

What is the Real Steric Impact of Triphenylphosphite? Solid-State and Solution Structural Studies of *cis*- and *trans*-Isomers of $M(CO)_4[P(OPh)_3]_2$ ($M = Mo$ and W)

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The steric requirements for the triphenylphosphite ligand in several molybdenum and tungsten carbonyl derivatives have been shown by X-ray crystallography to exceed the original Tolman's cone angle of 128° . That is, due to various accessible conformers possible for $P(OPh)_3$, solid-state data predict a considerably larger cone angle for the ligand of between 140° and 160° . Importantly, the solution behavior of *cis*- $M(CO)_4[P(OPh)_3]_2$ ($M = Mo$ or W), coupled with similarly reported observations on a series of *cis*- $Mo(CO)_4[PR_3]_2$ derivatives, support this conclusion, for these molecules both undergo thermal rearrangement to the more stable *trans*-isomers. On the other hand, the electronically similar but sterically much smaller *cis*- $Mo(CO)_4[P(OCH_2)_3Ct]_2$ complex is thermally stable under much harsher conditions. Furthermore, a comprehensive survey of structural data for transition-metal–triphenylphosphite derivatives available in the Cambridge Crystallographic Database reveals that most molecules display conformations that dictate cone angles much greater than that originally suggested by Tolman.

Introduction

Tolman's cone angles for quantifying the spatial requirements of phosphine and phosphite ligands have played a prominent role in organometallic chemistry.¹ Indeed, it is not possible to teach a course in modern inorganic/organometallic chemistry without discussing this concept, which is well-covered in most major textbooks.² Tolman utilized space-filling CPK models to define the angle of the cone formed having the metal atom as its apex and encompassing the tertiary phosphine ligand employing the surface of the van der Waals spheres of the outermost hydrogen atoms of the substituents as the periphery. Since Tolman's landmark contribution, there have been numerous alternative methods employed to refine these steric parameters for phosphine ligands, including molecular mechanics models and X-ray structural data.³

When the substituents on the phosphorus atom were not spherical, Tolman choose to fold them back to assume the conformation requiring the least amount of space. From their inception it has been recognized that the use of Tolman's cone angles as indicators of the steric influence of phosphine and phosphite ligands has limitations and must be employed with some discretion. This is particularly true when assessing the steric impact of unsymmetric phosphines, or phosphines where

different conformations of the substituents are readily accessible. Relevant to the ensuing discussion, Tolman realized early on that phosphine ligands like PPh_3 experienced a great deal of steric strain when its cone angle was compressed beyond 145° , while phosphite ligands like $P(OPh)_3$ endured no major barrier when its phenoxide substituents were folded upward to minimize its spatial requirements.⁴ Parenthetically, using this argument there should be no significant barrier to folding the phenoxide substituents down in the phosphite ligand. Indeed, studies by Ernst and co-workers have demonstrated that the $P(OMe)_3$ ligand generally adopts configurations where all three methoxy groups are not bent back away from the metal center.^{5,6} More recently, Coville and co-workers have examined several metal complexes containing (alkoxy)₃P ligands and shown these to exhibit conformation flexibility, with crystallographically determined cone angles significantly greater than their minimized values reported by Tolman.^{7,8} Furthermore, these larger steric requirements for $P(OR)_3$ ligands were substantiated in solution via equilibrium studies of *cis* $\rightleftharpoons$ *trans* isomers of $Mo(\eta^5-C_5H_5)(CO)_2(P(OR)_3)_2$. Pertinent to our report herein, Yarger and co-workers have established experimentally that $P(OPh)_3$ at low temperature exists in two configurations, C_3 (all phenoxide substituents bent toward the lone pair of electrons on the phosphorus center) and C_s (two toward lone pair and one away).⁹ These conformations were supported by theoretical studies as well.

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(1) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.
(2) (a) See for example: Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry*, 3rd ed.; Pearson, Prentice Hall, 2004; p 523. (b) Housecroft, C. E.; Sharpe, A. G.; *Inorganic Chemistry*, 2nd ed.; Pearson, Prentice Hall, 2005; p 703. (c) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley-Interscience: New York, 2005; p 102.
(3) (a) White, D.; Coville, N. J. *Adv. Organomet. Chem.* **1994**, *36*, 95–158. (b) Brown, T. L.; Lee, K. J. *Coord. Chem. Rev.* **1993**, *128*, 89–116. (c) Alyea, E. C.; Dias, S. A.; Ferguson, G.; Restivo, R. J. *Inorg. Chem.* **1977**, *16*, 2329–2334. (d) Mingos, D. M. P.; Muller, T. E. J. *Organomet. Chem.* **1995**, *500*, 251–259. (e) Guzei, I. A.; Wendt, M. *Dalton Trans.* **2006**, 3991–3999.

(4) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53–60.

(5) Stahl, L.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 5673–5680.

