(1) With the proof that $ReH_5(PCy_3)_2$ is a transient produced at or above 60 °C, there arises the question of why there is no evidence for "dimerization" of this unsaturated fragment to $Re_2H_8(PCy_3)_4$. Several additional conclusions derived from this work warrant explicit mention: (1) With the proof that $ReH_5(PCy_3)_2$ is a transient produced at or above 60 °C, the re arises the question of why there is no evidence for "dimerization" of this unsaturated fragment to $Re_2H_8(PCy_3)_4$. $ReH_7(PPh_3)_2$, $ReH_7(PMePh_2)_2$, and $ReH_7(PMe_2Ph)_2$ all transform thermally to $Re_2H_8(PR_3)_4$, with decreasing ease along the series as written. One might then expect the complex of the bulkiest phosphine, PCy_3, to dimerize most rapidly. The mechanism of formation of $Re_2H_8(PR_3)_4$ dimers from monomers has been established only for the case of photogenerated $ReH_5(PMe_2Ph)_2$,[4] and it proceeds not by dimerization of two transients but instead by reaction of $ReH_5(PMe_2Ph)_2$ with $ReH_5(PMe_2Ph)_3$. Perhaps $ReH_5(PCy_3)_2$ does not effectively condense with $ReH_7(PCy_3)_2$ for steric reasons. On the other hand, the above trend in ease of conversion from ReH_7P_2 to $Re_2H_8P_4$ also correlates inversely with phosphine basicity. Since PCy_3 is very basic, it may be that dimerization of $ReH_7(PCy_3)_2$ fails because re-addition of H_2 to $ReH_5(PCy_3)_2$ is very fast compared to attack by $ReH_7(PCy_3)_2$.

(2) In spite of the high formal oxidation state and low d electron count (d^2) of rhenium in transient $ReH_5(PCy_3)_2$, it is subject to "oxidative" addition by H_2 and the C–H bonds of benzene and pendant cyclohexyl groups. An electron-rich metal center is not essential to aliphatic C–H activation in this system. For example, the substitution kinetics with PPh_3 allows calculation of a value for $k_{-1}[H_2]/k_2$ of 0.25. An estimate of the hydrogen concentration yields $k_{-1}/k_2 \simeq 10^2$, indicating addition of H_2 to $ReH_5(PCy_3)_2$ is more favorable than addition of PPh_3.

(3) In spite of the evidence for activation of the C–H bonds of benzene, and the likelihood that a η^2-C_6H_6 complex mediates this reaction, the transient $Re(C_6H_6)H_5(PCy_3)_2$ never proceeds on to stable products containing a coordinated C_6-cycle in any state of hydrogenation. A hydrogen acceptor (e.g., acenaphthalene) is required to generate sub-16-electron species before η^4 binding of aromatic-derived fragments can be produced. This is also a feature of the C–H activation systems of the Ephritikhine/Felkin group.[20] It is also noteworthy that our work (with PCy_3) provides concrete evidence for the proposal of these French workers that H_2 elimination is a thermal equilibrium process from $ReH_7(PPh_3)_2$.

Returning to the original objectives of this work, the complex $ReH_5(PCy_3)_3$ does not form from borohydride reduction of $ReOCl_3(PCy_3)_2$ in the presence of excess PCy_3. The pentahydride complex can be made, however, by inefficient displacement of H_2 by PCy_3 from the actual product of the borohydride reaction, $ReH_7(PCy_3)_2$. While there is no evidence for our initial objective of an isolable unsaturated polyhydride, $ReH_7(PCy_3)_2$ has been shown to produce $ReH_5(PCy_3)_2$ in a thermal reaction at moderate temperatures, and this species exhibits the intermolecular hydrogen isotope exchange reactions detected for photogenerated $ReH_5(PMe_2Ph)_2$.[2] The attempt to preclude interactions between rhenium and pendant aryl phosphine by utilizing an alkyl phosphine reveals transient interactions even with certain aliphatic C–H bonds of coordinated PCy_3. $ReH_5(PCy_3)_2$ is therefore characterized as a transient of high reactivity.

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Registry No. B, 92284-94-1; C, 208-96-8; D, 91-20-3; E, 83-32-9; $ReOCl_3(PCy_3)_2$, 92284-89-4; $ReH_7(PCy_3)_2$, 92284-90-7; $ReH_5(PCy_3)_2(PEt_2Ph)$, 92284-91-8; $ReH_5(PCy_3)_2PPh_3$, 92284-92-9; $ReH_5(PCy_3)_3$, 92284-93-0; $ReOCl_3(PPh_3)_2$, 17442-18-1.

