give equivalent resonances for the *t*-Bu and Ph substituents. The alkylidene protons of **1-dppz-Ph** and **1-dtpz-Ph** resonate at 13.35 and 13.10 ppm, respectively, and both show a J_{CH} of 124 Hz. In contrast using the Li or K salt of (3,5-dimethylpyrazole) only leads to $\text{Mo}(\text{NAr})_2(\text{Me}_2\text{pz})_2$ in approximately 50% yield as the only isolable product, as determined by ^1H NMR spectroscopy.



Scheme 1 Synthesis of **1**.

X-Ray quality crystals of **1-dppz-Ph** were grown from a mixture of pentane and toluene at $-30\text{ }^{\circ}\text{C}$ and a thermal ellipsoid plot is shown in Fig. 1 (see Table 1 for crystal data). The complex **1-dppz-Ph** contains a near linear imido ($\text{Mo}(1)\text{-N}(1)\text{-C}(11)$ 175.41°) and the $\text{Mo}(1)\text{-C}(1)\text{-C}(2)$ angle of 143.45° is similar to other molybdenum imido alkylidenes.¹² The dppz ligands assume two different coordination modes. The dppz ligand containing N(2) and N(3) is coordinated in a $\sigma, \sigma\text{-}\eta^2$ fashion according to the near symmetrical $\text{Mo}\text{-N}$ bond lengths of 2.1026(16) \AA and 2.1496(15) \AA . The other dppz ligand is pseudo η^2 coordinated with $\text{Mo}(1)\text{-N}(4)$ equal to 2.0762(15) \AA , which is similar to $\text{Mo}^{\text{VI}}\text{-N}_{\text{pyrazolide}}$ bond lengths,^{12b} and the $\text{Mo}(1)\text{-N}(5)$ distance equal to $\sim 2.5\text{ \AA}$. The reason for this η^2 , η^1 coordination which gives a formally 16 electron complex vs. a η^2, η^2 configuration which would give a 18 electron complex is not known.

Reaction of bis-pyrazolide complexes with alcohols and phenols

Reaction of **1-dppz-Ph** or **1-dtpz-Ph** with two equivalents of either *t*-butanol, trifluoro-*t*-butanol, hexafluoro-*t*-butanol, nonafluoro-

Table 1 Crystal data and structure refinement of **1-dppz-Ph**

Empirical formula	$\text{MoC}_{53}\text{H}_{51}\text{N}_5$
Formula weight	841.92
Temperature	100(2) K
Wavelength	0.71073 \AA
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a 13.0553(17) \AA b 19.823(3) \AA c 16.594(2) \AA α 90° β $100.415(2)^{\circ}$ γ 90° 4223.6(9) \AA^3
V	4
Z	1.324 Mg m^{-3}
D_{calc}	0.353 mm^{-1}
μ	1760
$F(000)$	0.50 \times 0.50 \times 0.50 mm^3
Crystal size	1.62–27.48 $^{\circ}$
Theta range for data collection	$16 \leq h \leq 16$ $-25 \leq k \leq 23$ $-21 \leq l \leq 21$
Index ranges	71 070
Reflections collected	9683 [R_{int} 0.0418]
Independent reflections	100%
Completeness to theta 29.13°	Semi-empirical
Absorption correction	0.8432 and 0.8432
Max. and min. transmission	9683/1/526
Data/restraints/parameters	1.054
Goodness-of-fit on F^2	R_1 0.0311
Final R indices [$I > 2\sigma(I)$]	wR_2 0.0729
R indices (all data)	R_1 0.0419
	wR_2 0.0795
Largest diffraction peak and hole	0.518 and -0.583 e \AA^{-3}

