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Structural Variation in Silver Acetylide Complexes: Syntheses and X-ray Structure Determinations of $[Ph_3PAgC\equiv CPh]_4\cdot 3.5THF$ and $[Me_3PAgC\equiv CSiMe_3]_\infty$

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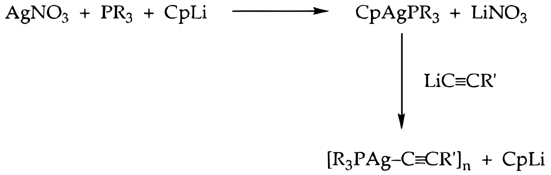
$[Ph_3PAgC\equiv CPh]_4\cdot 3.5THF$ (**2**) can be prepared by the reaction of $CpAgPPh_3$ (**1**) with lithium phenylacetylide (1:1 equiv). Similarly $[Me_3PAgC\equiv CSiMe_3]_\infty$ (**4**) can be prepared by the reaction of $CpAgPMe_3$ (**3**) and lithium (trimethylsilyl)acetylide (1:1 equiv). Both complexes have been characterized by elemental analyses, solid-state IR spectroscopy, ^1H and ^{31}P NMR spectroscopy, and low-temperature X-ray diffraction studies. The structure of **2** consists of a tetranuclear "flat-butterfly" core, with the two "hinge" silver atoms σ-bonded to two acetylide fragments, which then π-complex the apical $Ag(PPh_3)_2$ fragments. In **4**, the smaller steric bulk of the phosphine employed allows this complex to crystallize as a polymer. Rather than being constructed from simple $[R_3PAg(acetylide)]$ units, both **2** and **4** are formed by the aggregation of $(acetylide)_2Ag^-$ and $Ag(PR_3)_2^+$ fragments. The preparation of complexes **2** and **4** demonstrates the synthetic utility of nucleophilic substitution of $CpAgPR_3$ in the synthesis of Ag organometallics. The different structural alternatives adopted by **2** and **4** point to the steric bulk of the phosphine ligands being the major influence on the structure of Ag acetylide complexes.

Introduction

Jonas *et al.* demonstrated the synthetic utility of using the Cp group as a mesomerically stabilized anionic leaving group in the preparation of highly reactive transition metal species.[1] Our own studies on p block cyclopentadienyls showed that these compounds are valuable precursors to a range of novel organometallic and metalloorganic compounds.[2] This led us to investigate the organometallic chemistry of the elements that form the boundary between the transition metals and the p block metals. We recently reported that nucleophilic substitution of $CpCuPPh_3$ was a potentially versatile and halide-free route to copper organometallics.[3] The ion-separated complex $[Li(THF)_4]^+[(Fluorenyl)_2CuPPh_3]^-$ and the dinuclear complex $[Cy_3PCu(\mu\text{-}C\equiv C^tBu)_2Cu(PPh_3)_2]$ were synthesized by nucleophilic substitution of $CpCuPPh_3$ with fluorenyllithium (1:1 or 1:2 equiv) and with lithium *tert*-butylacetylide and tricyclohexylphosphine (1:1:1 equiv), respectively.[3] $[Li(THF)_4]^+[(Fluorenyl)_2CuPPh_3]^-$ was the first crystallographically characterized example of a phosphine-stabilized Gilman reagent, whereas $[Cy_3PCu(\mu\text{-}C\equiv C\text{-}^tBu)_2Cu(PPh_3)_2]$ is an unsymmetrical complex containing an extremely short Cu···Cu distance. This work illustrated that the Cp ligand of $CpCuPPh_3$ is readily substituted and has led us to investigate whether similar reactivity could be found for other group 11 cyclopentadienyl complexes.

We now report that this route *can* be extended to form silver organometallics from $CpAgPR_3$. The two silver acetylides reported herein represent only the second and third X-ray crystal structures on pure silver acetylides. The only previous study was that of Corfield and Shearer, who in 1966 reported the polymeric structure of $[Me_3PAgC\equiv CPh]_\infty$.[4] An analysis of the structure of this compound in conjunction with the two structures reported herein—molecular $[Ph_3PAgC\equiv CPh]_4\cdot 3.5THF$ (**2**) and polymeric $[Me_3PAgC\equiv CSiMe_3]_\infty$ (**4**)—shows that the compounds are constructed from similar $Ag(acetylide)_2^-$ and $Ag(PR_3)_2^+$ units but realize two separate aggregational alternatives. In so doing, the complexes give a fascinating insight into the factors dictating the structures of silver acetylides.

Scheme 1



For **2**: R = R' = Ph, n = 4
For **4**: R = Me, R' = $SiMe_3$, n = ∞

Results and Discussion

Addition of $LiC\equiv CPh$ to a freshly prepared solution of $CpAgPPh_3$ (**1**) (1:1 equiv) in THF at −30 °C leads to the formation of $[Ph_3PAgC\equiv CPh]_4\cdot 3.5THF$ (**2**) (Scheme 1). In a similar fashion, reaction of $CpAgPMe_3$ (**3**) and $LiC\equiv CSiMe_3$ under the same conditions leads to the formation of the polymeric $[Me_3PAgC\equiv CSiMe_3]_\infty$ (**4**) (Scheme 1). Evidently both products result from the substitution of the Cp ligand from the parent $CpAgPR_3$ complexes.

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(1) Jonas, K. *Angew. Chem.* **1985**, *97*, 292; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295.

(2) Paver, M. A.; Russell, C. A.; Wright, D. S. *Angew. Chem.* **1995**, *107*, 1677; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1545.

(3) Edwards, A. J.; Paver, M. A.; Raithby, P. R.; Russell, C. A.; Wright, D. S. *Organometallics* **1994**, *13*, 4967.

(4) Corfield, P. W. R.; Shearer, H. M. M. *Acta Crystallogr.* **1966**, *20*, 502.

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Prior to the determination of the crystal structures of the products **2** and **4**, both species (and the new complex **3**) were characterized by their melting points, elemental analyses (C, H, and P), solid-state IR spectroscopy, and solution ^{1}H and ^{31}P NMR. These preliminary studies confirmed the basic identities of complexes **2**−**4**. Complex **1** was characterized by comparison with literature data.[5] All of the complexes **1**−**4** are extremely air- and moisture-sensitive. Additionally, complexes **1** and **3** are thermally unstable, decomposing in a matter of minutes to black solids if left under an inert atmosphere at room temperature.

