Tris(pyrazolyl)methane Ligands: Syntheses and Structures of Monometallic and Metallodendritic Complexes

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The substituted ligands $Me_3SiC(pz)_3$ (**1**) and $Me_3SiOCH_2C(pz)_3$ (**2**) have been prepared starting from $HC(pz)_3$ and $HOCH_2C(pz)_3$. The molecular structure of compound **1** has been determined by X-ray diffraction studies, which show a propeller-like conformation of the pyrazolyl rings. Compound **2** has been found to be useful for the synthesis of $[Mo(CO)_3\{Me_3SiOCH_2C(pz)_3\}]$ (**3**), $[TiCl_2(N\textit{t}Bu)\{Me_3SiOCH_2C(pz)_3\}]$ (**4**), and $[PdCl_2\{Me_3SiOCH_2C(pz)_3\}]$ (**5**), through ligand exchange reactions. The characterization of the new complexes is compatible with a tridentate coordination of the ligands in complexes **3** and **4**, and a bidentate coordination in **5** as confirmed by an X-ray analysis carried out with the palladium complex. The procedure has been extended for the synthesis of the carbosilane G1–$[OCH_2C(pz)_3]_4$ (**6**) and the tetrametallic compound G1–$[OCH_2C(pz)_3Mo(CO)_3]_4$ (**7**) (G1 = $Si(CH_2CH_2CH_2Me_2Si)_4$–).

Introduction

Since their introduction by Trofimenko's pioneering work,[1] tris(pyrazolyl)-borates, or scorpionates, have become a very important class of tripodal nitrogen-donating ligands in modern coordination chemistry. These versatile family of substituted and non substituted ligands have been used to synthesize complexes of most metals of the periodic table, some of which have useful applications in a wide range of areas.[2] The isoelectronic and isosteric tris(pyrazolyl)methane ligands have received much less attention until the significant improvement of their synthetic procedures.[3] Subsequently, this area of chemistry has rapidly developed new modified ligands and complexes, including those functionalized at the methine central carbon atom of tris(pyrazoly)methane[4–7] and related systems.[5] The substitution of the reactive methine proton by other functional groups have led, for instance, to the preparation of ligands and complexes soluble and stable in water,[6] and offered the opportunity to synthesize multitopic ligands and polynuclear compounds by linking tris(pyrazolyl)methane units in a molecular core.[7]

In the last few years we have focused our research work into the chemistry of carbosilane dendrimers containing early transition metal complexes, located at the dendritic periphery or at the focal point, and usually bonded through O- or N-donor anchoring ligands.[8] Since poly(pyrazolyl)-methanes can be functionalized with different groups at the central carbon atom while coordinated to metallic moieties at the other side, we decided to evaluate the possible application of this type of neutral ligands in the field of carbosilane metallodendritic chemistry.

This paper describes our results using silyl and siloxy derivatives of tris(1-pyrazolyl)methane and -ethane for the synthesis of early and late transition metal complexes. In addition, the preparation and characterization of a molybdenum tetranuclear compound with a carbosilane core is presented.

Results and Discussion

Synthesis of Ligands

$Me_3SiC(pz)_3$ (**1**) was prepared by the deprotonation reaction of tris(pyrazolyl)methane with LiMe in THF, followed by the addition of chlorotrimethylsilane in the same solvent (Scheme 1). The preparation of compound **1** with *n*-butyllithium as a base has been reported during the course of this work; **1** was described as an orange yellow solid, which was characterized by ^1H NMR spectroscopy, and the molecular peak observed by MS.[4] The procedure used here, including the isolation and purification of the intermediate $LiC(pz)_3$ (**I**, see Scheme 1 and the Exp. Sect.), allows for the synthesis of **1** in 75% yield as an analytically pure white solid. The product is stable in air and soluble in all common organic solvents. Single crystal of **1** suitable for X-ray structure determinations were obtained by recrystallization from pentane.

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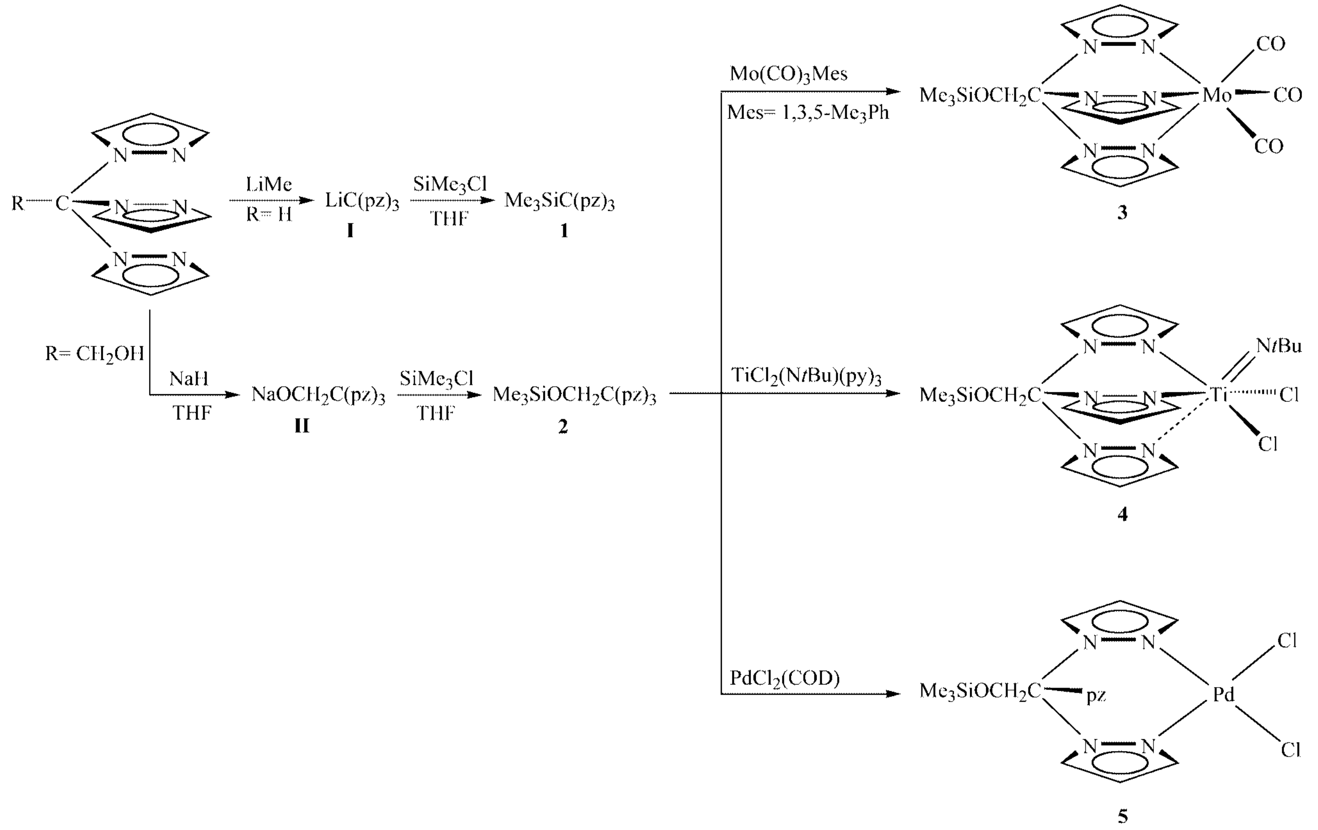


