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Tri-*N*-pyrrolylsilyl Complexes of Ruthenium and Osmium[1]

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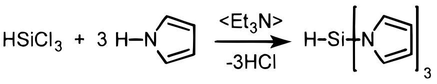
The development of a new, simple synthesis of tri-*N*-pyrrolylsilane (**1**) from trichlorosilane and pyrrole provides a convenient starting point for a series of interesting transition-metal complexes with the tri-*N*-pyrrolylsilyl ligand. Oxidative addition of **1** to $M(CO)_2(PPh_3)_3$ gives the six-coordinate compounds $M(SiPyr_3)H(CO)_2(PPh_3)_2$ (Pyr = 1-NC_4H_4; **2a**, M = Ru; **2b**, M = Os), whereas overall phenyl group-silyl group exchange between $MPhCl(CO)(PPh_3)_2$ and **1** yields the five-coordinate species $M(SiPyr_3)Cl(CO)(PPh_3)_2$ (**3a**, M = Ru; **3b**, M = Os). The nitrosyl complex $Os(SiPyr_3)HCl(NO)(PPh_3)_2$ (**4**) can be prepared from $OsCl(NO)(PPh_3)_3$ and **1**. The carbonyl groups in these compounds show relatively high C−O stretching frequencies, which fall between those found for the trihydroxysilyl and trichlorosilyl analogues. Bond lengths and angles obtained from the X-ray structure determinations of $HSiPyr_3$ (**1**) and $Os(SiPyr_3)H(CO)_2(PPh_3)_2$ (**2b**) indicate that the $SiPyr_3$ moiety undergoes significant changes on coordination to osmium.

Introduction

Ligands of the type PX_3, where X is alkyl, alkoxy, or halide, are often used to modify the reactivities of transition-metal complexes due to the σ-donor and π-acceptor abilities of the particular phosphine. In this context Moloy and Petersen recently reported that *N*-pyrrolylphosphines can act as very weak σ-donors and possibly good π-acceptors.[2] Remarkably shorter metal−phosphorus bonding distances and significantly higher C−O stretching frequencies relative to analogous triphenylphosphine complexes were reported for transition-metal complexes of this ligand. The substantial influence of the pyrrolyl fragments as potent electron-withdrawing groups caused us to consider if a comparable influence could be attained with *N*-pyrrolylsilyl compounds. Structural characterizations have revealed that the substituents on silicon have an important influence on the M−Si distances.[3] The observation that electronegative groups lead to a shortening of this parameter has frequently been explained by invoking π-bonding, and for a few examples photoelectron spectroscopy has affirmed multiple-bond formation between silicon and the metal center through participation of the σ^*-orbitals on the silyl group.[4]

Scheme 1



The chemistry of *N*-silyl-substituted pyrrole is largely unexplored, even though silyl functions are commonly used as protecting groups in organic synthesis. Except for compounds where the pyrrolyl function is part of larger conjugated systems such as those found in indoles, porphyrins, or tetraazaporphyrins, only the structures of 1-silylpyrrole,[5] 1-[bis(trimethylsilyl)(trimethylsiloxy)silyl]-2,3,4-tris(1,1-dimethylethyl)-5-phenylpyrrole[6] and, very recently, tetra-*N*-pyrrolylsilane[7] have been reported. To our knowledge, transition-metal complexes with *N*-pyrrolylsilyl ligands have not yet been published.

The new tri-*N*-pyrrolylsilyl complexes reported in this paper were prepared from tri-*N*-pyrrolylsilane, $HSiPyr_3$ (**1**, Pyr = 1-NC_4H_4). This silane has been synthesized previously from potassium pyrrolide and trichlorosilane[8] or from pyrrole and *n*-tetrasilane.[9] However, neither of these preparations provide easy access to large amounts of material with high purity, and we therefore devised a new synthesis for this useful starting material.

Results and Discussion

Syntheses. Tri-*N*-pyrrolylsilane (**1**) can easily be prepared from trichlorosilane and pyrrole in the presence of triethylamine in tetrahydrofuran at −78 °C (Scheme 1). After the mixture is warmed to room temperature, addition of *n*-hexane causes the precipitation of a solid which is removed by filtration. The desired product can be obtained from the filtrate as a colorless solid by reducing the volume and precipitation with *n*-hexane at −40 °C. Alternatively, removal of the solvent from the filtrate, followed by distillation under

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(1) Dedicated to Professor Dr. Wolfgang Beck on the occasion of his 65th birthday.

(2) Moloy, K. G.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 7696.

(3) Clark, G. R.; Flower, K. R.; Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *J. Organomet. Chem.* **1993**, *462*, 331.

(4) Lichtenberger, D. L.; Rai-Chaudhuri, A. *J. Am. Chem. Soc.* **1991**, *113*, 2923.

(5) Glidewell, C.; Robiette, A. G.; Sheldrick, G. M. *J. Mol. Struct.* **1971**, *9*, 476.

(6) Richter, H.; Arenz, S.; Michels, G.; Schneider, J.; Wagner, O.; Regitz, M. *Chem. Ber.* **1988**, *121*, 1363.

(7) Frenzel, A.; Herbst-Irmer, R.; Klingebiel, U.; Noltemeyer, M.; Schäfer, M. *Z. Naturforsch.* **1995**, *B50*, 1658. Allen, F. H.; Kennard, O. 3D Search and Research Using the Cambridge Structural Database. *Chemical Design Automation News* **1993**, *8* (1), 31.

(8) Atwood, J. L.; Cowley, A. H.; Hunter, W. E.; Sena, S. F. *Gov. Rep. Announce. Index* (*U.S.*) **1982**, *82*, 4027; *Chem. Abstr.* **1983**, *98*, 45906q.