(6) Stahl, L.; Trakarnpruk, W.; Freeman, J. W.; Arif, A. M.; Ernst, R. D. *Inorg. Chem.* **1995**, *34*, 1810–1814.

(7) Smith, J. M.; Coville, N. J.; Cook, L. M.; Boeyens, J. C. A. *Organometallics* **2000**, *19*, 5273–5280.

(8) Smith, J. M.; Coville, N. J. *Organometallics* **2001**, *20*, 1210–1215.

(9) Ghalsasi, P. S.; Yarger, J. 227th ACS National Meeting, Anaheim, CA, Abstracts of Papers, 2004. Also see: <http://yarger.asu.edu/Presentations/Prasanna04.ppt> (accessed Sept 28, 2007).

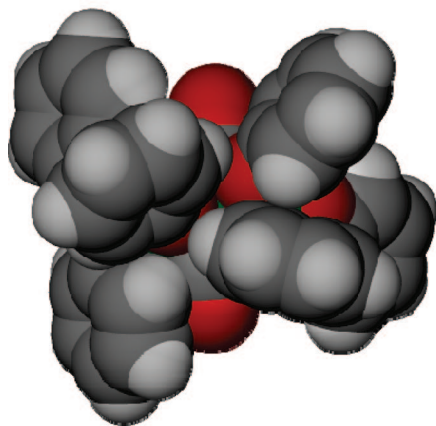


Figure 1. Thermal ellipsoid representation of complex **1** at 50% probability with atomic numbering scheme, and space-filling model illustrating the intertwining of the two triphenylphosphite ligands.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for *cis*-Mo(CO)₄[phosphite]₂

	phosphite	
	P(OPh) ₃	P(OCH ₂) ₃ CC ₂ H ₅
Mo(1)–C(1)	2.060(4)	2.044(5)
Mo(1)–C(3)	2.025(4)	2.051(5)
Mo(1)–C(2)	2.035(4)	2.032(5)
Mo(1)–C(4)	2.034(4)	2.026(5)
Mo(1)–P(1)	2.4318(10)	2.4247(14)
Mo(1)–P(2)	2.4360(10)	2.4218(13)
C–O _{av}	1.134(5)	1.137(6)
P(1)–Mo(1)–P(2)	89.05(3)	93.76(4)
P(1)–Mo(1)–C(1)	89.36(10)	87.10(13)
P(1)–Mo(1)–C(3)	87.83(11)	89.40(12)
P(1)–Mo(1)–C(2)	94.44(11)	87.97(13)
P(2)–Mo(1)–C(1)	95.90(10)	89.40(13)
P(2)–Mo(1)–C(3)	86.59(11)	85.93(12)
P(2)–Mo(1)–C(4)	88.62(11)	88.51(12)
P(1)–Mo(1)–C(4)	177.65(11)	174.93(12)
P(2)–Mo(1)–C(2)	174.01(11)	177.40(13)
Mo(1)–P(1)–O _{av}	116.8(11)	116.5(12)
Mo(1)–P(2)–O _{av}	117.9(11)	116.7(13)
O–P(1)–O	(96.97–103.61)	(100.96–102.20)
O–P(2)–O	(97.30–104.05)	(100.77–101.81)

readily rearranges to the *trans*-isomer in solution (*vide infra*). Relevant to this issue, the orientation of the phenolate substituents on the triphenylphosphite ligands in *cis*-Mo(CO)₄[P(OPh)₃]₂ are for P(1) one *down* and two *up*, and for P(2) two *down* and one *up*. Figure 2 illustrates with stick drawings the conformers of P(OPh)₃, where *up* and *down* are defined. A more precise description of the conformers of P(OPh)₃ entails determining τ , the angle that indicates whether the aryl substituent is *gauche* (*down*) or *anti* (*up*) to the metal bonded to the phosphorus atom of the phosphite ligand (Figure 3).¹⁴ As is apparent in Figure 1, these

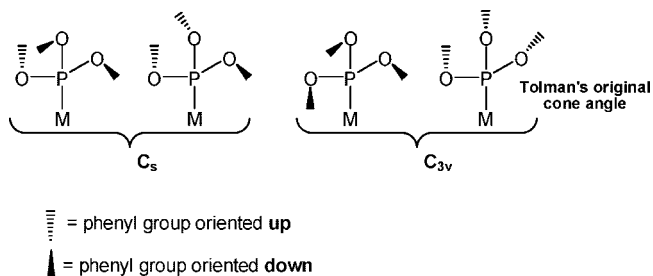


Figure 2. Conformers of P(OPh)₃.

