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# Synthesis, Structure, and Binding of the Open Titanocene−Cage Phosphite Complex $Ti(2,4\text{-}C_7H_{11})_2[P(OCH_2)_3CC_2H_5]$: Further Implications for Phosphite Cone Angles

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The 16 electron cage phosphite complexes of the open titanocene $Ti(2,4-C_7H_{11})_2$ can be prepared by direct interaction of the open titanocene with the cage phosphite, $P(OCH_2)_3CR$ ($C_7H_{11}$ = dimethylpentadienyl; R = $CH_3$, $C_2H_5$). Competitive equilibria studies involving the binding to $Ti(2,4\text{-}C_7H_{11})_2$ by $PMe_3$ and the R = $C_2H_5$ cage phosphite lead to an estimation of $\Delta H = -16.3 \pm 0.9$ kcal/mol and $\Delta S = -34.6 \pm 2.5$ eu for the binding of the cage phosphite. The $\Delta H$ value greatly exceeds those of other open phosphites such as $P(OMe)_3$ and $P(OEt)_3$, indicating that these latter phosphites are not nearly so small as once believed. A structural study of the R = $C_2H_5$ complex has provided further insight into the differences between cage and noncage phosphites. The complex crystallized in the monoclinic space group $P2_1/n$, with $a = 9.261(3)$ Å, $b = 7.976(3)$ Å, $c = 27.196(6)$ Å, $\beta = 94.37(2)°$, and $V = 2002.8$ Å$^3$ for $Z = 4$.

In a previous study, we reported that the 14 electron open titanocene, $Ti(2,4\text{-}C_7H_{11})_2$ ($C_7H_{11}$ = dimethylpentadienyl), bound phosphite ligands anomalously weakly relative to the good donor $PMe_3$ or the good acceptor $PF_3$.[1] Because of the crowding inherent even in the 14 electron "open titanocene,"[1,2] and the fact that $P(OR)_3$ ligands are electronically intermediate between $PR_3$ and $PF_3$ ligands, a steric explanation seemed necessary. This was provided by the fact that the original model of phosphite ligands utilized in cone angle estimations,[3] although seemingly reasonable at the time, has proven to date to be a nonexistent species,[1,4] due to steric repulsions that would arise by having more than one arm bent back from the metal center. Indeed, the smallest phosphite conformation commonly observed in metal phosphite complexes, one having only one arm bent back, clearly had a much larger cone angle, thereby explaining the poor phosphite binding. As an additional piece of evidence in support of a larger phosphite cone angle (which others had also proposed[5] ), we noted our qualitative observation that the cage phosphites ($P(OCH_2)_3CR$, R = $CH_3$, $C_2H_5$) seemed to bind $Ti(2,4\text{-}C_7H_{11})_2$ better than $PMe_3$, being possibly comparable to $PF_3$. Herein we report a more quantitative assessment of the binding between $Ti(2,4\text{-}C_7H_{11})_2$ and the cage phosphites, including structural support for the additional steric requirements imposed by the normal phosphite ligands.

## Experimental Section

All titanium complexes described herein are air-sensitive, and were therefore prepared and handled under a nitrogen atmosphere. Hydrocarbon and ethereal solvents were distilled under nitrogen from Na/benzophenone ketyl. The cage phosphites were either purchased commercially or prepared according to a published procedure (*Caution*! toxic).[6] The open titanocene, $Ti(2,4\text{-}C_7H_{11})_2$ was also prepared according to a published procedure.[7] Spectroscopic data were obtained as previously described.[8] The $^{13}C$ NMR spectra were not integrated, but numbers of carbon atoms were included in accord with the given assignments.

**$Ti(2,4\text{-}C_7H_{11})_2[P(OCH_2)_3CCH_3]$.** To a solution of $Ti(2,4\text{-}C_7H_{11})_2$ (ca. 2 mmol) in 20 mL of THF was added a solution of 1 equiv of $P(OCH_2)_3CCH_3$ in 10 mL of THF. The solution immediately changed from emerald green to golden-yellow. Crystals of the adduct began to form at room temperature. The solution was then cooled to −30 °C. The thermochromic product was isolated by syringing off the solvent, and dried under vacuum. With further concentration and cooling of the solution, nearly quantitative yields may be obtained; the limiting factor is the effort required to isolate the product. The thermochromic product (mp 187 °C, dec) is soluble in THF and could be purified by recrystallization. Room temperature samples are orange but change to red above ca. 100 °C. Cooling to −20 °C results in a change in the color to yellow. Cooling the solid to dry ice temperatures results in a greenish yellow color while cooling the solid in liquid nitrogen results in a bright green-yellow color.