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Monomeric Manganese(II) Alkoxides: Syntheses and X-ray Crystal Structures of Novel Three- and Four-Coordinate Manganese Complexes of the Tri-*tert*-butylmethoxide Ligand

Brendan D. Murray and Philip P. Power*

Contribution from the Department of Chemistry, University of California, Davis, Davis, California 95616. *Received December 12, 1983*

Abstract: Two novel alkoxides of manganese(II) containing the tri-*tert*-butylmethoxide ligand have been prepared in high yield. X-ray diffraction and elemental analysis were used to identify the products. The new alkoxide complexes are extremely air and moisture sensitive in solution and in the solid state. The molecular structures of $[Li\{Mn(N(SiMe_3)_2)(OC\text{-}t\text{-}Bu_3)_2\}]$ (**4**) and $[Li_2\{MnBr_2(OC\text{-}t\text{-}Bu_3)_2\}\cdot(THF)_2]$ (**5**) have been determined by X-ray diffraction. The crystal data at 140 K are as follows: **4**, Mo Kα (λ = 0.71069 Å), a = 21.243 (4) Å, b = 11.814 (1) Å, c = 20.334 (3) Å, β = 133.60 (1)°, Z = 4, space group Cc; **5**, Cu Kα (λ = 1.54178 Å), a = 17.868 (11) Å, b = 8.563 (6) Å, c = 26.075 (20) Å, β = 98.39 (6)°, Z = 4, space group $P2_1/c$. For **4**, R = 0.033, and for **5**, R = 0.088. The geometry at the manganese atom in **4** is distorted trigonal planar. Complexes **4** and **5** are the first manganese alkoxides to be structurally characterized. Both **4** and **5** contain a close Li···CH_3 interaction. Complex **4** is also unique in that it is a rare example of three-coordinate manganese(II).

In recent years, a number of authentic three-coordinate monomeric transition-metal complexes have been isolated.[1-9] These compounds usually involve sterically hindering groups such as $N(SiMe_3)_2^-$, $CH(SiMe_3)_2^-$, or a bulky phosphine which reduce

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intermolecular association and lead to lower metal coordination numbers. While the range of isolated three-coordinate transition-metal alkyls and amides is not extensive, a number of these complexes have been structurally characterized by X-ray diffraction. Some of these complexes exhibit unusual geometries at the metal center.[1,9]

For manganese, three-coordination is limited to very few compounds; these are the dimers $[Mn_2\{N(SiMe_3)_2\}_4]$[10] and $[Mn_2(CH_2CMe_2Ph)_4]$,[11] the trimers $[Mn_3(mesityl)_6]$[12] and $[Mn_3(OCH\text{-}t\text{-}Bu_2)_6]$,[13,14] and the tetramer $[\{Mn(CH_2CMe_3)_2\}_4]$.[11] The complex $[Mn\{N(SiMe_3)_2\}_2(THF)]$ is the only three-coordinate mononuclear compound reported, but detailed structural information is not yet available.[6,15] In comparison to the alkyls and amides, the isoelectronic monomeric transition-metal alkoxides have received less attention.[1,13,14,16-18] This may be due to the greater tendency of alkoxides to associate, yielding difficult to handle oligomeric species. This is a consequence of the lower steric requirements and excellent bridging ability of the alkoxo group. However, by using sterically demanding alkoxides it is possible to reduce the tendency to oligomerize. For example, the bulky tri-*tert*-butylmethoxide ligand ($OC\text{-}t\text{-}Bu_3^-$) has recently allowed the synthesis of the monomeric distorted T-shaped Cr(II) complex, $[Cr(OC\text{-}t\text{-}Bu_3)_2\cdot LiCl(THF)_2]$ (**1**).[1]

In this paper we describe the high-yield preparation of two new alkoxides of manganese(II) and their X-ray crystal structures. The X-ray crystal structures of **4** and **5** are the first structural characterizations of manganese(II) alkoxides; **4** is also the first detailed X-ray structure of a monomeric three-coordinate manganese(II) species.

Experimental Section

General Procedures. All reactions were performed by using either modified Schlenk techniques (under N_2) or a Vacuum Atmospheres HE43-2 drybox (under argon). Solvents were freshly distilled from drying agents and degassed three times immediately before use. Solutions of these manganese complexes are exceptionally air sensitive and immediately darken to violet or brown solutions if small controlled amounts of O_2 are added. When excess oxygen is present these solutions turn black/brown rapidly and deposit solids that are only soluble in concentrated mineral acids. Anhydrous $MnBr_2$ (Aldrich) was used as purchased. 2,2,4,4-Tetramethyl-3-*tert*-butylpentan-3-ol ($t\text{-}Bu_3COH$)[19] and lithium bis(trimethylsilyl)amide[4] were prepared by previously described procedures. Melting points were determined in capillaries sealed under argon. Elemental microanalyses were performed at the University of California, Berkeley and at the University of California, Davis.