The IR spectrum of **4** shows a C≡C stretch at 2018 cm^{-1} (cf. 2047 cm^{-1} in free $HC{\equiv}CSiMe_3$).[6] However, no C≡C stretch could be discerned for complex **2**. The absence of this absorption is also a characteristic of the related copper acetylides $[Cy_3PCu(\mu\text{-}C{\equiv}C^tBu)_2Cu(PPh_3)_2]$[3] and $[Cu\{S(2\text{-}Me_2NCH_2C_6H_4)\}_2(C{\equiv}C^tBu)]_2$.[7] The proton-decoupled ^{31}P NMR spectra of **2** and **4** show single absorptions at $\delta = -0.94$ and -42.51 ppm (s), respectively, indicating that there is only one phosphine ligand environment in both complexes. The ^{1}H-NMR spectrum of **2** shows a broad multiplet at $\delta = 7.40{-}6.91$ as a result of the two phenyl environments (PPh_3 and $-C{\equiv}CPh$) and two peaks at $\delta = 3.62{-}3.56$ and $\delta = 1.82{-}1.70$ due to the three uncomplexed THF molecules. In the ^{1}H-NMR spectrum of **4**, a doublet at $\delta = 1.29$ ($^{2}J_{P-H}$ 5.3 Hz) due to PMe_3 protons and a singlet at $\delta = 0.23$ due to the acetylide $Si(CH_3)_3$ protons are observed. Thus, the NMR data (combined with elemental analyses) are in accord with the later structural characterizations of both compounds.

Low-temperature X-ray crystallographic studies were performed on **2** and **4**. A key interest from the start in these studies was the investigation of the potentially different aggregation states of these species. Details of the X-ray analyses of both complexes are given in Table 1, with atomic coordinates given in Tables 2 (for complex **2**) and 3 (for complex **4**). Tables 4 and 5 list selected bond lengths and angles for complexes **2** and **4**, respectively.

Table 1. Crystal Data and Structure Solutions for 2 and 4[a]

	2	**4**
empirical formula	$C_{104}H_{80}Ag_4P_4(THF)_{3.5}$	$C_{32}H_{72}Ag_4P_4Si_4$
M_r	2136.40	1124.62
cryst size/mm^3	0.32 × 0.26 × 0.23	0.36 × 0.23 × 0.22
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a/Å	19.571(4)	12.189(2)
b/Å	18.994(4)	25.437(5)
c/Å	26.968(5)	17.660(4)
α/deg	90	90
β/deg	97.46(3)	108.17(3)
γ/deg	90	90
V/Å^3	9940(4)	5203(2)
Z	4	4
D_c/Mg m^{-3}	1.430	1.436
θ range	$4.01 \le \theta \le 22.51$	$3.51 \le \theta \le 21.51$
reflcns collcd	13 677	9000
indpdt reflcns	12 825	5944
R_1, wR_2 [$F > 4\sigma(F)$][b]	0.0611, 0.1570	0.0409, 0.0724
R_1, wR_2 (all data)[b]	0.0827, 0.2033	0.0752, 0.0889
final diff peak, hole	1.418, −1.200	0.876, −0.425

[a] Details in common: $T = 153(2)$ K, $\lambda = 0.710\,73$ Å. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma F_o$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o)^4]^{0.5}$.

The X-ray crystallographic study of **2** shows it to be $[Ph_3PAgC{\equiv}CPh]_4{\cdot}3.5THF$ (Figure 1). Three lattice bound THF molecules occupy the asymmetric unit. In addition, a further THF molecule is located on a crystallographic center of inversion and has half-occupancy in the asymmetric unit. None of the THF molecules interact with the central Ag_4 core. This core consists of four silver atoms in a "flat-butterfly" arrangement, with each of the apical Ag atoms [Ag(3) and Ag(4)] complexed by two PPh_3 ligands, and the Ag centers [Ag(1) and Ag(2)] σ-bonded to two acetylide ligands at the "hinge" of the butterfly. The C≡C groups of the acetylide ligands further π-bond to the apical silver atoms. The Ag⋯Ag distances in the core vary from 2.921(1) to 3.084(1) Å (cf. 2.89 Å in silver metal).[8] While this does not necessarily imply that there are genuine interactions, it is noteworthy that the shortest Ag⋯Ag contact occurs across the core between the "hinge" Ag centers [Ag(1)−Ag(2) 2.921(1) Å]. The "hinge" Ag centers are approximately linearly coordinated by the acetylide ligands (average C−Ag−C 173.1°). In contrast, the apical silver atoms have pseudotetrahedral geometries, being coordinated by two phosphine and two acetylide ligands.

The structure of **2** differs markedly from its symmetrical copper analogue, $[Ph_3PCuC{\equiv}CPh]_4$,[9] but shows similarities to a further copper acetylide $[Me_3PCuC{\equiv}CPh]_4$.[10,11] In $[Me_3PCuC{\equiv}CPh]_4$, one observes Cu(acetylide)$_2$ units interacting with $Cu(PMe_3)_2$ groups in a similar fashion to that observed for **2**. However, maintaining short (i.e., strong) Cu−acetylide bonds necessitates the distortion of the "flat-butterfly" geometry, with two Cu⋯Cu edges being opened up to give the observed zigzag chain of Cu atoms.[10] In contrast to both $[Me_3PCuC{\equiv}CPh]_4$ and **2**, the copper atoms of $[Ph_3PCuC{\equiv}CPh]_4$ form a tetrahedral metal skeleton, with each copper being bonded to one triphenylphosphine and each face of the tetrahedron being capped by a $\mu_3\text{-}\eta^1$-acetylide ligand. In $[Me_3PCuC{\equiv}CPh]_4$ and **2**, the unusual isomeric alternatives adopted in which there is asymmetrical phosphine complexation of the core (two metal centers being complexed by two phosphines each and the other two metal centers being uncomplexed) precludes formation of a tetrahedral metal core structure.

