Synthesis and Reactivity of a Phosphavinylidene Complex of Molybdenum

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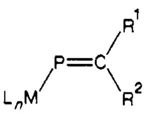
Received November 1, 1988

The reaction between $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$ and the phosphaalkene, $ClP{=}C(SiMe_3)_2$, affords the molybdenum phosphavinylidene complex $[Mo(CO)_2(\eta^1\text{-}P{=}C(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (1) which has been characterized by X-ray crystallography. The reaction of 1 with HX species has also been examined and affords the molybdenum phosphido species $[Mo(CO)_2(\eta^1\text{-}P(X)CH(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (5, X = EtO; 6, X = Me_2N; 7, X = C_6F_5S). Compounds 5 and 7 have been characterized by X-ray crystallography. In addition, the reaction of 1 with excess CD_3OD affords $[MoD(CO)_2(P(OCD_3)_2CD(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (8) which was characterized by X-ray diffraction. Extended Hückel molecular orbital calculations have also been carried out on 1 which account for the orientational preference of the phosphavinylidene ligand and the observed regioselectivity of HX addition across the P=C double bond in terms of orbital-controlled reactivity.

Introduction

Compounds containing multiple bonds to phosphorus are now well-known. These include diphosphenes ($RP{=}PR$),[1] phosphaalkenes ($RP{=}CR_2$),[2] and phosphaalkynes ($P{\equiv}CR$)[2,3] where R is, in general, a sterically demanding group imparting kinetic stability to these complexes. This R group is usually an organic moiety (alkyl, aryl, silyl, amido, etc.), but more recent work, particularly by Weber et al., has established that bulky organo-transition-metal fragments can also be used.[4] In particular, a number of metalladiphosphenes ($L_nMP{=}PR$)[5] and metallaphosphaalkenes ($RP{=}C(R)ML_n$[6] and $L_nMP{=}CR_2$[7]) have recently been reported. Of particular interest with regard to the present work is the latter class of compounds, namely, the P-bonded metallaphosphaalkenes or phosphavinyl complexes. Most of the reported complexes adopt a structure of type A[7] in which the phosphorus atom is singly bonded to the transition-metal center and carries a nonbonded lone pair resulting in a bent, two-coordinate geometry at phosphorus. In addition to this mode, examples exist in which additional bonding occurs involving the phosphorus lone pair. This can be either of type B, wherein bonding to the same metal center results in formal three-electron donation by a phosphavinylidene species,[7f,8] or of type C in which donation occurs to a second metal center resulting in a bridging phosphavinylidene complex.[9]



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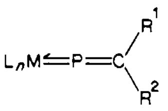

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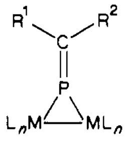

C

Table I. Bond Lengths (Å) for $[Mo(CO)_2(\eta^1\text{-}P{=}C(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (1)[a]

Mo1-P1	2.174 (1)	P1-C10	1.649 (4)	Si2-C23	1.873 (6)
Mo1-C1	1.958 (6)	Si1-C10	1.852 (5)	O1-C1	1.159 (9)
Mo1-C2	1.944 (6)	Si1-C11	1.889 (5)	O2-C2	1.163 (7)
Mo1-C51	2.338 (5)	Si1-C12	1.879 (7)	C51-C52	1.333 (10)
Mo1-C52	2.361 (6)	Si1-C13	1.897 (7)	C51-C55	1.451 (11)
Mo1-C53	2.358 (7)	Si2-C10	1.871 (5)	C52-C53	1.319 (11)
Mo1-C54	2.340 (6)	Si2-C21	1.875 (7)	C53-C54	1.410 (11)
Mo1-C55	2.326 (5)	Si2-C22	1.880 (6)	C54-C55	1.437 (11)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit in this and all other tables.

Table II. Selected Bond Angles (deg) for $[Mo(CO)_2(\eta^1\text{-}P{=}C(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (1)

P1-Mo1-C1	91.9 (2)	P1-C10-Si1	116.7 (3)
P1-Mo1-C2	88.9 (1)	P1-C10-Si2	116.9 (3)
C1-Mo1-C2	84.4 (3)	Si1-C10-Si2	126.3 (2)
Mo1-P1-C10	178.3 (2)		

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[4] The coordination chemistry of diphosphenes, phosphaalkenes, and phosphaalkynes containing organo R groups is well developed wherein these complexes act as ligands donating a formal even number of electrons to a transition-metal center. In contrast, the compounds described herein contain a univalent metalla R group and thus differ in a formal sense from the donor-acceptor, ligand-metal complexes mentioned above.

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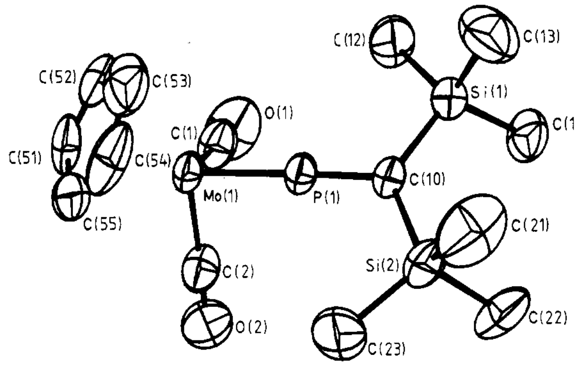
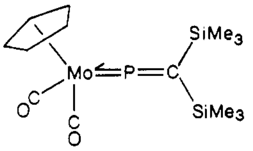


Figure 1. A view of the molecular structure of 1 showing the atom-numbering scheme adopted.

It is the synthesis of a type B complex and a study of its reactivity that are the subjects of this paper.

Results and Discussion

Synthetic and Structural Studies. Treatment of K[Mo(CO)$_3$(η-C$_5$H$_5$)] with the chlorophosphaalkene species ClP=C(SiMe$_3$)$_2$[10] at room temperature in THF solution afforded high yields of the orange crystalline molybdenum–phosphavinylidene complex 1. If the reaction is carried out at low temperature, an intermediate tricarbonyl phosphavinyl species, 2, is formed which on warming to room temperature readily loses CO affording 1. Details of the preparation of 2 and the analogous tungsten complex 3 are reported in ref 7f. Spectroscopic data for 1 were consistent with a dicarbonyl, phosphavinylidene formulation, but in order to more fully characterize this product, an X-ray structure determination was undertaken. The results of this study are shown in Figure 1 while tables of bond distances, bond angles, and atomic positional parameters are presented in Tables I, II, and III, respectively. The compound consists of a central molybdenum atom bonded to a cyclopentadienyl ligand, two terminal carbonyls, and the η^1-P=C(SiMe$_3$)$_2$ phosphavinylidene group, the geometry around the molybdenum atom being of the familiar "three-legged piano-stool" type. The Mo–P bond length (Mo(1)–P(1) = 2.174 (1) Å) is significantly shorter than those found in phosphine–Mo complexes (2.40–2.57 Å)[11] and also slightly shorter than typical values of 2.213 (1) and 2.207 (1) Å that have been reported for the η^1-phosphido complexes [Mo(CO)$_2$(η^1-PR$_2$)(η-C$_5$H$_5$)], in which Mo–P multiple bonding is implied.[12] (See also ref 16b for a discussion of these bond lengths.) The P–C bond length (1.649 (4) Å) is shorter but similar to those found in uncoordinated phosphaalkenes which span the range 1.665 (4)–1.72 Å[2,13] and is therefore consistent with a P=C double bond. In addition, the ligand configuration is such that the angle at phosphorus (Mo(1)–P(1)–C(10) = 178.3 (2)°) is almost linear and the methylene carbon, C(10), is trigonal-planar. Moreover, this plane (i.e. that defined by P(1), C(10), Si(1), and Si(2)) is essentially orthogonal to the symmetry plane of the Mo(CO)$_2$(η-C$_5$H$_5$) fragment. The reason for this is electronic in nature and is discussed in a later section. All other ligand and group geometries are normal and deserve no special comment.