$[MnBr_2(THF)_2]$ (2). Anhydrous $MnBr_2$ (4.0 g) was added to THF (60 mL) and refluxed for 10 h. The pink product crystallized upon cooling to 0 °C. The THF was decanted off, and the crystals were collected on a medium-porosity fritted funnel and then dried for 2 h at 25 °C/1 × 10^{-2} torr (98% yield). This procedure is similar to the synthesis of $MnCl_2(THF)_2$ described earlier by Horvath et al.[7]

Table I. Crystallographic Data and Summary of Intensity Data Collection and Structure Refinement for **4** and **5**

formula	$[Li\{Mn(N(SiMe_3)_2)\text{-}(OC\text{-}t\text{-}Bu_3)_2\}]$	$[Li_2\{MnBr_2(OC\text{-}t\text{-}Bu_3)_2\}\text{-}(THF)_2]$
fw	620.98	771.57
crystal system	monoclinic	monoclinic
space group	*Cc*	$P2_1/c$
T, K	140	140
a, Å	21.243 (4)	17.868 (11)
b, Å	11.814 (1)	8.563 (6)
c, Å	20.334 (3)	26.075 (20)
β, deg	133.60 (1)	98.39 (6)
V, Å^3	3695.3	3946.9
Z	4	4
d_{calcd}, g·cm^{-3}	1.12	1.30
crystal size, mm	0.48 × 0.46 × 0.43	0.40 × 0.26 × 0.10
radiation-graphite monochromated	Mo Kα (λ = 0.710 69 Å)	Cu Kα (λ = 1.541 78 Å)
μ, cm^{-1}	4.31	53.62
scan speed, deg·min^{-1}	60	30
scan type	ω	ω
scan range, deg	1.0	1.5
ω background offset, deg	1.0	1.5
2θ limits, deg	0–50	0–139
no. of unique data	2912	7194
std reflns (no decay observed)	(2,0,4) (2,4,–3)	(0,0,6) (1,1,1)
no. of reflns used in LS ($F > 6\sigma(F)$)	2558	3991
no. of parameters	446	440
R	0.033	0.088
R_w ($w = 1/\sigma^2(\lvert F_0 \rvert)$	0.034	0.088

$[Mn\{N(SiMe_3)_2\}_2(THF)]$ (3). A procedure similar to one by Burger and Wannagat[20] was followed. Anhydrous $MnBr_2$ (3.93 g) and $LiN(SiMe_3)_2$ (6.60 g) were refluxed in THF (60 mL) for 5 h. The solvent was removed in vacuo, and the residue was extracted with hexane and then filtered to remove LiBr. The hexane was removed in vacuo and the residue distilled as a light rose colored liq. (90–100 °C/1 × 10^{-3} torr), which crystallized as a pale flesh colored solid upon standing at room temperature.

$[Li\{Mn(N(SiMe_3)_2)(OC\text{-}t\text{-}Bu_3)_2\}]$ (4). To a stirred solution of **3** (2.00 g) and $LiN(SiMe_3)_2$ (0.75 g) in hexane (30 mL) was added $t\text{-}Bu_3COH$ (1.79 g) in THF (10 mL). The solution was stirred for 20 h. The volume was reduced to 15 mL and cooled slowly to –30 °C to give pale pink crystals in 86% yield, mp 158–160 °C. Anal. Calcd for $C_{32}H_{72}NO_2LiMnSi_2$: C, 61.9; H, 11.7; N, 2.3; O, 5.2; Li, 1.1; Mn, 8.8; Si, 9.0. Found: C, 62.0; H, 11.9; N, 2.3; O, not tested; Li, 1.6; Mn, 8.8; Si, not tested.

$[Li_2\{MnBr_2(OC\text{-}t\text{-}Bu_3)_2\}\cdot(THF)_2]$ (5). $t\text{-}Bu_3COH$ (1.13 g) in THF (35 mL) was quantitatively converted into a solution containing $LiOC\text{-}t\text{-}Bu_3$ by treatment with 1 equiv of *n*-BuLi in hexane (1.7 M). The $LiOC\text{-}t\text{-}Bu_3$ solution was added dropwise to a stirred slurry of $MnBr_2(THF)_2$ (1.0 g) in THF (20 mL) at –78 °C. The mixture was warmed slowly to 25 °C to yield a pale yellow solution. The solvent was removed in vacuo, and hexane/THF (30 mL) was added. The solution was filtered and the hexane/THF was removed. Fresh THF (30 mL) was added and upon slow evaporation pale pink rods were formed (73% yield): mp 145–149 °C. Anal. Calcd for $C_{34}H_{70}O_4Br_2Li_2Mn$: C, 52.9; H, 9.2; O, 8.3; Br, 20.7; Li, 1.8; Mn, 7.1. Found: C, 53.0; H, 9.1; O, not tested; Br, 20.7; Li, 2.0, Mn, 7.0.