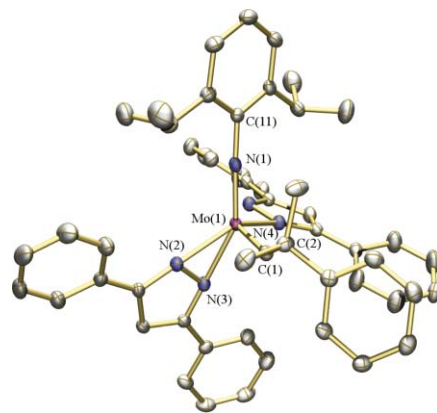
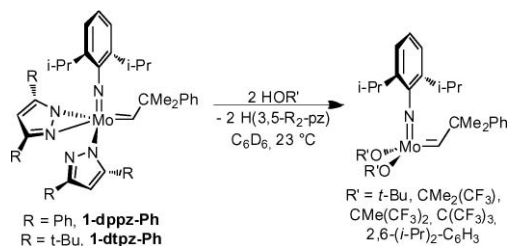


Fig. 1 Solid state structure of compound **1-dppz-Ph**. Selected bond lengths (\AA) and angles ($^{\circ}$): $\text{Mo}(1)\text{-N}(1)$ 1.7432(15), $\text{Mo}(1)\text{-C}(1)$ 1.8926(19), $\text{Mo}(1)\text{-N}(2)$ 2.1026(16), $\text{Mo}(1)\text{-N}(3)$ 2.1496(15), $\text{Mo}(1)\text{-N}(4)$ 2.0762(15); $\text{Mo}(1)\text{-N}(1)\text{-C}(11)$ $175.41(14)$, $\text{Mo}(1)\text{-C}(1)\text{-C}(2)$ $143.45(14)$.

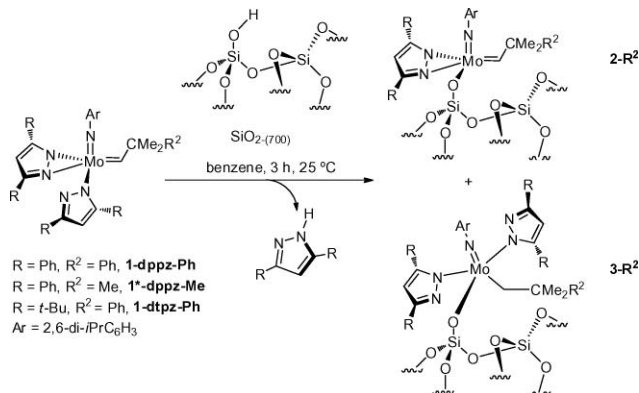
t-butanol, or diisopropylphenol in C_6D_6 solution ($\sim 40\text{ mM}$) at 23 $^{\circ}\text{C}$ cleanly produces $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OR})_2$ and two equivalents of either 3,5-di-*t*-butylpyrazole or 3,5-diphenylpyrazole (Scheme 2), as determined by ^1H NMR spectra of the reaction mixture. Formation of byproducts is not observable at the concentrations studied. Additionally, no monoalkoxide intermediates were observed during ^1H NMR monitoring of the reaction mixture. All the *in situ* prepared bisalkoxide complexes were shown to be competent catalysts for the ring-closing metathesis of

Scheme 2 Reactivity of **1** with alcohols.

diallyltosylamine or allylether to give 1-tosyl-2,5-dihydro-pyrrole or 2,5-dihydrofuran, respectively, in full conversion. Reactions with one equivalent of an alcohol or phenol were explored in an effort to prepare monoalkoxide(aryloxide) monopyrazolide which would be analogous to MAP catalysts.³ Reaction of **1-dppz-Ph** or **1-dtpz-Ph** with one equivalent of $\text{HOCMe}_x(\text{CF}_3)_y$ ($x = 0, 1, 2$, or 3 ; $y = 3 - x$) in either toluene or pentane-benzene between $-30 - 23^\circ\text{C}$, gave a complex mixture of products from which no monoalkoxide monopyrazolide complex could be obtained. Similarly, reaction of **1-dppz-Ph** or **1-dtpz-Ph** with 2,6-diisopropylphenol or 2-bromo-4,6-ditertbutylphenol gave mixtures of approximately 50:50 monoalkoxide monopyrazolide:bisalkoxide. Attempts to selectively crystallize the monophenoxide monopyrazolide product were unsuccessful. Reaction of **1-dppz-Ph** or **1-dtpz-Ph** with $[(R)\text{-}2'\text{-(di-tert-butyl(phenyl)silyloxy)-1,1'-naphthol}]^{\text{3b}}$ ($\text{H}(\text{Br}_2\text{Bitet-TBS})$) failed to yield any of $\text{Mo}(\text{NAr})(\text{CH}_2\text{CMe}_2\text{Ph})(3,5\text{-R}_2\text{pz})(\text{Br}_2\text{Bitet-TBS})$ although full consumption of the molybdenum starting material was observed after heating the reaction to 60°C for 18 h in C_6D_6 solution.