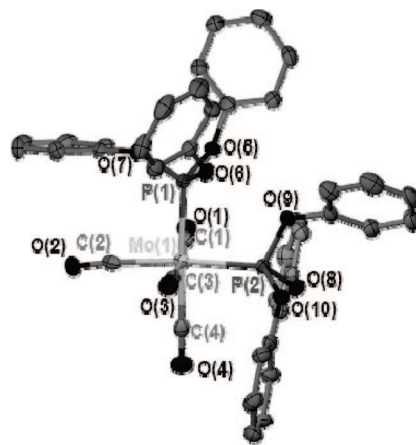


Figure 3. τ defines the angle that indicates whether the aryl substituent is *gauche* ($\tau \sim 60^\circ$) or *anti* ($\tau \sim 180^\circ$) to the metal bonded to the phosphite ligand.

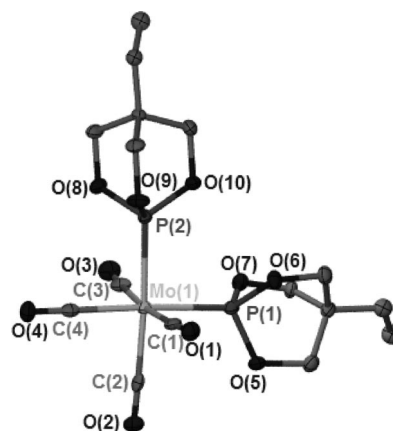


Figure 4. Thermal ellipsoid plot of **5** at 50% probability level.

conformers of P(OPh)₃ and their spatial orientation readily allow for a *cis* arrangement of these phosphite ligands about the molybdenum octahedral center. This is best illustrated in the space-filling model also illustrated in Figure 1.

We have also determined the solid-state structure of the sterically nonencumbering phosphite complex *cis*-Mo(CO)₄[P(OCH₂)₃CET]₂ (**5**). A thermal ellipsoid drawing of complex **5** is depicted in Figure 4. The structural parameters for this derivative are also listed in Table 2 for an easy comparison with those of complex **1**. As listed in Table 2, although the metal–ligand distances are quite similar the P–Mo–P angle is somewhat more open at 93.76(4)°. In this instance only one conformation of the phosphite ligand exists. The spatial requirements of P(OCH₂)₃CET are quite small; that is, the calculated cone angle from crystal structure data was determined to be between 68° and 72° (*vide infra*). Hence, the *cis*-isomer of complex **5** is anticipated to be the thermodynamically more stable isomer on the basis of both electronic (minimize *trans* CO ligands) and steric arguments. Indeed, upon heating complex **5** in solution for an extended period of time at 80–95°, no

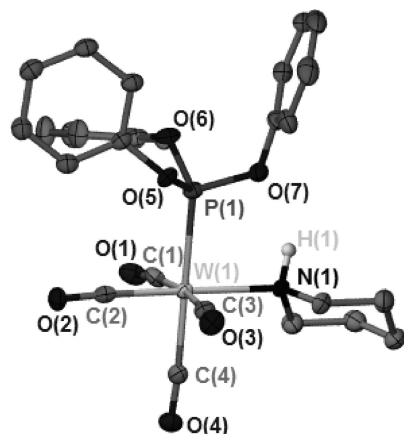


Figure 5. Thermal ellipsoid drawing of complex **2** at 50% probability level.

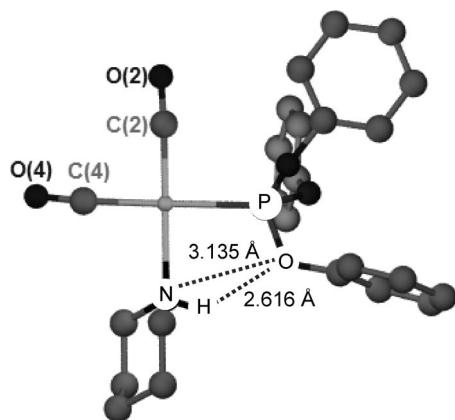


Figure 6. Ball-and-stick view of complex **2** shown down the *trans*-Mo(CO)₂ axis.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) in *cis*-W(CO)₄[P(OPh)₃][NHC₅H₁₀]

C(2)–O(2)	1.171(7)	C(2)–W(1)–P(1)	91.88(14)
C(4)–O(4)	1.157(6)	C(4)–W(1)–P(1)	176.23(14)
C(1)–O(1)	1.159(7)	C(3)–W(1)–P(1)	85.90(14)
C(3)–O(3)	1.155(6)	C(1)–W(1)–P(1)	98.23(15)
W(1)–C(1)	2.039(5)	C(2)–W(1)–C(4)	87.2(2)
W(1)–C(2)	1.947(6)	C(2)–W(1)–C(3)	86.1(2)
W(1)–C(3)	2.027(5)	C(4)–W(1)–C(3)	90.4(2)
W(1)–C(4)	1.995(5)	C(2)–W(1)–C(1)	87.8(2)
W(1)–N(1)	2.332(5)	C(4)–W(1)–C(1)	85.4(2)
W(1)–P(1)	2.4465(12)	C(3)–W(1)–C(1)	172.7(2)
N(1)–W(1)–P(1)	88.23(10)	W(1)–P(1)–O _{av}	117.08(13)
C(2)–W(1)–N(1)	178.00(17)	O–P(1)–O _{av}	100.7(2)
C(4)–W(1)–N(1)	92.58(18)		
C(3)–W(1)–N(1)	91.96(19)		
C(1)–W(1)–N(1)	94.16(18)		