(9) Schmidbaur, H.; Schuh, H. *Z. Naturforsch.* **1990**, *B45*, 1679.

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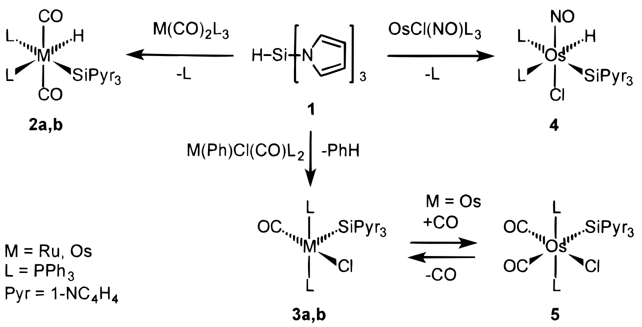
Scheme 2



high vacuum, gives the product as a colorless oil which solidifies within a few hours. Both methods give **1** in high purity. For further reactions, tri-*N*-pyrrolylsilane can be used as a solid or, with a melting point of only 32 °C, as a liquid. Because of the sensitivity of the compound to moisture, the latter possibility was generally more convenient. The product is stable under nitrogen, but the solid hydrolyzes slowly in air and much faster on dissolution in undried chloroform to give pyrrole and unidentified silicon products.

The six-coordinate compounds $M(SiPyr_3)H(CO)_2(PPh_3)_2$ (**2a**, M = Ru, **2b**, M = Os) were prepared from $M(CO)_2(PPh_3)_3$[10,11] and tri-*N*-pyrrolylsilane (**1**) in toluene. For the ruthenium complex the originally orange mixture instantaneously turned pale yellow on addition of **1** and after 10 min **2a** was obtained as a white powder on addition of *n*-hexane. The analogous osmium derivative, on the other hand, was formed only after irradiation with a quartz–iodine lamp for 5 min at room temperature, during which time the solution turned from yellow to colorless.

$Os(SiPyr_3)HCl(NO)(PPh_3)_2$ (**4**) was synthesized by adding air-sensitive green $OsCl(NO)(PPh_3)_3$[12] to a solution of tri-*N*-pyrrolylsilane (**1**) in benzene. The reaction proceeded immediately at room temperature with the solution changing from colorless to orange. After reduction of the solvent volume, $Os(SiPyr_3)HCl(NO)(PPh_3)_2$ (**4**) was precipitated by addition of *n*-hexane.

With the phenyl compounds $MPhCl(CO)(PPh_3)_2$[13] and tri-*N*-pyrrolylsilane (**1**) as starting materials, the corresponding five-coordinate silyl complexes $M(SiPyr_3)Cl(CO)(PPh_3)_2$ (**3a**, M = Ru; **3b**, M = Os) were formed by irradiation with a quartz–iodine lamp in toluene for 2 h (**3a**) or 10 h (**3b**). The reaction flasks were not cooled, and therefore the solutions reached approximately 50 °C.

In contrast to the parent tri-*N*-pyrrolylsilane (**1**) all tri-*N*-pyrrolylsilyl complexes are surprisingly stable to moisture. They can be kept in a desiccator for months without decomposition and are stable even in undried solvents for days. This reduced susceptibility toward hydrolysis has been observed for other transition-metal silyl complexes. An explanation could be that the electrophilicity of the silyl group is reduced because of electron donation from the metal to the silicon.[14] This results in a diminished susceptibility to nucleophilic attack, e.g. by water molecules. A mechanism has been described for hydridosilyliridium complexes in which the silyl ligand hydrolyzes after a reductive elimination to give the free silane, and subsequently the resulting hydroxysilane oxidatively adds to form a hydroxysilyl complex.[14] However, a similar reaction was not observed for the oxidative addition products **2a**,**b** and **4**, possibly because of the strength of the metal–silicon bond in these compounds.

Table 1. C–O Stretching Frequencies (cm^{-1}) for Silyl Complexes of Ruthenium and Osmium

R	$Ru(SiR_3)Cl(CO)(PPh_3)_2$	$Os(SiR_3)Cl(CO)(PPh_3)_2$	$Os(SiR_3)Cl(CO)_2(PPh_3)_2$
Me	1911[15]	1895[15]	1998, 1940[15]
OH	1937[15]	1919[16]	2023, 1962[15]
Py	1943	1915	2041, 1967
Cl	1956[15]	1944[15]	2045, 1985[15]
F	1964[17]	1946[17]	

The five-coordinate $Os(SiPyr_3)Cl(CO)(PPh_3)_2$ (**3b**) adds CO, but the reaction is easily reversed. When the six-coordinate, almost colorless $Os(SiPyr_3)Cl(CO)_2(PPh_3)_2$ (**5**) is quickly precipitated from solution with *n*-hexane, the loss of the second CO ligand after redissolution in $CDCl_3$ can be easily detected by a color change to yellow or *via* NMR spectroscopy over a 15 min period. In the following section a selection of IR and NMR parameters for the new silyl compounds reported here are compared with values for related compounds. A full list of spectroscopic data can be found in the Experimental Section.