$^1H$ NMR (toluene-$d_8$, ambient): $\delta$ 4.67 (s, 2H, H-3), 3.72 (d, 6H, $P(OCH_2)_3CCH_3$, $J$ = 3 Hz), 2.86 (s, 4H, H-1,$5_{exo}$), 1.68 (s, 12H, $CH_3$), 1.32 (d of d, 4H, H-1,$5_{endo}$, $J$ = 5, 11 Hz), −0.18 (s, 3H, $P(OCH_2)_3CCH_3$).

$^{13}C$ NMR (toluene-$d_8$, ambient): $\delta$ 116.0 (s, C), 99.3 (d, CH, $J$ = 156 Hz), 74.5 (t of d, $P(OCH_2)_3CCH_3$, $J$ = 6, 141 Hz), 56.5 (t of d, $CH_2$, $J$ = 10, 152 Hz), 31.5 (d, $P(OCH_2)_3CCH_3$, $J$ = 28 Hz), 29.8 (q, $CH_3$, $J$ = 134 Hz), 15.0 (q, $P(OCH_2)_3CCH_3$, $J$ = 130 Hz).

Anal. Calcd for $C_{19}H_{31}O_3PTi$: C, 59.07; H, 8.09. Found: C, 59.38; H, 8.29.

**$Ti(C_7H_{11})_2[P(OCH_2)_3CC_2H_5]$.** This compound was prepared by a procedure exactly like that of the $P(OCH_2)_3CCH_3$ complex. The compound was somewhat more soluble than the above species, rendering equilibria studies more feasible. Single crystals of this compound (mp 196 °C, dec) could be obtained by slow evaporation of hexane solutions over a period of several days.

$^1H$ NMR (benzene-$d_6$, ambient): $\delta$ 4.60 (s, 2H, H-3), 3.79 (d, 6H, $CH_2$, $J_{H-P}$ = 3.3 Hz), 2.87 (s, 4H, $H_{exo}$-1,5), 1.69 (s, 12H, $CH_3$), 1.31 (d of d, 4H, $H_{endo}$-1,5, $J$ = 4.4, 13.1 Hz), 0.30 (q, 2H, $CH_2$, $J$ = 7.7 Hz), 0.11 (t, 3H, $CH_3$, $J$ = 7.7 Hz).

Mass spectrum (EI, 17 eV), *m/z* (relative intensity): 238 (27), 234 (36), 175 (20), 162 (50), 140 (51), 132 (100), 117 (25), 109 (47), 107 (25), 96 (89), 95 (76), 81 (100), 68 (100).

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**Table 1.** Crystallographic Data for $Ti(2,4\text{-}C_7H_{11})_2[P(OCH_2)_3CC_2H_5]$

| | |
|---|---|
| chem formula: $C_{20}H_{33}TiO_3P$ | fw = 400.4 |
| $a = 9.261(3)$ Å | space group: $P2_1/n$ (no. 14) |
| $b = 7.976(3)$ Å | $T = 293$ °C |
| $c = 27.196(6)$ Å | $\lambda = 0.710\,73$ Å |
| $\beta = 94.37(2)°$ | $\varrho_{calcd} = 1.33$ g cm$^{-3}$ |
| $V = 2002.8$ Å$^3$ | $\mu = 5.15$ cm$^{-1}$ |
| $Z = 4$ | rel transm coeff: 0.8798–0.9985 |
| $R(F_o)^a = 0.048$ | $R_w(F_o)^b = 0.052$ |