isomerization to the *trans*-isomer was observed (*vide infra*). Furthermore, it should be noted that the two different phosphite ligands in complexes **1** and **5**, respectively, exhibit quite similar electronic properties, as revealed by infrared spectroscopy in the ν_{CO} region; that is, ν_{CO} values for **1** are 2047, 1965, and 1947 cm^{-1} and for **5** are 2046, 1957, and 1937 cm^{-1} .

As illustrated in eq 2, while attempting to synthesize the *cis*-W(CO)₄[P(OPh)₃]₂ derivative, because of the greater kinetic stability of the W–amine bond as compared to that in molybdenum, an intermediate, *cis*-W(CO)₄[P(OPh)₃][NHC₅H₁₀] (**2**), was isolated. An X-ray structure of complex **2** was determined, and a thermal ellipsoid drawing of this molecule is shown in Figure 5. Table 3 contains a compilation of selected

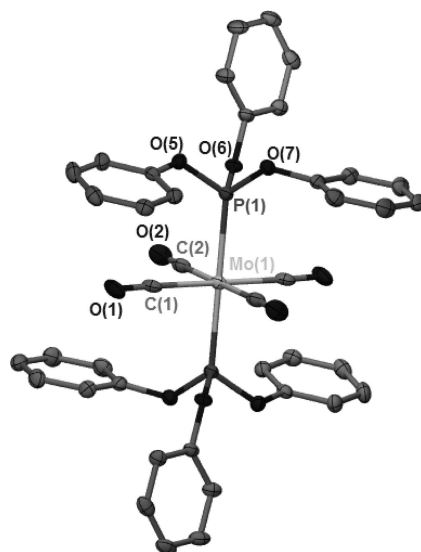


Figure 7. Thermal ellipsoid drawing of complex **6** at 50% probability level.

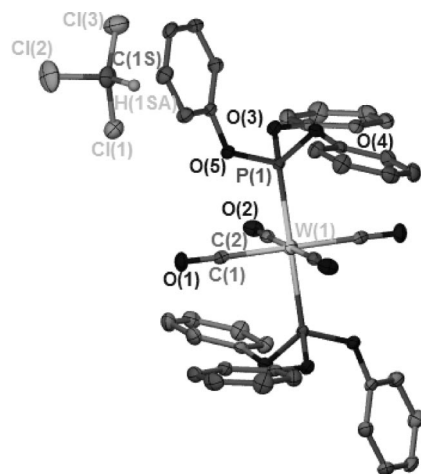


Figure 8. Thermal ellipsoid drawing of complex **4** at 50% probability level.

bond distances and bond angles. There are several interesting features in this complex worthy of note. As depicted in Figure 6, the phosphite and piperidine ligands are positioned to minimize steric interaction concomitantly providing H-bonding capability.¹⁷ Furthermore, the Mo–C(2) distance *trans* to piperidine is shorter (1.947(6) Å) than the Mo–C(4) distance *trans* to P(OPh)₃ of 1.995(5) Å, and both are shorter than the Mo–C distances *trans* to each other (2.033(5) Å).

The *trans*-M(CO)₄[P(OPh)₃]₂ (M = W (**4**) and Mo (**6**)) complexes were isolated from the thermal isomerization of the initially afforded *cis*-isomers obtained via reactions 1 and 2. Crystals suitable for X-ray analysis were obtained from a chloroform solution of the respective complex layered with methanol. Thermal ellipsoid representations of the two molecules are provided in Figures 7 and 8, with metric parameters compiled in Table 4. As depicted in Figures 7 and 8, the phenolate groups in the two phosphite ligands adopt a conformation where two groups are *down* and one is *up*. At this point it should be noted that the average steric requirements of the P(OPh)₃ ligand are greatly increased as the phenolate groups point downward (*vide infra*). A similar conformer of P(OPh)₃ was found for the phosphite ligand in Mo(CO)₅P(OPh)₃ (**7**), as indicated in Figure 9.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for *trans*-M(CO)₄[P(OPh)₃]₂, M = Mo and W

	Mo	W
C–O _{av}	1.143(4)	1.144(3)
M(1)–C(1)	2.045(3)	2.036(3)
M(1)–C(2)	2.040(3)	2.047(3)
M(1)–P(1)	2.4063(7)	2.4017(7)
P(1)–M(1)–C(1)	92.74(8)	87.86(8)
P(1)–M(1)–C(2)	86.35(8)	86.50(8)
M(1)–P(1)–O _{av}	118.42(8)	118.23(7)
O–P(1)–O	95.79–103.8	96.32–103.43