Inorganic Ag compounds containing Ag_4 cores have previously been observed, most commonly for Ag chalconides but also for halides and succinates. The structures of these complexes vary considerably, from those containing tetrahedral metal cores to "bent-butterfly" structures and "flat-butterfly" structures akin to **2**. Tetrahedral metal cores are observed in the anions of the complexes $[Pr^n{}_4N]_2[Ag_4(Me_3C_6H_2CS_2)_6]$,[12] $[Pr^n{}_4N]_2[Ag_4(Se_4)_3]$,[13] $[Ph_4P]_2[Ag_4(Te_4C_4H_3S)_6]$,[14] and $[Ph_4P]_2[Ag_4(SCH_2C_6H_4CH_2S)_3]$[15] and in the neutral complexes

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(5) Hofstee, H. F.; Boersma, J.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1976**, *120*, 313.

(6) Dolphin, D.; Wick, A. *Tabulation of Infrared Spectral Data*; Wiley-Interscience: New York, 1977; p 549.

(7) Knotter, D. M.; Spek, A. L.; Grove, D. M.; van Koten, G. *Organometallics* **1992**, *11*, 4083.

(8) Emsley, J. *The Elements*; Clarendon: Oxford, U.K., 1989; p 174.

(9) Demartin, F.; Manassero, M.; Naldini, L.; Rassu, G.; Sansoni, M.; Zoroddu, M. A. *J. Organomet. Chem.* **1985**, *279*, C42.

(10) Corfield, P. W. R.; Shearer, H. M. M. *Acta Crystallogr.* **1966**, *21*, 957.

(11) Coates, G. E.; Parkin, C. *J. Inorg. Nucl. Chem.* **1961**, *22*, 59.

(12) Schuerman, J. A.; Fronczek, F. R.; Selbin, J. *Inorg. Chim. Acta* **1989**, *160*, 43.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å × 10^3) for 2[a]