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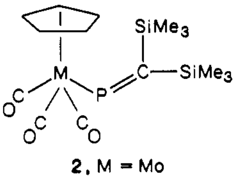

2, M = Mo
3, M = W

Table III. Positional Parameters and Their Estimated Standard Deviations for [Mo(CO)$_2$(η^1-P=C(SiMe$_3$)$_2$)(η-C$_5$H$_5$)] (1)

atom	x	y	z	B,[a] Å^2
Mo1	0.36804 (2)	0.19514 (6)	0.05071 (2)	3.725 (8)
P1	0.27278 (6)	0.0569 (2)	–0.04046 (6)	3.67 (2)
Si1	0.21050 (7)	–0.1350 (2)	–0.20706 (8)	4.59 (3)
Si2	0.11284 (7)	–0.0668 (2)	–0.07652 (8)	4.66 (3)
O1	0.4097 (3)	0.4591 (9)	–0.0823 (3)	9.9 (1)
O2	0.2697 (3)	0.5709 (7)	0.0656 (3)	8.1 (1)
C1	0.3928 (3)	0.362 (1)	–0.0335 (3)	6.0 (1)
C2	0.3060 (3)	0.4309 (9)	0.0579 (3)	5.4 (1)
C10	0.1990 (2)	–0.0446 (7)	–0.1083 (2)	3.61 (8)
C11	0.1363 (3)	–0.016 (1)	–0.2966 (3)	6.9 (2)
C12	0.3028 (3)	–0.050 (2)	–0.2161 (3)	8.7 (2)
C13	0.1988 (5)	–0.428 (1)	–0.2151 (4)	9.9 (2)
C21	0.0834 (4)	–0.345 (1)	–0.0772 (6)	9.4 (2)
C22	0.0350 (3)	0.077 (1)	–0.1527 (4)	7.3 (2)
C23	0.1281 (3)	0.046 (1)	0.0290 (3)	8.1 (2)
C51	0.4810 (3)	0.225 (1)	0.1563 (3)	6.4 (1)
C52	0.4895 (3)	0.064 (1)	0.1104 (4)	7.4 (2)
C53	0.4437 (4)	–0.090 (1)	0.1105 (4)	7.9 (2)
C54	0.4010 (3)	–0.036 (1)	0.1624 (3)	8.9 (2)
C55	0.4234 (4)	0.170 (1)	0.1928 (3)	8.7 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

While 1 is the first example of a phosphavinylidene complex, a number of examples of the nitrogen analogues (azavinylidene) are known.[14] Of particular interest are

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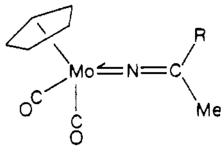
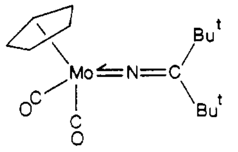
(14) (a) Kilner, M.; Midcalf, C. *J. Chem. Soc. A* **1971**, 292. (b) Kilner, M. *Adv. Organomet. Chem.* **1972**, *10*, 115. (c) Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Dalton Trans.* **1986**, 377. (d) Chatt, J.; Dosser, R. J.; King, F.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2435. (e) Green, M.; Mercer, R. J.; Morton, C. E.; Orpen, A. G. *Angew. Chem.* **1985**, *97*, 422; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 422. (f) Erker, G.; Frömberg, W.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1984**, *96*, 72; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 68. (g) Fromberg, W.; Erker, G. *J. Organomet. Chem.* **1985**, *280*, 343. (h) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443. (i) Werner, H.; Knaup, W.; Dziallas, M. *Angew. Chem.* **1987**, *99*, 277; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 248. (j) Shearer, H. M. M.; Sowerby, J. D. *J. Chem. Soc., Dalton Trans.* **1973**, 2629.

those reported in ref 14e and 14j, namely, **4a** and **4b**, respectively, which both contain the $Mo(CO)_2(\eta\text{-}C_5H_5)$ fragment analogous to **1**. Compound **4b** was the subject of a crystal structure determination[14j] which revealed a linear two-coordinate nitrogen atom and a ligand–metal fragment orientation similar to that found in **1**.



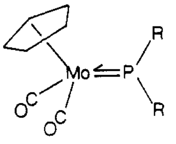
4a, R = Ph, 4-C_6H_4Me



4b

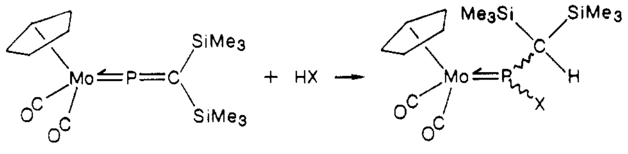
The novel nature of **1** also prompted a study of its reactivity, particularly with regard to HX species, the results of which are presented in Scheme I. Thus, treatment of **1** with EtOH, Me_2NH, or C_6F_5SH afforded the molybdenum–phosphido species **5**, **6**, or **7**, respectively. Spectroscopic evidence was consistent with addition of the HX species across the P=C double bond in such a way as to produce C—H and P—X bonds. This regioselectivity was confirmed for **5** and **7** by X-ray crystallographic studies.

The results for **5** are shown in Figure 2 with bond distances, bond angles, and atomic positional parameters presented in Tables IV–VI. The molecule consists of a $Mo(CO)_2(\eta\text{-}C_5H_5)$ fragment of normal geometry bonded to a phosphido ligand, $P(OEt)CH(SiMe_3)_2$, derived from addition of EtOH to the phosphavinylidene P=C bond. This phosphido ligand behaves as a neutral three-electron donor to the molybdenum center, an interpretation confirmed by the trigonal-planar geometry at phosphorus (sum of angles = 359.8 (3)°) and the short Mo–P bond length (Mo(1)–P(1) = 2.207 (2) Å). These geometrical features are characteristic of compounds of the general formula $[Mo(CO)_2(\eta^1\text{-}PR_2)(\eta\text{-}C_5H_5)]$ which contain a three-electron donor phosphido ligand. The bonding may be represented as shown in D with formal donation of the phosphorus lone pair from a 3p orbital to a vacant metal orbital. This accounts for the trigonal-planar geometry at phosphorus and for the relatively short M–P bond distances resulting from some degree of multiple bonding.[12,15,16] In addition to **5**, a range of compounds of type D with a variety of R groups have been synthesized, particularly by Malisch,[15b] Paine,[12,15a,c] and Cowley[16] and their co-workers. A more detailed account of the bonding in these species is given by Paine et al.[15c] and Cowley et al.[16b] Examination of the orbital interactions between the PR_2 and $Mo(CO)_2(\eta\text{-}C_5H_5)$ fragments suggests that the $MoPR_2$ plane should coincide with the symmetry plane of the $Mo(CO)_2(\eta\text{-}C_5H_5)$ fragment. This feature is observed in **5** in which the plane at phosphorus, i.e. that defined by Mo(1), P(1), C(10), O(3), bisects the angle at molybdenum defined by the two carbonyls, i.e. C(1)–Mo(1)–C(2). We note also that the