We have previously established a relationship between the size of the phosphorus donor, as estimated by the Tolman cone angle, and the relative thermodynamic stability of the *cis*/*trans* isomers in Mo(CO)₄[PR₃]₂ derivatives (eq 3).^{10,11} For example, the *K*_{eq} value for the reaction defined in eq 3 when R = *n*-Bu (Tolman cone angle = 132°) was determined to be 5.3 at 60–80 °C. On the other hand, for the more compact PMe₃ ligand (Tolman cone angle = 118°) the *cis*-isomer is slightly favored, with Δ*G* for reaction 3 in this instance being slightly positive, i.e., 0.32 kcal mol^{−1} at 65 °C. In both of these rearrangement processes, the isomerization mechanism was definitively established as being *intramolecular*. That is, ligand rearrangement occurred via a trigonal-prismatic intermediate where no ligand dissociation took place (Scheme 1a). By way of contrast, when R = Ph where the PPh₃ ligand is sterically more demanding (Tolman cone angle = 145°), rearrangement to the highly favored *trans*-isomer proceeds by way of phosphine dissociation with isomerization of the five-coordinate intermediate followed by phosphine recombination (Scheme 1b).



Based on electronic arguments, in the absence of steric demands made by phosphine or phosphite ligands, Mo(CO)₄[PR₃]₂ or Mo(CO)₄[P(OR)₃]₂ derivatives would be anticipated to exhibit *cis* stereochemistry. As indicated earlier, this was indeed found to be the case for the sterically compact P(OCH₂)₃CEt derivative of molybdenum tetracarbonyl. On the other hand for the electronically quite similar P(OPh)₃ derivative with a reported Tolman angle of 128°, that is, 4° smaller than *n*-Bu₃P, our initial thoughts were that Mo(CO)₄[P(OPh)₃]₂ would

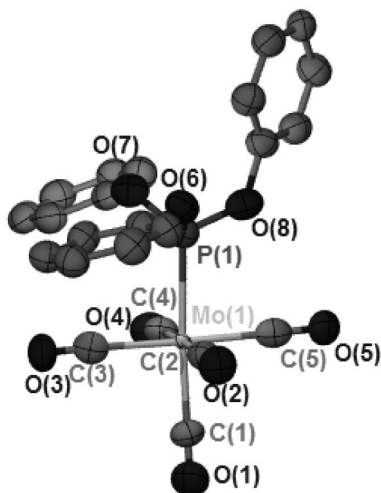
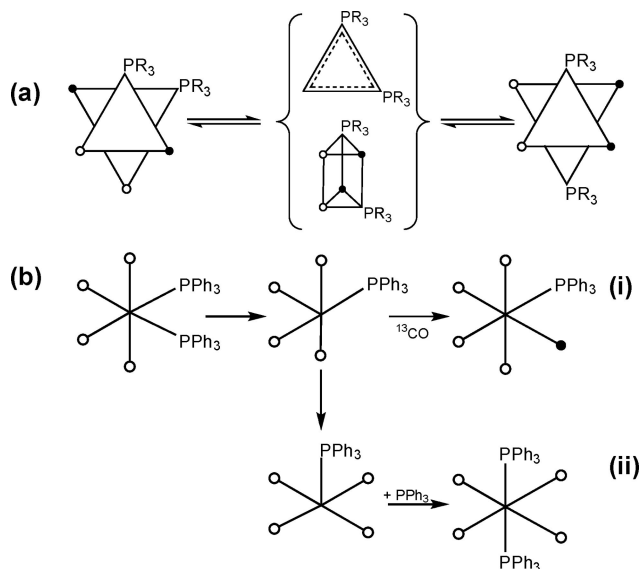


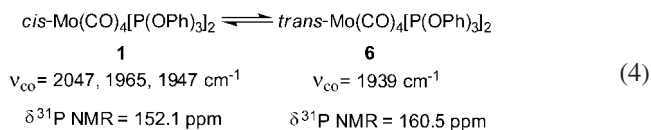
Figure 9. Thermal ellipsoid view of complex **7** at 50% probability level. Selected bond distances (Å) and bond angles (deg): Mo–C_{eq}(av) = 2.061(9), Mo–C_{ax} = 2.066(9), Mo–P = 2.448(2), P–Mo–C_{eq}(av) = 90.1(2).

Scheme 1

exist as a thermodynamically stable mixture of *cis*/*trans*-isomers. Furthermore, isomerization of a kinetically isolated *cis*-Mo(CO)₄[P(OPh)₃]₂ complex would be expected to rearrange to the *trans*-isomer or *cis*/*trans* mixture via an *intramolecular* mechanism. However, herein quite the opposite situation was observed for the behavior of *cis*-Mo(CO)₄[P(OPh)₃]₂. Specifically, *cis*-Mo(CO)₄[P(OPh)₃]₂ was found to readily isomerize 100% to the *trans*-isomer with P(OPh)₃ dissociation, i.e., via Scheme 1b.