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

**Table 2.** Positional Parameters for the Non-Hydrogen Atoms of $Ti(2,4\text{-}C_7H_{11})_2[P(OCH_2)_3CC_2H_5]$

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ti | 0.9370(1) | 0.1976(1) | 0.15294(4) |
| P | 1.0852(2) | 0.3926(2) | 0.10962(5) |
| O1 | 1.2020(4) | 0.5051(6) | 0.1416(2) |
| O2 | 1.0064(4) | 0.5349(5) | 0.0752(2) |
| O3 | 1.1902(5) | 0.3138(6) | 0.0704(2) |
| C1 | 0.9423(6) | 0.0705(8) | 0.0768(2) |
| C2 | 0.8775(6) | −0.0442(7) | 0.1083(2) |
| C3 | 0.9362(6) | −0.0917(7) | 0.1551(2) |
| C4 | 1.0650(6) | −0.0386(8) | 0.1819(2) |
| C5 | 1.1647(6) | 0.0760(8) | 0.1641(2) |
| C6 | 0.7341(7) | −0.1199(9) | 0.0898(2) |
| C7 | 1.0947(7) | −0.109(1) | 0.2335(2) |
| C8 | 0.7543(6) | 0.3909(8) | 0.1262(2) |
| C9 | 0.6949(6) | 0.2787(8) | 0.1590(2) |
| C10 | 0.7557(6) | 0.2338(7) | 0.2069(2) |
| C11 | 0.8870(6) | 0.2905(8) | 0.2311(2) |
| C12 | 0.9784(6) | 0.4105(8) | 0.2119(2) |
| C13 | 0.5557(6) | 0.187(1) | 0.1409(3) |
| C14 | 0.9326(8) | 0.212(1) | 0.2805(2) |
| C15 | 1.2941(7) | 0.6182(9) | 0.1154(2) |
| C16 | 1.0963(6) | 0.6510(8) | 0.0499(2) |
| C17 | 1.2778(7) | 0.4269(9) | 0.0443(2) |
| C18 | 1.2559(6) | 0.6062(8) | 0.0600(2) |
| C19 | 1.3541(6) | 0.7234(8) | 0.0317(2) |
| C20 | 1.3408(7) | 0.9082(9) | 0.0425(2) |

**Table 3.** Pertinent Bonding Parameters for $Ti(2,4\text{-}C_7H_{11})_2[P(OCH_2)_3CC_2H_5]$

| | | | |
|---|---|---|---|
| | Bond Distances (Å) | | |
| Ti–P | 2.437(2) | C1–C2 | 1.418(10) |
| Ti–C1 | 2.310(8) | C2–C3 | 1.396(10) |
| Ti–C2 | 2.322(7) | C2–C6 | 1.510(10) |
| Ti–C3 | 2.308(7) | C3–C4 | 1.414(10) |
| Ti–C4 | 2.330(7) | C4–C5 | 1.410(10) |
| Ti–C5 | 2.319(7) | C4–C7 | 1.518(10) |
| Ti–C8 | 2.362(7) | C8–C9 | 1.404(10) |
| Ti–C9 | 2.352(7) | C9–C10 | 1.425(10) |
| Ti–C10 | 2.330(7) | C9–C13 | 1.529(10) |
| Ti–C11 | 2.331(7) | C10–C11 | 1.413(10) |
| Ti–C12 | 2.348(8) | C11–C12 | 1.404(10) |
| P–O1 | 1.609(5) | C11–C14 | 1.513(11) |
| P–O2 | 1.610(5) | C15–C18 | 1.524(10) |
| P–O3 | 1.624(5) | C16–C18 | 1.525(10) |
| O1–C15 | 1.463(8) | C17–C18 | 1.511(11) |
| O2–C16 | 1.454(8) | C18–C19 | 1.550(10) |
| O3–C17 | 1.437(9) | C19–C20 | 1.510(12) |
| | Bond Angles (deg) | | |
| C1–C2–C3 | 124.9(7) | O1–P–O2 | 100.2(3) |
| C1–C2–C6 | 117.3(7) | O1–P–O3 | 99.2(3) |
| C2–C3–C4 | 129.9(7) | O2–P–O3 | 99.1(3) |
| C3–C2–C6 | 117.8(7) | P–O1–C15 | 118.3(5) |
| C3–C4–C5 | 124.5(7) | P–O2–C16 | 118.3(4) |
| C3–C4–C7 | 116.8(7) | P–O3–C17 | 118.1(5) |
| C5–C4–C7 | 118.7(7) | O1–C15–C18 | 110.0(6) |
| C8–C9–C10 | 126.4(7) | O2–C16–C18 | 110.3(6) |
| C8–C9–C13 | 117.6(7) | O3–C17–C18 | 111.1(6) |
| C9–C10–C11 | 127.8(7) | C15–C18–C16 | 108.3(6) |
| C10–C9–C13 | 116.0(7) | C15–C18–C17 | 108.3(7) |
| C10–C11–C12 | 124.5(7) | C15–C18–C19 | 110.7(6) |
| C10–C11–C14 | 116.9(7) | C16–C18–C17 | 108.7(6) |
| C12–C11–C14 | 118.5(7) | C16–C18–C19 | 111.4(6) |
| Ti–P–O1 | 118.4(2) | C17–C18–C19 | 109.4(6) |
| Ti–P–O2 | 118.9(2) | C18–C19–C20 | 115.6(6) |
| Ti–P–O3 | 117.3(2) | | |