	x	*y*	*z*	*U*(eq)		*x*	*y*	*y*	*U*(eq)
Ag(1)	10568(1)	4633(1)	2704(1)	27(1)	C(92)	10661(5)	2875(5)	776(4)	42(2)
Ag(2)	9512(1)	5710(1)	2466(1)	28(1)	C(93)	11034(5)	3503(6)	809(4)	46(3)
Ag(3)	9071(1)	4210(1)	2322(1)	26(1)	C(94)	10865(6)	4021(6)	1134(4)	53(3)
Ag(4)	10928(1)	6137(1)	2812(1)	25(1)	C(95)	10346(5)	3917(5)	1416(3)	33(2)
P(1)	7854(1)	4239(1)	2527(1)	26(1)	C(100)	9496(1)	2334(4)	2067(3)	29(2)
P(2)	9277(1)	3180(1)	1772(1)	25(1)	C(101)	9956(5)	2332(5)	2506(4)	34(2)
P(3)	11762(1)	6205(1)	3610(1)	25(1)	C(102)	10211(5)	1715(5)	2719(4)	35(2)
P(4)	11054(1)	7163(1)	2240(1)	27(1)	C(103)	10001(5)	1077(5)	2505(4)	44(3)
C(10)	9903(5)	4082(5)	3095(3)	31(2)	C(104)	9531(5)	1063(5)	2080(4)	47(3)
C(11)	9630(5)	3756(5)	3398(3)	27(2)	C(105)	9284(5)	1675(5)	1853(4)	35(2)
C(12)	9316(5)	3330(5)	3748(3)	35(2)	C(110)	12650(5)	5936(4)	3593(3)	30(2)
C(13)	8856(6)	3589(6)	4041(4)	46(3)	C(111)	12766(5)	5338(5)	3332(4)	43(3)
C(14)	8530(6)	3155(7)	4347(5)	62(3)	C(112)	13415(5)	5085(6)	3319(4)	51(3)
C(15)	8687(7)	2440(7)	4375(4)	58(3)	C(113)	13980(5)	5437(6)	3539(4)	46(3)
C(16)	9150(6)	2180(6)	4089(4)	54(3)	C(114)	13878(5)	6046(6)	3808(4)	44(3)
C(17)	9470(5)	2604(5)	3780(4)	38(2)	C(115)	13230(5)	6281(5)	3835(4)	44(3)
C(20)	9086(5)	5254(5)	1804(4)	34(2)	C(120)	11791(4)	7109(4)	3851(3)	27(2)
C(21)	8859(5)	5238(5)	1369(4)	40(3)	C(121)	11373(4)	7310(5)	4196(3)	31(2)
C(22)	8577(2)	5233(5)	849(3)	40(3)	C(122)	11304(5)	8026(5)	4312(4)	38(2)
C(23)	8921(7)	4958(6)	483(4)	58(3)	C(123)	11672(5)	8523(5)	4097(3)	33(2)
C(24)	8621(8)	4963(6)	−19(4)	67(4)	C(124)	12116(5)	8328(5)	3761(4)	38(2)
C(25)	7989(8)	5273(7)	−154(5)	66(4)	C(125)	12178(5)	7625(5)	3635(3)	33(2)
C(26)	7644(7)	5561(8)	195(5)	73(4)	C(130)	11528(4)	5679(4)	4127(3)	28(2)
C(27)	7921(6)	5544(6)	707(4)	56(3)	C(131)	10944(5)	5270(4)	4070(3)	31(2)
C(30)	11301(5)	5117(5)	2343(4)	35(2)	C(132)	10772(5)	4866(5)	4463(4)	43(4)
C(31)	11744(5)	5215(4)	2070(4)	28(2)	C(133)	11191(6)	4860(5)	4915(4)	49(3)
C(32)	12292(5)	5353(5)	1772(4)	35(2)	C(134)	11783(6)	5260(5)	4978(4)	49(3)
C(33)	12952(5)	5081(5)	1898(4)	39(2)	C(135)	11952(5)	5670(5)	4594(4)	41(2)
C(34)	13475(6)	5229(6)	1629(5)	51(3)	C(140)	10561(4)	7945(5)	2345(4)	37(2)
C(35)	13363(6)	5669(6)	1226(5)	54(3)	C(141)	10243(5)	8371(5)	1961(4)	44(3)
C(36)	12714(7)	5942(6)	1079(4)	56(3)	C(142)	9870(6)	8952(6)	2073(6)	62(4)
C(37)	12178(6)	5777(5)	1348(4)	44(3)	C(143)	9815(5)	9131(5)	2560(5)	60(4)
C(40)	9826(4)	6274(5)	3101(3)	26(2)	C(144)	10127(5)	8725(6)	2939(5)	51(3)
C(41)	9745(4)	6578(5)	3492(3)	28(2)	C(145)	10487(5)	8123(5)	2838(4)	39(2)
C(42)	9647(4)	6938(5)	3946(3)	31(2)	C(150)	11944(4)	7469(4)	2358(4)	28(2)
C(43)	9451(5)	7646(5)	3934(4)	39(2)	C(151)	12462(5)	6978(5)	2443(3)	31(2)
C(44)	9379(5)	8006(6)	4365(4)	52(3)	C(152)	13136(5)	7174(6)	2575(4)	44(3)
C(45)	9494(5)	7672(7)	4821(4)	55(3)	C(153)	13313(5)	7873(5)	2621(4)	43(3)
C(46)	9681(5)	6969(6)	4852(4)	47(3)	C(154)	12806(5)	8376(5)	2535(4)	48(3)
C(47)	9750(5)	6609(5)	4421(4)	40(2)	C(155)	12126(5)	8180(5)	2401(4)	40(2)
C(50)	7237(5)	4636(5)	2042(4)	35(2)	C(160)	10891(5)	7039(4)	1563(3)	31(2)
C(51)	6813(5)	5201(5)	2125(4)	38(2)	C(161)	10361(5)	6589(5)	1374(4)	41(2)
C(52)	6338(5)	5459(5)	1723(5)	50(3)	C(162)	10221(6)	6465(6)	865(4)	50(3)
C(53)	6296(6)	5159(6)	1259(4)	53(3)	C(163)	10590(6)	6788(6)	542(4)	56(3)
C(54)	6725(6)	4623(6)	1170(4)	54(3)	C(164)	11146(6)	7225(6)	724(4)	58(3)
C(55)	7196(5)	4353(5)	1564(4)	39(2)	C(165)	11279(6)	7344(6)	1233(4)	51(3)
C(60)	7482(5)	3366(4)	2604(3)	29(2)	O(1T)	13006(4)	7601(4)	623(3)	82(3)
C(61)	6805(5)	3184(5)	2448(4)	38(2)	C(11T)	12767(5)	8271(4)	452(3)	63(3)
C(62)	6567(5)	2519(6)	2515(4)	50(3)	C(12T)	12827(6)	8734(4)	928(4)	79(4)
C(63)	7006(6)	2019(6)	2765(5)	60(3)	C(13T)	13440(6)	8412(6)	1249(3)	111(6)
C(64)	7677(6)	2190(5)	2918(5)	65(4)	C(14T)	13367(6)	7638(5)	1128(3)	108(6)
C(65)	7922(5)	2860(5)	2846(4)	41(3)	O(2T)	14282(6)	4217(6)	4628(3)	146(5)
C(70)	7696(4)	4724(4)	3088(3)	24(2)	C(21T)	13788(6)	4691(5)	4773(3)	84(4)
C(71)	7121(5)	4616(5)	3326(4)	36(2)	C(22T)	13618(5)	4405(7)	5281(4)	58(6)
C(72)	7008(5)	5036(5)	3722(4)	41(2)	C(23T)	14293(7)	4069(7)	5499(3)	58(6)
C(73)	7464(6)	5565(5)	3893(3)	41(3)	C(24T)	14565(5)	3772(5)	5044(4)	81(4)
C(74)	8044(5)	5664(5)	3663(4)	43(3)	C(22′)	13992(7)	4779(6)	5358(4)	38(5)
C(75)	8169(5)	5247(5)	3266(4)	43(3)	C(23′)	14047(7)	3776(6)	5381(4)	76(8)
C(80)	8529(4)	2982(4)	1304(4)	31(2)	O(3T)	11504(6)	1959(7)	−159(4)	131(4)
C(81)	8499(6)	3247(6)	818(4)	47(3)	C(31T)	11674(7)	2650(6)	−294(4)	111(6)
C(82)	7912(6)	3136(8)	482(5)	70(4)	C(32T)	11727(8)	2606(7)	−861(4)	101(5)
C(83)	7369(7)	2787(8)	614(5)	71(4)	C(33T)	11209(9)	2036(9)	−1034(4)	181(11)
C(84)	7376(5)	2532(6)	1102(6)	62(4)	C(34T)	11278(9)	1534(6)	−597(6)	190(12)
C(85)	7973(5)	2631(5)	1443(4)	41(3)	C(41T)	4733(9)	5432(9)	234(6)	89(5)
C(90)	9970(4)	3300(4)	1392(3)	29(2)	C(42T)	5298(9)	5598(10)	77(7)	93(5)
C(91)	10151(5)	2776(5)	1063(4)	37(2)	C(43T)	5395(12)	5275(14)	−226(10)	149(9)

[a] *U*(eq) is defined as one-third of the trace of the orthogonolized $\mathbf{U}_{ij}$ tensor.

$Ag_4(Me_3C_6H_2CS_2)_4$·$(py)_3$ and $Ag_4(MeC_6H_5CS_2)_4$·$(py)_4$.[12] Upon disconnecting of one Ag···Ag contact in a tetrahedron, a "bent-butterfly" metal-core arrangement is observed as in $Ag_4[SCH(SiMe_3)_8]_2$.[16] Finally, as the tetrahedron is fully opened, one observes "flat-butterfly" cores akin to **2**, as in the anions of the complexes

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(13) Kanatzidis, M. G.; Huang, S.-P. *Angew. Chem.* **1989**, *101*, 1556; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1513.

(14) Zhao, J.; Adcock, D.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1990**, *29*, 4358.

(15) Henkel, G.; Betz, P.; Krebs, B. *Angew. Chem.* **1987**, *99*, 131; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 145.

