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Triphenylsiloxy Complexes. A Novel Compound Containing a Mo(VI)–P Bond: $MoO_2(OSiPh_3)_2(PPh_3)$

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Triphenylsiloxy complexes have been synthesized through direct silylation of silver metalates by triphenylchlorosilane. The Mo dioxo complex $MoO_2(OSiPh_3)_2$ (**1**) is tetrahedral and crystallizes in the *Fdd*2 space group with a = 19.556(7) Å, b = 34.187(4) Å, c = 9.748(5) Å, V = 6517.3(3.6) Å^3, and D_{calcd} = 1.38 g/cm^3 for Z = 8; final residuals R = 4.4% and R_w = 4.4%. An interesting compound, $MoO_2(OSiPh_3)_2(PPh_3)$ (**2**), containing the first Mo(VI)–phosphine bond was also synthesized in this study and characterized by single-crystal X-ray diffraction. X-ray crystallographic data for compound **2**: a = 18.498(4) Å, b = 10.818(3) Å, c = 24.844(3) Å, β = 107.08(1)°, V = 4753(2) Å^3, D_{calc} = 1.315 g/cm^3 for Z = 4; final residuals R = 5.2% and R_w = 5.6% for 1236 ($I > 3\sigma(I)$) reflections and 194 variables. Compound **2** has a distorted trigonal bipyramidal structure with a Mo–P bond length equal to 2.759 Å. The preparation and a single-crystal X-ray structure of $VO(OSiPh_3)_3$ are also reported.

Introduction

In the past few years there has been an increasing reasearch interest in the use of the sterically demanding trialkylsiloxy group as a ligand in coordination chemistry. The very bulky ligand tri-*tert*-butylsiloxy (Bu^t_3SiO) has been used to stabilize low coordination number transition metal compounds, yielding interesting structures and chemistry.[1,2] The triphenylsiloxy (Ph_3SiO) group has been extensively used in lanthanide alkoxide chemistry.[3,4]

Our interest has been in the development of new oxo siloxy complexes of Mo^{VI}. The use of triphenylsiloxy in place of trimethylsiloxy not only increases the solubility of the product but also increases the air stability and prevents the possible oligomerization through the siloxy group.

Direct silylation (eq 1) of the metal oxo moieties of silver metalates by trimethylchlorosilane has been used by others[5] to

$$AgMO_4 + Me_3SiCl \xrightarrow[-AgCl]{25\ ^\circ C} Me_3SiOMO_3 \qquad (1)$$

$$M = Re, Tc$$

prepare trimethylsiloxy compounds. In this paper we expand on this strategy to prepare a series of triphenylsiloxy compounds and report the crystal structure of the compounds $MoO_2(OSiPh_3)_2$ (**1**) and its triphenylphosphine adduct $MoO_2(OSiPh_3)_2(PPh_3)$ (**2**). Compound **2** was found during a study of the reaction of **1** with triphenylphosphine and contains the first example of a Mo^{VI}–phosphine bond.

Experimental Section

The operations were carried out under an atmosphere of purified nitrogen. Anhydrous 1,2-dichloroethane and acetonitrile were used as purchased from Aldrich; all other solvents were dried and distilled before use by standard methods. Silver vanadate and silver molybdate were synthesized from analytical grade silver nitrate and ammonium vanadate and sodium molybdate, respectively, and dried in a vacuum oven at 60 °C for several days. Triphenylchlorosilane was purchased from Petrach Systems (Huls-America, Inc.) and used as received. Infrared spectra were recorded with a Nicholet 510P FTIR spectrometer, and NMR spectra, with an AC-300 Bruker instrument.

Synthesis of $MoO_2(OSiPh_3)_2$ (1). In a typical synthesis, a flask was loaded with Ag_2MoO_4 (2.38 g, 6.33 mmol), Ph_3SiCl (2.44 g, 8.29 mmol), 40 mL of 1,2-dichloroethane, and about 1 mL of acetonitrile and the mixture was stirred and heated in an 82 °C bath overnight to yield a bluish solution. A pale bluish solution was recovered by filtration through Celite. Removal of the solvent under vacuum gave a white or sometimes slightly bluish solid. Yields based on Ph_3SiCl were typically >90%. Frequently, the solid is sufficiently pure for further reactions. If desired, it can be crystallized from *n*-hexane/1,2-dichloroethane or hot acetonitrile. Anal. Calcd for $C_{36}H_{30}O_4Si_2Mo$: C, 63.53; H, 4.45; Mo, 14.12. Found: C, 63.37; H, 4.50; Mo, 13.71. IR (KBr, cm^{-1}): 3070 m, 3024 m, 1588 m, 1485 m, 1428 s, 1188 w, 1119 s, 948 m, 933 m, 886 vs, 743 m, 712 s, 697 s, 556 m, 512 s. ^1H NMR ($CDCl_3$/TMS, ppm): 7.5 (dd, J = 7, 2 Hz, 2 H), 7.46 (tt, J = 7, 2 Hz, 1 H), 7.33 (t, J = 7 Hz, 2H).