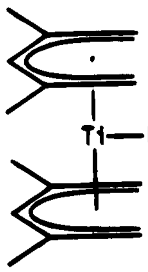
**X-ray Diffraction Study of $Ti(2,4\text{-}C_7H_{11})[P(OCH_2)_3CC_2H_5]$.** Single crystals of this compound were mounted and sealed in glass capillaries under nitrogen. Unit cell, space group, and intensity data were obtained through standard software programs on a Nicolet-Siemens $P\bar{1}$ autodiffractometer, refurbished by Crystal Logic Co. The systematic absences uniquely identified the space group as $P2_1/n$. The structure was solved by direct methods, after which full anisotropic refinement of all non-hydrogen atoms was carried out. Subsequently the hydrogen atom positions could be found, and these were then placed in idealized positions. A summary of data collection and refinement parameters is given in Table 1, while pertinent positional and bonding parameters are presented in Tables 2 and 3.

**Equilibria Studies for Phosphite Binding.** A competitive study of the binding of $PMe_3$ relative to $P(OCH_2)_3CEt$ was carried out essentially as previously described for the $PF_3/PMe_3$ competition.[1] Approximately equimolar quantities of $Ti(2,4\text{-}C_7H_{11})_2PMe_3$ and $P(OCH_2)_3CEt$ were carefully sealed in a high quality NMR tube with THF as solvent. The equilibria were studied by variable temperature $^{31}P$ NMR spectroscopy over the temperature range 276–306 K. Lower temperatures were avoided in order to prevent precipitation of the phosphite adduct. The spectra were obtained on a Bruker AC 200P instrument at 81.02 MHz, using a protocol similar to that employed previously.

## Results and Discussion

The addition of either $P(OCH_2)_3CR$ cage ($R = CH_3, C_2H_5$) to the 14 electron open titanocene, $Ti(2,4\text{-}C_7H_{11})_2$, led immediately to a reaction (eq 1) in which a 16 electron mono(phosphite) adduct was formed. The solutions lost all trace of the deep green color of $Ti(2,4\text{-}C_7H_{11})_2$, in marked contrast to the behavior exhibited by the very reversible reactions involving $P(OCH_3)_3$ or $P(OC_2H_5)_3$.[1] Spectroscopic data were consistent with the high symmetry expected for the *syn*-eclipsed structure adopted by related adducts (e.g., $PMe_3$, $PF_3$, $P(OEt)_3$, etc.),[9] as in I.

$$Ti(2,4\text{-}C_7H_{11})_2 + P(OCH_2)_3CR \rightarrow Ti(2,4\text{-}C_7H_{11})_2[P(OCH_2)_3CR] \quad (1)$$



I

To confirm the structural assignment, and to allow for comparison to the related $P(OEt)_3$ structure, a single crystal X-ray diffraction study was carried out. The solid state structure of $Ti(2,4\text{-}C_7H_{11})_2[P(OCH_2)_3CC_2H_5]$ is shown in Figure 1, and pertinent bonding parameters are given in Table 2. The structure does correspond to the expected *syn*-eclipsed model, with only small tilts and twists between the two ligands, 0.8 and 3.0°, respectively.[10] One interesting, although slight, difference concerning this structure involves the orientation of the three