X-ray Crystallographic Studies. All X-ray data were collected with a Syntex $P2_1$ diffractometer equipped with a locally modified Syntex LT-1 low-temperature device, using a procedure described earlier.[21] Further details are in Table I.

All calculations were carried out on a Data General ECLIPSE computer using the SHELXTL program system. The atomic form factors, including anomalous scattering, were from "International Tables of Crystallography".[22] Both structures were solved by direct methods,

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(15) The complex $[Mn\{N(SiMe_3)_2\}_2(THF)]$ is reported to be a three-coordinate monomer. Unfortunately, the data collection on this low-melting solid ($\sim$50 °C) was obtained at room temperature and many of the important structural details are obscured by high thermal motion.[6]

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Table II. Atom Coordinates ($\times 10^4$) and (esd's) for Non-Hydrogen Atoms in Crystalline **4**

atom	*x*	*y*	*z*
Mn(1)	9472 (1)	4099 (1)	2485 (1)
Si(1)	8503 (1)	6412 (1)	1437 (1)
Si(2)	10252 (1)	6495 (1)	3392 (1)
O(1)	10071 (2)	2941 (2)	2344 (2)
O(2)	9199 (2)	2826 (2)	2887 (2)
N(1)	9392 (3)	5790 (2)	2427 (3)
C(1)	10594 (2)	2661 (3)	2171 (3)
C(2)	11591 (3)	2819 (4)	3121 (3)
C(3)	10318 (3)	3491 (4)	1373 (3)
C(4)	10357 (3)	1322 (4)	1830 (3)
C(5)	11738 (3)	2438 (4)	3943 (3)
C(6)	11865 (3)	4068 (4)	3349 (3)
C(7)	12288 (3)	2240 (5)	3193 (3)
C(8)	10940 (3)	3504 (4)	1218 (3)
C(9)	10210 (3)	4742 (4)	1501 (3)
C(10)	9418 (3)	3197 (4)	444 (3)
C(11)	10743 (4)	474 (4)	2601 (4)
C(12)	10642 (3)	895 (4)	1350 (3)
C(13)	9362 (4)	1102 (4)	1162 (4)
C(14)	8661 (3)	2421 (3)	3020 (3)
C(15)	8276 (3)	3499 (4)	3127 (3)
C(16)	9291 (3)	1644 (4)	3931 (3)
C(17)	7900 (3)	1672 (4)	2109 (3)
C(18)	7577 (3)	4130 (4)	2231 (4)
C(19)	8970 (4)	4435 (4)	3735 (4)
C(20)	7869 (4)	3253 (5)	3518 (4)
C(21)	9900 (3)	2339 (5)	4813 (3)
C(22)	8824 (3)	799 (4)	4046 (3)
C(23)	9952 (3)	963 (4)	3997 (4)
C(24)	8205 (4)	518 (4)	2066 (4)
C(25)	7563 (3)	2246 (4)	1227 (3)
C(26)	7089 (3)	1416 (5)	1949 (3)
C(27)	7865 (3)	5319 (4)	506 (3)
C(28)	7729 (3)	7055 (4)	1483 (4)
C(29)	8798 (3)	7573 (4)	1056 (3)
C(30)	9914 (4)	7598 (4)	3750 (4)
C(31)	10980 (3)	5469 (4)	4366 (3)
C(32)	10975 (4)	7197 (4)	3287 (4)
Li(1)	9822 (6)	1914 (6)	2796 (7)

phasing difference electron density maps in consecutive steps.

Large, well-shaped, pale pink single crystals of [Li{Mn(N-$(SiMe_3)_2$)(OC-*t*-Bu_3)$_2$}] (**4**) were obtained by cooling a concentrated hexane/THF solution to −30 °C. After the crystals were removed from a Schlenk tube inside the drybox they were protected from air contamination by a layer of hydrocarbon oil. A large crystal was cut to a suitable size, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream (140 K). Although the precise stoichiometry was unknown initially, the correct structure was found and subsequently refined by least-squares methods, with anisotropic thermal parameters for the non-hydrogen atoms. Seventy of the seventy-two H atoms were detected in a difference electron density map; their sites compared well with coordinates calculated according to carbon hybridization. The H atoms bound to C11 and C23 were located and refined isotropically. The remaining hydrogen atoms were included in the refinements with fixed methyl group geometry. The refinement converged with $R = 0.033$ for the 2558 reflections used.

Long, pale pink rods of **5** were obtained by slow evaporation of a concentrated THF solution. The crystals were very brittle and were prone to twinning. A long rod was cut to an acceptable size and handled by the procedure described earlier. The crystal that was finally chosen was of lower quality than we would have preferred, due mainly to desolvation and the extreme air sensitivity of **5**. However, the difficulty in obtaining high-quality metal alkoxide crystals has been mentioned by other workers.[13,23] The structure was solved and refined by a similar method to that used for **4**. The data were corrected for absorption. Thirty-nine of the seventy H atoms were detected in a difference electron map; their sites compared well with coordinates calculated according to carbon hybridization. All of the H atoms were included in the refinements with fixed group geometry. The refinement converged with $R = 0.088$ for the 3991 reflections used. Tables II and III contain the atomic coordinates for **4** and **5**.