Reaction of bis-pyrazolide complexes with $\text{SiO}_{2-(700)}$

In view of the high reactivity of complexes **1** with alcohols, we studied their reactivity with the surface silanols of silica partially dehydroxylated at 700°C , $\text{SiO}_{2-(700)}$, with the hope to obtain monosiloxy complexes **2** (Scheme 3).¹³ Monitoring the grafting of **1-dppz-Ph** on a pellet of $\text{SiO}_{2-(700)}$ by IR spectroscopy showed that the peak associated with the surface silanols at 3747 cm^{-1} disappeared as new IR bands associated with the $\nu(\text{C-H})$ and $\delta(\text{C-H})$ of hydrocarbyl ligands appeared in the $3000\text{--}2800$ and $1500\text{--}1350\text{ cm}^{-1}$ region, respectively (ESI, Fig. S1).[†] Moreover, a broader

Scheme 3 Reactivity of **1** with the surface silanols of $\text{SiO}_{2-(700)}$.

signal appeared at 3608 cm^{-1} in agreement with the presence of residual SiOH interacting with the hydrocarbyl ligands.¹⁴ Grafting was also carried out by contacting **1-dppz-Ph** and $\text{SiO}_{2-(700)}$ in C_6H_6 , and elemental analysis of the resulting solid shows the presence of 1.62% Mo in the solid, which is also consistent with grafting and a partial consumption of surface silanols. This corresponds to 0.17 mmol of grafted Mo and to a consumption of *ca.* 65% of the surface SiOH (0.26 mmol g^{-1}). Additionally, during grafting, only 0.2 equiv. of $\text{H}(\text{dppz})$ was liberated per grafted Mo. This shows that grafting is probably not a simple exchange of one pyrazolide by a siloxy ligand but most probably involves the formation of two grafted species **2-dppz-Ph** and **3-dppz-Ph** in $20:80$ ratio. The ^1H magic-angle spinning (MAS) (Figure S2a) of the resulting solid displays 5 resolved signals at 12.7 ($=\text{CHMe}_2\text{Ph}$), 7.8 ($\text{Csp}^2\text{-H}$), 4.4 ($\text{C}_3\text{N}_2\text{H}$), and 1.8 (free OH , $=\text{CHCMe}_2\text{Ph}$ and CHMe_2). Note that the proton of the alkylidene ligand at 12.7 ppm is only observed as a very weak signal. The ^{13}C CP MAS NMR spectrum (ESI, Fig. S2b)[†] exhibits resonances assigned to the aromatic carbons ($152\text{--}128\text{ ppm}$), and four more signals assigned as follow: 107 (pyrazolide $\text{Csp}^2\text{-H}$), 54 ($=\text{CHCMe}_2\text{Ph}$), 28 (CHMe_2Ph) and 22 ppm (CHMe_2). As is typically the case for the alkylidene signals of samples at natural ^{13}C abundance (*ca.* 0.02 mmol g^{-1} of sample) no signal corresponding to the alkylidene carbon resonance ($\text{Mo}=\text{CHCMe}_2\text{Ph}$) was observed. We therefore investigated the grafting of the corresponding ^{13}C labelled neopentylidene complex, **1*-dppz-Me**, 99% ^{13}C labelled on the α -carbon to Mo. In this case, the ^{13}C CP-MAS NMR was very informative by showing two new isotropic signals of ^{13}C enriched carbons at 70 and 298 ppm (ESI, Fig. S3b).[†] The signal at 298 ppm is readily assigned to the alkylidene carbon of the neopentylidene and is consistent with the formation of **2-dppz-Me**, which results from the protolysis of one of the pyrazolide ligand (Scheme 3). The other signal at 70 ppm can however be attributed to the carbon of a neopentyl ligand bound to the metal center, and we propose the formation of **3-dppz-Me** having two remaining dppz ligands, which results from the addition of the silanol across the double bond of the alkylidene ligand. Such species have already been observed before, *e.g.* in the grafting on silica of bis-(2,5-dimethylpyrrolyl) Mo complexes.^{4c} Thus, combining available analytical data (*in situ* IR, mass balance analysis and solid state NMR spectroscopy), speaks for the formation of the desired surface complex **2-dppz-R²** ($\text{R}^2 = \text{Me}$ or Ph) as a minor surface species ($20\text{--}30\%$), the major species being **3-dppz-R²** (*ca.* $70\text{--}80\%$) where no alkylidene is present (Scheme 3).