Scheme 1

A computer molecular modeling study of this compound shows several close contacts between the atoms in the 5-position of the pyrazolyl rings (C and H) and the $SiMe_3$ fragment. Maximum interaction occurs when the three rings are parallel to the C_3 axis (Figure 1a) in the tripodal arrangement expected in coordination complexes, and this steric hindrance minimizes by rotation of the pyrazolyl rings about the N−C(methine) bond (Figure 1b). These results are confirmed in the solid-state structure determined by X-ray diffraction studies, and in solution by the chemical behavior found for compound **1** (vide infra). At this point it is worth mentioning that our attempts to functionalize the central carbon atom of $HC(3,5\text{-}Me_2pz)_3$ failed, as was also noted by Reger who explained that the methyl groups in the 5-position block the reaction at that carbon atom.[4]

The reaction of 2,2,2-tris(pyrazolyl)ethanol with NaH in THF at room temperature resulted in the quantitative formation of the alkoxide **II** as an intermediate (Scheme 1), which was isolated as a hygroscopic white solid and characterized spectroscopically.[9] Subsequent addition of $SiMe_3Cl$ in THF gave $Me_3SiOCH_2C(pz)_3$ (**2**) in 80% yield after workup. Compound **2** was isolated as a colorless oil, which is stable in air and very soluble in all common organic solvents. Molecular modeling of the siloxy derivative **2** reveals a much more relaxed structure. Only some close contacts are observed between the 5-position atoms and the CH_2OSiMe_3 moiety, if the tripodal arrangement is in the eclipsed conformation along the $(pz)_3C{-}CH_2O$ bond (Figure 1c). These interactions become negligible for the staggered conformation (Figure 1d) or by rotation of the pyrazolyl ring. The latter is in agreement with the small rotation barrier along the central $C{-}CH_2OR$ bond proposed by Reger in related rhenium compounds.[7b]

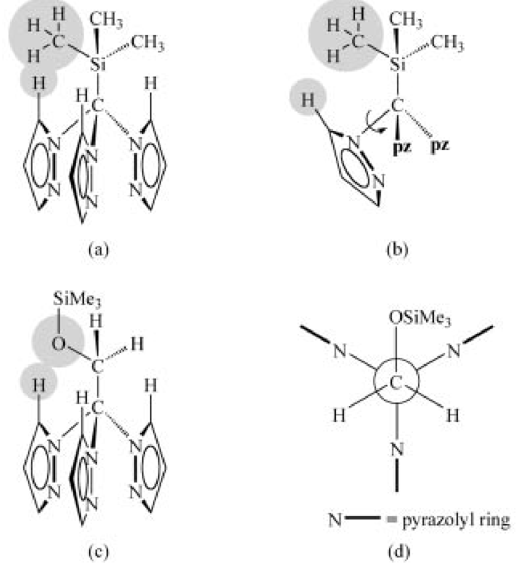


Figure 1. Representations of close contacts in compound **1** (a) and a more relaxed disposition (b); representations of close contacts in compound **2** (c) and the staggered conformation (d)

The NMR spectra of compounds **1** and **2** confirm the presence of three equivalent pyrazolyl rings in each molecule. The ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data for both compounds are almost the same for the atoms in the 3- and 4-position of the rings. However, those in the 5-position are assigned more up field for compound **1** (δ = 6.63 and 128.5 ppm, proton and carbon, respectively) than for **2** (δ = 7.44 and 131.0 ppm), an effect probably related to the significant steric hindrance discussed above between the pyrazolyl rings and the $SiMe_3$ group in compound **1**. Both derivatives show an IR band $\nu_{C=N}$ around 1515 cm^{-1} in the usual range for free pyrazolyl rings.

Complexes Syntheses

The labile ligand substitution in $[Mo(CO)_3\{1,3,5\text{-}(CH_3)_3C_6H_3\}]$, $[TiCl_2(NtBu)(py)_3]$, and $[PdCl_2(COD)]$ by ligand **2**, leads to the formation of $[Mo(CO)_3\{Me_3SiOCH_2C(pz)_3\}]$ (**3**), $[TiCl_2(NtBu)\{Me_3SiOCH_2C(pz)_3\}]$ (**4**), and $[PdCl_2\{Me_3SiOCH_2C(pz)_3\}]$ (**5**), respectively, in high yields (see Scheme 1, and the Exp. Sect.). The formation of the molybdenum compound **3** required the use of a polar solvent such as THF or acetonitrile, whereas no reaction was observed in toluene. Instead, compounds **4** and **5** were readily prepared in toluene under reflux conditions. They are found to be stable (**5**), or moderately sensitive as a solid (**3**), or very sensitive to air (**4**). They are insoluble in alkanes, complex **3** is only soluble in polar solvents (THF, CH_3CN, acetone), compound **4** in chlorinated solvents, and complex **5** in aromatic solvents.

Similar attempts that use compound **1** as the entering ligand resulted in a mixture of the starting materials for the titanium and palladium compounds, and an untreatable insoluble greenish solid for the reaction with $[Mo(CO)_3(\text{mesitylene})]$. The different chemical behavior showed by compounds **1** and **2** in these reactions can arise as a result of the important steric interaction between the $SiMe_3$ fragment and the pyrazolyl rings in compound **1**. Its tripodal arrangement to form complexes analogous to **3** or **4**, or the bidentate coordination as in **5** are hindered probably because the molecule minimizes the steric hindrance, thus positioning the three pyrazolyl rings in a three-bladed propeller conformation similar to that observed in the solid state (vide infra).

A number of tricarbonyl tris(pyrazolyl)methane metal complexes have been described,[3a,7] including molybdenum compounds[10] with tris(pyrazolyl)silane ligands.[11] The titanium examples are much more limited,[12] although some interesting heteroscorpionate-like complexes have recently been reported.[13] In the case of palladium(II), bis(pyrazolyl)methane as well as tris(pyrazolyl)methane compounds have been described.[14,15]

Complexes **3−5** were characterized by NMR and IR spectroscopy and elemental analysis, and the molecular structure of compound **5** has been determined by X-ray diffraction studies.