Table III. Atom Coordinates ($\times 10^4$) and (esd's) for Non-Hydrogen Atoms in Crystalline **5**

atom	*x*	*y*	*z*
Br(1)	2482 (1)	1049 (2)	1358 (1)
Br(2)	3592 (1)	−2603 (2)	1968 (1)
Mn(1)	2508 (1)	−1910 (2)	1240 (1)
O(1)	2610 (4)	−2822 (8)	540 (2)
O(2)	1471 (4)	−2873 (8)	1171 (2)
C(1)	3000 (6)	−2965 (13)	108 (4)
C(2)	3860 (6)	−2298 (14)	264 (4)
C(3)	2984 (6)	−4849 (14)	−42 (4)
C(4)	2498 (6)	−1915 (15)	−353 (4)
C(5)	4297 (7)	−1972 (16)	−192 (4)
C(6)	3882 (6)	−775 (14)	596 (4)
C(7)	4373 (6)	−3423 (16)	628 (4)
C(8)	3530 (7)	−5387 (16)	−408 (4)
C(9)	2200 (6)	−5474 (15)	−284 (4)
C(40)	3150 (7)	−5862 (15)	460 (5)
C(11)	2628 (7)	−2280 (15)	−915 (4)
C(12)	2628 (6)	−137 (14)	−284 (5)
C(13)	1645 (6)	−2042 (15)	−331 (4)
C(14)	777 (5)	−3132 (14)	1372 (4)
C(15)	848 (6)	−2472 (14)	1957 (4)
C(16)	128 (6)	−2206 (14)	980 (4)
C(17)	810 (7)	−611 (14)	1988 (5)
C(18)	1653 (7)	−2805 (16)	2257 (4)
C(19)	250 (7)	−3027 (15)	2282 (4)
C(20)	392 (7)	−565 (14)	834 (5)
C(21)	−74 (6)	−2986 (15)	437 (4)
C(22)	−650 (6)	−1974 (16)	1171 (5)
C(23)	653 (6)	−5023 (13)	1355 (4)
C(31)	−164 (6)	−5611 (15)	1358 (4)
C(32)	933 (7)	−5768 (14)	874 (4)
C(33)	1153 (7)	−5920 (14)	1796 (4)
O(7)	3225 (4)	1162 (11)	2754 (3)
C(71)	2479 (8)	1423 (23)	2881 (5)
C(72)	2491 (7)	2809 (20)	3214 (6)
C(73)	3263 (9)	3465 (22)	3238 (8)
C(74)	3715 (7)	2077 (19)	3139 (6)
O(8)	4374 (4)	1467 (10)	2014 (3)
C(81)	5073 (7)	799 (16)	1911 (5)
C(82)	5433 (9)	2021 (20)	1588 (5)
C(83)	5058 (8)	3528 (22)	1710 (7)
C(84)	4290 (9)	3046 (17)	1797 (7)
Li(1)	1635 (10)	−3610 (28)	544 (7)
Li(2)	3476 (11)	422 (29)	2140 (7)

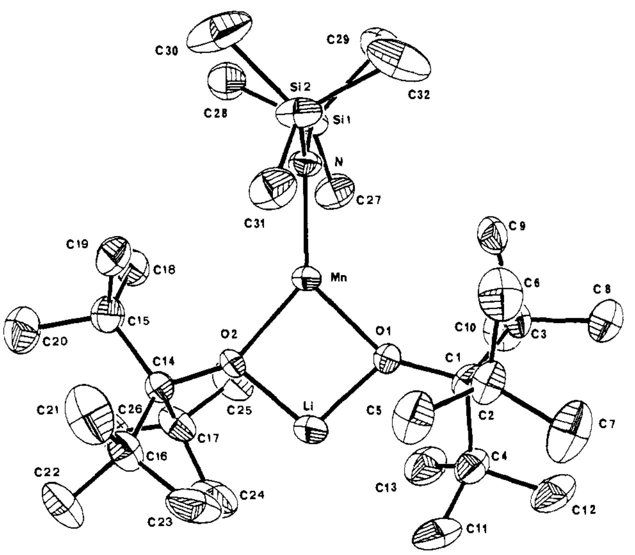

Figure 1. Computer-generated perspective diagram of **4**. The hydrogen atoms have been omitted for clarity.