Compound **1** is a white or sometimes pale bluish solid that is stable in air for several months. It is soluble in most organic solvents, except nonpolar solvents like hexane. Once exposed to air, the 1,2-dichloroethane solution of **1** became bluish.

Synthesis of $MoO_2(OSiPh_3)_2(PPh_3)$ (2). A 207-mg sample of **1** was dissolved in a small amount of dichloromethane; the solution was then cooled to –78 °C. To this solution was slowly added about 1 mL of dichloromethane solution containing 96 mg of triphenylphosphine. The adduct was precipitated by the addition of 30 mL of cold hexane and then recovered by cold cannular filtration to yield 148 mg of a gray solid after drying under vacuum. IR (KBr, cm^{-1}): 3050 m, 1590 m, 1482 m, 1437 w, sh 1429 s, 1187 w, 1117 s, 989 w, 965 w, 898 vs (Mo=O), 873 vs (Mo=O), 712 s, 698 s, 564 w, 536 w, 507 s. ^{31}P NMR (in $CDCl_3$, 85% H_3PO_4 as external standard, ppm): 30.44 (Mo–PPh_3), –4.823 (PPh_3), area ratio 3:2, obtained by removing the NOE effect through a gated decoupling pulse sequence.

Synthesis of Oxotris(triphenylsiloxy)vanadium (3). A mixture of $AgVO_3$ (0.490 g, 2.37 mmol), Ph_3SiCl (0.700 g, 2.37 mmol), and 30 mL of 1,2-dichloroethane was stirred and refluxed for 70 h, yielding a bluish solution. Filtration through Celite gave a pale yellowish solution, and from this solution was recovered 0.676 g of a white solid upon solvent removal and *n*-hexane wash. The IR spectrum (909.6 cm^{-1}, V=O), the elemental analysis (Anal. Calcd for $C_{54}H_{45}O_4Si_3V$: C, 72.69; H, 5.08. Found: C, 72.26; H, 4.92), and the ^1H NMR spectrum ($CDCl_3$/TMS) [7.49 (d, J = 8.9 Hz, 2H), 7.37 (m, 1H), 7.18 ppm (t, J = 8.3 Hz, 2H)] as well as the x-ray diffraction study of this solid confirmed the formula of $VO(OSiPh_3)_3$. The yield is 93% based on Ph_3SiCl.

Crystallographic Studies. In all cases, X-ray reflection data were collected at 23 °C with a Rigaku AFC6R diffractometer using with graphite-monochromated Mo Kα (λ = 0.710 73Å) radiation. Three

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Table I. Crystallographic Data and Experimental Conditions for **1–3**

	1	**2**	**3**
empirical formula	$MoSi_2O_4C_{36}H_{30}$	$MoSi_2O_4C_{54}H_{45}P$	$VSi_3O_4C_{54}H_{45}$
fw	678.7416	941.03	893.1451
dimens, mm	0.2 × 0.2 × 0.5	0.2 × 0.2 × 0.4	0.2 × 0.2 × 0.3
crystal system	orthorhombic	monoclinic	triclinic
a, Å	19.556(7)	18.498(4)	13.477(5)
b, Å	34.187(4)	10.818(3)	18.577(4)
c, Å	9.748(5)	24.844(3)	10.014(3)
α, deg			98.66(3)
β, deg		107.08(1)	101.22(3)
γ, deg			73.14(2)
V, $Å^3$	6517.3(3.6)	4753(2)	2341.7(1.4)
space group	*Fdd*2 (No. 43)	$P2_1/a$ (No. 14)	$P\bar{1}$ (No. 2)
Z	8	4	2
D_{calc}, g cm^{-3}	1.3833	1.315	1.2665
$F(000)$	2784	1944	932
μ(Mo Kα), cm^{-1}	4.9975	3.9368	3.22
diffractometer	Rigaku AFC6R	Rigaku AFC6R	Rigaku AFC6R
λ(Mo Kα), Å (graphite monochromated)	0.710 690	0.710 690	0.710 690
temp, °C	23	23	23
$2\theta_{max}$, deg	53.2	45	53
scan method	ω–2θ	ω	ω
data colln speed, deg min^{-1} in ω	16.0	16.0	16.0
hkl limits	0,0,0 to 24, 42,12	–21,0,0 to 21,12,29	0,–23,–17 to 16,23,17
total no. of measd data	1921	6546	6839
no. of observns ($I > 3\sigma(I)$)	1236	2768	3011
no. of variables	194	559	559
residuals: R, R_w	0.044, 0.044	0.052, 0.056	0.0651, 0.0679
GOF	1.523	1.34	1.90
max shift	0.07	0.02	0.05
largest residual peak	0.339	0.527	0.269