IR and NMR Spectra. The IR spectrum of the free tri-*N*-pyrrolylsilane (**1**) shows a significant band for the Si–H stretch at 2233 cm^{-1} as well as a very strong, characteristic absorption at 1199 cm^{-1}. Similarly, a characteristic absorption for the tri-*N*-pyrrolylsilyl ligand is found between 1179 and 1182 cm^{-1} in the IR spectra of **2**–**5**, which makes it very easy to identify the presence of this ligand in a transition-metal complex. The second important feature when one analyzes the IR data of complexes **2**–**5** is the location of the C–O stretching frequencies, which are considered to be an indication of the electron density at the metal center. In all tri-*N*-pyrrolylsilyl complexes the values of ν(CO) are approximately 30 cm^{-1} higher than the frequencies for the corresponding trialkylsilyl derivatives (see Table 1) and in each case they fall between the values found for analogous compounds containing trihydroxysilyl or trichlorosilyl groups. This suggests a highly electron withdrawing nature for the tri-*N*-pyrrolylsilyl ligand. In $Os(SiPyr_3)H(CO)_2(PPh_3)_2$ (**2b**), for example, ν(CO) is 1953 cm^{-1}, whereas for the isostructural $Os(SiEt_3)H(CO)_2(PPh_3)_2$ a parameter of only 1925 cm^{-1} is reported.[3] This can be explained in terms of either an inductive

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[10] Cavit, B. E.; Grundy, K. R.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1972**, 60.

[11] Collins, T. J.; Grundy, K. R.; Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 161.

[12] Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939.

[13] Rickard, C. E. F.; Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1990**, *389*, 375.

[14] Aizenberg, M.; Goikhman, R.; Milstein, D. *Organometallics* **1996**, *15*, 1075.

[15] Salter, D. M. The Synthesis and Reactivity of New Ruthenium and Osmium Silyl Complexes. Thesis, The University of Auckland, Auckland, New Zealand, 1993.

[16] Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *J. Am. Chem. Soc.* **1992**, *114*, 9682.

[17] Maddock, S. M. Studies of Ruthenium and Osmium Silyl Complexes. Thesis, The University of Auckland, Auckland, New Zealand, 1995.

[18] (a) Hahn, T., Ed. *International Tables for Crystallography*, 2nd ed.; Reidel: Dordrecht The Netherlands, 1984; Vol. A (Space-Group Symmetry). (b) Sheldrick, G. M. SHELXTL/PC, Version 5.0; Siemens Industrial Automation Inc., Madison, WI, 1995.

or mesomeric electron-withdrawing effect. The fact that only one C−O stretching band is observed for the compounds of the type $M(SiPyr_3)H(CO)_2(PPh_3)_2$ (**2a**, M = Ru; **2b**, M = Os) indicates the presence of two mutually *trans* carbonyl groups, and this has been confirmed by analysis of NMR and X-ray data (see below).

In the ^1H NMR spectrum of tri-*N*-pyrrolylsilane (**1**) the resonance for the silicon-bound hydrogen is observed at 6.14 ppm, accompanied by silicon satellites with $^1J_{HSi}$ = 284.5 Hz, along with two pseudo triplets of an AA′XX′ pattern for α- and β-protons of the pyrrolyl rings at 6.86 and 6.47 ppm, respectively. The corresponding α- and β-carbon atoms can be found as singlets at 113.5 and 123.6 ppm, respectively in the $^{13}C\{^1H\}$ NMR spectrum. The ^{29}Si NMR spectrum shows a doublet at −37.8 ppm with a very large $^1J_{HSi}$ coupling constant of 284.5 Hz and no fine structure due to coupling with the protons of the pyrrolyl rings. The ^1H resonances of comparable silanes such as triethyl- and triphenylsilane show much smaller $^1J_{HSi}$ values of 177.7 and 196.8 Hz, respectively, and are shifted upfield to 3.68 and 5.60 ppm, respectively.

The ^1H NMR spectra of the six-coordinate hydride complexes $M(SiPyr_3)H(CO)_2(PPh_3)_2$ (**2a**, M = Ru; **2b**, M = Os) show the characteristic resonances for the hydrogen atoms bound to the metal center at −8.17 (**2a**) and −9.32 ppm (**2b**) in the form of doublets of doublets with coupling constants of $^2J_{HPcis}$ = 18.7 and $^2J_{HPtrans}$ = 52.7 Hz for **2a** and $^2J_{HPcis}$ = 21.2 and $^2J_{HPtrans}$ = 36.0 Hz for **2b**. The coupling pattern clearly indicates that the two triphenylphosphine groups are mutually *cis* and that the hydride is *trans* to one phosphorus atom. The presence of *cis* PPh_3 ligands can also be seen from the ^{13}C NMR data. Most compounds with two triphenylphosphine ligands such as $M(SiPyr_3)Cl(CO)(PPh_3)_2$ (**3a**,**b**) have a *trans* arrangement of these two bulky groups with resulting pseudo triplets for the *ipso*, *ortho*, and *meta* carbon atoms of the phenyl rings. The ^{13}C NMR spectra of the six-coordinate complexes **2a** and **2b**, however, show two sets of doublets for these atoms, and this requires the existence of two chemically different triphenylphosphine ligands.

X-ray Structures of Compounds 1 and 2b. The solid-state structures of **1** and **2b**, which were determined by single-crystal X-ray studies, contain one free tri-*N*-pyrrolylsilane molecule or one $Os(SiPyr_3)H(CO)_2(PPh_3)_2$ molecule accompanied by a solvate water molecule, respectively, per asymmetric unit. Crystal data and data collection parameters are listed in Table 2, and Figures 1 and 2 show perspective views of the two structures. Obtaining an X-ray structure of both the free tri-*N*-pyrrolylsilane and a metal complex of the novel tri-*N*-pyrrolylsilyl ligand provides the opportunity for a direct comparison to be made between the bond lengths and angles observed for the silyl group in these two bonding situations. Parameters within the tri-*N*-pyrrolylsilyl group for both **1** and **2b** are compared in Table 3, and additional interatomic distances and angles for complex **2b** are given in Table 4.