(16) Tang, K.; Aslam, M.; Block, E.; Nicholson, T.; Zubieta, J. *Inorg. Chem.* **1987**, *26*, 1488.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å $\times 10^3$) for 4[a]

	x	y	z	U(eq)
Ag(1)	5591(1)	8745(1)	7470(1)	39(1)
Ag(2)	3087(1)	8834(1)	7499(1)	43(1)
Ag(3)	515(1)	8589(1)	7448(1)	39(1)
Ag(4)	−1846(1)	8646(1)	7698(1)	36(1)
Si(11)	3354(2)	7052(1)	7291(1)	38(1)
Si(12)	7961(2)	10354(1)	7324(1)	40(1)
Si(31)	3984(2)	8234(1)	9859(1)	42(1)
Si(32)	−3252(2)	8822(1)	5185(1)	46(1)
P(21)	3856(2)	9701(1)	8120(2)	53(1)
P(22)	2053(2)	8895(1)	6049(1)	49(1)
P(41)	−2253(2)	7684(1)	7715(1)	40(1)
P(42)	−625(2)	8899(1)	9078(1)	37(1)
C(111)	4479(6)	8126(3)	7395(5)	39(2)
C(112)	3973(6)	7714(3)	7339(4)	37(2)
C(113)	1828(6)	7095(3)	7306(5)	52(2)
C(114)	3403(7)	6732(4)	6360(5)	66(3)
C(115)	4249(7)	6658(4)	8150(5)	64(3)
C(121)	6697(6)	9366(3)	7510(4)	36(2)
C(122)	7258(6)	9746(3)	7480(4)	34(2)
C(123)	6834(7)	10797(3)	6673(5)	57(3)
C(124)	9082(8)	10193(4)	6864(6)	70(3)
C(125)	8625(8)	10702(4)	8294(5)	71(3)
C(311)	2027(6)	8492(3)	8366(4)	41(2)
C(312)	2866(6)	8411(3)	8939(5)	40(2)
C(313)	5394(7)	8191(5)	9693(6)	86(4)
C(314)	3976(10)	8711(4)	10634(6)	102(4)
C(315)	3621(8)	7585(4)	10188(6)	78(3)
C(321)	−1046(7)	8668(3)	6572(4)	37(2)
C(322)	−1952(6)	8711(3)	6035(4)	35(2)
C(323)	−4342(7)	8315(4)	5153(6)	74(3)
C(324)	−2854(9)	8796(4)	4248(5)	80(3)
C(325)	−3845(8)	9480(3)	5274(5)	70(3)
C(211)	2839(10)	10033(4)	8523(9)	115(5)
C(212)	4145(8)	10194(3)	7473(6)	70(3)
C(213)	5170(9)	9720(4)	8964(5)	82(3)
C(221)	3090(9)	9059(5)	5546(6)	104(5)
C(222)	1382(10)	8298(4)	5545(6)	100(4)
C(223)	939(8)	9382(4)	5645(6)	84(4)
C(411)	−3218(7)	7350(3)	6867(5)	60(3)
C(412)	−2701(7)	7424(3)	8533(5)	55(2)
C(413)	−894(7)	7334(3)	7847(6)	63(3)
C(421)	471(7)	9405(3)	9243(5)	52(2)
C(422)	163(6)	8372(3)	9731(4)	46(2)
C(423)	−1561(7)	9159(3)	9628(5)	50(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Selected Bond Lengths and Angles for Complex 2

Distances/Å			
Ag(1)−Ag(2)	2.921(1)	Ag(1)−Ag(3)	3.084(1)
Ag(1)−Ag(4)	2.948(1)	Ag(2)−Ag(3)	2.987(1)
Ag(2)−Ag(4)	2.923(1)	Ag(1)−C(10)	2.065(11)
Ag(1)−C(30)	2.053(11)	Ag(2)−C(20)	2.061(9)
Ag(2)−C(40)	2.044(9)	Ag(3)−C(10)	2.486(8)
Ag(3)−C(20)	2.426(9)	Ag(4)−C(30)	2.476(10)
Ag(4)−C(40)	2.399(9)	C(10)−C(11)	1.203(13)
C(20)−C(21)	1.202(13)	C(30)−C(31)	1.222(13)
C(40)−C(41)	1.230(12)	Ag(3)−P(1)	2.515(2)
Ag(3)−P(2)	2.518(2)	Ag(4)−P(3)	2.530(2)
Ag(4)−P(4)	2.517(2)		
Angles/deg			
C(30)−Ag(1)−C(10)	174.6(3)	C(40)−Ag(2)−C(20)	171.6(3)
Ag(1)−C(10)−C(11)	166.5(7)	Ag(1)−C(30)−C(31)	161.4(8)
Ag(2)−C(20)−C(21)	156.1(8)	Ag(2)−C(40)−C(41)	154.8(7)
C(20)−Ag(3)−C(10)	120.5(3)	C(20)−Ag(3)−P(1)	101.0(2)
C(20)−Ag(3)−P(2)	106.4(2)	C(10)−Ag(3)−P(1)	110.7(3)
C(10)−Ag(3)−P(2)	106.3(2)	P(2)−Ag(3)−P(1)	112.0(1)
C(40)−Ag(4)−C(30)	126.0(3)	C(30)−Ag(4)−P(3)	105.9(2)
C(30)−Ag(4)−P(4)	103.5(2)	C(40)−Ag(4)−P(3)	102.9(3)
C(40)−Ag(4)−P(4)	106.2(2)	P(4)−Ag(4)−P(3)	112.2(1)

Table 5. Selected Bond Lengths and Angles for Complex 4[a]