D

Scheme I



5, X = EtO
6, X = Me_2N
7, X = C_6F_5S

Table IV. Bond Lengths (Å) for $[Mo(CO)_2(\eta^1\text{-}P(OEt)CH(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (5)

Mo1–P1	2.207 (2)	P1–C10	1.794 (9)	O1–C1	1.138 (11)
Mo1–C1	1.964 (9)	Si1–C10	1.901 (9)	O2–C2	1.168 (11)
Mo1–C2	1.937 (10)	Si1–C11	1.888 (13)	O3–C8	1.466 (12)
Mo1–C3	2.369 (10)	Si1–C12	1.896 (11)	C3–C4	1.383 (15)
Mo1–C4	2.369 (10)	Si1–C13	1.904 (12)	C3–C7	1.42 (2)
Mo1–C5	2.355 (10)	Si2–C10	1.909 (8)	C4–C5	1.44 (2)
Mo1–C6	2.347 (10)	Si2–C14	1.891 (13)	C5–C6	1.42 (2)
Mo1–C7	2.364 (11)	Si2–C15	1.886 (11)	C6–C7	1.420 (15)
P1–O3	1.616 (6)	Si2–C16	1.891 (12)	C8–C9	1.480 (15)

Table V. Selected Bond Angles (deg) for $[Mo(CO)_2(\eta^1\text{-}P(OEt)CH(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (5)

P1–Mo1–C1	91.9 (3)	Mo1–C1–O1	178.2 (9)
P1–Mo1–C2	95.5 (3)	Mo1–C2–O2	177.6 (8)
C1–Mo1–C2	82.4 (4)	O3–C8–C9	107.8 (9)
Mo1–P1–O3	132.9 (3)	P1–C10–Si1	112.9 (4)
Mo1–P1–C10	129.0 (3)	P1–C10–Si2	112.1 (4)
O3–P1–C10	97.9 (3)	Si1–C10–Si2	117.9 (4)
P1–O3–C8	122.4 (6)		

Table VI. Positional Parameters and Their Estimated Standard Deviations for $[Mo(CO)_2(\eta^1\text{-}P(OEt)CH(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (5)

atom	*x*	*y*	*z*	*B*, Å^2
Mo1	0.75277 (6)	0.22067 (6)	0.64001 (5)	3.69 (1)
P1	0.5859 (2)	0.2345 (2)	0.6846 (1)	3.52 (4)
Si1	0.5210 (3)	0.2254 (2)	0.8721 (2)	5.06 (6)
Si2	0.3960 (2)	0.0779 (2)	0.7051 (2)	4.78 (6)
O1	0.6345 (8)	0.2462 (7)	0.4386 (5)	8.3 (2)
O2	0.7920 (6)	0.4572 (5)	0.6204 (5)	5.9 (2)
O3	0.4741 (5)	0.3081 (5)	0.6532 (4)	4.7 (1)
C1	0.6770 (8)	0.2353 (8)	0.5125 (6)	5.0 (2)
C2	0.7760 (6)	0.3687 (7)	0.6294 (6)	4.1 (2)
C3	0.8063 (9)	0.0487 (8)	0.6864 (8)	6.8 (3)
C4	0.8500 (9)	0.1131 (8)	0.7584 (7)	6.2 (3)
C5	0.9340 (9)	0.1807 (9)	0.7312 (8)	7.2 (3)
C6	0.9382 (8)	0.153 (1)	0.6410 (8)	7.8 (3)
C7	0.8579 (9)	0.0722 (8)	0.6114 (8)	7.3 (3)
C8	0.4722 (8)	0.3926 (8)	0.5879 (7)	5.8 (2)
C9	0.3780 (9)	0.4648 (9)	0.5983 (8)	7.0 (3)
C10	0.5288 (6)	0.1549 (6)	0.7629 (5)	3.4 (2)
C11	0.464 (1)	0.132 (1)	0.9490 (7)	8.8 (3)
C12	0.428 (1)	0.3469 (8)	0.8553 (7)	6.6 (3)
C13	0.676 (1)	0.262 (1)	0.9266 (8)	8.4 (4)
C14	0.406 (1)	0.051 (1)	0.5838 (8)	7.6 (3)
C15	0.2557 (8)	0.148 (1)	0.7058 (9)	7.3 (3)
C16	0.4001 (9)	−0.0497 (8)	0.7675 (9)	7.0 (3)

Table VII. Bond Lengths (Å) for $[Mo(CO)_2(\eta^1\text{-}P(SC_6F_5)CH(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (7)

Mo1–P1	2.221 (2)	Si1–C10	1.874 (9)	C3–C4	1.416 (15)
Mo1–C1	1.946 (9)	Si1–C11	1.868 (11)	C3–C7	1.437 (13)
Mo1–C2	1.937 (10)	Si2–C8	1.912 (8)	C4–C5	1.429 (13)
Mo1–C3	2.384 (9)	Si2–C12	1.875 (11)	C5–C6	1.427 (13)
Mo1–C4	2.388 (8)	Si2–C13	1.879 (15)	C6–C7	1.42 (2)
Mo1–C5	2.360 (9)	Si2–C14	1.883 (15)	C15–C16	1.37 (2)
Mo1–C6	2.336 (8)	F1–C16	1.28 (2)	C15–C20	1.41 (2)
Mo1–C7	2.338 (9)	F2–C17	1.15 (3)	C16–C17	1.71 (2)
S1–P1	2.147 (3)	F3–C18	1.52 (2)	C17–C18	1.14 (3)
S1–C15	1.740 (10)	F4–C19	1.40 (2)	C18–C19	1.26 (3)
P1–C8	1.805 (7)	F5–C20	1.35 (2)	C19–C20	1.43 (2)
Si1–C8	1.915 (9)	O1–C1	1.143 (11)		
Si1–C9	1.892 (10)	O2–C2	1.154 (12)		

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(15) (a) Light, R. W.; Paine, R. T. *J. Am. Chem. Soc.* **1978**, *100*, 2230. (b) Bross, E.; Jorg, K.; Fiederling, K.; Göttlein, A.; Malisch, W.; Boese, R. *Angew. Chem.* **1984**, *96*, 705; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 738. (c) Paine, R. T.; Hutchins, L. D.; Dubois, D. A.; Duesler, E. N. *Phosphorus Sulfur* **1983**, *18*, 263.

(16) (a) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367. (b) Cowley, A. H.; Giolando, D. M.; Nunn, C. M.; Pakulski, M.; Westmoreland, D.; Norman, N. C. *J. Chem. Soc., Dalton Trans.* **1988**, 2127.