The rearrangement of *cis*-Mo(CO)₄[P(OPh)₃]₂ to *trans*-Mo(CO)₄[P(OPh)₃]₂ was monitored by infrared spectroscopy in toluene at 85 °C over 48 h (eq 4). When this isomerization process was carried out under an atmosphere of carbon monoxide, Mo(CO)₅P(OPh)₃ (**7**) was afforded quantitatively, indicative of a process proceeding by way of Scheme 1b. Importantly, *trans*-Mo(CO)₄[P(OPh)₃]₂ does not undergo phosphine dissociation under these reaction conditions. By way of contrast, *cis*-W(CO)₄[P(OPh)₃]₂ (**4**) was shown via this protocol to undergo quantitative isomerization to its *trans*-isomer by an *intramolecular* pathway. Hence, the added strength of the W–P bonds in **4** allows for a trigonal twist rearrangement without bond disruption. It should be noted that we have previously reported a Δ*H*[‡] value of 31.9 kcal/mol for the dissociation of P(*o*-tolyl)₃ from *cis*-Mo(CO)₄[P(*o*-tolyl)₃]₂, whereas the similar process involving the tungsten analogue would be expected to be on the order of 10 kcal/mol higher in energy.¹¹

We have estimated the steric requirements of P(OPh)₃ in the



various group 6 metal–carbonyls discussed herein by calculating the *average* and *maximum* cone angles from crystallographic parameters employing the method of Müller and Mingos.¹⁸ Although Tolman's original cone angles obtained from CPK models of the most compact conformer of phosphine and phosphite ligands have served us well when discussing ligand

(17) (a) Atwood, J. L.; Darensbourg, D. J. *Inorg. Chem.* **1977**, *16*, 2314–2317. (b) Darensbourg, D. J. *Inorg. Chem.* **1979**, *18*, 2821–2825.

(18) Müller, T. W.; Mingos, D. M. P. *Transition Met. Chem.* **1995**, *20*, 533–539.

Table 5. Calculated Cone Angles of Triphenylphosphite in Group 6 Metal–Carbonyl Derivatives^a

complex	phenyl orientations (τ values, deg)	cone angle (deg)	
		average	maximum
<i>cis</i> -Mo(CO) ₄ [P(OPh) ₃] ₂ (1)	two down (160, 55, 44)	140	162
	one down (165, 125, 48)	125	152
<i>trans</i> -Mo(CO) ₄ [P(OPh) ₃] ₂ (6)	two down (179, 52, 40)	139	154
<i>trans</i> -W(CO) ₄ [P(OPh) ₃] ₂ (4)	two down (168, 53, 37)	143	166
Mo(CO) ₅ P(OPh) ₃ (7)	two down (160, 55, 44)	143	162

^a θ_i values calculated from crystallographic data using the method of Müller and Mingos, where $\theta_i = \alpha + 180/\pi \times \sin^{-1}(r_{H/d})$.¹⁸ The angle α is defined as the angle between the phosphorus and metal centers and the center of the outermost hydrogen atom on the phenyl substituent. The distance d is the crystallographic distance between the metal center and the outmost hydrogen atom, and r_H is the van der Waals radius of hydrogen.

spatial requirements, these values fail to take into account variations in cone angles with ligand conformation. As depicted in Figure 2, triphenylphosphite can exist as several conformers. In the crystallographically defined metal-carbonyls in this study two of the commonly observed conformers of P(OPh)₃ were observed, i.e., those of C_s symmetry with either two phenyl groups oriented *up* (*anti*) or *down* (*gauche*). The latter conformer is found in the low-temperature structure of triphenylphosphite derived from a single crystal study at 119 K.¹⁹ Furthermore, no phase changes as a function of temperature were noted from powder X-ray diffraction measurements of P(OPh)₃ over the temperature range 150–290 K. Indeed, of the 362 triphenylphosphite ligands bound to transition metal centers in the Cambridge Crystallographic Database as of May 2007, only 1.7% (6) of these displayed the Tolman's all (*up*, *anti*) arrangement,²⁰ whereas, 33.7% (122) and 62.4% (226) were two (*up*, *anti*) and one (*down*, *gauche*) or two (*down*, *gauche*) and one (*up*, *anti*), respectively.²¹ The remaining 2.2% (8) of the TM–P(OPh)₃ structures exhibit all three aryl substituents *down* (*gauche*).²²