The average bond lengths within the pyrrolyl rings of **1** (N−Cα, 139.2 pm, Cα−Cβ, 134.9 pm; Cβ−Cβ′. 140.3 pm) and **2b** (N−Cα, 138.6 pm; Cα−Cβ, 135.8 pm; Cβ−Cβ′, 141 pm) show no significant differences (Table 3). Very similar values were also found for tetra-*N*-pyrrolylsilane (N−Cα, 139.3 pm; Cα−Cβ, 135.5 pm; Cβ−Cβ′, 141.9 pm)[7] and for tri-*N*-pyrrolylphosphine complexes (N−Cα, 138.7 pm; Cα−Cβ, 134.9 pm; Cβ−Cβ′, 139.5 pm).[2] There are, however, differences between the structures **1** and **2b**, and the most obvious of these are found in the interatomic distances and angles involving silicon.

Table 2. X-ray Data for $HSiPyr_3$ (1) and $Os(SiPyr_3)H(CO)_2(PPh_3)_2 \cdot H_2O$ (2b·H₂O)

	1	2b·H₂O
chem formula	$C_{12}H_{13}N_3Si$	$C_{50}H_{45}N_3O_3OsP_2Si$
fw	227.34	1016.12
cryst descripn	colorless needles	colorless blocks
cryst dimens (mm)	0.30 × 0.20 × 0.15	0.38 × 0.28 × 0.28
cryst syst, space group	orthorhombic, *Pcab* (No. 61)[18a]	triclinic, $P\bar{1}$ (No. 2)[18a]
mp (°C)	32	218
a (pm)	931.88(2)	1037.7(3)
b (pm)	974.32(2)	1277.8(5)
c (pm)	2647.98(4)	1870.6(2)
α (deg)	90	86.83(2)
β (deg)	90	89.71(2)
γ (deg)	90	66.76(3)
V (m³)	$[2404.23(8)] \times 10^{-30}$	$[2275.2(11)] \times 10^{-30}$
Z	8	2
ρ_{calcd} (kg m⁻³)	1.256×10^3	1.483×10^3
$F(000)$	960	1020
radiation, temp (K)	Mo Kα, 203(2)	Mo Kα, 193(2)
μ_{calcd} (m⁻¹)	171	2944
range of rflns	$-11 \le h \le 11$, $-10 \le k \le 12$, $-33 \le l \le 32$	$-12 \le h \le 11$, $-15 \le k \le 0$, $-22 \le l \le 22$
range of θ (deg)	$1.5 \le \theta \le 21.5$	$1.7 \le \theta \le 25.0$
no. of rflns		
collected	8581	8327
unique	1372	7932
included	1371	7589
$F_o > 4\sigma(F_o)$	1113	6676
no. of params/restraints	197/0	536/0
wR2, R1[a]	0.149, 0.073	0.168, 0.057
GOF[a]	1.29	1.02

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$; $GOF = \{\sum w(F_o^2 - F_c^2)^2/(n - p)\}^{1/2}$.

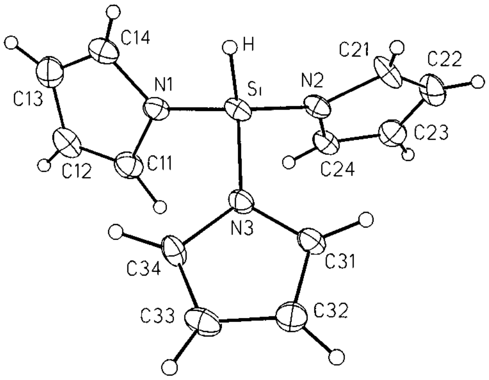

Figure 1. Molecular structure of $HSiPyr_3$ (**1**).

The average Si−N bond length of 172.9 pm in **1** is comparable to the 172.5 pm found for tetra-*N*-pyrrolylsilane.[7] The sum of the covalent radii for the Si−N bond is approximately 188 pm.[19] However, most of the observed Si−N bond lengths for simple molecules (e.g. $Me_3SiNHMe$ 172 pm;[20] H_3SiNMe_2, 171.5 pm[21]) are much

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(19) Pauling, L.; Huggins, M. L. *Z. Kristallogr.* **1934**, *87*, 205.

(20) Roper, W. R.; Wilkins, C. J. *Trans. Faraday Soc.* **1962**, *58*, 1686.

(21) Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M. *J. Mol. Struct.* **1970**, *6*, 231.

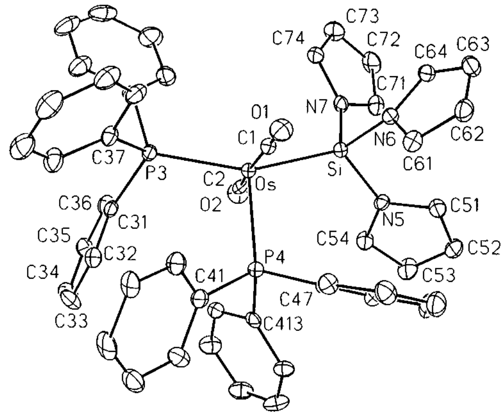

Figure 2. Molecular structure of Os(SiPyr$_3$)H(CO)$_2$(PPh$_3$)$_2$·H$_2$O (**2b·H$_2$O**). All hydrogen atoms are omitted for clarity. The solvent water molecule is not displayed.

shorter, and the mean value for 170 compounds with silicon bound to a three-coordinate nitrogen atom[22] is 174.8 pm.