intense reflections were monitored every 300 reflections to check stability. No significant intensity loss was found in all cases. Crystallographic programs used were TEXSAN[6] installed on a microVAX or SHELXS-86 for direct methods.[7] Crystallographic data are given in Table I. Hydrogen positions, bond angles, and bond lengths can be found in the supplementary material.

$MoO_2(OSiPh_3)_2$ (1). A colorless single crystal (0.2 × 0.2 × 0.5 mm) of **1**, crystallized from a 1,2-dichloroethane and hexane mixed solvent, was coated with epoxy and mounted on a Rigaku AFC6R diffractometer. The unit cell parameters were determined from a least-squares fit of 19 accurately centered reflections ($27.8 < 2\theta < 31.7°$). The heavy atom was located by the deconvolution of the Patterson pattern (PHASE[8]). The remaining atoms were expanded by the DIRDIF program[9] and difference Fourier techniques. All H atoms were included in the calculated positions (C–H = 0.95 Å) in the structure factor calculations. H parameters were not refined. Anisotropic temperature factors were refined for all non-hydrogen atoms. The largest residue on a final difference electron density map was 0.339 e Å^{-3}. Fractional positional parameters and B(eq) values for the non-hydrogen atoms of $MoO_2(OSiPh_3)_2$ are given in Table II.

$MoO_2(OSiPh_3)_2(PPh_3)$ (2). Some crystals were obtained by recrystallization from a toluene/hexane solvent mixture at –15 °C. One crystal, ~0.2 × 0.2 × 0.4 mm, was carefully chosen under a microscope and coated with epoxy resin. Unit cell parameters were determined from a least-squares fit of 12 accurately centered reflections ($22 < 2\theta < 24.6°$). The structure was solved by a combination of direct methods (SHELXS-86[7]) and a difference Fourier synthesis. All H atoms were included in the calculated positions (C–H = 0.95 Å) in the structure factor calculations. H parameters were not refined. Anisotropic temperature factors were refined for all non-hydrogen atoms. The largest residue on a final difference electron density map was 0.527 e Å^{-3}. Fractional positional parameters and B(eq) values for the non-Hydrogen atoms of $MoO_2(OSiPh_3)2(PPh_3)$ are given in Table III.

Table II. Fractional Positional Parameters and B(eq) Values for the Non-Hydrogen Atoms of $MoO_2(OSiPh_3)_2$ (**1**)

atom	x	y	z	B(eq), Å^2
Mo	0	0	0	3.42(4)
Si(1)	0.0935(1)	0.07143(6)	–0.1649(3)	3.6(1)
O(2)	–0.0577(3)	0.0219(2)	0.1038(8)	7.6(4)
O(1)	0.0417(3)	0.0364(2)	–0.1068(6)	4.6(3)
C(1)	0.1822(4)	0.0533(2)	–0.1504(9)	3.3(3)
C(2)	0.2192(5)	0.0423(2)	–0.265(1)	4.5(4)
C(3)	0.2855(5)	0.0285(3)	–0.256(1)	5.5(5)
C(4)	0.3146(4)	0.0258(3)	–0.129(1)	6.0(6)
C(5)	0.2809(5)	0.0358(3)	–0.014(1)	5.7(5)
C(6)	0.2140(4)	0.0501(2)	–0.025(1)	4.5(5)
C(7)	0.0803(4)	0.1154(2)	–0.0571(8)	3.6(4)
C(8)	0.1320(4)	0.1425(2)	–0.035(1)	5.1(5)
C(9)	0.1223(5)	0.1761(2)	0.039(1)	6.2(6)
C(10)	0.0610(6)	0.1842(3)	0.096(1)	6.1(5)
C(11)	0.0067(5)	0.1581(3)	0.077(1)	5.7(5)
C(12)	0.0169(4)	0.1245(2)	0.003(1)	4.6(4)
C(13)	0.0711(4)	0.0795(3)	–0.344(1)	4.0(4)
C(14)	0.0865(5)	0.1143(3)	–0.413(1)	5.8(6)
C(15)	0.0712(8)	0.1179(4)	–0.548(1)	9.4(8)
C(16)	0.0455(7)	0.0897(5)	–0.624(1)	9.6(9)
C(17)	0.0283(9)	0.0550(4)	–0.562(1)	9.7(9)
C(18)	0.0420(6)	0.0507(3)	–0.425(1)	7.6(7)