Distances/Å			
Ag(1)−Ag(2)	3.0768(10)	Ag(2)−Ag(3)	3.1700(10)
Ag(3)−Ag(4)	3.0472(10)	Ag(1)−Ag(#4)	3.0339(10)
Ag(1)−C(111)	2.054(8)	Ag(1)−C(121)	2.065(8)
Ag(3)−C(311)	2.055(8)	Ag(3)−C(321)	2.053(8)
Ag(2)−C(111)	2.521(7)	Ag(2)−C(311)	2.450(7)
Ag(4)−C(#121)	2.500(7)	Ag(4)−C(321)	2.473(7)
Ag(2)−P(21)	2.511(2)	Ag(2)−P(22)	2.482(2)
Ag(4)−P(41)	2.500(2)	Ag(4)−P(42)	2.511(2)
C(111)−C(112)	1.204(10)	C(121)−C(122)	1.194(10)
C(311)−C(312)	1.211(10)	C(321)−C(322)	1.216(9)
Angles/deg			
C(111)−Ag(1)−C(121)	178.3(3)	C(311)−Ag(3)−C(321)	176.7(3)
Ag(1)−C(111)−C(112)	169.4(7)	Ag(1)−C(121)−C(122)	174.1(7)
Ag(3)−C(311)−C(312)	174.5(7)	Ag(3)−C(321)−C(322)	177.9(7)
C(311)−Ag(2)−P(21)	103.7(2)	C(311)−Ag(2)−P(22)	118.1(2)
C(111)−Ag(2)−P(21)	119.4(2)	C(111)−Ag(2)−P(22)	96.1(2)
P(21)−Ag(2)−P(22)	113.33(9)	C(111)−Ag(2)−C(311)	106.9(3)
C(321)−Ag(4)−P(41)	99.3(2)	C(321)−Ag(4)−P(42)	120.8(2)
C(#121)−Ag(4)−P(41)	125.7(2)	C(#121)−Ag(4)−P(42)	97.1(2)
P(41)−Ag(4)−P(42)	107.38(7)	C(#121)−Ag(4)−C(321)	108.6(3)

[a] # denotes an equivalent atom in an adjoining asymmetric unit.

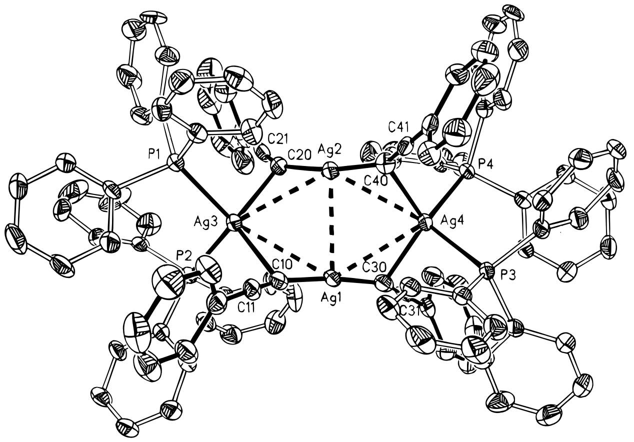

Figure 1. ORTEP drawing of **2**. Thermal ellipsoids at the 40% level are shown. All hydrogen atoms and lattice-bound THF molecules have been omitted for clarity.

$[Et_4N]_4[Ag(Se_4)]_4$[13] and $[C_{15}H_{30}N_2]_2[Ag_4I_8]$[17] and in the neutral complexes $Ag[SC(SiMe_3)_3]_4$,[16] $[Ag(FC_6H_4N_3C_6H_4F)_4$,[18] $(Ph_3P)_2Ag_4(C_3H_4NS_2)_4$,[19] $[Ag_4(OOC(CH_2)_2COO)_2]_\infty$,[20] $Ag_4[C_6H_4O_2(Me_2SiNBu^t)_2]_2$,[21] and $Ag_4(SSi(OBu^t)_3)_4$.[22] Although Ag organometallics have rarely been structurally elucidated, there are three structurally characterized examples of Ag organometallics which have tetrameric structures, *viz.* $[CpFe(C_5H_3CH_2NMe_2)Ag]_4$ (**5**),[23] $[Me_3C_6H_2Ag]_4$ (**6**),[24] and $[CF_3CF{=}C(CF_3)Ag]_4$ (**7**).[25] In all three compounds, the silver atoms are linearly coordinated by two sp^2 carbon atoms in square core structures. The sp^2 carbon atoms bridge the Ag···Ag vectors symmetrically in **5**−**7**, unlike the unsymmetrical bridging by the sp carbon atoms in **2**

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(17) Estienne, J. *Acta Crystallogr.* **1986**, *C42*, 1516.

(18) Hartmann, A.; Strähle, J. *Z. Anorg. Allg. Chem.* **1990**, *583*, 31.

(19) Fackler, J. P., Jr.; López, C. A.; Staples, R. J.; Wang, S.; Winpenny, R. E. P.; Lattimer, R. P. *J. Chem. Soc., Chem. Commun.* **1992**, 146.

(20) Michaelides, A.; Kiritsis, V.; Skoulika, S.; Aubrey, A. *Angew. Chem.* **1993**, *105*, 1525; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1495.

(21) Veith, M.; Woll, K. L. *Chem. Ber.* **1993**, *126*, 2383.

(22) Wojnowski, W.; Wojnowski, M.; Peters, K.; Peters, W.-M.; von Schnering, H. G. Z. *Anorg. Allg. Chem.* **1985**, *530*, 79.

(23) Nesmeyanov, A. N.; Sedova, N. N.; Struchkov, Y. T.; Andrianov, V. G.; Stakheeva, E. N.; Sazonova, V. A. *J. Organomet. Chem.* **1978**, *153*, 149.

(24) Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067.

(25) Jeffries, P. M.; Wilson, S. R.; Girolami, G. S. *J. Organomet. Chem.* **1993**, *449*, 203.

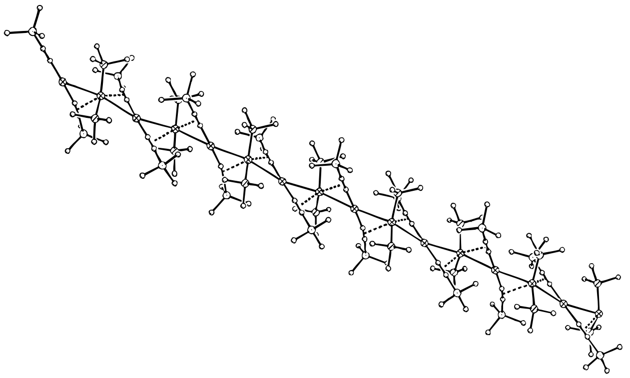

Figure 2. Polymeric chains of **4**. All hydrogen atoms have been omitted for clarity.