The average Si−N distance in the tri-*N*-pyrrolylsilyl complex **2b** is 5.3 pm longer than in the free silane, which suggests weaker bonds between silicon and the three nitrogen atoms. An important factor in explaining this difference lies in the special nature of the free electron pairs on the pyrrolyl nitrogen atoms. On the one hand, they are involved in the aromatic systems of the five-membered rings, but on the other hand, they can also potentially act as donors to silicon, thereby strengthening the Si−N bonds and equalizing the electron deficiency (via "back-donation") at silicon which arises from the electron-withdrawing, electronegative nitrogen atoms. With hydrogen being the fourth substituent at silicon in compound **1**, there is no alternative to this back-donation from the pyrrolyl groups, but in the case of complex **2b** the transition-metal fragment can partially overcome the electron deficiency at silicon by back-bonding into a combination of the σ*-orbitals of the SiN$_3$ group. Consequently, the three Si−N bonds would be weakened and the Os−Si bond strengthened. In fact, the Os−Si distance in **2b** (237.5(2) pm) is much shorter than the one found for the analogous triethylsilyl compound (249.3 pm).[3] While some other six-coordinate SiR$_3$ complexes of osmium with electron-withdrawing groups R show similar short Os−Si distances, for example 237.7 pm in Cl$_3$Si−Os(CO)$_4$−Os(CO)$_4$−Os(CO)$_4$−SiCl$_3$, in which a second-transition metal center is *trans* to the trichlorosilyl group,[23] others show much larger values, for example 246.4 pm in Os[Si(OH)$_3$]Cl(CO)$_2$(PPh$_3$)$_2$, in which CO is *trans* to silicon.[15] This illustrates the important effect another strong π-acceptor *trans* to the silyl ligand has on the Os−Si distance.

An alternative explanation arises from the discussion of the bond angles at silicon. While the average N−Si−N angle within the SiN$_3$ group drops from 109.0 to 100.3° as one goes from the free silane **1** to the silyl complex **2b**, the average angle from one pyrrolyl ring to the fourth substituent at silicon, hydrogen or osmium, rises from 110 to 117.5°. According to Bent's rule,[24] smaller angles are found between electronegative groups with these bonds having more p character and in turn more s character is concentrated in bonds to electropositive bonding partners. An increased s character in the Os−Si bond would also explain the much shorter distance in **2b** in comparison with the analogous triethylsilyl compound. *Ab initio* calculations to clarify the influence of electronegative substituents in general and *N*-pyrrolyl groups in particular on the nature of the transition-metal−silicon bond have been undertaken.[25]

Fully in accord with the IR and NMR spectroscopic data, the arrangement of the two carbonyl groups in Os(SiPyr$_3$)H(CO)$_2$(PPh$_3$)$_2$ (**2b**) is *trans* (C1−Os−C2, 171.6(4)°) and the two triphenylphosphine ligands take up mutually *cis* positions (P3−Os−P4, 103.47(8)°). The tri-*N*-pyrrolylsilyl ligand is located *trans* to one of the latter groups, which results in a *mer* arrangement of the three bulky ligands in this complex. The fourth coordination site in this *mer* plane is occupied by the hydride, which could not be found in the X-ray structure determination. Due to the steric demands of the three bulky groups the Si−Os−P3 angle of 153.49(8)° is much smaller than 180° and the angles between *cis*-positioned silyl and phosphine ligands are much larger than 90° (101.92(8) and 103.47(8)°), showing that Si and P3 are bent toward the hydride position. In addition to that, two larger and one smaller Os−Si−N angle around silicon (120.8(2), 119.3(3), and 112.4(2)°) show that one of the pyrrolyl rings of the tri-*N*-pyrrolylsilyl ligand points in the direction of the hydride. It might be expected that a comparison of the Os−C and C−O bond lengths in complex **2b** and its triethylsilyl analogue, Os(SiEt$_3$)H(CO)$_2$(PPh$_3$)$_2$, would also be revealing, but unfortunately the corresponding parameters do not differ by more than 3 times their standard deviations.[3]

Conclusions

Tri-*N*-pyrrolylsilane is a versatile reagent which undergoes reactions with a number of osmium and ruthenium complexes in different oxidation states. Unusually short Os−Si and particularly long Si−N distances in Os(SiPyr$_3$)H(CO)$_2$(PPh$_3$)$_2$ compared to the parent tri-*N*-pyrrolylsilane as well as the lack of reactivity of all the tri-*N*-pyrrolylsilyl complexes are signs of a strong interaction between silicon and the metal center, and this is probably due to back-bonding. Relatively high CO stretching frequencies of the tri-*N*-pyrrolylsilyl complexes fall between the values found for compounds containing trihydroxysilyl or trichlorosilyl groups and suggest that the tri-*N*-pyrrolylsilyl group acts as a π-acceptor.

Experimental Section

General Comments. All reactions were carried out using standard Schlenk techniques under a dry atmosphere of oxygen-free dinitrogen. The solvents were carefully dried and distilled from the appropriate drying agents prior to use.[26] NMR spectra were measured at 25 °C on a Bruker DRX 400 spectrometer at 400.128 MHz (^{1}H), 100.625 MHz (^{13}C), or 79.495 MHz (^{29}Si). All chemical shifts were recorded in ppm downfield from tetramethylsilane on the δ scale. The carbon−

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(22) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1.

(23) Willis, A. W.; van Bouren, G. N.; Pomeroy, R. K.; Einstein, F. W. B. *Inorg. Chem.* **1983**, *22*, 1162.

(24) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

(25) Hübler, K.; Hübler, U.; Roper, W. R.; Schwerdtfeger, P.; Wright, L. J. *Chemistry*, in press.