Table 5 contains the calculated phosphite cone angles for the seven P(OPh)₃ ligands found in complexes **1**, **4**, **6**, and **7**, along with the three τ angles as described in Figure 3. The Müller and Mingos¹⁸ algorithm for calculating cone angles uses the center of the outermost hydrogen atom in the substituent as defined by crystallographic data. The *average* cone angle is defined as $2/3 \sum_i \theta_i$, where θ_i is the half-angle to the van der Waals radius of the outermost hydrogen atom of the substituent i , whereas, our *maximum* cone angle is ascribed to twice the largest half-angle, θ_i (see Supporting Information). For the conformer where two of the phenyls are oriented downward, the *average* and *maximum* cone angles were found to have average values of $141 \pm 2^\circ$ and $161 \pm 5^\circ$, respectively. On the other hand, the P(OPh)₃ ligand with two phenyl substituents oriented upward was found to have an *average* cone angle of 125° and a *maximum* cone angle of 152° . Hence, the *cis*-Mo(CO)₄[P(OPh)₃]₂ structure contains one phosphite ligand with two phenyl substituents down and the other phosphite ligand with two phenyl substituents up, thereby allowing for a meshing of the two ligands minimizing steric interactions. That is, the one up and two up areas are in closest proximity to one another

in the solid-state *cis* structure. Furthermore, rearrangement to the *trans* structures of both molybdenum and tungsten tetracarbonyl (complexes **4** and **6**) allows for both phosphites to possess what is evidently their favored conformation, two phenyl substituents *down*. This conformer is also found in the sterically unencumbered monosubstituted Mo(CO)₅P(OPh)₃ complex (**7**) and as was previously observed in the unbound P(OPh)₃ molecule. It is worthy of note that in the sterically more bulky tris(2-methoxyphenyl)phosphite molecule the C_3 conformer was observed crystallographically, where all three phenyl substituents are oriented downward as defined herein.¹⁴

Conclusions

Although Tolman's cone angles for tertiary phosphines and phosphites have served the organometallic community well, there are instances where their absolute values must be utilized with some degree of skepticism. This is particularly true when various conformers of the ligands are readily accessible. Herein, we have shown that triphenylphosphite displays four different conformers in the solid state, two of which are dominant, accounting for 96% of the structures currently contained in the Cambridge Crystallographic Database. Importantly, these latter conformers in group 6 carbonyl derivatives are spatially much larger than the original Tolman cone angle for P(OPh)₃ of 128° .

Significantly, the steric requirements of P(OPh)₃ found in these solid-state structures persist in solution as demonstrated by *cis*–*trans* equilibria and isomerization mechanisms. That is, phosphite ligands with cone angles $\sim 128^\circ$ would be expected to thermodynamically favor *cis*-M(CO)₄[P(OPh)₃]₂ (M = Mo or W) structures and their isomerization pathways to the analogous *trans*-isomers would be anticipated to be *intramolecular*. However, *cis*-Mo(CO)₄[P(OPh)₃]₂ and *cis*-W(CO)₄[P(OPh)₃]₂ isomers undergo essentially complete thermal rearrangement to the *trans*-isomers, with the former complex proceeding via an *intermolecular* process. Current studies are aimed at more extensively exploring the steric effects of various triarylphosphite and triaryllarsenite ligands in metal-carbonyl derivatives employing the X-ray crystallographic and isomerization reaction probes described herein.

Experimental Section

Methods and Materials. Unless otherwise stated all synthesis and manipulations were carried out on a double-manifold Schlenk vacuum line under an argon atmosphere or in an argon-filled glovebox. Molybdenum hexacarbonyl, tungsten hexacarbonyl, and triphenylphosphite were purchased from ACROS. Trimethylolpropanephosphite was obtained from TCI. All solvents were freshly purified using an MBraun solvent purification system packed with Alcoa F200 activated alumina desiccant. Infrared spectra were recorded on a Mattson 6021 Galaxy series FTIR, and ³¹P NMR spectra were collected on an Inova 300 MHz spectrometer. *cis*-M(CO)₄[NHC₅H₁₀]₂ (M = Mo and W) were prepared in 90% yield by the method previously described in the literature.¹⁵

Compound Preparations. (a) *cis*-Mo(CO)₄L₂ (L = P(OPh)₃) (**1**) and P(OCH₂)₃CEt (**5**). Derivatives were prepared from *cis*-Mo(CO)₄[NHC₅H₁₀]₂ and excess ligand (L) in refluxing dichloromethane as previously reported.¹⁵ White crystals of complex **1** suitable for X-ray analysis were obtained from chloroform and cold methanol in 66.3% yield. The ν_{CO} values of **1** in hexane were observed at 2047, 1965, and 1947 cm⁻¹, with the ³¹P NMR resonance found at 152.1 ppm. White crystals of complex **5** were obtained from dichloromethane/methanol in 57.2% yield. The ν_{CO} frequencies of **5** in toluene were observed at 2046, 1957, and 1937 cm⁻¹, with the ³¹P NMR signal found at 139.7 ppm.

(19) Senker, J.; Lüdecke, J. Z. *Naturforsch.* **2001**, 56b, 1089–1099.