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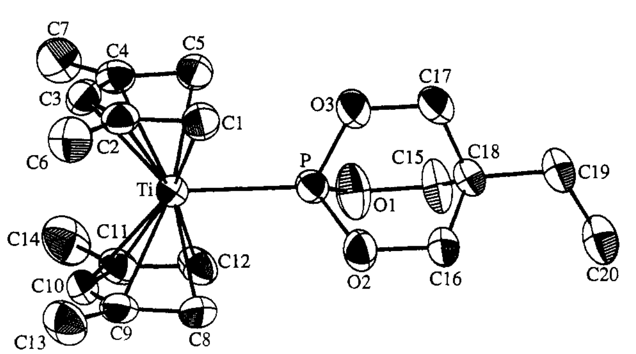
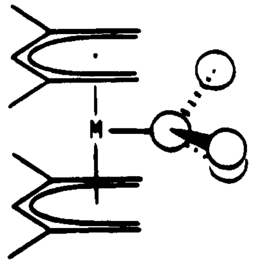
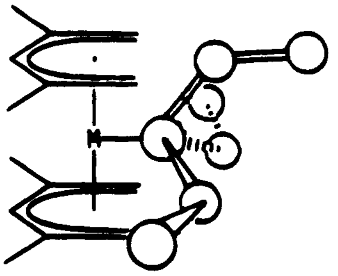


**Figure 1.** Perspective view and numbering scheme for Ti(2,4-$C_7H_{11})_2[P(OCH_2)_3CC_2H_5]$.

phosphite arms. For the related $PF_3$ and $PMe_3$ complexes, one phosphine substituent is unique in that it points between the $CH_2$ groups of two different ligands, leading to the other two substituents pointing at the remaining two $CH_2$ groups, as in **II**.[11] However, for the $PEt_3$[9] and $P(OEt)_3$[11] complexes, one substituent preferentially points between the two $CH_2$ groups of a single ligand, leading to the other two substituents pointing at the two $CH_2$ groups of the other ligand, as in **III**. A twist of 30° would convert one of these forms to the other. For the cage phosphite complex, however, the structure lies between these two idealized forms. The C3−Ti−P3−O3 and C10−Ti−P−O3 torsion angles of 7.97 and −173.88° indicate a twist of 7.0° from **II** to **III**. The Ti−P bond length of 2.437(2) Å is 0.035(4) Å shorter than the corresponding distance of 2.472(4) Å in the $P(OEt)_3$ analog. This difference is essentially identical to that found between the $Ti(C_5H_5)_2(CO)(PR_3)$ complexes, for R = $CH_3$ (2.544(1) Å) or $C_2H_5$ (2.585(1) Å).[12] This would appear to be no coincidence, but attributable to a similar steric difference in each case. Thus, for the $P(CH_3)_3$ and $P(OCH_2)_3CC_2H_5$ compounds, the ligands are held in fairly compact forms, as no substituents dangle off to the sides. For the $P(C_2H_5)_3$ and $P(OC_2H_5)_3$ adducts, however, one observes only one arm bent back away from the metal center, with the other two situated to the sides, as in **III**, where they encounter the other ligands. The relative constancy in the differences in Ti−P bond lengths for these two situations provides further evidence that the differences in cone angles between normal phosphites and cage phosphites (Tolman values,[3] 107° for $P(OCH_3)_3$ and 101° for $P(OCH_2)_3CCH_3$, respectively) should be more comparable in magnitude to the differences between the cone angles of $P(CH_3)_3$ and $P(C_2H_5)_3$, 118° and 132°, respectively. On the basis of common, compact phosphine conformations such as represented in **III**, revised cone angles of 128, 134, and 137° were estimated for $P(OMe)_3$, $P(OEt)_3$, and $PEt_3$, respectively.[1]



**II**



**III**

The bonding parameters for the bound cage phosphite are remarkably unchanged as compared to those for a free analog, $P(OCH_2)_3CCH_2Br$.[13] Thus, the respective P−O bond lengths average 1.614(3) and 1.615(3) Å. Similarly, the P−O−C bond angles average 118.2(3) and 117.5(2)°, while the O−P−O bond angles average 99.5(2) and 100.1(2)°, respectively.

The average Ti−C[1,5], −C[2,4], and −C[3][10b] bond lengths for the first $C_7H_{11}$ ligand (C1−C7) are 2.315(5), 2.326(5), and 2.308(7) Å, respectively, while those for the second ligand are longer at 2.345(5), 2.342(5), and 2.330(7) Å. This may clearly be attributed to the proximity of the two lower phosphite arms to the two terminal $CH_2$ groups of the second (lower) $C_7H_{11}$ ligand (see Figure 1). As is usual, the presence of methyl groups on the internal pentadienyl carbon atoms leads to a contraction in C−C−C bond angles,[14] cf., ∠C[1]−C[2]−C[3] = 125.1(4)° vs ∠C[2]−C[3]−C[4] = 128.8(5)°. The methyl groups tilt an average of 2.5° toward the titanium center in an apparent attempt to optimize overlap between the ligand and metal orbitals.[15] The magnitude of the tilt is smaller than usually observed, but comparable to those observed in other *syn*-eclipsed structures.[9] As in these other eclipsed structures, the degree of tilting is clearly retarded by the $CH_3$--$CH_3$ steric repulsions that are generated by the tilting.