(26) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

Table 3. Selected Interatomic Distances (pm) and Angles (deg) within the Tri-*N*-pyrrolylsilyl Group of $HSiPyr_3$ (1, $n = 1-3$) and $Os(SiPyr_3)H(CO)_2(PPh_3)_2 \cdot H_2O$ (2b·H_2O: $n = 5-7$) Together with Their Averaged Values

	$n = 1$	$n = 2$	$n = 3$	av	$n = 5$	$n = 6$	$n = 7$	av
Si−N*n*	171.1(4)	173.5(4)	174.0(4)	172.9	178.8(7)	178.7(7)	177.0(7)	178.2
N*n*−C*n*1	140.7(7)	140.3(7)	137.3(7)		137.4(11)	139.1(12)	140.6(12)	
N*n*−C*n*4	138.4(7)	137.1(7)	141.1(6)	139.2	138.0(11)	137.7(12)	138.8(12)	138.6
C*n*1−C*n*2	133.4(8)	134.6(9)	136.8(8)		135.8(14)	136.1(14)	134(2)	
C*n*3−C*n*4	134.4(9)	135.6(8)	134.8(8)	134.9	137.3(14)	134.5(14)	137(2)	135.8
C*n*2−C*n*3	140.2(9)	141.2(9)	139.5(8)	140.3	142(2)	142(2)	140(2)	141
H/Os−Si−N*n*	105(2)	116(2)	109(2)	110	120.8(2)	119.3(3)	112.4(2)	117.5
N*n*−Si−N(*n*+1)	112.8(2)	106.8(2)	107.3(2)[a]	109.0	100.3(3)	101.1(3)	99.5(3)[b]	100.3
Si−N*n*−C*n*1	128.7(4)	125.0(4)	125.4(4)		125.9(6)	124.0(6)	126.0(6)	
Si−N*n*−C*n*4	126.1(4)	128.3(4)	127.4(4)	126.8	126.6(6)	125.5(6)	127.5(7)	125.9
C*n*1−N*n*−C*n*4	105.1(5)	106.2(5)	106.9(4)	106.1	107.4(7)	107.7(7)	104.9(8)	106.7
Si−H/Os	136(4)				237.5(2)			

[a] N3−Si−N1. [b] N7−Si−N5.

Table 4. Additional Bond Lengths (pm) and Angles (deg) for $Os(SiPyr_3)H(CO)_2(PPh_3)_2 \cdot H_2O$ (2b·H_2O)

Os−C1	189.6(9)	Os−C2	188.5(9)
C1−O1	116.9(11)	C2−O2	119.4(11)
Os−P3	240.7(2)	Os−P4	241.1(2)
Si−Os−C1	88.0(3)	C1−Os−P3	100.1(2)
Si−Os−C2	83.9(3)	C1−Os−P4	88.5(3)
Si−Os−P3	153.49(8)	C2−Os−P3	86.2(3)
Si−Os−P4	101.92(8)	C2−Os−P4	95.5(3)
C1−Os−C2	171.6(4)	Os−C1−O1	180.0(9)
P3−Os−P4	103.47(8)	Os−C2−O2	174.7(8)

phosphorus coupling $^{n/m}J_{CP}$ in the triphenylphosphine ligands stands for $|^nJ_{CP} + {}^mJ_{CP}|$; the hydrogen−hydrogen coupling $^{n/m}J_{HH}$ in the pyrrolyl rings means $|^nJ_{HH} + {}^mJ_{HH}|$. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000PC FT-IR spectrometer. High-resolution mass spectra (fast atom bombardment, FAB^+ at 8 kV) were determined on a VG 70-SE mass spectrometer. Melting points are reported in degrees Celsius (uncorrected). Analytical data were obtained from the Microanalytical Laboratory, University of Otago. Evidence of solvation of some analytical samples was apparent from the ^1H NMR spectrum (H_2O, δ 1.58 (s); CH_2Cl_2, 5.29 (s)). $Ru(CO)_2(PPh_3)_3$,[10] $Os(CO)_2(PPh_3)_3$,[11] $OsCl(NO)(PPh_3)_3$,[12] $RuPhCl(CO)(PPh_3)_2$,[13] and $OsPhCl(CO)(PPh_3)_2$[13] were all prepared according to literature procedures.

$HSiPyr_3$ (1). To a solution of pyrrole (8.4 mL, 120 mmol) and triethylamine (20 mL) in 50 mL of tetrahydrofuran at −78 °C was added trichlorosilane (4.1 mL, 40 mmol) within 1 min. After the mixture was warmed to room temperature, *n*-hexane was added and the solution filtered. Reduction of the volume of the filtrate under vacuum and distillation at 86 °C/1 Torr leads to pure tri-*N*-pyrrolylsilane (25.1 g, 15.1 mL, 110.4 mmol, 92%). Mp: 32 °C. ^1H NMR ($CDCl_3$): δ 6.86 (t′, $^{3/4}J_{HH}$ = 4.0 Hz; α-*H*, Pyr), 6.47 (t′, $^{3/4}J_{HH}$ = 4.0 Hz; β-*H*, Pyr), 6.14 (s; Si*H*). ^{13}C NMR ($CDCl_3$): δ 123.6 (s; β-C, Pyr), 113.5 (s; α-C, Pyr). ^{29}Si NMR ($CDCl_3$): δ −37.8 (d, $^1J_{SiH}$ = 284.5 Hz). IR (Nujol): ν 2233 (SiH), 1199 cm^{-1} ($SiPyr_3$). Because of difficulties with the moisture sensitivity of **1**, no satisfactory chemical analysis could be obtained.