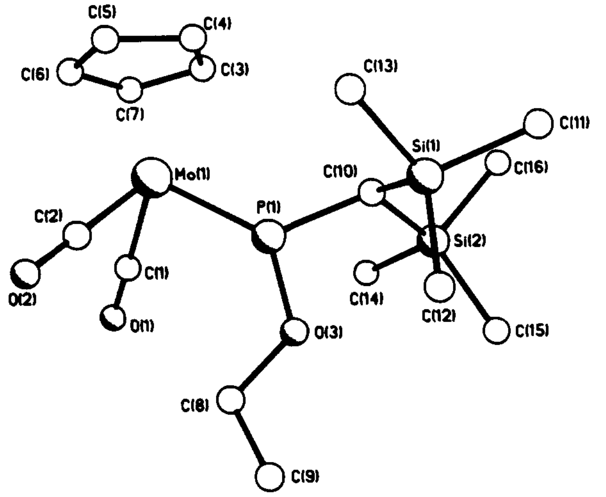


Figure 2. A view of the molecular structure of 5 showing the atom-numbering scheme adopted.

Table VIII. Selected Bond Angles (deg) for $[Mo(CO)_2(\eta^1\text{-}P(SC_6F_5)CH(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (7)

P1–Mo1–C1	87.7 (2)	S1–P1–C8	97.1 (2)
P1–Mo1–C2	86.5 (3)	Mo1–C1–O1	176.6 (7)
C1–Mo1–C2	84.1 (4)	Mo1–C2–O2	178.6 (9)
P1–S1–C15	101.6 (3)	P1–C8–Si1	114.9 (4)
Mo1–P1–S1	132.9 (1)	P1–C8–Si2	115.7 (4)
Mo1–P1–C8	129.9 (2)	Si1–C8–Si2	117.6 (4)

stereochemistry associated with the Mo═P bond is such as to place the $CH(SiMe_3)_2$ group in a syn position relative to the cyclopentadienyl ligand which probably results from minimization of intramolecular steric effects.

The structure of 7 is shown in Figure 3 while relevant metric parameters are presented in Tables VII–IX. The important features of 7 are the same as those described for 5. Thus the phosphorus adopts a trigonal-planar geometry (sum of angles = 359.9 (2)°), the Mo–P bond length is short (Mo(1)–P(1) = 2.221 (2) Å), and the plane defined by Mo(1), P(1), S(1), and C(8) is coplanar with the molybdenum fragment symmetry plane. All other geometries are normal and deserve no special comment although large thermal motion effects in the C_6F_5 group resulted in some distortion in the derived parameters for the C_6 ring. In 7 the orientation of the phosphido ligand is such as to place the $CH(SiMe_3)_2$ group anti to the cyclopentadienyl ligand. This is opposite to that observed for 5, but as mentioned previously, the stereochemistry about the Mo═P bond is probably governed by intramolecular steric considerations and will therefore be quite dependent on the size of the attached groups.

Finally we note that the Mo–P bond lengths in 5 and 7 together with other reported values for type D phosphido complexes[12,15,16b] are all slightly longer than the Mo–P bond length in 1. Although the formal nature of the bonding in both the phosphavinylidene and the phosphido complexes is similar (i.e. Mo$\overset{\leftarrow}{=}$P), two factors associated with the former might account for the observed shortening. First in 1 the phosphorus is formally sp hybridized rather than sp^2 in 5, 7, and other type D species. Second, the availability of a vacant P═C π^* orbital in 1 may allow back-donation from molybdenum to phosphorus, thereby increasing the formal bond order. This aspect will be addressed more fully in the next section.

Table IX. Positional Parameters and Their Estimated Standard Deviations for $[Mo(CO)_2(\eta^1\text{-}P(SC_6F_5)CH(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (7)

atom	x	y	z	B, Å^2
Mo1	0.30275 (6)	0.45205 (6)	0.11407 (9)	3.99 (1)
S1	0.3474 (2)	0.1350 (2)	−0.0874 (4)	7.03 (7)
P1	0.2612 (2)	0.2970 (2)	−0.0469 (3)	3.92 (5)
Si1	0.0475 (2)	0.1780 (2)	−0.1417 (3)	5.09 (6)
Si2	0.1608 (3)	0.2487 (2)	−0.4040 (3)	6.19 (7)
F1	0.3825 (8)	0.1137 (9)	0.241 (1)	16.2 (3)
F2	0.564 (1)	0.134 (1)	0.453 (1)	28.3 (5)
F3	0.7498 (7)	0.1858 (8)	0.360 (1)	27.5 (4)
F4	0.7444 (7)	0.2000 (8)	0.066 (2)	23.6 (6)
F5	0.5615 (7)	0.1813 (6)	−0.137 (1)	14.7 (3)
O1	0.0606 (5)	0.5015 (6)	0.1676 (9)	7.4 (2)
O2	0.2189 (7)	0.5647 (6)	−0.1688 (8)	8.7 (2)
C1	0.1492 (7)	0.4812 (7)	0.143 (1)	4.9 (2)
C2	0.2514 (7)	0.5222 (7)	−0.064 (1)	5.7 (2)
C3	0.4309 (7)	0.4266 (8)	0.342 (1)	5.9 (2)
C4	0.4915 (7)	0.4464 (7)	0.233 (1)	5.5 (2)
C5	0.4546 (7)	0.5538 (7)	0.202 (1)	5.9 (2)
C6	0.3706 (7)	0.6009 (7)	0.295 (1)	6.1 (2)
C7	0.3549 (8)	0.5225 (9)	0.380 (1)	6.5 (3)
C8	0.1406 (6)	0.2695 (6)	−0.1909 (9)	4.0 (2)
C9	−0.0910 (8)	0.1981 (9)	−0.269 (2)	8.6 (4)
C10	0.0964 (9)	0.0279 (8)	−0.177 (2)	8.1 (3)
C11	0.0319 (9)	0.2264 (9)	0.068 (1)	8.4 (3)
C12	0.170 (1)	0.1013 (9)	−0.506 (1)	9.0 (4)
C13	0.041 (1)	0.333 (1)	−0.501 (1)	12.5 (5)
C14	0.292 (1)	0.301 (1)	−0.416 (1)	11.3 (4)
C15	0.4664 (8)	0.1503 (8)	0.050 (1)	7.0 (3)
C16	0.468 (1)	0.134 (1)	0.198 (2)	11.5 (4)
C17	0.583 (2)	0.148 (1)	0.338 (2)	17.4 (7)
C18	0.637 (2)	0.173 (1)	0.263 (2)	19.1 (6)
C19	0.6578 (9)	0.1805 (9)	0.133 (3)	15.7 (7)
C20	0.5642 (9)	0.1744 (9)	0.013 (2)	9.4 (4)

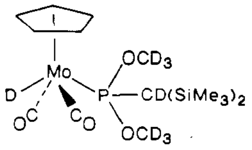
Table X. Bond Lengths (Å) for $[MoD(CO)_2(P(OCD_3)_2CD(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (8)