In order to allow for a direct comparison of $Ti(2,4\text{-}C_7H_{11})_2$'s relative preferences for binding normal ($P(OR)_3$, R=$CH_3$, $C_2H_5$) and cage phosphites, equilibrium constants were obtained for a competition involving $P(OCH_2)_3CC_2H_5$ and $PMe_3$ (eq 2). The

$$Ti(2,4\text{-}C_7H_{11})_2(PMe_3) + P(OCH_2)_3CC_2H_5 \rightleftharpoons Ti(2,4\text{-}C_7H_{11})_2[P(OCH_2)_3CC_2H_5] + PMe_3 \quad (2)$$

absolute values for $PMe_3$, $P(OMe)_3$, and $P(OEt)_3$ binding had been determined earlier,[1] yielding respective $\Delta H$ values of −14.5 ± 0.8, −11.4 ± 0.9, and −10.6 ± 0.6 kcal/mol, respectively. In the case of the cage phosphite (as well as for $PF_3$, with $\Delta H = -17.4 \pm 0.8$ kcal/mol), it was clear that the binding was too strong for meaningful data to be determined through dissociation (eq 3), hence requiring the competition.

$$Ti(2,4\text{-}C_7H_{11})_2[P(OCH_2)_3CC_2H_5] \rightleftharpoons Ti(2,4\text{-}C_7H_{11})_2 + P(OCH_2)_3CC_2H_5 \quad (3)$$

In fact, over the temperature range 276−306 K, the values of

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(10) (a) The tilt between planes is simply the angle between the two planes, each defined by the five metal-bound carbon atoms. The twist is the angle formed between the two Ti−C[3]−$\frac{1}{2}$(C[1] + C[5]) planes, one constructed from each ligand. (b) The use of brackets designates the inclusion of all (noncrystallographically) symmetry related bonding parameters in the presented average value.

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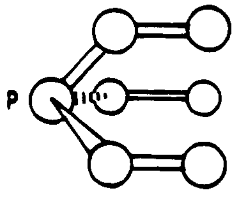
**Table 4.** Equilibrium Parameters for the $Ti(2,4\text{-}C_7H_{11})_2(PMe_3)$ + $P(OCH_2)_3C_2H_5$ Competitive Reaction

| 1000/*T* | ln *K* | 1000/*T* | ln *K* |
|---|---|---|---|
| 3.268 | 2.65 | 3.497 | 2.88 |
| 3.378 | 2.81 | 3.623 | 2.98 |

$\Delta H = -1.8 \pm 0.3$ kcal/mol $\Delta S = -0.5 \pm 0.8$ eu

the equilibrium constant for eq 2 ranged from 14.1 to 19.6 (Table 4), and a reasonable straight line was obtained for a plot of ln $K$ vs $1/T$ (Figure 2). From this plot, respective values for $\Delta H$ and $\Delta S$ of $-1.8 \pm 0.3$ kcal/mol and $-0.5 \pm 0.8$ eu could be obtained. Combined with the earlier absolute determination for $PMe_3$ binding[1] (*vide supra*), the respective absolute values for $P(OCH_2)_3CC_2H_5$ binding can be obtained as $-16.3 \pm 0.9$ kcal/mol and $-34.6 \pm 2.5$ eu.