$VO(OSiPh_3)_3$ (3). Crystals suitable for an X-ray diffraction study were obtained by crystallization from a 1,2-dichloroethane and hexane mixed solvent. Unit cell parameters were determined from a least-squares fit of 15 accurately centered reflections ($20.5 < 2\theta < 23.7°$). The structure was solved by a combination of direct methods (SHELXS-86) and a difference Fourier synthesis. All H atoms were included in calculated positions (C–H = 0.95 Å) in structure factor calculations. H parameters were not refined. Anisotropic temperature factors were refined for all non-hydrogen atoms. The largest residue on a final difference electron density map was 0.269 e Å^{-3}.

Results and Discussion

Synthesis of Metal Oxo Triphenylsiloxides. In the synthesis of **1**, an excess amount of silver molybdate was used to ensure complete reaction of Ph_3SiCl, which can be identified by the disappearance of the 542-cm^{-1} (Si–Cl vibration) band in the infrared spectrum of the liquid phase of the reaction mixture. The only compound remaining in the filtrate was **1**. Yields based on Ph_3SiCl were typically 90% or better. The reaction can be described as

$$Ag_2MoO_4 + 2Ph_3SiCl \xrightarrow{83\ °C} MoO_2(OSiPh_3)_2 + 2AgCl \tag{2}$$

It is interesting to note that, without a small amount of acetonitrile, a deep bluish mixture was usually obtained which contains a high concentration of hexaphenyldisiloxane, instead of compound **1**.

The stoichiometric preparation of $VO(OSiPh_3)_3$ can be written as eq 3. Although there are other ways[10] to prepare $VO(OSiPh_3)_3$,

$$3AgVO_3 + 3Ph_3SiCl \xrightarrow{\text{reflux}} VO(OSiPh_3)_3 + V_2O_5 + 3AgCl \tag{3}$$

the current method has the advantages that the starting materials are easily available and that the product is easy to isolate and purify. The yield is high based on Ph_3SiCl, although it is low (31%) based on silver vanadate.

While Ph_3SiCl silylates three V=O bonds in the $\{VO_4\}$ tetrahedron to form $VO(OSiPh_3)_3$, the reaction between $(^tBu)_3SiOH$ and V_2O_5 gives a dimer $(^tBu_3SiO)_2VO$–O–VO-