Mo1–P1	2.387 (2)	P1–O4	1.627 (6)	O1–C1	1.163 (9)
Mo1–C1	1.945 (7)	P1–C10	1.818 (7)	O2–C2	1.136 (12)
Mo1–C2	1.957 (9)	Si1–C10	1.920 (8)	O3–C3	1.449 (12)
Mo1–C5	2.334 (9)	Si1–C12	1.887 (12)	O4–C4	1.444 (10)
Mo1–C6	2.318 (11)	Si1–C13	1.901 (11)	C5–C6	1.41 (2)
Mo1–C7	2.376 (11)	Si2–C10	1.919 (6)	C5–C9	1.40 (2)
Mo1–C8	2.378 (8)	Si2–C14	1.885 (9)	C6–C7	1.43 (2)
Mo1–C9	2.358 (9)	Si2–C15	1.898 (11)	C7–C8	1.44 (2)
P1–O3	1.617 (5)	Si2–C16	1.887 (10)	C8–C9	1.40 (2)

Table XI. Selected Bond Angles (deg) for $[MoD(CO)_2(P(OCD_3)_2CD(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (8)

P1–Mo1–C1	83.3 (3)	O4–P1–C10	96.4 (3)
P1–Mo1–C2	112.7 (3)	P1–O3–C3	123.2 (4)
C1–Mo1–C2	81.5 (4)	P1–O4–C4	122.7 (5)
Mo1–P1–O3	106.1 (2)	Mo1–C1–O1	177.6 (9)
Mo1–P1–O4	119.1 (2)	Mo1–C2–O2	176.4 (7)
Mo1–P1–C10	125.2 (3)	P1–C10–Si1	115.6 (4)
O3–P1–O4	102.1 (3)	P1–C10–Si2	115.8 (4)
O3–P1–C10	105.1 (3)	Si1–C10–Si2	114.6 (4)

The addition of methanol to 1 was also studied, the reaction being carried out by dissolving a small sample of 1 in deuteromethanol, CD_3OD. After several days, small pale brown crystals had precipitated from solution and the spectroscopic data obtained on this material were consistent with a double addition of CD_3OD to the Mo═P═C functionality resulting in the phosphonite derivative 8.



8

The formulation was confirmed by an X-ray crystallographic study, the results of which are shown in Figure 4 and Tables X–XII. The structure consists of a central molybdenum atom residing in a "$CpML_4$ piano stool" environment with L_4 comprising two carbonyl ligands, a

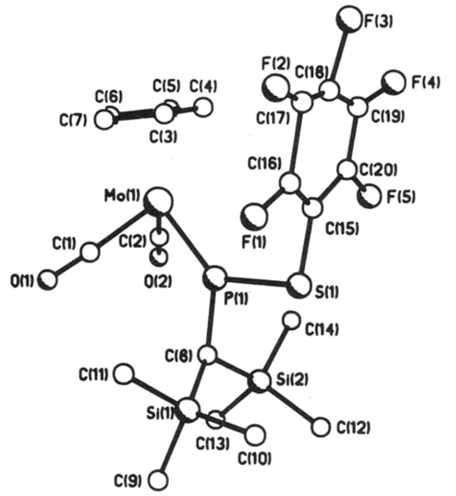


Figure 3. A view of the molecular structure of **7** showing the atom-numbering scheme adopted.

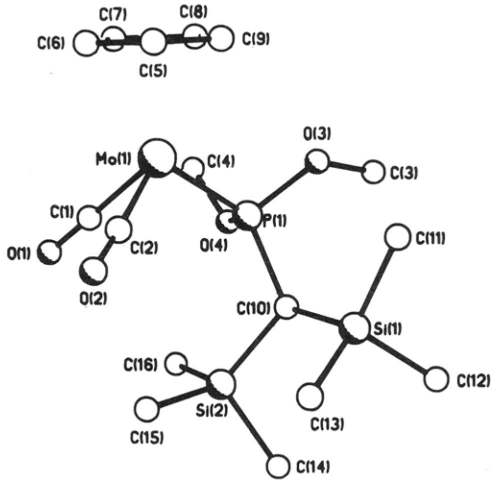


Figure 4. A view of the molecular structure of **8** showing the atom-numbering scheme adopted.

deuterium (not located directly), and the phosphonite ligand $P(OCD_3)_2CH(SiMe_3)_2$ with a stereochemistry defined by *trans* carbonyls. Double HX (X = OCD_3) addition has therefore occurred such as to place both X groups on the phosphorus atom with protonation (or, more precisely, deuteration) taking place at the metal center and the unique carbon atom of the phosphavinylidene fragment. On the basis of the results observed with 1 equiv of HX (X = EtO, Me_2N, C_6F_5S), it is assumed that initial addition of CD_3OD occurs across the P=C double bond, resulting in a complex analogous to **5**, followed by a further addition across the Mo=P multiple bond.

Theoretical Studies. In order to gain an understanding of the various properties of the phosphavinylidene complex **1**, we have carried out extended Hückel molecular orbital calculations[17] on a model for **1**, $[Mo(CO)_2(\eta^1\text{-}PCH_2)(\eta\text{-}C_5H_5)]$ (**9**). The geometry imposed on **9** had exact C_s symmetry, with angles C(O)–Mo–C(O) = 90.0, Mo–C–O = 180.0, Mo–P–C = 180.0, P–C–H = 120.0, and H–C–H = 120.0°, the MoC_5H_5 moiety having local C_{5v} symmetry, and bond lengths Mo–C(C_5H_5) = 2.34, Mo–C(O) = 1.978, C–O = 1.145, C–C = 1.41, C–H = 1.09, Mo–P = 2.174, and P–C = 1.649 Å. Hückel parameters were taken from the literature.[18]

Table XII. Positional Parameters and Their Estimated Standard Deviations for $[MoD(CO)_2(P(OCD_3)_2CD(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (8)

atom	*x*	*y*	*z*	*B*, Å^2
Mo1	0.39927 (4)	0.24083 (8)	0.04231 (4)	3.56 (1)
P1	0.2708 (1)	0.3149 (2)	0.0666 (1)	3.19 (4)
Si1	0.2046 (2)	0.6125 (3)	−0.0274 (2)	4.20 (6)
Si2	0.0883 (1)	0.3287 (3)	−0.1173 (2)	3.95 (5)
O1	0.2632 (4)	0.0077 (7)	−0.0749 (4)	6.1 (2)
O2	0.3851 (5)	0.3315 (9)	−0.1408 (4)	7.8 (2)
O3	0.3144 (3)	0.4022 (6)	0.1596 (3)	3.9 (1)
O4	0.2085 (3)	0.1959 (6)	0.0848 (3)	4.3 (1)
C1	0.3134 (5)	0.0945 (9)	−0.0296 (5)	4.3 (2)
C2	0.3872 (5)	0.298 (1)	−0.0748 (5)	4.6 (2)
C3	0.2598 (5)	0.451 (1)	0.2032 (5)	5.1 (2)
C4	0.2485 (7)	0.073 (1)	0.1399 (6)	5.6 (3)
C5	0.5588 (6)	0.283 (2)	0.1129 (7)	9.5 (4)
C6	0.5446 (7)	0.136 (2)	0.0998 (7)	9.1 (3)
C7	0.5028 (7)	0.085 (1)	0.1540 (7)	8.1 (4)
C8	0.4910 (6)	0.208 (1)	0.1986 (6)	6.9 (3)
C9	0.5247 (7)	0.327 (1)	0.1727 (7)	7.7 (3)
C10	0.1743 (5)	0.4220 (8)	−0.0102 (5)	3.4 (2)
C11	0.6793 (6)	0.181 (1)	0.4384 (6)	5.6 (3)
C12	0.1112 (6)	0.727 (1)	−0.0223 (7)	7.0 (3)
C13	0.2050 (6)	0.639 (1)	−0.1398 (5)	5.5 (2)
C14	−0.0176 (6)	0.445 (1)	−0.1691 (7)	6.0 (3)
C15	0.1344 (6)	0.298 (1)	−0.2022 (5)	5.2 (2)
C16	0.0479 (6)	0.153 (1)	−0.0939 (6)	5.5 (2)