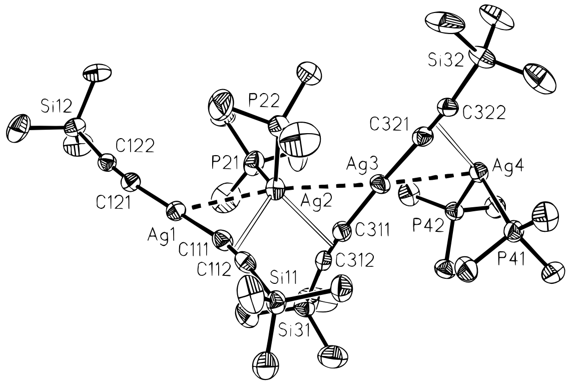

Figure 3. ORTEP drawing of **4** showing the asymmetric unit. Thermal ellipsoids at the 40% level are shown. All hydrogen atoms have been omitted for clarity.

(average Ag−C 2.17 Å in **5**, 2.20 Å in **6**, 2.19 Å in **7**; cf. 2.05 Å (Ag−C$_{short}$) and 2.45 Å (Ag−C$_{long}$) in **2**). The Ag···Ag distances are much shorter in **5**−**7** than in **2** (average Ag···Ag 2.740 Å in **5**, 2.744 Å in **6**, 2.761 Å in **7**; cf. 2.921−3.084 Å in **2**). These features may reflect the fact that **5**−**7** are built up from simple "AgR" units with no phosphine solvation of the core, whereas **2** can be visualized as being formally constructed from Ag(acetylide)$_2^-$ and Ag(PR$_3$)$_2^+$ units.

In contrast to the oligomeric structure of **2**, the structure of **4** is polymeric (Figure 2). The asymmetric unit consists of an Ag$_4$ segment (Figure 3). However, rather than forming an infinite array utilizing basic [Me$_3$PAgC≡CSiMe$_3$] building blocks, the complex is constructed from strands in which alternating Ag(acetylide)$_2^-$ units π-donate to adjacent Ag(PMe$_3$)$_2^+$ units.

The structure of **4** closely resembles the only other structurally characterized silver acetylide complex, that of [Me$_3$PAgC≡CPh]$_\infty$ (**8**).[4] The structure is highly unsymmetrical, with the formally anionic and cationic Ag centers being separated by long-range Ag···Ag contacts (ranging from 3.034(1) to 3.170(1) Å; cf. 2.89 Å in silver metal) in a zigzag chain (average Ag−Ag−Ag 163.6°). Each of the "anionic" silver fragments [Ag(1) and Ag(3)] are σ-bonded to two acetylide ligands [Ag−C ranging from 2.053(8) to 2.065(8) Å], giving an approximately linear coordination geometry (average C−Ag−C 177.5°). The "cationic" Ag centers [Ag(2) and Ag(4)] have pseudotetrahedral geometries, being bonded to two phosphines and asymmetrically π-bonded to two acetylide ligands. The bond angles about these Ag centers range from 96.1(2) to 120.8(2)°.

Table 6. Comparison of Ligand Environment and Degree of Oligomerization in the Solid State for Silver Acetylide Complexes [R′$_3$PAgC≡CR]$_n$

complex	R′	R	*n*
2	Ph	Ph	molecular (n = 4)
4	Me	SiMe$_3$	polymer
8	Me	Ph	polymer

The unsymmetrical π-bonding of the acetylides observed in both **2** and **4** and the previously reported silver acetylide (**8**)[4] is of interest. Corfield *et al.* suggest that the unsymmetrical side-on bonding in **8** is necessarily weak because Ag−P back-bonding occurs.[4] This effect is also seen in complexes **2** and **4**. The small reduction in the C≡C stretching frequency in **4** (2018 cm^{-1}; cf. 2047 cm^{-1} in free HC≡CSiMe$_3$)[6] and the small deviation from linearity of the C≡CR unit in both **2** and **4** (average 2.1° in **2**, 6.8° in **4**, and 8.1° in **8**) reflect only a slight formal change in hybridization of the β-carbon.

Although there are obvious electronic differences in the natures of the acetylide ligands present in **2** and **4**, it seems unlikely that the terminal substituents in these ligands (Ph in **2** and SiMe$_3$ in **4**) will have much steric influence on the nature of the complex formed. The steric bulk of the phosphine ligand is far more likely to play a significant role in determining the structural motif adopted. In this respect it is useful to compare the structures of **2**, **4**, and of the previously reported complex **8** (Table 6).

In **4** and **8**, in which different acetylide ligands but the same phosphine ligand are present, similar polymeric structures are observed. However, changing the PMe$_3$ ligands of **8** to PPh$_3$ gives rise to a molecular structure. Although the current structural studies are admittedly limited, for Ag acetylide complexes it is therefore to be expected that ligands with lower steric bulk will favor the formation of polymeric structures akin to **4** and **8**, whereas phosphine ligands with higher steric bulk drive the complex toward a molecular structure.

Conclusion

The syntheses of **2** and **4** illustrate the synthetic utility of substitution of the Cp group of CpAgPR$_3$ as a route to new silver organometallics. Particularly the solubility of CpAgPMe$_3$ in organic solvents circumvents one of the most commonly occurring problems with less soluble Ag inorganic precursors, that of a significant amount of reduction of the metal. Complex **2** is the first structurally characterized oligomeric silver acetylide complex. The structures of **2** and **4** show that these complexes are constructed from the interactions of Ag(acetylide)$_2^-$ with Ag(PR$_3$)$^+$ fragments rather than from simple (acetylide)Ag(PR$_3$) units. Despite this, two very different structural alternatives are adopted in the molecular and polymeric structures of **2** and **4**. The adoption of the differing structural motifs appears to be dictated largely by the steric influence of the phosphine ligands employed.

We are continuing to investigate the synthetic utility of CpAgPR$_3$ in forming new Ag organometallic and metalloorganic complexes and in preparing further silver acetylides in order to probe further the nature of the bonding in these species.