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Table III. Fractional Positional Parameters and *B*(eq) Values for the Non-Hydrogen Atoms of $MoO_2(OSiPh_3)_2(PPh_3)$ (**2**)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Mo	–0.00209(5)	0.0737(1)	0.26813(4)	4.23(4)
P	0.1009(2)	0.1266(3)	0.3708(1)	4.7(1)
Si(1)	0.0733(2)	–0.2011(3)	0.2564(1)	4.0(1)
Si(2)	–0.1273(2)	0.0291(3)	0.1401(1)	4.7(2)
O(1)	0.0558(3)	–0.0759(6)	0.2875(2)	4.4(3)
O(2)	–0.0603(4)	0.0017(6)	0.1991(3)	5.1(3)
O(3)	–0.0664(4)	0.1092(7)	0.3019(3)	7.2(4)
O(4)	0.0317(4)	0.2035(7)	0.2474(3)	7.2(4)
C(1)	–0.0069(6)	–0.311(1)	0.2454(4)	4.3(5)
C(2)	–0.0007(7)	–0.430(1)	0.2244(5)	5.8(6)
C(3)	–0.0606(9)	–0.515(1)	0.2158(5)	6.7(7)
C(4)	–0.1230(8)	–0.485(1)	0.2294(6)	6.6(7)
C(5)	–0.1294(7)	–0.372(1)	0.2512(6)	6.7(8)
C(6)	–0.0715(7)	–0.285(1)	0.2594(5)	5.3(6)
C(11)	0.1601(6)	–0.2753(9)	0.3048(5)	4.2(5)
C(12)	0.1678(7)	–0.286(1)	0.3626(5)	5.4(6)
C(13)	0.228(1)	–0.343(1)	0.3981(5)	7.4(8)
C(14)	0.2829(8)	–0.393(1)	0.3782(7)	7.7(8)
C(15)	0.2781(7)	–0.384(1)	0.3217(7)	7.3(8)
C(16)	0.2151(6)	–0.328(1)	0.2857(5)	5.5(6)
C(21)	0.0938(6)	–0.160(1)	0.1898(4)	4.3(5)
C(22)	0.0568(7)	–0.212(1)	0.1386(6)	6.9(7)
C(23)	0.078(1)	–0.182(2)	0.0910(6)	8(1)
C(24)	0.132(1)	–0.099(2)	0.0926(7)	10(1)
C(25)	0.1698(8)	–0.044(2)	0.1422(7)	10(1)
C(26)	0.1485(7)	–0.076(1)	0.1901(5)	7.4(7)
C(31)	–0.2166(6)	0.064(1)	0.1562(5)	4.9(6)
C(32)	–0.2211(7)	0.163(1)	0.1901(6)	6.8(8)
C(33)	–0.287(1)	0.193(1)	0.2021(5)	7.7(8)
C(34)	–0.3501(8)	0.126(2)	0.1793(7)	7.5(9)
C(35)	–0.3482(8)	0.026(1)	0.1451(7)	7.9(8)
C(36)	–0.2811(9)	–0.006(1)	0.1348(5)	6.9(7)
C(41)	–0.1015(7)	0.166(1)	0.1046(5)	4.9(6)
C(42)	–0.0299(8)	0.185(1)	0.1019(5)	7.5(8)
C(43)	–0.013(1)	0.283(2)	0.0709(8)	10(1)
C(44)	–0.070(1)	0.356(2)	0.0421(7)	9(1)
C(45)	–0.142(1)	0.339(1)	0.0422(7)	9(1)
C(46)	–0.1562(7)	0.243(1)	0.0739(6)	6.8(7)
C(51)	–0.1392(6)	–0.108(1)	0.0926(5)	4.7(6)
C(52)	–0.1319(7)	–0.097(1)	0.0397(6)	6.9(7)
C(53)	–0.1401(8)	–0.197(2)	0.0035(5)	8.2(8)
C(54)	–0.1539(9)	–0.311(1)	0.0210(6)	8.3(9)
C(55)	–0.1620(8)	–0.325(1)	0.0733(7)	7.8(8)
C(56)	–0.1531(7)	–0.224(1)	0.1093(5)	6.5(7)
C(61)	0.1959(6)	0.138(1)	0.3647(4)	4.4(5)
C(62)	0.2254(6)	0.253(1)	0.3577(4)	5.0(6)
C(63)	0.2962(8)	0.260(1)	0.3489(5)	6.5(7)
C(64)	0.3353(7)	0.157(2)	0.3466(5)	6.9(8)
C(65)	0.3078(7)	0.044(1)	0.3536(5)	6.3(7)
C(66)	0.2385(8)	0.033(1)	0.3635(5)	6.1(7)
C(71)	0.0865(6)	0.271(1)	0.4035(5)	4.9(6)
C(72)	0.1086(7)	0.290(1)	0.4596(6)	6.9(8)
C(73)	0.099(1)	0.401(2)	0.4837(6)	9(1)
C(74)	0.063(1)	0.498(2)	0.4488(8)	9(1)
C(75)	0.0397(8)	0.481(1)	0.3924(8)	8.0(8)
C(76)	0.0502(7)	0.368(1)	0.3673(6)	6.6(7)
C(81)	0.1022(7)	0.012(1)	0.4237(4)	4.5(5)
C(82)	0.1666(7)	–0.026(1)	0.4658(5)	5.6(6)
C(83)	0.162(1)	–0.115(1)	0.5047(5)	7.4(8)
C(84)	0.093(1)	–0.165(1)	0.5024(6)	8(1)
C(85)	0.0301(8)	–0.131(1)	0.4609(6)	7.7(8)
C(86)	0.0330(7)	–0.043(1)	0.4226(5)	6.1(7)

$(OSi^tBu_3)_2$ with only two V═O bonds being silylated.[11] This is a reflection of the greater steric bulkiness of $^tBu_3SiO$ over Ph_3SiO. The cone angle of $^tBu_3Si$ (187°) is significantly larger than that of Ph_3Si (150°).[12]