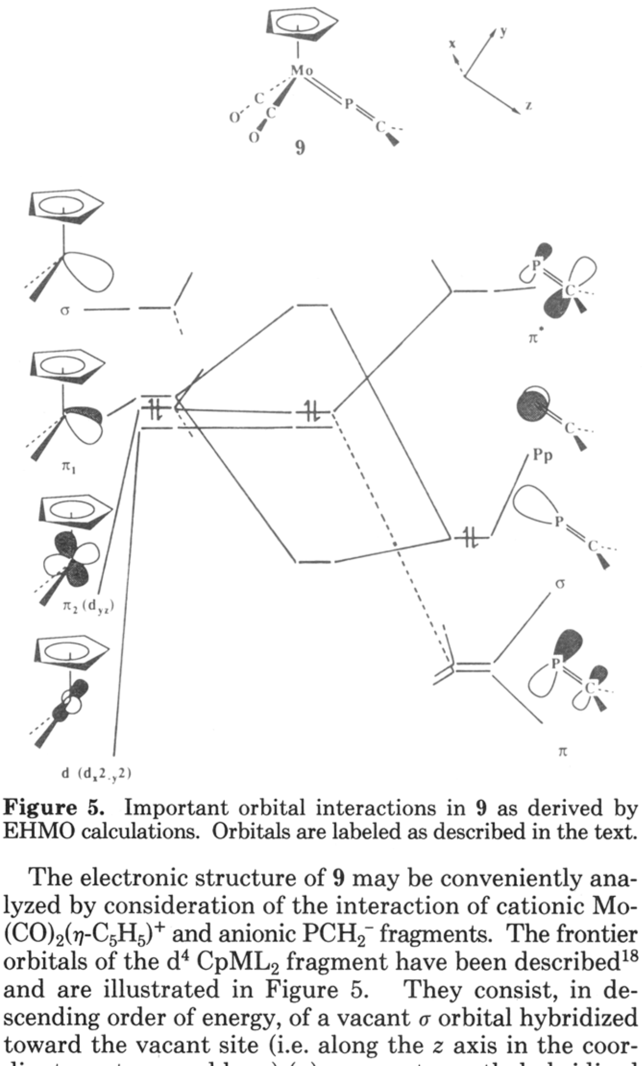


Figure 5. Important orbital interactions in **9** as derived by EHMO calculations. Orbitals are labeled as described in the text.

The electronic structure of **9** may be conveniently analyzed by consideration of the interaction of cationic $Mo(CO)_2(\eta\text{-}C_5H_5)^+$ and anionic PCH_2^- fragments. The frontier orbitals of the d^4 $CpML_2$ fragment have been described[18] and are illustrated in Figure 5. They consist, in descending order of energy, of a vacant σ orbital hybridized toward the vacant site (i.e. along the *z* axis in the coordinate system used here) (σ), an empty partly hybridized orbital of π pseudosymmetry with respect to the z axis with

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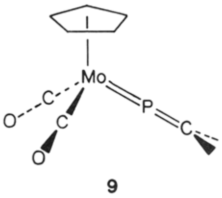
[17] Howell, J.; Rossi, A.; Wallace, D.; Harak, I. K.; Hoffmann, R. *QCPE* **1977**, *10*, 344.

[18] Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

its nodal plane coincident with the symmetry plane of the $Mo(CO)_2(\eta\text{-}C_5H_5)^+$ fragment (π_1), a filled, essentially unhybridized, d orbital (≈d_{yz} in the coordinate system of Figure 5) also of π pseudosymmetry, orthogonal to π_1, having its nodal plane orthogonal to the fragment symmetry plane (π_2), and a second filled d orbital (≈$d_{x^2-y^2}$) of near δ pseudosymmetry (δ). The frontier orbitals of the PCH_2^- fragment are, of course, qualitatively similar to those of the vinylidene (CCH_2) moiety. As shown in Figure 5, they consist, in descending order of energy, of the vacant P–C π^* orbital (π^*), the filled phosphorus unhybridized p orbital (Pp), the phosphorus lone pair (Pσ), and the P–C π orbital (π). Given the parameterization used here the P–C π orbital is predominantly centered on phosphorus (≈75%) and the π^* on carbon (≈75%).



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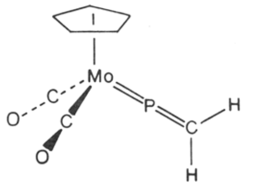
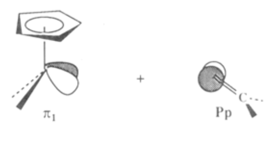


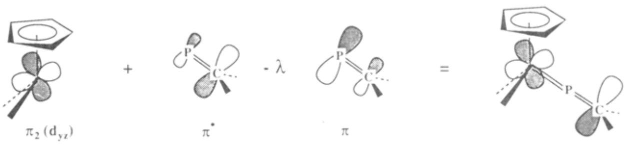
9a

EHMO calculations were performed for 9 in geometries approximating that observed in the crystal structure of 1 and with the PCH_2 moiety rotated through 90° about the Mo–P–C axis (9a). These indicated a preference for the observed geometry of ca. 6 kcal mol^{-1}. A similar but slightly smaller energy preference for this geometry was calculated for the analogous $CpFe(CO)_2CCH_2$ cation.[18] The preferred orientation coincides with the position that allows maximum overlap of the better hybridized d_π function of the Mo fragment (π_1) with the phosphorus π donor orbital (Pp). The LUMO of 9 is substantially localized on Mo and P, arising as it does from interaction E below. This implies that if nucleophilic attack is orbital-controlled (as has been postulated for related carbyne complexes),[19] the most probable site is at the two-coordinate phosphorus (or less likely, at the sterically protected molybdenum) and not carbon. The concentration of the LUMO on P is also a major contributory cause of the very low-field NMR chemical shift observed for this nucleus.[19] In contrast the HOMO is localized primarily on Mo and C(H_2) (see F below). As a consequence, orbital-controlled eletrophilic attack is most likely at the carbon of the phosphavinylidene ligand. Partial charges on the phosphavinylidene P and C atoms are −0.38e and −0.18e respectively (cf. Mo + 1.06e). Thus the observed regioselectivity in reactions of 1 with reagents HX (see Scheme I) is consistent with orbital control of these reactions but not consistent with charge control. These conclusions hold also for 9a which shows qualitatively similar atomic localization of HOMO and LUMO.