Experimental Section

General Experimental Methods. Compounds **1**−**4** are air- and moisture-sensitive. They were handled on a vacuum line using standard inert-atmosphere techniques[26] and under dry/oxygen-free argon. THF was dried by distillation over sodium/benzophenone and degassed prior to the reactions. Complexes **1**−**4** were isolated and characterized with the aid of an argon-filled glovebox (Faircrest Mark 4A) fitted with an O_2 and H_2O recirculation system (type B). Melting points were determined by using a conventional apparatus and sealing samples in capillaries under argon. IR spectra were recorded as Nujol mulls using NaCl plates and were run on a Perkin-Elmer 2400 spectrophotometer. Elemental analyses were performed by first sealing the samples under argon in airtight aluminum boats (1−2 mg), and C and H content was analyzed using a Perkin-Elmer 240 elemental analyzer. Proton NMR spectra were recorded on a Bruker WH 250 MHz spectrometer in dry [$^2H_8$]-THF (using the resonances of C_4D_7HO as the internal reference standard). ^{31}P NMR were recorded using a Bruker WH 250 MHz spectrometer in the same solvent (using 85% H_3PO_4 as the external reference standard).

Synthesis of $CpAgPPh_3$ (1). **1** was prepared by a variation on literature methods.[5] A suspension of freshly ground $AgNO_3$ (0.68 g, 4 mmol) in THF (30 mL) was placed in an ultrasound bath for 5 min, this treatment leading to finely divided material. To this was added PPh_3 (1.05 g, 4 mmol) and CpLi (8.0 ml, 0.5 mol L^{-1} in THF/hexane, 4 mmol) at −78 °C. A white solid was precipitated in 85% (1.48 g) yield. The sample is extremely air- and moisture-sensitive and thermally unstable, but if kept cool (<−20 °C), it can be isolated.

Synthesis of $[Ph_3PAgC{\equiv}CPh]_4{\cdot}3.5THF$ (2). A 2.5 mmol amount of **1** was prepared *in situ* at −78 °C. Then freshly prepared $LiC{\equiv}CPh$ (2.5 mmol, prepared by literature methods[27]) in 10 mL of THF was added and the cooled solution was filtered immediately. The solvent was then reduced *in vacuo* to ca. 10 mL, and storage at 5 °C (24 h) gave colorless crystals of **2** (0.52 g, 41%). Mp: decomposition at 100 °C to a black solid (which melts at 134−136 °C). Anal. Found: C, 66.0; H, 5.2; P, 5.9. Calc: C, 66.3; H, 5.2; P, 5.7. IR: no definitive absorptions. ^1H-NMR (250 MHz, [$^2H_8$]-THF, +25 °C): δ = 7.40−6.91 [m, 80 H, Ph], 3.62−3.56 [m, 12 H, THF], 1.82−1.70 [m, 12 H, THF]. ^{31}P-NMR (101.27 MHz, [$^2H_8$]-THF, +25 °C): $\delta = -0.94$ [s, PPh_3].

Synthesis of $CpAgPMe_3$ (3). A suspension of freshly ground $AgNO_3$ (0.68 g, 4 mmol) in THF (10 mL) was placed in an ultrasound bath for 5 min. To this was added PMe_3 (0.30 g, 4 mmol) and CpLi (8.0 mL, 0.5 mol L^{-1} in THF/hexane, 4 mmol) at −78 °C. A clear solution resulted, which was reduced *in vacuo* to ca. 7 mL. Storage at −35 °C (24 h) gave colorless crystals of **3** (0.25 g, 25%). On being left in a sealed vessel under argon at 20 °C, the product decomposes over 5 min, but immediate analysis following isolation of the crystals yielded the following results. Mp: decomposition at 60−62 °C to a black solid. Anal. Found: C, 38.1; H, 5.7. Calc: C, 38.6; H, 5.7. IR: ν (Nujol) = 3064 cm^{-1} (m, Cp str). ^1H-NMR (250 MHz, [$^2H_8$]-THF, +25 °C): δ = 5.91 [s, 5H, Cp], 1.09 [d, 9H, ^2J(P−H) = 3.3 Hz, CH_3]. ^{31}P-NMR (101.27 MHz, [$^2H_8$]-THF, +25 °C): $\delta = -46.51$ [s, PMe_3].

Synthesis of $[Me_3PAgC{\equiv}CSiMe_3]_\infty$ (4). A 2.5 mmol amount of **3** was prepared *in situ* at −78 °C. Then freshly prepared $LiC{\equiv}CSiMe_3$ (2.5 mmol, prepared by literature methods[28]) in 5 mL of THF was added and the mixture was filtered immediately while being kept cool. The solvent was reduced to ca. 5 mL. Hexane (1 mL) was added, and storage at −35 °C (24 h) produced colorless blocks of **4** (0.50 g, 71%). Mp: decomposition at 118−126 °C to a black solid. Anal. Found: C, 33.0; H, 6.4; P, 10.9. Calc: C, 34.0; H, 6.4; P, 11.0. IR: ν (Nujol) = 2018 cm^{-1} ($C{\equiv}C$ str). ^1H-NMR (250 MHz, [$^2H_8$]-THF, +25 °C): δ = 1.29 [d, $^2J_{P-H}$ 5.3 Hz, 9H $P(CH_3)_3$], 0.23 [s, 9H, $-Si(CH_3)_3$]. ^{31}P-NMR (101.27 MHz, [$^2H_8$]-THF, +25 °C): $\delta = -42.51$ [s, PMe_3].

X-ray Structure Determinations of 2 and 4. Crystals were mounted directly from solution under argon using a perfluorocarbon oil which protects them from atmospheric oxygen and moisture.[29] The oil "freezes" at reduced temperature and holds the crystal static in the X-ray beam. Data were collected on a Stoe-Siemens AED diffractometer by the θ/ω method. Details of the structure solutions and refinements of both complexes are shown in Table 1. Both structures were solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXL-93).[30] Atomic coordinates, bond lengths and angles, and thermal parameters for **2** and **4** have been deposited with the Cambridge Crystallographic Data Centre.

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Supporting Information Available: Tables giving a summary of the crystal structure determinations, atomic coordinates, bond lengths and angles, and displacement parameters for **2** and **4** (17 pages). Ordering information is given on any current masthead page.

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[26] Shriver, D. F.; Dredzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

[27] Gilman, H.; Young, R. V. *J. Org. Chem.* **1937**, *1*, 315.

[28] Mukaimama, T.; Suzuki, K.; Soai, K.; Sato, T. *Chem. Lett.* **1979**, 447.

[29] Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615.

[30] Sheldrick, G. M. SHELXL-93, Göttingen, Germany, 1993.