ORGANOMETALLICS

Article

Cite This: *Organometallics* XXXX, XXX, XXX–XXX

pubs.acs.org/Organometallics

XL-Xantphos: Design and Synthesis of a Mechanistic Probe of Xantphos *O*-Coordination in Catalytic Reactions

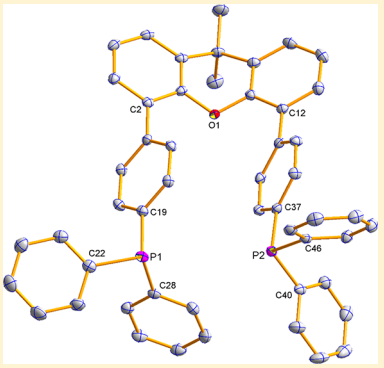
Gregory T. Whiteker,*[†] Fangzheng Li,[†] Robert D. J. Froese,[‡] Michael L. Tulchinsky,[‡] Amaruka Hazari,[†] and Jerzy Klosin[‡]

[†]Process Chemistry, Corteva Agriscience, Agriculture Division of DowDuPont, 9330 Zionsville Road, Indianapolis, Indiana 46268, United States

[‡]Core R&D, The Dow Chemical Company, 1776 Building, Midland, Michigan 48674, United States

Supporting Information

ABSTRACT: The synthesis and characterization of an analog of the Xantphos ligand that is geometrically incapable of coordination of the xanthene bridging oxygen atom is reported. This new ligand, XL-Xantphos, ((9,9-dimethyl-9*H*-xanthene-4,5-diyl)bis(4,1-phenylene))bis(diphenylphosphane), was studied in homogeneous, catalytic reactions for comparison with Xantphos. The XL-Xantphos ligand performed essentially identically to Xantphos in Rh-catalyzed hydroformylation of 1-octene, which suggests that the high regioselectivity for linear aldehyde is due to the large bite angle of these ligands and is not influenced by oxygen coordination to the metal. The Pd-catalyzed amidocarbonylation of 4-bromoanisole with dimethylhydroxylamine hydrochloride similarly showed no difference between Xantphos and XL-Xantphos. Computations on Pd(II) phosphine complexes at the DLPNO−CCSD(T) level of theory indicated that these ligands have different preferences for *cis* and *trans* coordination modes. The XL-Xantphos ligand has a thermodynamic preference for *trans*-chelated structures, whereas the *cis*-[(Xantphos)$PdCl_2$] isomer was calculated to be thermodynamically more stable than its *trans* isomer. Given the key role of d^8 square planar Pd intermediates in many catalytic cycles, the greater preference of Xantphos to form *cis* chelates may indeed be a factor which has made this ligand particularly effective.



INTRODUCTION

Chelating ligands have played a prominent role in the development of homogeneous, transition metal catalysis. Diphosphines, in particular, are important for a variety of late transition metal catalytic processes, including asymmetric hydrogenation, hydroformylation, and cross-coupling reactions. Compared to monodentate phosphines, diphosphine ligands allow more precise control of metal to phosphine ratio in catalytic intermediates. In addition, through appropriate design of the linking structure, diphosphines can provide control of coordination geometry, or P−M−P bite angle, which has been found to be important in a variety of catalytic reactions.[1] The effects of diphosphines with large bite angles have been studied extensively, especially in rhodium-catalyzed hydroformylation. Xantphos, the most important of these ligands, was designed by van Leeuwen to adopt structures with large bite angles that place the two phosphorus atoms in the equatorial plane of five-coordinate intermediates in the hydroformylation catalytic cycle.[2] This coordination mode imparts very high selectivity for linear aldehyde and has led to Xantphos becoming one of the most widely utilized ligands for regioselective hydroformylation.

Xantphos is a privileged ligand that has shown utility in a wide variety of catalytic reactions in addition to hydroformylation.[3] It is a particularly effective ligand for α-arylation of ketones,[4] amide arylation,[5] carbonylation of aryl bromides,[6] and olefin hydroamination.[7] In addition to the wide bite angle adopted by Xantphos in metal complexes, the oxygen atom in the xanthene bridge is capable of coordination to the metal center to form tridentate P−O−P pincer complexes. Initially, the ability of ether-bridged "POP" ligands, such as Xantphos, to coordinate in a tridentate fashion was not widely recognized.[8] On the basis of analysis of data from the Cambridge Structural Database, a correlation between large P−M−P bite angles and short M···O distances was reported recently by Williams et al.[9] Such correlation is expected since a large, *trans* P−M−P angle should result geometrically in close proximity of the oxygen atom to the metal. The possible catalytic importance of a hemilabile interaction between the Xantphos oxygen atom and a metal center has been raised previously.[10] For example, in rhodium-catalyzed hydroformylation, stabilization of four-coordinate intermediates could potentially be stabilized by a coordination of the Xantphos bridging oxygen atom. Xantphos has been found to be more conformationally flexible than originally expected, and both *cis* and *trans* coordination modes have been observed. Indeed, this flexibility to adopt a variety of geometries during a catalytic cycle is often invoked as an explanation for the widespread utility of Xantphos.