The ^1H NMR spectrum of complex **3** at room temperature exhibits one set of three multiplets for the pyrazolyl protons, whereas at lower temperature each type of pyrazolyl proton gives two resonances in the ratio 2:1. This finding is consistent with a staggered conformation of the ligand, as represented in Figure 1d, with a small rotation barrier along the central $C-CH_2OR$ bond, as earlier proposed by Reger for dinuclear rhenium compounds.[7b]

The ^1H NMR spectra of complexes **4** and **5** are simple at 50 °C because at this temperature their different conformers rapidly interconvert on the NMR time-scale. Only one type of pyrazolyl ring is observed for compound **4**, and two are observed for **5** in a 2:1 ratio due to the bidentate coordination of ligand **2** to the palladium atom. On cooling the NMR samples, the spectra become more complicated, indicating the presence of conformational isomers in both complexes.

Thus, the spectra for the imide complex **4** at −80 °C in CD_2Cl_2 exhibits ten resonances in the range δ = 7.60−8.40 ppm assigned to the pyrazolyl protons H^3 and H^5, and two singlets assigned to the Me_3Si- (δ = 0.36 and 0.41 ppm) and to the Me_3C groups (δ = 0.90 and 0.97 ppm), indicating the presence of two conformers in a 1:1.25 ratio, with a total of five different pyrazolyl environments. Mixtures of conformers have also been described for related titanium compounds with tridentate N-donor ligands.[16] For the current case (**4**), the observation of two conformers can be attributed to the presence of the *tert*-butyl imide group with an important *trans* influence and to the presumable rotation barrier for the Me_3SiOCH_2 moiety (see conformers A and B in Figure 2).

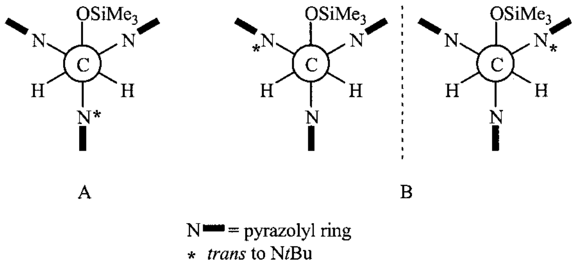
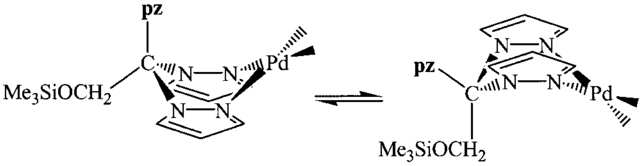


Figure 2. Conformer projections for compound **4**

The ^1H NMR spectra of derivative **5** at −50 °C in $CDCl_3$ shows twelve resonances for the pyrazolyl protons (δ = 6.40−8.40 ppm) and two singlets for the Me_3Si group (δ = 0.06 and 0.28 ppm). The splitting of these resonances and their relative intensities are in agreement with the presence of two conformers in an approximate ratio of 1:3, each with two equivalent pyrazolyl rings. These data are interpreted as the result of a boat-to-boat conformational exchange between the isomers depicted in Scheme 2,[14,15] which are observable at low temperature in an unequal population because of the different natures of the substituents in the axial position on the methine carbon (pz or Me_3SiOCH_2). It is worth noting that the exchange process between the non-coordinated and the coordinated pyrazolyl rings, a feature described as a "tumbling" process[1a] and commonly found in related complexes,[15,17] was not observed for compound **5** below 50 °C. A similar result has been reported for some palladium(II) complexes containing the rigid ligand 2-pyridyl-bis(3,5-dimethylpyrazolyl)methane, in which the pyridine group remains uncoordinated.[14a] However, the tris(pyrazolyl)methane ligand in compound **5** is flexible as demonstrated by the observation of the boat-to-boat inversion. The effect, nevertheless, could be ascribed to the presence of the Me_3SiOCH_2 substituent, which might hinder the ability of the free-pyrazolyl ring to coordinate to the metal center and, therefore, preclude the formation of the pentacoordinate intermediate involved during the tumbling process.



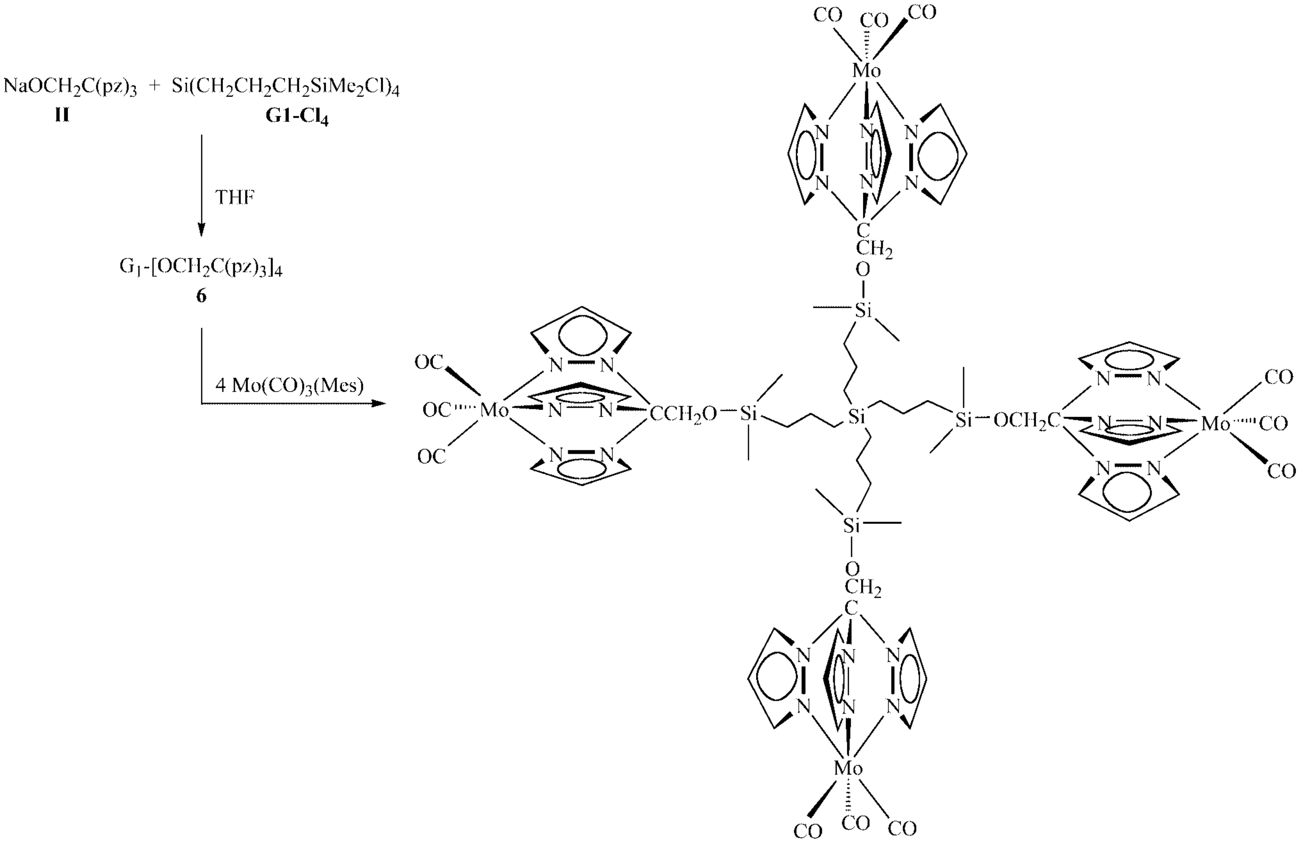
Scheme 2

The $^{13}C\{^1H\}$ NMR spectroscopic data for derivatives **3**–**5** are in agreement with a tripodal coordination of the tris(pyrazolyl)methane ligand in compounds **3** and **4**, and a bidentate *cis* coordination in a square-planar geometry for **5**. The spectra for **3** and **4** show one set of pyrazolyl resonances, whereas the spectrum for **5** shows the presence of nonequivalent rings in a 2:1 ratio; no mixtures of conformers are detected by $^{13}C\{^1H\}$ NMR spectroscopy at room temperature.