$Ru(SiPyr_3)H(CO)_2(PPh_3)_2$ (2a). The orange solution of $Ru(CO)_2(PPh_3)_3$ (411 mg, 0.436 mmol) in 30 mL of toluene immediately turned pale yellow when $HSiPyr_3$ (300 μL, 498 mg, 2.19 mmol) was added. After 10 min at room temperature the solution was concentrated to ca. 2 mL, and 10 mL of *n*-hexane was added. Recrystallization from CH_2Cl_2/*n*-hexane yields pure, white **2a** (300 mg, 0.330 mmol, 76%). Mp: 225 °C dec. ^1H NMR ($CDCl_3$): δ 7.7−6.8 (m, 30H; $P(C_6H_5)_3$), 6.26 (t, $^2J_{HH}$ = 1.7 Hz, 6H; α-*H*, Pyr), 6.13 (t, $^2J_{HH}$ = 1.7 Hz, 6H; β-*H*, Pyr), −8.17 (dd, $^2J_{HP}$ = 18.7 and 52.7 Hz, 1H; OsH). ^{13}C NMR ($CDCl_3$): δ 202.9 (t, $^2J_{CP}$ = 12 Hz; CO−C_6H_5), 135.6 and 135.0 (d, $^{1/3}J_{CP}$ = 38 and 39 Hz; *i*-C_6H_5), 133.2 (d, $^{3/5}J_{CP}$ = 12 Hz; *m*-C_6H_5), 129.8 (s; *p*-C_6H_5), 128.4 and 128.3 (d, each $^{2/4}J_{CP}$ = 10 Hz; *o*-C_6H_5), 124.7 (s; β-C, Pyr), 110.0 (s; α-C, Pyr). IR (Nujol): ν 1966 (CO), 1899 (RuH), 1181 cm^{-1} ($SiPyr_3$). MS (*m*/*e* (%)): 910 (13) [M^+], 654 (100) [M^+ − $HSiPyr_3$ − CO]. Anal. Calcd for $C_{50}H_{43}N_3O_2SiP_2Ru$ (909.10): C, 66.07; H, 4.77; N, 4.62. Found: C, 66.12; H, 5.00; N, 4.30.

$Os(SiPyr_3)H(CO)_2(PPh_3)_2$ (2b). The yellow solution of $Os(CO)_2(PPh_3)_3$ (130 mg, 0.126 mmol) and $HSiPyr_3$ (69 mg, 41.6 μL, 0.304 mmol) in 20 mL of toluene turned colorless after 5 min irradiation with a quartz−iodine lamp. After a further 5 min of irradiation concentration of the solution under vacuum to approximately 1 mL and addition of 20 mL of *n*-hexane leads to a white solid which can be recrystallized out of CH_2Cl_2/*n*-hexane to give pure **2b** (96 mg, 0.096 mmol, 76%). Mp: 218 °C dec. ^1H NMR ($CDCl_3$): δ 8.0−6.5 (m, 30H; $P(C_6H_5)_3$), 6.21 (t, $^2J_{HH}$ = 1.7 Hz, 6H; α-*H*, Pyr), 6.11 (t, $^2J_{HH}$ = 1.7 Hz, 6H; β-*H*, Pyr), −9.32 (dd, $^2J_{HP}$ = 36.0 and 21.2 Hz, 1H; OsH). ^{13}C NMR ($CDCl_3$): δ 188.4 (t, $^2J_{CP}$ = 10 Hz; CO−C_6H_5), 135.5 and 135.0 (d, $^1J_{CP}$ = 47 and 42 Hz; *i*-C_6H_5), 133.3 and 133.2 (d, each $^3J_{CP}$ = 10 Hz; *m*-C_6H_5), 130.1 and 130.0 (s; *p*-C_6H_5), 128.3 and 128.2 (d, each $^2J_{C,P}$ = 10 Hz; *o*-C_6H_5), 124.6 (s; β-C, Pyr), 110.0 (s; α-C, Pyr). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 4.9 (d, $^2J_{SiPtrans}$ = 74.8 Hz). IR (Nujol): ν 2039 (OsH), 1953 (CO), 1179 cm^{-1} ($SiPyr_3$). MS (*m*/*e* (%)): 1000 (17) [M^+], 263 (100) [$P(Ph_3)_3H^+$]. Anal. Calcd for $C_{50}H_{43}N_3O_2SiP_2Os \cdot H_2O$ (1016.16): C, 59.10; H, 4.46; N, 4.14. Found: C, 59.43; H, 4.49; N, 4.03.

$Ru(SiPyr_3)Cl(CO)(PPh_3)_2$ (3a). After 2 h of irradiation with a quartz−iodine lamp without cooling (50 °C) the red-orange solution of $RuPhCl(CO)(PPh_3)_2$ (179 mg, 0.234 mmol) and $HSiPyr_3$ (100 μL, 166 mg, 0.730 mmol) in 20 mL of toluene turned yellow. The crude product obtained by reducing the volume and adding *n*-hexane is recrystallized out of CH_2Cl_2/*n*-hexane to give pure **3a** (175 mg, 0.191 mmol, 82%). Mp: 198 °C dec. ^1H NMR ($CDCl_3$): δ 7.7−6.9 (m, 30H; $P(C_6H_5)_3$), 6.18 (t, $^2J_{HH}$ = 1.9 Hz, 6H; α-*H*, Pyr), 5.90 (t, $^2J_{HH}$ = 1.9 Hz, 6H; β-*H*, Pyr). ^{13}C NMR ($CDCl_3$): δ 199.5 (t, $^2J_{CP}$ = 12 Hz; CO−C_6H_5), 134.8 (t′, $^{3/5}J_{CP}$ = 12 Hz; *m*-C_6H_5), 131.2 (t′, $^{1/3}J_{CP}$ = 46 Hz; *i*-C_6H_5), 130.3 (s; *p*-C_6H_5), 128.2 (t′, $^{2/4}J_{CP}$ = 10 Hz; *o*-C_6H_5), 125.5 (s; β-C, Pyr), 110.4 (s; α-C, Pyr). IR (Nujol): ν 1936 (CO), 1927 (CO), 1181 cm^{-1} ($SiPyr_3$). MS (*m*/*e*): 916 [M^+]. Anal. Calcd for $C_{49}H_{42}N_3OSiP_2ClRu \cdot 2.5H_2O$ (960.49): C, 61.28; H, 4.93; N, 4.37. Found: C, 61.48; H, 4.82; N, 4.35.