A summary of the $\Delta H$ and $\Delta S$ values for $Ti(2,4\text{-}C_7H_{11})_2\text{-}PX_3$ binding is presented in Table 5. Given that the range spans only some 7.4 kcal/mol between $PF_3$ and $PEt_3$ and that the difference between $PMe_3$ and $PEt_3$ is 4.5 kcal/mol, the extra binding of ca. 5.3 kcal/mol for the cage phosphite compared to the open phosphites is quite impressive. Since both $PMe_3$ and $PF_3$ bind $Ti(2,4\text{-}C_7H_{11})_2$ strongly, the poor binding of $P(OR)_3$ ($R = CH_3$, $C_2H_5$) ligands can not be ascribed to an electronic effect. Furthermore, the differences between the Tolman cone angles for the cage (101°) and noncage (107−109°) phosphites are also too small to account for the difference, particularly given the significant binding for both the similarly-sized $PF_3$ (104°) and the much larger $PMe_3$ (118°) ligands. As was surmised earlier, there is clearly something greatly retarding the binding of the noncage phosphites. The root of this may again be traced to the fact that the phosphite model employed by Tolman, **IV**, in fact represents a nonexistent species, as a result of the significant interchain van der Waals repulsions that it would generate. The conformation represented by **III** is actually the most compact of the commonly observed forms, and through the general procedure employed by Tolman,[3] its cone angle has been estimated to be 128° (134° for $P(OEt)_3$).[1] These increases nicely account for the poorer binding of $P(OR)_3$ ($R = CH_3$, $C_2H_5$) ligands relative to $PF_3$, $PMe_3$, and $P(OCH_2)_3CC_2H_5$.



**IV**

It seems worth noting that if one retained the Tolman phosphite cone angle values, it would lead to the interesting situation in which the larger $PF_3$ would be bound more strongly (by $1.1 \pm 0.4$ kcal/mol—a value that would certainly be larger were the $Ti{-}PF_3$ bond length not significantly shorter than the Ti−phosphite bond length) than $P(OCH_2)_3CC_2H_5$, while the larger $PMe_3$ would be bound more strongly ($3.9 \pm 1.0$ kcal/mol) than $P(OEt)_3$. In one case a larger better acceptor would be favored, while in the other, a larger, better donor would be favored. An explanation for these trends would appear difficult to come by. With the revision of the $P(OR)_3$ ($R$ = Me, Et) cone angles to the larger values, one is left only with a need to explain the stronger binding of $PF_3$ relative to the cage phosphite. This can then readily be attributed to an electronic effect favoring accepting ligands.[16] This electronic contribution seemed necessary anyway, in order to offset the greater steric repulsions that would be generated by the accepting $PX_3$ ligands, due to the Ti−P bond shortening that they experience.

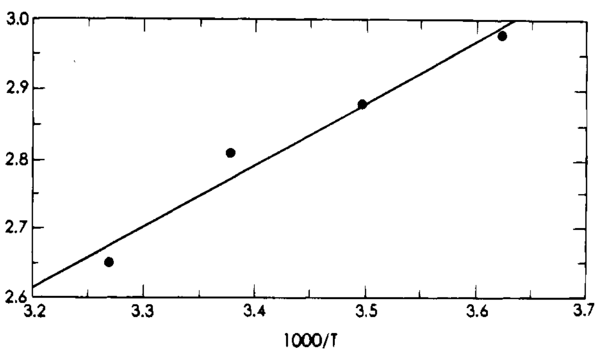


**Figure 2.** Plot of ln $K$ vs $1000/T$ for the reaction $Ti(2,4\text{-}C_7H_{11})_2(PMe_3)$ + $P(OCH_2)_3CC_2H_5 \rightleftharpoons Ti(2,4\text{-}C_7H_{11})_2[P(OCH_2)_3CC_2H_5]$ + $PMe_3$.

**Table 5.** Binding of Phosphines and Phosphites to $Ti(2,4\text{-}C_7H_{11})_2$

| L | $-\Delta H$, kcal/mol | TCA,[a] deg | RCA,[b] deg |
|---|---|---|---|
| $PF_3$ | $17.4 \pm 0.8$ | 104 | |
| $P(OCH_2)_3CC_2H_5$ | $16.3 \pm 0.9$ | 101 | |
| $P(CH_3)_3$ | $14.5 \pm 0.8$ | 118 | |
| $P(CH_3)_2C_6H_5$ | $12.9 \pm 0.5$ | 122 | |
| $P(OCH_3)_3$ | $11.4 \pm 0.9$ | 107 | 128 |
| $P(OC_2H_5)_3$ | $10.6 \pm 0.6$ | 109 | 134 |
| $P(C_2H_5)_3$ | $10.0 \pm 0.1$ | 132 | 137 |

[a] Tolman cone angle. [b] Revised cone angle.