The IR spectra of compounds **3** and **5**, obtained as KBr pellets, show a band $\nu_{C=N}$ at around 1519 cm^{-1} not far from the absorption observed in the free ligand. In addition, the spectrum for the molybdenum complex shows two strong absorptions in the carbonyl region at 1901 cm^{-1} (a_1 mode) and 1764 cm^{-1} (e mode), as expected for a C_{3v} symmetry in an octahedral tricarbonyl complex. The observed ν_{CO} values are similar to those reported for related group 6 metal complexes.[11]

Synthesis of Dendritic Molecules

The methodology described above for the preparation of ligand **2** and compound **3** was extended to synthesize $G1-[OCH_2C(pz)_3]_4$ (**6**) and $G1-[OCH_2C(pz)_3Mo(CO)_3]_4$ (**7**) (Scheme 3), whereas attempts to prepare the corresponding tetrametallic analogues of compounds **4** and **5** yielded untreatable mixtures of insoluble solids. Thus, the reaction of chloro-containing carbosilane $G1-Cl_4$[18] with the sodium salt **II** in THF results in the formation of $G1-[OCH_2C(pz)_3]_4$ (**6**) as a colorless oil in a 76% yield. Subsequent treatment with $[Mo(CO)_3(mesitylene)]$ in refluxing THF leads to the dendritic compound **7**. Compounds **6** and **7** are found to be fairly stable in air. The



7

Scheme 3

organic compound is soluble in all common organic solvent, whereas the tetra-molybdenum complex is only slightly soluble in polar solvents such us acetone. The latter fact is relevant since it severely limits the preparation of higher generations of this type of metallodendrimers.

^1H and $^{13}C\{^1H\}$ NMR chemical shifts of the terminal $-OCH_2C(pz)_3$ groups for **6** are similar to those for **2**; the spectra are also quite similar, with additional signals for the methylene groups of the $SiCH_2CH_2CH_2Si$ chains in **6**. The most significant difference in the NMR spectroscopic data of **6** relative to that of the starting material G1$-Cl_4$, is the shift of the $SiMe_2$ resonances form $\delta = 0.38$ (^1H) and 0.2 (^{13}C) to 0.00 (^1H) and -2.4 (^{13}C) for **6**. The ^1H and $^{13}C\{^1H\}$ NMR spectra for compound **7** are consistent with the structure depicted in Scheme 3, and the peripheral organometallic units are in an electronic environment like that described for the mononuclear complex **3**.

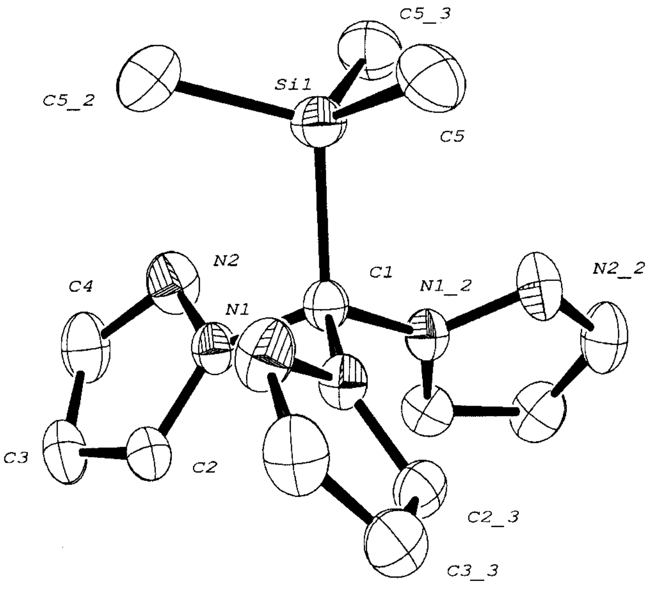


Figure 3. Molecular structure of compound **1**

The IR spectra of compounds **6** and **7** show a band $\nu_{C=N}$ at around 1518 cm^{-1}, and two strong ν_{CO} bands at 1906 cm^{-1} and 1757 cm^{-1} in the case of **7**.

Structures of $Me_3SiC(pz)_3$ (1) and $[PdCl_2\{Me_3SiOCH_2C(pz)_3\}]$ (5)

The molecular structures of both compounds have been determined by single-crystal X-ray diffraction studies. Figure 3 and Figure 4 show ORTEP representations of them, and Table 1 and Table 2 summarize their relevant structural data.

The molecular structure of **1** consists of discrete molecules and provides the first reported structure containing a tris(pyrazolyl)methane$-$Si linkage. The C$-$Si bond lies on a threefold axis in the *R*-3 space group, and only one third of the molecule appears in the asymmetric part of the unit cell. The geometry around the silicon atom is tetrahedral, but the Si(1)$-$C(1) bond length is clearly longer [1.968(3) Å] than the other Si$-$C bond lengths [1.858(3) Å]. The geometry around C(1) is distorted tetrahedral as shown by the Si(1)$-$C(1)$-$N(1) angle [111.5(1)°]. The three methyl groups bonded to the Si atom are located in a staggered configuration with respect to the C$-$N(pyrazolyl) bonds. The pyrazolyl rings are tilted with respect to the threefold axis to give the molecule a propeller-like shape. The Si$-$C$-$N$-$N torsion angle [46.4(2)°] provides a measure of this twist.