$Os(SiPyr_3)Cl(CO)(PPh_3)_2$ (3b). A solution of $OsPhCl(CO)(PPh_3)_2$ (315 mg, 0.368 mmol) and $HSiPyr_3$ (100 μL, 166 mg, 0.730 mmol) in 20 mL of toluene turned reddish brown after 10 h of irradiation with a quartz-iodine lamp without cooling (50 °C). After the volume is reduced under vacuum to approximately 2 mL and 15 mL of *n*-hexane is added, the solid obtained can be recrystallized out of CH_2Cl_2/*n*-hexane. This yields pure **3b** (286 mg, 0.285 mmol, 77%) in the form of an orange powder. Mp: 185 °C dec. ^1H NMR ($CDCl_3$): δ 7.45−6.90 (m, 30H; $P(C_6H_5)_3$), 6.13 (t, $^2J_{HH}$ = 1.9 Hz, 6H; α-*H*, Pyr), 5.88 (t, $^2J_{HH}$ = 1.9 Hz, 6H; β-*H*, Pyr). ^{13}C NMR ($CDCl_3$): δ 182.1 (t, $^2J_{CP}$ = 8 Hz; CO−C_6H_5), 134.9 (t′, $^{3/5}J_{CP}$ = 11 Hz; *m*-C_6H_5), 130.4 (s; *p*-C_6H_5), 128.2 (t′, $^{2/4}J_{CP}$ = 10 Hz; *o*-C_6H_5), 125.3 (s; β-C, Pyr), 110.1 (s; α-C, Pyr). IR (Nujol): ν 1915 (CO), 1182 cm^{-1} (SiPyr$_3$). MS (*m*/*e* (%)): 1006 (28) [MH$^+$], 263 (100) [P(Ph$_3$)$_3$H$^+$]. Anal. Calcd for $C_{49}H_{42}N_3OSiP_2ClOs\cdot1.5H_2O$ (1031.60): C, 57.05; H, 4.40; N, 4.07. Found: C, 57.12; H, 4.42; N, 4.08.

Os(SiPyr$_3$)HCl(NO)(PPh$_3$)$_2$ (4). To a solution of tri-*N*-pyrrolylsilane (**1**) (100 μL, 166 mg, 0.730 mmol) in 10 mL of benzene was added, OsCl(NO)(PPh$_3$)$_3$ (184 mg, 0.177 mmol), and the color changed instantly to orange. After 10 min of heating under reflux the volume of the solution was reduced under vacuum. Addition of *n*-hexane (10 mL) gives a crude product; recrystallization from CH$_2$Cl$_2$/*n*-hexane leads to pure **4** in the form of a cream-colored powder (84 mg, 0.083 mmol, 48%). Mp: 178 °C dec. ^{1}H NMR (CDCl$_3$): δ 7.8−7.0 (m, 30H; P(C$_6$*H*$_5$)$_3$), 6.33 (s, 6H; α-*H*, Pyr), 6.12 (s, 6H; β-*H*, Pyr), −0.38 (dd, $^2J_{HP}$ = 112.0 and 18.0 Hz, 1H; Os*H*). ^{13}C NMR (CDCl$_3$): δ 134.3 and 134.0 (d, each $^3J_{CP}$ = 10 Hz; *m*-C$_6$H$_5$), 132.0 and 131.2 (d, $^1J_{CP}$ = 43 and 41 Hz; *i*-C$_6$H$_5$), 130.5 and 130.4 (s; *p*-C$_6$H$_5$), 128.3 (d, $^2J_{C,P}$ = 10 Hz; *o*-C$_6$H$_5$), 125.3 (s; β-C, Pyr), 110.1 (s; α-C, Pyr). IR (Nujol): ν 2083 (OsH), 1783 (NO), 1181 cm^{-1} (SiPyr$_3$). MS: (*m*/*e* (%)): 1009 (24) [MH$^+$], 263 (100) [P(Ph$_3$)$_3$H$^+$]. Anal. Calcd for $C_{48}H_{43}N_4OSiP_2ClOs\cdot1.6CH_2Cl_2$ (1143.47): C, 52.10; H, 3.99; N, 4.90. Found C, 52.42; H, 4.04; N, 4.24.

X-ray Experimental Data for 1. Crystals of **1** were grown at −40 °C from an *n*-hexane solution of the compound. Data were collected on a Siemens Smart CCD diffractometer. A SADABS absorption correction was applied. The structure was solved by direct methods, and refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL Plus).[18b] Anisotropic temperature factors were used for all non-hydrogen atoms. All hydrogen atoms were refined freely with isotropic temperature factors. Further results of the refinement are listed in Table 2.

X-ray Experimental Data for 2b·H$_2$O. Suitable crystals were obtained by diffusion of *n*-hexane into a chloroform solution of the compound at room temperature. Data were collected on an Enraf-Nonius CAD4 diffractometer. An XEMP (SHELXTL Plus)[18b] absorption correction was applied. The structure was solved by Patterson methods, and refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXTL Plus).[18b] Anisotropic temperature factors were used for all non-hydrogen atoms except for the water molecule. Hydrogen atoms were included in calculated positions with isotropic temperature factors 20% higher than the corresponding carbon atoms. Further results of the refinement are listed in Table 2.

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Supporting Information Available: Tables giving descriptions of X-ray procedures and all atomic coordinates, thermal parameters, and interatomic distances and angles (13 pages). Ordering information is given on any current masthead page.

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