The reactivity of metalates toward Ph_3SiCl displays an interesting pattern. It was found in this study that while $CrO_2(OSiPh_3)_2$ can be prepared from the reaction of silver chromate with Ph_3SiCl at room temperature, higher temperatures (83 °C) are required for silver molybdate to react with Ph_3SiCl. For silver tungstate, no reaction with Ph_3SiCl was observed even at 110 °C for 15 h. Because this direct silylation is a heterogeneous reaction, the lattice energies of the silver metalates are very important in determining the reactivity for direct silylation. On the basis of metal ionic radii, it can be expected that, going from silver chromate to tungstate, the lattice energy of the silver metalates gradually decreases. This is supported by the solubility product data of silver metalates in aqueous solution: 7.1×10^{-13}, 6.4×10^{-12}, and 5.2×10^{-10} at 25 °C for silver chromate, molybdate, and tungstate, respectively.[13] It is interesting to note that although the tungstate has the lower lattice energy (higher solubility), it does not react with triphenylchlorosilane at all! There must be other factors that play an important role in determining the reactivity. Metal–oxo bond strength is one of the factors which is parallel to the reactivity of the silver metalate silylation reactions. The W═O bond strength in WO_3, 150 kcal/mol, is greater than the Mo═O bond strength in MoO_3, 141 kcal/mol,[14] which in turn is greater than that of the Cr═O bond of a diatomic Cr–O species (102.6 ± 7.0 kcal/mol).[15]

One of the advantages of using Ph_3Si^+ instead of $(CH_3)_3Si^+$ [16,17] for direct silylation is that for Ph_3SiCl the loss of $(R_3Si)_2O$ either by intramolecular extrusion from the $\{M(OSiR_3)_2\}$ moiety or by the side reaction shown in (4) is reduced due to the relative steric bulkiness of Ph_3Si– compared to the $(CH_3)_3Si$– group.

$$M\text{–}OSiR_3 + R_3Si^+Cl^- \rightarrow M\text{–}Cl + (R_3Si)_2O \qquad (4)$$

In the synthesis of **1**, a small amount of acetonitrile is needed to avoid the formation of $(Ph_3Si)_2O$. Among many possible explanations, it may be that the acetonitrile saturates the inner coordination sphere of Mo, thus protecting the Mo–$OSiPh_3$ bond from attack by $Ph_3Si^+Cl^-$ (eq 4) or preventing the elimination of $(Ph_3Si)_2O$ by an intramolecular pathway.

Structure of $MoO_2(OSiPh_3)_2$ (1). The structure of **1** and some selected bond angles and lengths are given in Figure 1 and its caption. Final fractional coordinates are given in Table II. There is a 2-fold axis in the molecule passing through the Mo atom and bisecting the O(1)–O(1A) linkage. The $\{MoO_2\}^{2+}$ unit is typical of that in four-coordinate Mo dioxo compounds. Mo–O(1)–Si(1) linkages are almost linear (163.6(4)°); on the contrary, one Cr–O–Si linkage in $CrO_2(OSiPh_3)_2$[18] is bent (133.1(6), 162.7(7)°). The Mo–O–Si linkages in compound **2** with a trigonal bipyramidal structure are bent (143.9(4), 138.7(4)°).

Structure of $VO(OSiPh_3)_3$ (3). An ORTEP drawing is shown in Figure 2. The coordination geometry around V is nearly tetrahedral with the O–V–O angle spanning the range 107.8–111.2°. The V–O–Si angles are 145.4, 154.7, and 156.6°, respectively. Feher has reported a crystal structure for $VO(OSiPh_3)_3 \cdot 0.5C_6H_6$[19] at –90 °C. His crystal of $VO(OSiPh_3)_3$ was grown from benzene solvent and contained one benzene molecule per unit cell. Feher's $VO(OSiPh_3)_3$ structure has an average V–O–Si angle and Si–O bond length of 154.6(1)° and 1.653(2) Å, respectively. His average V–O–Si bond angle (154.6(1)°) is slightly larger than that in our $VO(OSiPh_3)_3$ compound (152.2(4)°). Other aspects of the two structures are very similar to each other.

Structure of $MoO_2(OSiPh_3)_2(PPh_3)$ (2). The structure of **2** and some selected bond lengths and bond angles as determined from a single-crystal X-ray diffraction study are given in Figure

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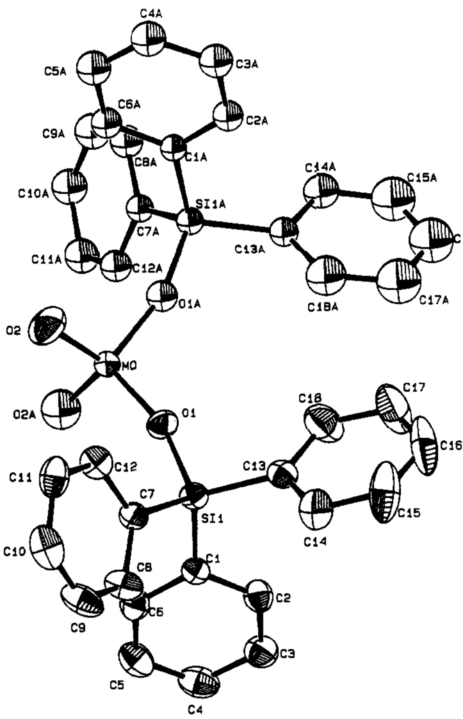