The fragment orbital populations in 9 show that there is significant back-donation (from Mo(π_2) to PCH_2(π^*)), resulting in net occupancies of 0.55e and 1.53e for PCH_2(π^*) and Mo(π_2), respectively, as well as both σ and π donation (from PCH_2(σ) to Mo(σ) and from PCH_2(Pp) to Mo(π_1)) leading to final occupancies for Mo(σ), Mo(π_1), PCH_2(σ), and PCH_2(Pp) of 0.49e, 0.52e, 1.69e, and 1.50e, respectively. As a result the net Mo–P bond order may be higher than two, since it arises from one σ and two π interactions.



E



F

Conclusions

The synthesis of a phosphavinylidene complex, 1, has been described together with details of its molecular and electronic structure. EHMO calculations allow an understanding of the ligand orientational preference in 1 and, in addition, account for the observed regioselectivity in the reactions of HX species with the P=C double bond. Further studies involving the reactivity of 1 toward nucleophiles and organo-transition-metal fragments are in progress and will be reported in a future publication.

Experimental Section

All experiments were performed by using standard Schlenk techniques under an atmosphere of dry oxygen-free dinitrogen. All solvents were freshly distilled over appropriate drying agents immediately prior to use. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a General Electric QE300 instrument operating at 300, 75.48, and 121.5 MHz respectively. ^1H and ^{13}C NMR spectra were referenced to Me_4Si (0.0 ppm) and ^{31}P spectra to 85% H_3PO_4, positive values to high frequency. Infrared spectra were recorded on a Digilab FTS-40 spectrophotometer and mass spectra on Du Pont Consolidated 21-491 and 21-100 spectrometers (the latter for high-resolution mass spectra, HRMS).

Preparations. Preparation of $[Mo(CO)_2(\eta^1\text{-}P{=}C(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (1). A solution of $(Me_3Si)_2C{=}PCl$[10] (2.30 g, 10.23 mmol) in THF (30 mL) was added to a stirred solution of $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$ [prepared by treatment of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (4.08 g, 8.33 mmol) with KH (0.70 g, 17.45 mmol) in THF (50 mL)][20] at room temperature, and the resulting mixture was stirred for 48 h. All volatiles were then removed resulting in a brown residue. Extraction with *n*-hexane afforded an orange solution from which orange crystals of 1 were obtained after filtration, concentration, and cooling to −20 °C (2.79 g, 41%).

Spectroscopic data: ^1H NMR (CD_2Cl_2) δ 5.48 (s, 5 H, C_5H_5), 0.24 (s, 18 H, $SiMe_3$); $^{13}C\{^1H\}$ NMR δ 230.4 (s, CO), 90.1 (s, C_5H_5), 2.8 (s, $SiMe_3$); $^{31}P\{^1H\}$ NMR δ +498.1; IR $\nu_{C\equiv O}$ (KBr) 1940, 1882 cm^{-1}; mass spectrum, 408 (P), 380 (P − CO), 352 (P − 2CO), 343 (P − C_5H_5); HRMS 408.00358 (observed), 408.00282 (calculated for $C_{14}H_{23}MoPO_2Si_2$); mp 98–105 °C dec. Anal. Calcd for $C_{14}H_{23}MoPO_2Si_2$: C, 41.37; H, 5.70; P, 7.62. Found: C, 40.87; H, 5.79; P, 7.59.

Preparation of $[Mo(CO)_2(P(OEt)CH(SiMe_3)_2)(\eta\text{-}C_5H_5)]$ (5). To a solution of 1 (1.00 g, 2.46 mmol) in THF (20 mL) was added 1 equiv of ethanol (0.11 g, 2.46 mmol), and the resulting solution was stirred at room temperature for 36 h. A color change from orange to orange-brown occurred during this time. Removal of the THF in vacuo followed by extraction with hexane (3 × 25 mL) afforded an orange-brown solution from which crystals of 5 were obtained after filtration, concentration, and cooling to −20 °C (0.78 g, 70%).

Spectroscopic data: ^1H NMR (CD_2Cl_2) δ 5.43 (s, 5 H, C_5H_5), 4.10 (dq, 2 H, OCH_2CH_3, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 9.2 Hz), 1.78 (d, 1 H, $CH(SiMe_3)_2$, $^2J_{PH}$ = 1.3 Hz), 1.35 (t, 3 H, OCH_2CH_3, $^3J_{HH}$ = 7.0 Hz), 0.21 (s, 18 H, $SiMe_3$); $^{13}C\{^1H\}$ NMR δ 237.2 (d, CO, $^2J_{PC}$ = 19.1 Hz), 90.2 (s, C_5H_5), 65.5 (s, OCH_2CH_3), 51.0 (d, $CH(SiMe_3)_2$, $^1J_{PC}$ = 13.3 Hz), 16.5 (d, OCH_2CH_3, $^3J_{PC}$ = 5.9 Hz), 1.6 (s, $SiMe_3$); $^{31}P\{^1H\}$ NMR δ +367.9; IR $\nu_{C\equiv O}$ (KBr) 1910, 1825 cm^{-1}; mass

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(19) Fenske, R. F. *Organomet. Compds.* **1983**, *305* and references therein.

(20) Inkrott, K.; Goetze, R.; Shore, S. G. *J. Organomet. Chem.* **1978**, *154*, 336.

Table XIII. Crystallographic Data

	1	5	7	8
formula	$C_{14}H_{23}MoPO_2Si_2$	$C_{16}H_{29}MoO_3PSi_2$	$C_{20}H_{24}F_5MoO_2PSSi_2$	$C_{16}H_{31}MoO_4PSi_2$
fw	406.43	452.49	606.56	470.51
cryst system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a, Å	18.90 (1)	11.775 (3)	12.446 (3)	16.127 (2)
b, Å	6.432 (1)	12.876 (2)	12.595 (3)	9.447 (2)
c, Å	17.009 (3)	15.107 (3)	8.881 (1)	16.737 (2)
α, deg			102.64 (2)	
β, deg	107.83 (3)	101.48 (2)	100.72 (2)	116.67 (1)
γ, deg			81.34 (2)	
U, Å^3	1968	2245	1326	2279
Z	4	4	2	4
d(calc), g cm^{-3}	1.507	1.339	1.520	1.371
radiatn	graphite-monochromated Mo radiation, λ = 0.71069 Å			
μ(Mo Kα), cm^{-1}	8.6	7.54	7.55	7.48
2θ range, deg	2–50	3–48	3–48	3–48
range of indices	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$+h,+k,\pm l$
no. of data collected	3944	3895	4452	3959
no. of unique data used	2857	2103	2870	2424
data omissn factor			$I \geq 3\sigma(I)$	
absorptn correctn	none		empirical	
transmissn factors		94.5–99.9	88.0–99.7	85.2–99.9
struct soln	Patterson		direct methods	
R^a	0.040	0.044	0.050	0.043
$R_w{}^b$	0.068	0.053	0.059	0.056
residual *e*(max)	0.51	0.43	0.64	0.48

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

spectrum, 454 (P). Anal. Calcd for $C_{16}H_{29}O_3PSi_2Mo$: C, 42.47; H, 6.46; P, 6.85; Si, 12.41. Found: C, 42.29; H, 6.40; P, 6.53; Si, 12.79.