(20) For example: Guss, J. M.; Mason, R. J. *Chem. Soc., Dalton Trans.* **1972**, 2193–2196.

(21) The three calculated values of τ for each triphenylphosphite ligand bound to a transition metal structure found in the Cambridge Crystallographic Database as of May 2007 are provided in the Supporting Information.

(22) For examples, see: (a) Rasmussen, P. G.; Anderson, J. E.; Bayón, J. C. *Inorg. Chim. Acta* **1984**, 87, 159–164. (b) Haumann, M.; Meijboom, R.; Moss, J. R.; Roodt, A. *Dalton Trans.* **2004**, 1679–1686.

(b) *cis*-W(CO)₄[NHC₅H₁₀]P(OPh)₃ (**2**). To 2.57 g of *cis*-W(CO)₄[NHC₅H₁₀]₂ suspended in 50 mL of dichloromethane was added 1.47 mL (1 equiv) of P(OPh)₃, and the solution was refluxed overnight. The resultant reaction solution was filtered through Celite, and the solvent was removed under vacuum. Small yellow crystals suitable for X-ray analysis were isolated upon recrystallization of the product from chloroform and cold methanol. The purified product was obtained in a 44.2% yield, or 1.68 g. The ν_{CO} infrared bands of **2** appeared in hexane at 2029, 1911, 1906, and 1895 cm⁻¹. The ³¹P NMR chemical shift was observed at 136.4 ppm, with J_{PW} = 419 Hz. Anal. Found: C, 46.48; H, 3.54. Calcd: C, 46.91; H, 3.79.

(c) *cis*-W(CO)₄[P(OPh)₃]₂ (**3**). To 0.174 g of **2** in 12 mL of toluene was added 0.066 mL of P(OPh)₃, and the solution was heated at 60 °C for 24 h. The product, which consisted mostly of **3** with a small quantity of **2** remaining, was isolated following removal of solvent under vacuum. The ν_{CO} infrared vibrations of **3** were observed at 2043, 1953, and 1933 cm⁻¹.

Isomerization Reactions. (a) Complete rearrangement of *cis*-Mo(CO)₄[P(OPh)₃]₂ (**1**) to *trans*-Mo(CO)₄[P(OPh)₃]₂ (**6**) occurred in toluene at 85 °C over a 48 h period. The ν_{CO} infrared absorption of **6** was observed at 1939 cm⁻¹ in toluene, with a ³¹P NMR signal appearing at 160.5 ppm. Crystals suitable for X-ray analysis were obtained from chloroform and cold methanol. When this process was similarly carried out under an atmosphere of carbon monoxide, the sole reaction product was Mo(CO)₅P(OPh)₃ (**7**).

(b) Isomerization of *cis*-W(CO)₄[P(OPh)₃]₂ (**3**) in toluene was performed as described above, leading to *trans*-W(CO)₄[P(OPh)₃]₂ (**4**). The ν_{CO} infrared absorption of **4** in toluene appeared at 1932 cm⁻¹, with the ³¹P NMR signal observed at 135.4 ppm (J_{PW} = 564 Hz). Complex **4** was crystallized from chloroform and cold methanol. This isomerization reaction was unaffected when carried out under an atmosphere of carbon monoxide.

(c) Complex **5**, *cis*-Mo(CO)₄[P(OCH₂)₃CET]₂, was heated in toluene solution for 48 h at 80 °C, followed by further heating at 95 °C for 24 h with no change occurring in its infrared ν_{CO} bands.

X-ray Crystallography Data Collection and Refinement. X-ray data for compounds **1**, **3**, **4**, **5**, **6**, and **7** were collected on a Bruker Smart 1000 CCD diffractometer and covered more than a hemisphere of reciprocal space by a combination of four sets of exposures. The structures were solved by direct methods utilizing SAINT,²³ SHELX,^{24–26} and WinGX²⁷ suite programs. Crystal details and details of data collection are provided in Table 1.

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Supporting Information Available: CIF files of complexes **1**, **2**, **4**, **5**, **6**, and **7** giving full details of the X-ray crystallographic studies. Observed τ angle values for the metal–P(OPh)₃ X-ray structures in the Cambridge Crystallographic Database as of May 2007. Calculated cone angles for the crystallographically defined metal–P(OPh)₃ units in this study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(23) SAINT-Plus, version 6.02; Bruker: Madison, WI, 1999.

(24) Sheldrick, G. *SHELXS-86: Program for Crystal Structure Solution*; Institut für Anorganische Chemie der Universität: Göttingen, Germany, 1986.

(25) Sheldrick, G. *SHELXL-97: Program for Crystal Structure Refinement*; Institut für Anorganische Chemie der Universität: Göttingen, Germany, 1997.

(26) SHELXTL, version 5.0; Bruker: Madison, WI, 1999.

(27) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, 32, 837–838.