Similar observations are found with the grafting of **1-dtpz-Ph** on $\text{SiO}_{2-(700)}$, *i.e.* partial consumption of OH groups and formation of OH groups interacting with hydrocarbyl ligands (ESI, Fig. S4),[†] a low Mo loading (1.58%) in agreement with the partial consumption of the surface silanols (0.16 mmol of Mo/g of silica, *ca.* 63%) and formation of 0.3 equiv. of $\text{H}(\text{dtpz})$ per grafted Mo. The ^1H MAS NMR and ^{13}C CP-MAS NMR spectra are also consistent with the grafting of molybdenum imido alkylidene pyrazolide complexes (ESI, Fig. S5).[†] However, the proton of the alkylidene ligand was only observed as a very weak signal at 12.7 ppm in ^1H NMR, and the alkylidene carbon not observed under ^{13}C CP-MAS NMR. Overall, the data are consistent with the formation of two grafted surface species: 30% of $[(\text{SiO})\text{Mo}(\text{NAr})(=\text{CHCMe}_2\text{Ph})(\text{dtpz})]$ (**2-dtpz-Ph**) and 70% of $[(\text{SiO})\text{Mo}(\text{NAr})(\text{CH}_2\text{CMe}_2\text{Ph})(\text{dtpz})_2]$ (**3-dtpz-Ph**).

Alkene metathesis

The catalytic activity of **1-Ph**/SiO₂ in propene metathesis was investigated (ESI, Fig. S6–9).[†] Firstly, contacting **1-dppz-Ph**/SiO₂, with propene in a flow reactor (*ca.* 400 mL × min^{−1}; 4800 (propene) × (Mo)^{−1} × min^{−1}), gives selectively ethene and 2-butenes (> 99.9%) with a very fast initial rate (1.7 s^{−1}), and overall 25,300 TON. However, **1-dtpz-Ph**/SiO₂ is not as active, with an initial rate of 0.5 s^{−1} and an overall TON of 3800 after 1500 min. Considering the number of active sites (*ca.* 20%), the initial rate and the overall number of turnover for **1-dppz-Ph**/SiO₂ can be estimated to 8.5 s^{−1} and 127 000, respectively, so that **2-dppz-Ph** displays catalytic performances similar to those previously reported using diphenylamido, pyrrolyl or 2,6-dimethylpyrrolyl precursors.⁴ Note that in contrast **1-Ph** is inactive in the metathesis of 1-alkene at room temperature, which illustrates the importance of the dissymmetry at the metal center to achieve high reactivity.⁵

4 Conclusions

Pyrazolide alkylidene Mo complexes can be readily synthesized by reaction of lithium pyrazolide with Mo(NAr)(CHCMe₂Ph)(OTf)₂(DME), when the pyrazolide ligand is sufficiently bulky to avoid decomposition of the product. These compounds readily react with alcohols to generate the corresponding bis-alkoxide, but so far it has been impossible to selectively generate the monopyrazolide alkoxide complexes. In contrast, the use of SiO₂-(700) could yield the correspond monosiloxy complexes, albeit with a low selectivity because the major product, a bis-pyrazolide siloxy complex, corresponds to the addition of the SiO–H to the alkylidene ligand. It is noteworthy however that these pyrazolide Mo alkylidene complexes display similar catalytic performances in alkene metathesis with the pyrrolyl systems, showing that catalytic performances are not affected by the multiple binding modes of pyrazolide ligands. Further studies are currently under way to establish structure-reactivity relationship in alkene metathesis.^{4d}

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