This shape is similar to that found in other molecules such as tris(3,5-dimethylpyrazol-1-yl)methane[19] and tris(3,5-dimethylpyrazol-1-yl)silane.[20] However, it is worth mentioning that only one of the possible conformers is present in the crystal of **1**; the isomer with the N(2) and the Si

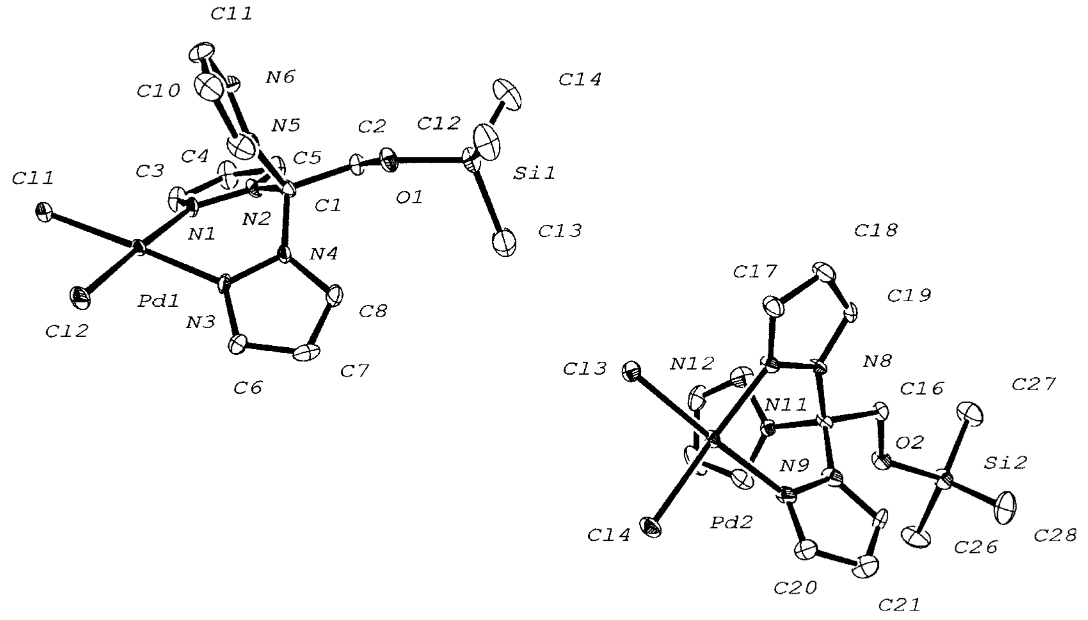


Figure 4. Molecular structure of the palladium complex **5**

Table 1. Bond lengths (Å) and angles (°) for compound **1**; symmetry transformations used to generate equivalent atoms: #1: $-x + y + 1$, $-x + 1$, z

Si(1)−C(5)	1.858(3)	N(1)−C(1)	1.460(2)
Si(1)−C(1)	1.968(3)	N(2)−C(4)	1.328(3)
N(1)−C(2)	1.357(2)	C(2)−C(3)	1.358(3)
N(1)−N(2)	1.354(2)	C(3)−C(4)	1.382(3)
C(5)#1−Si(1)−C(5)	111.2(1)	N(1)−C(2)−C(3)	106.9(2)
C(5)−Si(1)−C(1)	107.7(1)	N(1)#1−C(1)−N(1)	107.4(1)
C(2)−N(1)−N(2)	111.7(2)	N(1)−C(1)−Si(1)	111.5(1)
C(2)−N(1)−C(1)	129.5(2)	C(2)−C(3)−C(4)	104.9(2)
N(2)−N(1)−C(1)	118.6(2)	N(2)−C(4)−C(3)	112.6(2)
C(4)−N(2)−N(1)	103.7(2)		

Table 2. Bond lengths (Å) and angles (°) for compound **5**

Molecule 1		Molecule 2	
Pd(1)−N(3)	2.003(4)	Pd(2)−N(9)	2.005(5)
Pd(1)−N(1)	2.027(4)	Pd(2)−N(7)	2.016(4)
Pd(1)−Cl(2)	2.2841(12)	Pd(2)−Cl(4)	2.2778(13)
Pd(1)−Cl(1)	2.2845(14)	Pd(2)−Cl(3)	2.2842(14)
Si(1)−O(1)	1.671(4)	Si(2)−O(2)	1.678(4)
Si(1)−C(12)	1.850(6)	Si(2)−C(26)	1.853(6)
Si(1)−C(13)	1.854(7)	Si(2)−C(27)	1.862(6)
Si(1)−C(14)	1.858(6)	Si(2)−C(28)	1.863(7)
N(1)−C(3)	1.321(7)	N(7)−C(17)	1.330(7)
N(1)−N(2)	1.358(6)	N(7)−N(8)	1.363(6)
N(2)−C(5)	1.366(7)	N(8)−C(19)	1.355(6)
N(2)−C(1)	1.478(6)	N(8)−C(15)	1.461(6)
N(3)−C(6)	1.332(7)	N(9)−C(20)	1.319(7)
N(3)−N(4)	1.363(5)	N(9)−N(10)	1.361(6)
N(4)−C(8)	1.362(7)	N(10)−C(22)	1.359(7)
N(4)−C(1)	1.437(6)	N(10)−C(15)	1.457(6)
N(5)−N(6)	1.351(7)	N(11)−C(23)	1.352(7)
N(5)−C(9)	1.371(7)	N(11)−N(12)	1.353(7)
N(5)−C(1)	1.465(6)	N(11)−C(15)	1.456(6)
N(6)−C(11)	1.315(8)	N(12)−C(25)	1.330(7)
O(1)−C(2)	1.415(6)	O(2)−C(16)	1.410(6)
C(1)−C(2)	1.523(7)	C(15)−C(16)	1.548(6)
C(3)−C(4)	1.397(8)	C(17)−C(18)	1.394(7)
C(4)−C(5)	1.382(8)	C(18)−C(19)	1.371(8)
C(6)−C(7)	1.379(9)	C(20)−C(21)	1.389(9)
C(7)−C(8)	1.350(8)	C(21)−C(22)	1.357(8)
C(9)−C(10)	1.360(9)	C(23)−C(24)	1.379(9)
C(10)−C(11)	1.389(10)	C(24)−C(25)	1.390(9)
N(3)−Pd(1)−N(1)	87.41(17)	N(9)−Pd(2)−N(7)	87.37(18)
N(3)−Pd(1)−Cl(2)	89.94(12)	N(9)−Pd(2)−Cl(4)	90.07(12)
N(1)−Pd(1)−Cl(2)	177.34(13)	N(7)−Pd(2)−Cl(4)	177.44(14)
N(3)−Pd(1)−Cl(1)	175.64(12)	N(9)−Pd(2)−Cl(3)	175.39(13)
N(1)−Pd(1)−Cl(1)	90.72(13)	N(7)−Pd(2)−Cl(3)	90.85(13)
Cl(2)−Pd(1)−Cl(1)	91.90(5)	Cl(4)−Pd(2)−Cl(3)	91.70(5)
O(1)−C(2)−C(1)	107.9(4)	O(2)−C(16)−C(15)	107.6(4)
C(2)−O(1)−Si(1)	123.9(3)	C(16)−O(2)−Si(2)	122.8(3)
N(4)−C(1)−N(5)	107.8(4)	N(11)−C(15)−N(10)	108.1(4)
N(4)−C(1)−N(2)	109.1(4)	N(11)−C(15)−N(8)	108.7(4)
N(5)−C(1)−N(2)	107.4(4)	N(10)−C(15)−N(8)	108.9(4)
N(4)−C(1)−C(2)	112.6(4)	N(11)−C(15)−C(16)	110.8(4)
N(5)−C(1)−C(2)	110.7(4)	N(10)−C(15)−C(16)	111.2(4)
N(2)−C(1)−C(2)	109.1(4)	N(8)−C(15)−C(16)	109.1(4)
Pd(1)−C(1)−C(2)−O(1)	−143.1	Pd(2)−C(15)−C(16)−O(2)	133.0
C(1)−C(2)−O(1)−Si(1)	159.4	C(15)−C(16)−O(2)−Si(2)	−159.9

atom located on the same side of the plane defined by the three nitrogen atoms bonded to the central carbon atom. Obviously, this arrangement found in the solid state is incompatible with a bi- or tridentate coordination of compound **1** to a metal center.