Results and Discussion

The structure of **4** (Figure 1) is of interest since it is the first monomeric three-coordinate manganese alkoxide. The geometry

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Table IV. Selected Bond Distances (Å) and Angles (deg) for **4**

	(a) Bond Distances		
Mn-O(1)	2.019 (4)	Mn-O(2)	1.980 (4)
Mn-N	2.001 (3)	Mn···Li	2.640 (7)
O(1)-C(1)	1.418 (8)	C(16)-C(23)	1.542 (10)
O(1)-Li	1.808 (14)	O(2)-Li	1.813 (14)
	(b) Bond Angles		
O(1)-Mn-N	134.8 (2)	O(2)-Mn-N	138.2 (3)
O(1)-Mn-O(2)	86.4 (2)	N-Mn-Li	171.3 (2)
Mn-O(1)-Li	87.1 (4)	Mn-O(1)-C(1)	150.7 (3)
Si(1)-N-Si(2)	125.4 (2)	O(1)-Li-O(2)	98.2 (4)

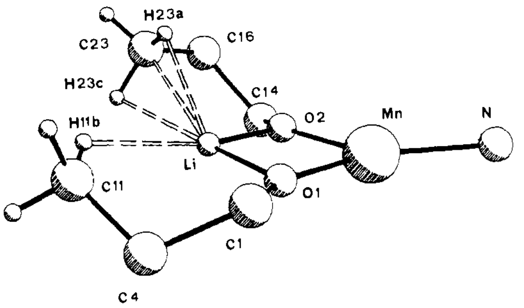

Figure 2. Computer-generated perspective diagram of the Li···CH_3 contact in **4**. Many of the nearby atoms have been omitted for clarity.

at manganese is distorted trigonal planar. Table IV contains some bond distances and angles for **4**. The Mn–O bond distances in **4** are much shorter than the Mn–O distance of 2.16 (2) Å reported for **3**.[6] The Mn–N distance in **4** is consistent with a normal terminal Mn–$N(SiMe_3)_2$ bond.[10] The average N–Si distance of 1.711 (3) Å is similar to the N–Si distances found in other metal amides bearing the $[N(SiMe_3)_2^-]$ group.[5,6] The two tri-*tert*-butylmethoxide ligands exhibit similar angles and distances to those found in $[Cr(OC\text{-}t\text{-}Bu_3)_2\cdot LiCl(THF)_2]$ and $[\{Li(OC\text{-}t\text{-}Bu_3)(THF)\}_2]$.[1] The Mn–O bond distances in **4** are similar to the Cr–O(2) distance of 1.991 (3) Å found in **1**. The angles and distances at the carbons bound to oxygen display considerable distortion from tetrahedral values. The angles at C(1) range from 105.2 (4)° to 113.4 (4)° and the average C(1)–CMe_3 distance is 1.632 (6) Å.

The *tert*-butyl groups in each alkoxo group are staggered with respect to each other, which disrupts the near C_2 axis through N, Mn, and Li. The staggering also allows weak interactions between the Li atom and C(23), H(23A), H(23B), and H(11B) (Figure 2). This interaction is similar to the type of CH_3···Li contact which has been proposed by Andersen and Wilkinson.[11,24] The Li···C(23) distance is 2.52 (3) Å. The Li···H(23A), Li···H(23B), and Li···H(11B) distances are 2.1 (1), 2.2 (1), and 2.2 (1) Å. The large steric bulk of the alkoxide prevents the formally two-coordinate lithium from complexing a THF molecule even when **4** is prepared in THF solutions. Further evidence for steric congestion in **4** is that it does not form a tris(alkoxy) complex even when it is treated with excess $t\text{-}Bu_3COH$ in refluxing toluene for 20 h. The starting material can be recovered in near quantitative yield. The Li atom may be responsible for reducing the O(1)–Mn–O(2) angle to 86.4 (2)°. This behavior has also been observed in the distorted T-shaped complex **1** where the Cl–Cr–O(2) angle is 91.1 (2)°. The data above suggest that $OC\text{-}t\text{-}Bu_3^-$ has even larger steric requirements than $N(SiMe_3)_2^-$.

If **3** is treated with less sterically demanding alkoxides the product obtained is quite different. For example, the reaction of **3** with 2 equiv of di-*tert*-butylcarbinol ($t\text{-}Bu_2CHOH$) in refluxing benzene/hexane yields the manganese trimer $[Mn_3(OCH\text{-}t\text{-}Bu_2)_6]$[13] (**6**), which contains two three-coordinate manganese atoms and a central four-coordinate manganese atom.[14] The bridging Mn–O distances range from 2.012 (3) to 2.095 (4) Å. The two terminal alkoxides have Mn–O bond distances of 1.856 (4) and 1.852 (4) Å. The difference in reactivity of the less bulky $t\text{-}Bu_2CHO^-$ group vs. the $t\text{-}Bu_3CO^-$ group has also been seen in chromium complexes.[1,13,14]

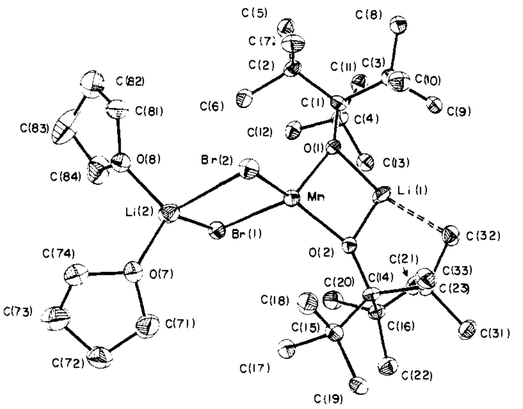

Figure 3. Computer-generated perspective diagram of **5**. The hydrogen atoms have been omitted for clarity.