Brown and co-workers have reached a similar conclusion for phosphites (as well as $P(i\text{-}C_4H_9)_3$), based on kinetic data for atom transfer reactions to 17 electron Re(O) species.[5] However, in their view, an increase for $P(OMe)_3$ to ca. 115° seemed reasonable. An empirical analysis by Poë of some of Brown's kinetic data also has indicated that an increase in the cone angle of $P(OMe)_3$ of some 10° might be warranted.[17] However, subsequent molecular mechanics calculations on $Cr(CO)_5(L)$ species have indicated that $P(OMe)_3$ and $P(OEt)_3$ generate interligand repulsive forces equivalent to phosphines having cone angles of 128 and 133 degrees, respectively.[18,19] Similar results were subsequently obtained for $Rh(C_5H_5)(CO)(L)$ complexes.[18b] Notably, the inter-ligand repulsion forces generated in each case for the cage phosphites were reasonably in line with their cone angle, *but less than half those generated by* $P(OMe)_3$ *or* $P(OEt)_3$.[19]

It may well be important, however, to recognize that what applies for a thermodynamic situation may not necessarily apply in other cases. Poë has also carried out molecular mechanics calculations on $P(OMe)_3$, and observed that another conformation, having an approximate cone angle of 117° (120° for $P(OEt)_3$) lies only ca. 1 kcal/mol higher in energy than that of **III**. It is conceivable that such a species could play an important role in kinetic experiments, and that the measure of steric demands for ligands may then be a function of the particular experiment under study, and the relative cost of the promotional energy (which could vary depending on the experiment and conditions). However, the results obtained for the Ti(2,4-

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$C_7H_{11})_2(L)$,[1] $Cr(CO)_5(L)$,[18d,19] and $Rh(C_5H_5)(CO)(L)$[18b] systems suggest that the M−L (L = $P(OMe)_3$) binding would be increased by more than the calculated promotional energy of 1 kcal/mol were the 128° $P(OMe)_3$ conformer replaced by the 117° form. This might indicate that the 117° form suffers from greater intramolecular repulsions than are apparent. While it appears that at most one can presently only infer the participation of a 117° form, the revised cone angle values of 128° and 134°, respectively, for $P(OMe)_3$ and $P(OEt)_3$ at least represent real, representative forms that are commonly found in crowded environments.[1]

It can be noted that other measures of the steric demands of phosphine and phosphite ligands have been proposed.[20] A recent compilation of "solid angles",[20a] whose values are based on actual ligand conformations, again provides an indication that the steric demands of "normal" phosphites greatly exceed those of the cage phosphites. Thus, for the cage phosphites, a solid angle ($\Omega$) of 82° is observed, whereas the values for $P(OMe)_3$ and $P(OEt)_3$ are much larger, at 113° and 117°, respectively.

Given the fact that estimated cone angles, including those suggested herein, do not take into account the differing M−P bond lengths (cf., $d$(Ti−P) in $Ti(2,4\text{-}C_7H_{11})_2PF_3$, 2.324(1) Å, vs $Ti(2,4\text{-}C_7H_{11})_2PMe_3$, 2.550(2) Å),[14] and the fact that these ligands are not true cones, and will have different abilities to mesh together with other ligands in various coordination environments, it appears that the whole estimation of ligand steric demands by cone angles is subject to sufficiently sizable complications that quantitative correlations should not be expected. Depending on the sampling of ligands included in a given correlation, one might expect a certain amount of scatter in such correlations, or at least some change in slope relative to what otherwise should be observed. Nevertheless, it is likely that reasonable insight may still be obtained from these correlations should appropriate measures be followed (*vide infra*).

While there may be some ambiguity regarding which cone angle would be appropriate under certain circumstances, there are some prudent measures that can at least promote more meaningful comparisons to be made. First, for studies involving phosphite ligands, the inclusion of a cage phosphite is of paramount importance, although significant differences between the two ligands may only be observed in situations for which steric crowding is significant, i.e., one is well past the "steric threshold" for the normal $P(OR)_3$ ligands.[21] Notably, other studies have also found the cage phosphites to be anomalous in their high reactivity.[22] Of course, in a more general sense, any correlation utilizing $n$ variable parameters should include adequate sampling of the $n$ dimensional space defined by these parameters. Unfortunately, there may not always be $PX_3$ ligands which allow for such sampling.

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**Supplementary Material Available:** Tables of data collection parameters, anisotropic thermal parameters, hydrogen atom positional parameters, least-square planes, and torsion angles (18 pages). Ordering information may be found on any current masthead page.

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