Preparation of [Mo(CO)$_2$(P(NMe$_2$)CH(SiMe$_3$)$_2$)(η-C$_5$H$_5$)] (6). A solution of 1 (0.46 g, 1.14 mmol) in hexane (20 mL) was cooled to −196 °C in a 100-mL Schlenk flask. A sample of dimethylamine (30 mL) was then distilled into this flask, and the contents were allowed to warm to −78 °C. The resulting solution was then stirred for 3 h and subsequently allowed to warm to room temperature. The resulting brown solution was then concentrated, and brown crystals were obtained at −20 °C. Two subsequent recrystallizations from hexane at −20 °C afforded brown crystals of 6 (0.33 g, 64%).

Spectroscopic data: ^{1}H NMR (CD$_2$Cl$_2$) δ 5.39 (s, 5 H, C$_5$*H*$_5$), 2.90 (d, 6 H, N*Me*$_2$, $^3J_{PH}$ = 12.0 Hz), 1.76 (d, 1 H, C*H*(SiMe$_3$)$_2$, $^2J_{PH}$ = 5.3 Hz), 0.24 (s, 18 H, Si*Me*$_3$); ^{13}C{^{1}H} NMR δ 92.7 (s, *C*$_5$H$_5$), 25.0 (s, N*Me*$_2$), 1.9 (s, Si*Me*$_3$), *C*H(SiMe$_3$)$_2$ signal obscured by solvent; ^{31}P{^{1}H} NMR δ +316.2; IR $\nu_{C\equiv O}$ (KBr) 1885, 1850 cm^{-1}; mass spectrum, 453 (P); HRMS 453.05826 (observed), 453.06068 (calculated for $C_{16}H_{30}NPO_2Si_2Mo$). Anal. Calcd for $C_{16}H_{30}NPO_2Si_2Mo$: C, 42.56; H, 6.70; N, 3.10; P, 6.86. Found: C, 42.37; H, 6.59; N, 2.97; P, 6.76.

Preparation of [Mo(CO)$_2$(P(SC$_6$F$_5$)CH(SiMe$_3$)$_2$)(η-C$_5$H$_5$)] (7). A sample of 1 (0.36 g, 0.89 mmol) was dissolved in THF (50 mL), cooled to −78 °C, and stirred. Pentafluorothiophenol (0.21 g, 1.05 mmol) was then added, leading to an immediate color change to dark red. After 2 h all volatiles were removed in vacuo and the resulting dark red residue was purified by column chromatography (silica gel/hexane) which afforded a single red fraction. Red crystals of 7 were obtained from concentrated hexane solutions at −20 °C (0.08 g, 15%).

Spectroscopic data: ^{1}H NMR (CD$_2$Cl$_2$) δ 5.23 (s, 5 H, C$_5$*H*$_5$), 2.40 (s, 1 H, C*H*(SiMe$_3$)$_2$), 0.38 (s, 18 H, Si*Me*$_3$); ^{13}C{^{1}H} NMR δ 91.4 (s, *C*$_5$H$_5$), 1.9 (s, Si*Me*$_3$), *C*H(SiMe$_3$)$_2$ signal obscured by solvent; ^{31}P{^{1}H} NMR δ +297.7; IR $\nu_{C\equiv O}$ (KBr) 1987, 1888 cm^{-1}; mass spectrum, 608 (P); HRMS 607.97085 (observed), 607.97474 (calculated for $C_{20}H_{24}F_5O_2PSSi_2Mo$). Anal. Calcd for $C_{20}H_{24}F_5O_2PSSi_2Mo$: C, 39.60; H, 3.99. Found: C, 39.13; H, 4.40.

Preparation of [MoD(CO)$_2$(P(OCD$_3$)$_2$CD(SiMe$_3$)$_2$)(η-C$_5$H$_5$)] (8). A sample of 1 (0.19 g, 0.47 mmol) was dissolved in CD$_3$OD (1 mL) and the solution left at room temperature without stirring. Over a period of 72 h, the solution changed color from orange-brown to pale brown with concomitant formation of pale brown crystals. After 1 week the crystals of 8 were removed and dried in vacuo (0.15 g, 67%).

Spectroscopic data: ^{1}H NMR (CD$_2$Cl$_2$) δ 5.30 (s, 5 H, C$_5$*H*$_5$), 0.20 (s, 18 H, Si*Me*$_3$); ^{13}C{^{1}H} NMR δ 238.9 (s, *C*O), 89.9 (s, *C*$_5$H$_5$), 51.9 (septet, O*C*D$_3$, $^1J_{CD}$ = 4.0 Hz), 35.7 (unresolved multiplet, *C*D(SiMe$_3$)$_2$), 2.8 (s, Si*Me*$_3$); ^{31}P{^{1}H} NMR δ +225.2; ^{2}H NMR δ 4.47 (OC*D*$_3$), −7.4 (Mo-*D*), C*D*(SiMe$_3$)$_2$ not observed; IR $\nu_{C\equiv O}$ (KBr) 1954, 1882 cm^{-1}; mass spectrum, 480 (P); HRMS 480.10631 (observed), 480.10547 (calculated for $C_{16}H_{23}D_8O_4PSi_2Mo$). Anal. Calcd for $C_{16}H_{31}O_4PSi_2Mo$: C, 40.16; H, 6.53; P, 6.47. Found: C, 40.45; H, 6.84; P, 6.06.

X-ray Crystallographic Studies. All data were collected on an Enraf-Nonius CAD4-F diffractometer at room temperature on crystals mounted in Lindemann capillaries. Initial lattice parameters were determined from a least-squares fit to 25 accurately centered reflections, 15 < 2θ < 25°, and subsequently refined using higher angle data. Data were collected by using the ω–2θ scan mode for indices as described in Table XIII.

Data were corrected for the effects of Lorentz, polarization, decay (minimal in all structures), and absorption (except 1). Pertinent crystallographic and data collection parameters are collected in Table XIII.

All structures were solved by Patterson or direct methods (see table) and difference Fourier syntheses using full matrix least squares. All programs used were from the SDP Program Package (B.A. Frenz and Associates, Inc., College Station, TX). All non-hydrogen atoms in the structures of 1, 5, 7, and 8 were refined anisotropically although large thermal motion effects in the C$_6$F$_5$ ring in 7 led to small distortions in some of the derived parameters.

Final refinement converged smoothly for all structures, and no chemically significant peaks were present in the final difference maps.

Acknowledgment. We thank the Robert A. Welch Foundation, National Science Foundation and SERC for financial support.

Supplementary Material Available: Tables of bond lengths, bond angles, and thermal parameters for 1, 5, 7, and 8 and a table of calculated hydrogen positional parameters for 1 (10 pages); tables of observed and calculated structure factors for 1, 5, 7, and 8 (54 pages). Ordering information is given on any current masthead page.