Table V. Selected Bond Distances (Å) and Angles (deg) for **5**

	(a) Bond Distances		
Mn-Br(1)	2.553 (2)	Mn-Br(2)	2.576 (2)
Mn-O(1)	2.019 (7)	Mn···Li(1)	2.650 (19)
Mn···Li(2)	3.36 (2)	O(1)-C(1)	1.412 (12)
C(23)-C(31)	1.545 (15)	C(23)-C(32)	1.555 (16)
	(b) Bond Angles		
Br(1)-Mn-O(1)	119.9 (2)	Br(1)-Mn-O(2)	112.6 (2)
Br(1)-Mn-Br(2)	99.5 (1)	O(1)-Mn-O(2)	87.9 (3)
Mn-O(2)-Li(1)	87.5 (6)	Mn-O(1)-C(1)	151.0 (6)
O(1)-Li(1)-O(2)	98.7 (9)	Li(1)-Mn-Li(2)	175 (1)

The structure of **5** is illustrated in Figure 3. The manganese atom is in a distorted-tetrahedral environment. Table V contains some selected bond distances and angles for **5**. The average Mn–O bond distance is 2.016 (7) Å. The manganese atom is located near two chemically different lithium atoms. The atom Li(1) possesses a similar environment to the lithium atom in **4**. The atom Li(2) is ligated by two THF molecules and two $[Nd\{\eta^5\text{-}[C_5H_3(SiMe_3)_2]\}_2(\mu\text{-}Cl)_2Li(THF)_2]$.[23] bromine atoms. The different structures for **4** and **5** are probably due to two reasons. Firstly, in **4** the bis(trimethylsilyl)amido group is very sterically demanding and prevents further association. Secondly, in **5** the presence of $MnBr_2(THF)_2$ in the reaction mixture permits halide bridging to a lithium atom; in addition, the lower steric requirements of two bromide atoms compared with $N(SiMe_3)_2^-$ permit higher coordination at the manganese center. A similar type of association has been seen in the chromium(II) complex, **1**, where a $(THF)_2LiCl$ moiety is in combination with $Cr(OC\text{-}t\text{-}Bu_3)_2$. The Li(2)–Br(1) distance of 2.560 (17) Å is very close to the sum of the ionic radii for Li^+ and Br^- (2.55 Å).[25] The Li–Cl distance in **1** (2.417 (8) Å) is also very close to ionic radius for LiCl (2.41 Å). The Li(2)–O(7) and Li(2)–O(8) distances are 1.837 (21) and 1.907 (22) Å. The coordination at Li(2) is distorted from tetrahedral geometry. The angles at Li(2) vary from 97.6 (7)° for Br(1)–Li(2)–Br(2) to 121.5 (11)° for O(7)–Li(2)–Br(2). A similar mode of bonding has been reported for the complex $[Nd\{\eta^5[C_5H_3(SiMe_3)_2]\}_2(\mu\text{-}Cl)_2Li(THF)_2]$.[23] The M-$(\mu\text{-}X)_2Li$ (X = Cl or Br) unit appears to be an important feature of transition and lanthanoid metal chemistry. The Li–C(32) interaction is responsible for the difference in the Li(1) to O distances in **5**. The Li(1)···C(32) distance is 2.46 (3) Å, which is shorter than the Li–C(23) distance of 2.52 (2) Å in **4**. The strength of this interaction allows the Li(1)–O(2) distance (1.816 (21) Å) to be shortened at the expense of Li(1)–O(1) bond (1.871 (19) Å). Packing effects may also play an important role.

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In summary, the use of the $t\text{-Bu}_3CO^-$ group permits the stabilization of low-coordinate transition-metal complexes which display novel geometries and can contain close Li···CH_3 interactions. The steric bulk of the ligand prevents the formation of multiply bridged manganese chains which result when less sterically demanding groups such as $t\text{-Bu}_2CHO^-$ or mesityl are used. The tri-*tert*-butylmethoxide ligand can be incorporated into transition-metal complexes by exchange with metal amides or by treating the lithium alkoxide with metal halides. These two methods permit the formation of different species even when a similar solvent system is employed.