Figure 1. ORTEP drawing of the structure of $MoO_2(OSiPh_3)_2$. Selected bond lengths (Å) and bond angles (deg): Mo–O(1) = 1.815(5), Mo–O(2) = 1.692(7), Si(1)–O(1) = 1.669(6); O(2)–Mo–O(2) = 106.4(5), O(1)–Mo–O(1) = 110.(4), O(1)–Mo–O(2) = 109.9(3), O(1A)–Mo–O(2) = 110.3(3), Mo–O(1)–Si(1) = 163.6(4). H atoms are omitted for clarity.

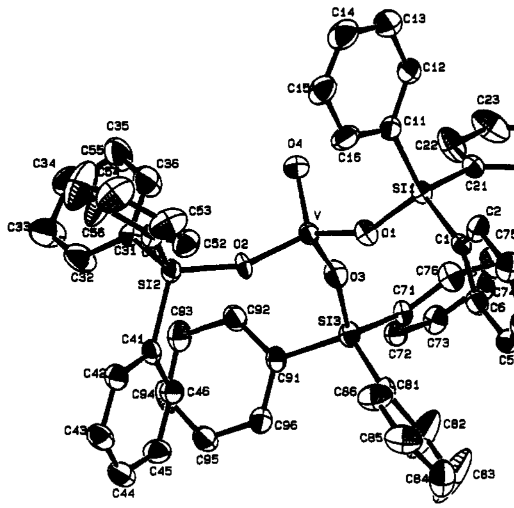

Figure 2. ORTEP drawing of $VO(OTPS)_3$. Selected bond lengths (Å) and bond angles (deg): V–O(1) - 1.742(6), V–O(2) = 1.740(6), V–O(3) = 1.737(6), V–O(4) = 1.566(7), Si(1)–O(1) = 1.649(7), Si(2)–O(2) = 1.650(6), Si(3)–O(3) = 1.643(7); V–O(1)–Si(1) - 145.4(4), V–O(2)–Si(2) - 154.7(4), V–O(3)–Si(3) = 156.6(5), O(1)–V–O(2) - 110.5(3), O(1)–V–O(3) = 107.8(3), O(1)–V–O(4) = 109.0(4), O(2)–V–O(3) = 111.2(3), O(2)–V–O(4) = 110.0(3), O(3)–V–O(4) = 108.1(4). H atoms are omitted for clarity.

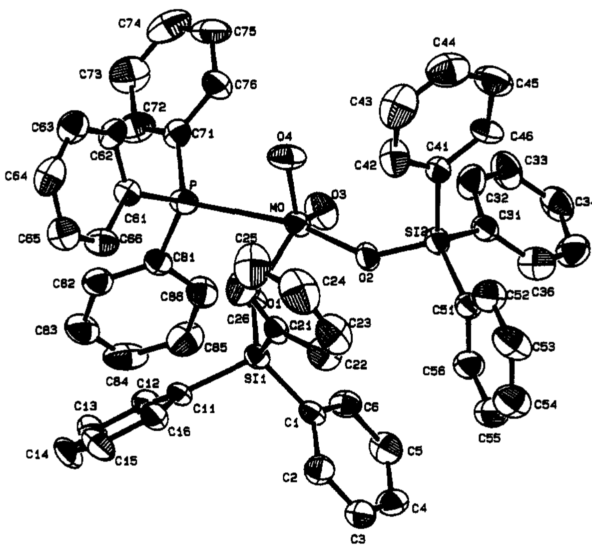

Figure 3. ORTEP drawing of the structure of $MoO_2(OSiPh_3)_2(PPh_3)$. Selected bond lengths (Å) and bond angles (deg): Mo–P = 2.759(3), Mo–O(1) = 1.922(6), Mo–O(2) = 1.903(6), Mo–O(3) = 1.688(7), Mo–O(4) = 1.678(7), P–O(1) = 2.961(7), P–O(3) = 3.071(7), P–O(4) = 3.071(7); P–Mo–O(1) = 76.2(2), P–Mo–O(2) = 166.5(2), P–Mo–O(3) = 83.7(3), P–Mo–O(4) = 83.8(3), O(1)–Mo–O(2) = 90.4(3), O(1)–Mo–O(3) = 119.3(3), O(1)–Mo–O(4) = 123.5(3), O(2)–Mo–O(3) = 104.2(3), O(2)–Mo–O(4) = 103.3(3), O(3)–Mo–O(4) = 110.0(4), Mo–O(1)–Si(1) = 138.7(4), Mo–O(2)–Si(2) = 143.9(4). H atoms are omitted for clarity.