The molecular structure of compound **5** consists of discrete molecules with one Pd atom with a *cis* configuration in a square-planar environment. The metal atom is bonded to two chlorine and two nitrogen atoms from the tris(pyrazolyl)methane ligand, whereas one of the pyrazolyl rings remains uncoordinated. The asymmetric part of the unit cell comprises two molecules. Both molecules are very similar, except for the position of the Me_3SiOCH_2 moiety, whose orientations differ with respect to the rest of the structure in such a way that the two molecules are enantiomers.

Two examples of palladium complexes containing the tris(pyrazolyl)methane ligand have been described and structurally characterized. The octahedral palladium(IV) complex $[PdMe_3\{HC(pz)_3\}]I$[21] and the square-planar Pd^{II} species $[Pd\{HC(pz)_3\}_2][BF_4]_2$,[15a] both cationic compounds, show the κ^3-and the κ^2-mode of coordination of the ligand, respectively. The neutral compound **5** is also a Pd^{II} square-planar complex, with Pd−N bond lengths [ranging from 2.003(4) Å to 2.027(4) Å] and N−Pd−N angle [87.41(1)°] very similar to those found in $[Pd\{HC(pz)_3\}_2][BF_4]_2$.[15a]

In contrast with the other examples, the two coordinated rings in both molecules of the asymmetric unit have different inclinations with respect to the coordination plane of the metal. The dihedral angle of this plane with the pyrazolyl ring closer to the Me_3SiOCH_2 moiety is 36.0(1)° [rings with N(3)−N(4) and N(9)−N(10)], whereas the angle with the other pyrazolyl ring is 29.3(1)° [rings with N(1)−N(2) and N(7)−N(8)]. This structural feature is probably caused by the orientation of the siloxy group and the different steric interactions over the coordinated pyrazolyl rings in the solid state.

In both molecules, the non-coordinated pyrazolyl ring is oriented towards the palladium coordination plane with an angle between the planes of 57.1°. The distances between the N apical and Pd atoms are 3.180 Å in Pd(1)−N(5) and 3.195 Å in Pd(2)−N(11), and the Pd(1)−N(6) and Pd(2)−N(12) distances are 3.738 Å and 3.762 Å, respectively. The donor nitrogen atoms N(6) and N(12) are pointing to the opposite side of the Me_3SiOCH_2 moieties.

Conclusion

Tris(pyrazolyl)methane compounds substituted at the methine carbon atom have been prepared and characterized. Their ability as coordination ligands is greatly affected by the substituent. Thus, $Me_3SiOCH_2C(pz)_3$ (**2**) allows the straightforward preparation of transition metal complexes **3−5**, whereas similar attempts using $Me_3SiC(pz)_3$ (**1**) all failed. The result is interpreted as a consequence of the "steric pressure" of the Me_3Si group over the pyrazolyl rings in **1**, which blocks their ability to coordinate. Ligand **2** is tridentately coordinated in $[Mo(CO)_3\{Me_3SiOCH_2C(pz)_3\}]$ (**3**) and $[TiCl_2(NtBu)\{Me_3SiOCH_2C(pz)_3\}]$ (**4**), and bidentately coordinated in $[PdCl_2\{Me_3SiOCH_2C(pz)_3\}]$ (**5**). The dynamic behavior of these complexes in solution is consistent with a staggered conformation of ligand **2** in complexes **3** and **4** at low temperature. In addition, the absence of chemical exchange between the free and the coordinated pyrazolyl rings in compound **5** is explained in terms of the steric effect exerted by the Me_3SiOCH_2 group over the tris(pyrazolyl)methane ligand. The preparation of poly(pyrazolyl)methane complexes can be readily extended to polymetallic systems as demonstrated by the synthesis of the carbosilane precursor **6**, and the tetramolybdenum complex **7**. However, modification of the ligand will be required to reduce its steric crowding and to obtain more soluble compounds, in order to apply this methodology in dendrimer chemistry. Further work along these lines is currently underway.

Experimental Section

General Remarks: All operations were performed under an argon atmosphere using Schlenk or dry-box techniques. Unless otherwise stated, reagents were obtained from commercial sources and used as received. $[TiCl_2(NtBu)(py)_3]$,[22] $[PdCl_2(COD)]$,[23] $[Mo(CO)_3\{1,3,5\text{-}(CH_3)_3C_6H_3\}]$,[24] carbosilane G1−$Cl_4$,[18] $HC(pz)_3$, and $HOCH_2C(pz)_3$[3a] were prepared according to literature procedures. Solvents were previously dried and distilled under argon as described elsewhere.[25] NMR spectra were recorded on Varian Unity 500+, VR-300 or 200 NMR spectrometers. Chemical shifts (δ) are reported in ppm referenced to $SiMe_4$ for ^1H and ^{13}C. IR spectra were recorded on a Perkin−Elmer FT-IR Spectrum-2000 spectrophotometer. Elemental analyses were performed by Microanalytical Laboratories of the University of Alcalá on a Heraeus CHN-O-Rapid mycroanalyzer. Molecular modeling was carried out using CambridgeSoft Chem. 3D Pro 5.0 for Mac and MM2 force field computations.

Preparation of (Trimethylsilyl)tris(1-pyrazolyl)methane (1): LiMe (3.0 mL, 1.6 M in diethyl ether, 4.80 mmol) was slowly added with a funnel equipped with a bubbler to a solution of $HC(pz)_3$ (1.00 g, 4.67 mmol) in THF (20 mL) at −78 °C, and the reaction mixture was stirred overnight and allowed to warm up to room temperature. Removal of the solvent under vacuum led to intermediate **I** as an off-white solid that was washed with pentane (10 mL). Solid **I** was dissolved in THF (20 mL), treated with an excess of $SiMe_3Cl$ (1.0 mL, 7.88 mmol) at 0 °C, and the resulting solution stirred for 4 h. The volatiles were removed in vacuo and the residue extracted into hexane (2 × 10 mL). Compound **1** was isolated as a white solid by evaporation of the filtrates under vacuum to dryness, and recrystallized from pentane. Yield: 1.00 g (75%). $C_{13}H_{18}N_6Si$ (286.41): calcd. C 54.52, H 6.33, N 29.34; found C 54.65, H 6.64, N 29.73%. ^1H NMR ($CDCl_3$): δ = 0.29 (s, 9 H, $SiMe_3$), 6.28 (dd, 3 H, $J_{H,H}$ = 1.5, 2.6 Hz, pz−H^4), 6.63 (d, $J_{H,H}$ = 2.6 Hz, 3 H, pz−H^5), 7.65 (d, $J_{H,H}$ = 1.5 Hz, 3 H, pz−H^3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = −0.6 ($SiMe_3$), 105.9 (pz−C^4), 128.5 (pz−C^5), 140.6 (pz−C^3) ppm, $C(pz)_3$ not observed. IR (KBr): ṽ = 1510 cm^{-1} (s, C=N).