We are currently investigating the properties of the $t\text{-Bu}_3CO^-$ ligand with later first-row transition metals and will present our results in a future article.[14]

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Supplementary Material Available: Complete tables of bond distances, angles, structure factors, and calculated hydrogen positional and thermal parameters for **4** and **5** (50 pages). Ordering information is given on any current masthead page.

Synthesis and Structures of Free and Coordinated Phosphaalkenes

A. H. Cowley,*[†] R. A. Jones,*[†] J. G. Lasch,[†] N. C. Norman,[†] C. A. Stewart,[†] A. L. Stuart,[†] J. L. Atwood,*[‡] W. E. Hunter,[‡] and H.-M. Zhang[‡]

Contribution from the Departments of Chemistry, University of Texas at Austin, Austin, Texas 78712, and University of Alabama, University, Alabama 35486.
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Abstract: Treatment of $(Me_3P)_2NiCl_2$ with $[(Me_3Si)_2CH]_2PNa$ affords the η^2-phosphaalkene complex $(Me_3P)_2Ni[(Me_3Si)_2CPC(H)(SiMe_3)_2]$ (**1**). The structure of **1** has been determined by single-crystal X-ray diffraction. Compound **1** crystallizes in the space group $P2_1/c$ with $Z = 4$ and $a = 8.742$ (6) Å, $b = 19.225$ (6) Å, $c = 20.111$ (8) Å, and $\beta = 99.21$ (9)°. The geometry at nickel is close to square planar, and the phosphaalkene is η^2-bonded. The free phosphaalkenes $(Me_3Si)_2C{=}PR$ ($R = (Me_3Si)_2CH$) (**2**), 2,4,6-$(t\text{-Bu})_3C_6H_2$ (**4**), and $(Me_3Si)_3C$ (**5**) have been prepared by treatment of $(Me_3Si)_2C{=}PCl$ (**3**) with the appropriate organolithium reagent. Compounds **3** and **5** are liquids at ambient temperature. However, **4** is a crystalline solid and has been investigated by single-crystal X-ray diffraction. Compound **4** crystallizes in the space group $P\bar{1}$ with $Z = 2$ and $a = 9.118$ (5) Å, $b = 11.860$ (8) Å, $c = 14.403$ (6) Å, $\alpha = 69.41$ (4)°, $\beta = 79.61$ (4)°, and $\gamma = 83.63$ (5)°. The molecule adopts a planar conformation about the P=C bond, and the C=P—C bond angle is 110.7 (2)°. The phosphorus–carbon bond lengths and ^{31}P NMR spectra of free and coordinated phosphaalkenes are discussed.

Compounds containing P=C double bonds, phosphaalkenes, have been known for many years. The first such compounds to be isolated contained resonance-stabilized double bonds.[1] However, following the pioneering work of Becker,[2] an increasingly large number of isolable, acyclic compounds featuring localized P=C double bonds have been discovered.[3] In contrast, the chemistry of phosphaalkenes coordinated to transition-metal species is less well developed. Interest in such complexes stems from a potential for two types of bonding mode, namely, η^1 through the phosphorus lone pair or η^2 through the P=C π bond. Prior to the commencment of this work, there were no definitive examples of η^2-complexation of phosphaalkenes. However, following our initial disclosure of the synthesis of the η^2-bonded complex $(Me_3P)_2Ni[(Me_3Si)_2CPC(H)(SiMe_3)_2]$ (**1**),[4] two other examples of this type of complex have been reported, namely, (triphos)Pt(P(mesityl)=CPh_2)[5] and (bpy)Ni(P(xylyl)=CPh_2).[6] Examples of η^1 complexation are somewhat more plentiful, this mode of phosphaalkene coordination now having been recognized for Ni(0),[6] Cr(0),[7,8] W(0),[7] Rh(I),[7] and Pt(II).[7] The compound $(Ph_3P)_2Pt(P(mesityl){=}CPh_2)$ is particularly intriguing because of the subtle equilibrium between the η^1 and η^2 bonding modes.[9] The implied closeness in energy of these bonding modes is consistent with MO calculations on the model phosphaalkene $HP{=}CH_2$, which indicate that the MO's corresponding to the phosphorus lone pair and the P=C π bond are closely spaced.[10]

In the present paper, we report details of the synthesis and structure of the η^2-phosphaalkene complex **1**. We also report the synthesis of the uncoordinated phosphaalkenes $(Me_3Si)_2C{=}PR$ [$R = (Me_3Si)_2CH$ (**2**)], 2,4,6-$(t\text{-Bu})_3C_6H_2$ (**4**), and $(Me_3Si)_3C$ (**5**). We have determined the structure of **4** by single-crystal X-ray diffraction. Although fragmentary information is available in the literature, e.g., the P=C bond lengths of phosphaalkenes,[3,6,11] to

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[†] University of Texas at Austin.

[‡] University of Alabama.

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