3 and its caption. Final fractional coordinates are given in Table III. Compound **2** has a distorted trigonal bipyramidal configuration around the Mo atom. The oxo atoms and one triphenylsiloxy oxygen atom occupy the equatorial plane. The Mo atom is not coplanar with the equatorial ligands but is slightly moved (by 0.276 Å) from the equatorial plane toward the axial triphenylsiloxy group. The triphenylsiloxy group above the equatorial plane is displaced from the axial position toward the equatorial triphenylsiloxy group. This causes the four oxygen atoms in the inner coordination layer to be in a quasi-tetrahedral setting. It is also noteworthy that the equatorial Mo–O(Si) bond length (1.922(6) Å) is longer than the axial one (1.903(6) Å).

The bond angle between the Mo dioxo bonds (110.0°) in **2** is close to that of the parent tetrahedral compound **1** (106.4°). The Mo=O bond lengths (1.638(7), 1.678(7) Å) are comparable to the corresponding Mo=O bond lengths in **1** (1.690(6) Å). It appears, from these structural data, that the $\{MoO_2\}$ unit is not sensitive to the uptake of triphenylphosphine. This is also true for the uptake of 2,2′-bipyridine by **1** to form $MoO_2(OSiPh_3)_2(2,2'\text{-bpy})$.[20] These results are in contrast to those from the infrared spectrum of **2**, which shows that ν(Mo=O) bands at 898 and 873 cm^{-1} are significantly lower than the bands at 948, 932, and 885 cm^{-1} for the parent compound, suggesting that the Mo=O bond strength in **2** may be weaker than that in **1**.

The most interesting structural feature of **2** is the coordination of the phosphorus atom to **1**. To our knowledge, no Mo(VI) compounds coordinated to alkyl or aryl P compounds have been observed. The Mo–P distance here is 2.759(3) Å. For comparison, Mo(IV)–P bond lengths in $MoOCl_2(PMe_2Ph)_3$ are 2.500, 2.541, and 2.588(3) Å,[21] Mo(II)–P lengths in $MoBr_2(CO)_3\{Ph_2P(CH_2)_2PPh_2\}\cdot CH_3COCH_3$ are 2.618 Å (trans to CO) and 2.500 Å (trans to Br),[22] Mo(O)–P in $Et_3P(OC)_3Mo(\mu\text{-}PMe_2)_2Mo(CO)_3PEt_3$ is 2.477(5) Å,[23] and Mo(IV)–P distances in $Mo(NTol)Cl_2(Me_3P)_3$ are 2.471(1) and 2.509(1) Å.[24] A Mo(V)–P bond is also known in $Mo(NPPh_3)Cl_4(PPh_3)$ and $Mo(NTol)Cl_3(Me_3P)_2$,[24] but no structural data are available. It appears that the Mo–P bond length is not very sensitive to the change of Mo oxidation state or, alternatively, the Mo–P bond length is not correlated with the Mo oxidation state. On the basis of the above arguments, we estimate the Mo(VI)–P single bond length to be between 2.5 and 2.6 Å. This suggests that the Mo–P (2.759 Å) bond in **2** is weaker than a single bond. This conclusion is supported by the following experimental fact: if **2** is stirred in

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hexane, in which both **1** and **2** are insoluble, some PPh_3 is found in the hexane, which must come from the decomposition of **2**. The ^{31}P NMR spectrum of **2** also shows that the signal at 30.44 ppm (assigned to Mo–PPh_3) is always accompanied by a peak at –4.823 ppm, which corresponds to free PPh_3.

Conclusion

In this study we have shown that triphenylsiloxy complexes can be synthesized easily from the direct silylation of silver metalates by triphenylchlorosilane Ph_3SiCl. The method has the advantages of high yield based on Ph_3SiCl, easy product isolation, and ease in monitoring the extent of the reaction. The reactivities of group 6 metalates toward silylation by Ph_3SiCl are opposite to their solubilities (lattice energies) but parallel to their M=O bond strengths.

Compound **2** is the first compound containing a Mo–P bond in which the Mo ion is in oxidation state +6.

Supplementary Material Available: Tables of bond lengths, bond angles, hydrogen coordinates, and anisotropic thermal parameters for **1–3** (10 pages). Ordering information is given on any current masthead page.