Preparation of 1-(Trimethylsiloxy)tris-2,2,2-(1-pyrazolyl)ethane (2): A solution of $HOCH_2C(pz)_3$ (1.00 g, 4.09 mmol) in THF (15 mL) was added to NaH (0.17 g, 60% dispersion in mineral oil, 4.25 mmol) previously washed with hexane and suspended in THF (15 mL). When the evolution of H_2 ceased, the solvent was removed under vacuum to lead to intermediate **II** as a white solid, which was washed with pentane (10 mL).[9] The solid was then dissolved in THF (20 mL), $SiMe_3Cl$ (0.6 mL, 4.73 mmol) was added at 0 °C, and the resulting solution stirred for 2 h at room temperature. The volatiles were removed in vacuo, and the residue extracted into hexane (2 × 10 mL) to give **2** as a colorless oil. Yield: 1.03 g (80%). $C_{14}H_{20}N_6OSi$ (316.44): calcd. C 53.14, H 6.37, N 26.56; found C 53.64, H 6.33, N 26.05%. ^1H NMR ($CDCl_3$): $\delta = 0.02$ (s, 9 H, $SiMe_3$), 5.19 (s, 2 H, CH_2O), 6.29 (dd, 3 H, $J_{H,H} = 1.7, 2.7$ Hz, pz−H^4), 7.44 (d, $J_{H,H} = 2.7$ Hz, 3 H, pz−H^5), 7.62 (d, $J_{H,H} = 1.7$ Hz, 3 H, pz−H^3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = -0.7$ ($SiMe_3$), 66.9 (CH_2O), 90.3 [C(pz)$_3$], 106.2 (pz−C^4), 131.0 (pz−C^5), 141.1 (pz−C^3) ppm. IR (CsI/Nujol): $\tilde{\nu} = 1518$ cm^{-1} (s, C=N).

Preparation of [Mo(CO)$_3${Me$_3$SiOCH$_2$C(pz)$_3$}] (3): In a Schlenk, [Mo(CO)$_3${1,3,5-(CH$_3$)$_3$C$_6$H$_3$}] (95 mg, 0.32 mmol) was added to a solution of **2** (100 mg, 0.32 mmol) in acetonitrile or THF (15 mL) at room temperature. The yellow solution was stirred overnight and evaporated to dryness, and the yellow solid was washed with hexane and recrystallized form THF. Yield: 143 mg (90%). $C_{17}H_{20}N_6O_4SiMo$ (496.41): calcd. C 41.13, H 4.06, N 16.93; found C 41.27, H 3.89, N 16.46%. ^1H NMR ([D$_6$]acetone): $\delta = 0.44$ (s, 9 H, $SiMe_3$), 5.99 (s, 2 H, CH_2O), 6.49 (m, 3 H, pz−H^4), 8.02 (m, 3 H, pz−H^5), 8.33 (m, 3 H, pz−H^3) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): $\delta = -0.7$ ($SiMe_3$), 63.0 (CH_2O), 85.6 [C(pz)$_3$], 107.5 (pz−C^4), 133.3 (pz−C^5), 146.0 (pz−C^3), 229.8 (CO)ppm. IR (KBr): $\tilde{\nu} = 1901$ and 1764 cm^{-1} (s, CO), 1518 cm^{-1} (m, C=N).

Preparation of [TiCl$_2$(N*t*Bu){Me$_3$SiOCH$_2$C(pz)$_3$}] (4): [TiCl$_2$(N*t*Bu)(py)$_3$] (452 mg, 1.06 mmol), **2** (335 mg, 1.06 mmol), and toluene (15 mL) were placed into a glass ampoule equipped with a high vacuum greaseless stopcock. The mixture was kept at reduced pressure, evacuating the vapors regularly through the stopcock, and heated at 100 °C for 24 h. The resulting salmon-color solid was filtered and washed with pentane (2 × 10 mL). Yield: 385 mg (72%). $C_{18}H_{29}N_7OSiTiCl_2$ (506.33): calcd. C 42.70, H 5.77, N 19.36; found C 43.17, H 5.36, N 18.82%. ^1H NMR ($CDCl_3$, 50 °C): $\delta = 0.47$ (s, 9 H, $SiMe_3$), 1.06 (s, 9 H, N*t*Bu), 5.45 (s, 2 H, CH_2O), 6.28 (m, 3 H, pz−H^4), 7.85 (m, 3 H, pz−H^5), 8.19 (m, 3 H, pz−H^3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = -0.3$ ($SiMe_3$), 30.6 (C*Me*$_3$), 62.2 (CH_2O), 69.4 (*C*Me$_3$), 83.3 [C(pz)$_3$], 106.8 (pz−C^4), 129.8 (pz−C^5), 145.9 (pz−C^3) ppm.

Preparation of [PdCl$_2${Me$_3$SiOCH$_2$C(pz)$_3$}] (5): [PdCl$_2$(COD)] (81 mg, 0.28 mmol) was added to a solution of compound **2** (90 mg, 0.28 mmol) in toluene (15 mL), and the mixture was refluxed for 1.5 h. The solvent was evaporated, and the yellow-orange residue was washed with hexane (2 × 10 mL) and recrystallized from acetone to afford **5** as orange crystals suitable for X-ray analysis. Yield: 130 mg (94%). $C_{14}H_{20}N_6OSiPdCl_2$ (493.76): calcd. C 34.06, H 4.08, N 17.02; found C 34.42, H 4.05, N 16.58%. ^1H NMR ($CDCl_3$, 50 °C): $\delta = 0.15$ (s, 9 H, $SiMe_3$), 5.48 (s, 2 H, CH_2O), 6.40, 6.63 (m, m, 2 H, 1 H, pz−H^4), 6.96, 7.89 (m, m, 2 H, 1 H,

Table 3. Crystal data and structure refinement for compounds **1** and **5**

	1	**5**
Empirical formula	$C_{13}H_{18}N_6Si$	$C_{14}H_{20}Cl_2N_6OPdSi$
Molecular weight	286.42	493.77
Color	colorless	yellow
Temperature, K	293(2)	150(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	trigonal, $R\bar{3}$	triclinic, $P\bar{1}$
a (Å)	13.293(1)	7.8816(13)
b (Å)	13.293(1)	14.796(3)
c (Å)	15.364(1)	17.1711(14)
α (°)	90	90.14(1)
β (°)	90	98.99(1)
γ (°)	120	90.24(1)
Volume [(Å)^3]	2351.2(3)	1977.8(5)
Z (g cm^{-3})	6, 1.214	4, 1.658
Absorption coefficient (mm^{-1})	0.150	1.284
F(000)	912	992
Crystal size, mm	0.40 × 0.35 × 0.20	0.50 × 0.45 × 0.30
θ ranges (°)	5.03−27.52	5.01−27.50
Limiting indices	$-17 \le h \le 17$, $-16 \le k \le 17$, $-19 \le l \le 19$	$-10 \le h \le 10$, $-19 \le k \le 19$, $-22 \le l \le 22$
Reflections collected/unique	12700/1197 [*R*(int) = 0.1416]	67152/8994 [*R*(int) = 0.3110]
Reflections observed	883 [$I > 2\sigma(I)$]	7161 [$I > 2\sigma(I)$]
Completeness to θ (%)	99.3	99.0
Absorption correction	none	analytical
Max. and min. transmission		0.7486 and 0.5459
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	1197/0/85	8994/0/508
Goodness of fit on F^2	1.062	1.092
Final $R^{[a]}$ indices [$I > 2\sigma(I)$]	$R_1 = 0.0432$, $wR_2 = 0.0994$	$R_1 = 0.0509$, $wR_2 = 0.1238$
R int (all data)	$R_1 = 0.0654$, $wR_2 = 0.1127$	$R_1 = 0.0709$, $wR_2 = 0.1513$
Largest diff. peak and hole, e/Å^3	0.140, −0.219	1.417, −1.881

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{[\Sigma\omega(F_o^2 - F_c^2)]/[\Sigma\omega(F_o^2)^2]\}^{1/2}$.

pz−H^5), 8.01, 8.49 (m, m, 1 H, 2 H, pz−H^3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = −0.5 ($SiMe_3$), 66.5 (CH_2O), 107.4, 108.9 and 146.0 (coord. pz−$C^{4,\,5,\,3}$) 109.1, 134.1 and 144.0 (non coord. pz−$C^{4,\,5,\,3}$) ppm. IR (KBr): $\tilde{\nu}$ = 1519 cm^{-1} (m, C=N).

Preparation of G1−[$OCH_2C(pz)_3$]$_4$ (6): This compound was prepared according to the procedure described above for **2**, from Na$OCH_2C(pz)_3$ (**II**, 1.288 g, 4.84 mmol) and carbosilane G1−Cl_4 (0.690 g, 1.21 mmol) in THF (20 mL). The resulting oil was dissolved in pentane (20 mL), washed with water, and the organic layer dried with $MgSO_4$. The solvent was removed under vacuum giving compound **6** as a colorless oil. Yield: 1.29 g (76%). $C_{64}H_{92}N_{24}O_4Si_5$ (1402.02): calcd. C 54.83, H 6.61, N 23.98; found C 53.89, H 6.82, N 23.57%. ^1H NMR ($CDCl_3$): δ = 0.00 (s, 6 H, $SiMe_2$), 0.44 (m, 2 H, SiCH_2), 0.56 (m, 2 H, CH_2SiMe_2), 1.24 (m, 2 H,$CH_2CH_2CH_2$), 5.19 (s, 2 H, CH_2O), 6.29 (dd, 3 H, $J_{H,H}$ = 1.4, 2.3 Hz, pz−H^4), 7.43 (d, $J_{H,H}$ = 2.3 Hz, 3 H, pz−H^5), 7.61 (d, $J_{H,H}$ = 1.4 Hz, 3 H, pz−H^3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = −2.4 ($SiMe_2$), 16.8 (CH_2), 17.5 (CH_2), 20.8 (CH_2), 66.8 (CH_2O), 90.1 [$C(pz)_3$], 106.1 (pz−C^4), 130.8 (pz−C^5), 140.9 (pz−C^3) ppm. IR (CsI/Nujol): $\tilde{\nu}$ = 1517 cm^{-1} (m, C=N).

Preparation of G1−[$OCH_2C(pz)_3Mo(CO)_3$]$_4$ (7): A yellow solution of [$Mo(CO)_3\{1,3,5\text{-}(CH_3)_3C_6H_3\}$] (137 mg, 0.46 mmol) and compound **6** (160 mg, 0.11 mmol) in THF (20 mL) was refluxed for 1.5 h. At room temperature, a greenish precipitate was filtered, washed with hexane (2 × 5 mL), and recrystallized from acetone to afford **7** as a mustard-yellow solid. Yield: 143 mg (61%). $C_{76}H_{92}N_{24}O_{16}Si_5Mo_4$ (2121.91): calcd. C 43.02, H 4.37, N 15.84; found C 42.62, H 4.72, N 15.75%. ^1H NMR ([D_6]acetone): δ = 0.41 (s, 6 H, $SiMe_2$), 0.58 (m, 2 H, SiCH_2), 0.89 (m, 2 H, CH_2SiMe_2), 1.35 (m, 2 H, $CH_2CH_2CH_2$), 5.98 (s, 2 H, CH_2O), 6.46 (m, 3 H, pz−H^4), 8.01 (m, 3 H, pz−H^3), 8.27 (m, 3 H, pz−H^5) ppm. $^{13}C\{^1H\}$ NMR ([D_6]acetone): δ = −1.9 ($SiMe_2$), 17.6 (CH_2), 18.6 (CH_2), 27.7 (CH_2), 63.5 (CH_2O), 107.0 (pz−C^4), 131.7 (pz−C^5), 146.0 (pz−C^3) ppm, $C(pz)_3$ and CO not observed. IR (KBr): $\tilde{\nu}$ = 1906 and 1757 cm^{-1} (s, CO), 1519 cm^{-1} (m, C=N).

X-ray Crystallography Studies: Suitable monocrystals of **1** and **5** were obtained from a saturated solution in pentane at −30 °C, and by slow evaporation of acetone at room temperature. A summary of crystal data, data collection, and refinement parameters for the structure analysis of both compounds is given in Table 3. A colorless (**1**) or yellow (**5**) crystal was glued to a glass fiber and mounted on Kappa-CCD Bruker-Nonius diffractometer with area detector, and data were collected with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). For compound **1**, data were collected at room temperature, with an exposure time of 30 s per frame (five sets; 224 frames; phi and omega scans 2° scan-width). For compound, **5** data collection was performed at 150 K, with an exposure time of 10 s per frame (12 sets; 510 frames; phi and omega scans 2° scan-width). Raw data were corrected for Lorenz and polarization effects.

Structures were solved by direct methods, completed by subsequent difference Fourier techniques, and refined by full-matrix least-squares on F^2(SHELXL-97).[26] Anisotropic thermal parameters were used in the last cycles of refinement for the non hydrogen atoms in both structures. Hydrogen atoms were found in the final Fourier maps and were refined with isotropic thermal displacement parameters.

All the calculations were made with the WINGX system.[27]

CCDC-232262 and -232263 contains the supplementary crystallographic data for compounds **1** and **5**, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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