Received: March 18, 2019

DOI: 10.1021/acs.organomet.9b00141
Organometallics XXXX, XXX, XXX–XXX

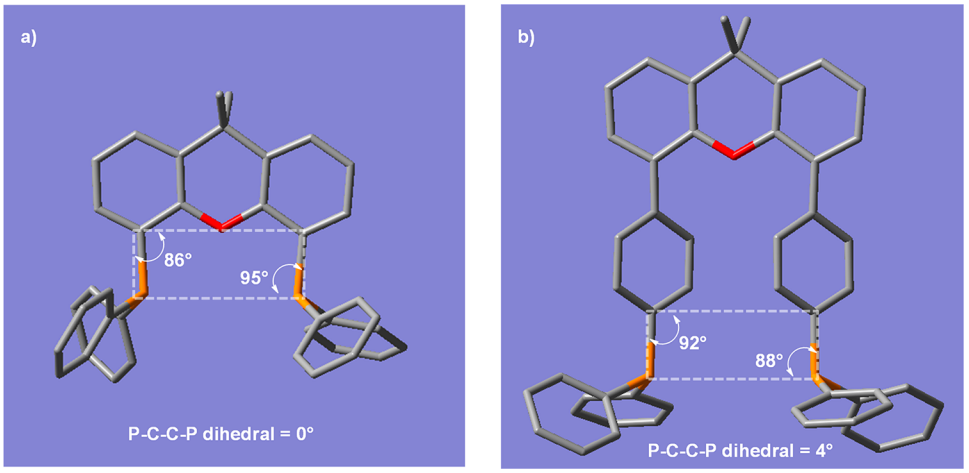
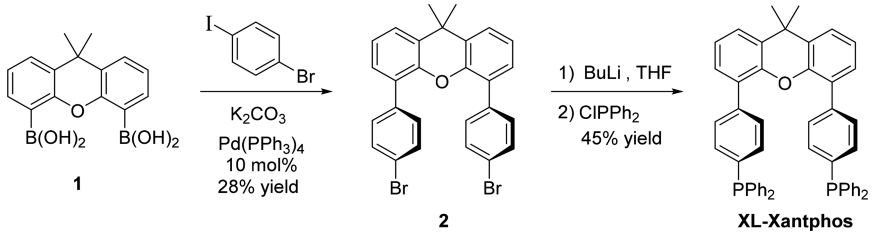
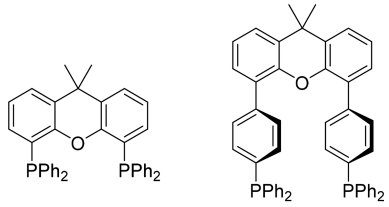


Figure 1. DFT (B3LYP-d/6-31+G*) optimized structures of (a) Xantphos and (b) XL-Xantphos.

Scheme 1. Synthesis of XL-Xantphos

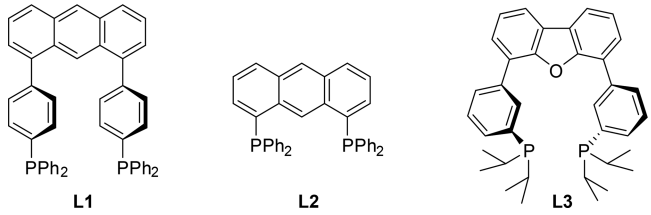


We describe a mechanistic probe of coordination of the oxygen atom in Xantphos in transition metal catalyzed reactions. The new diphosphine, XL-Xantphos, was designed to be identical to Xantphos in bite angle and ligand basicity but precluded from interaction of the xanthene oxygen atom with metal centers. The synthesis of this new ligand and its performance in rhodium-catalyzed hydroformylation and palladium-catalyzed arylation chemistry are presented. Computational studies of the potential differences in coordination geometry between these two ligands are also reported.



RESULTS AND DISCUSSION

Ligand Design and Synthesis. We sought to design a diphosphine analog which maintained the bite angle of Xantphos but prevented coordination of the oxygen atom by insertion of a rigid spacer unit. Figure 1 shows the structures of Xantphos and XL-Xantphos obtained from density functional theory calculations at the B3LYP-d/6-31G* level (see the Supporting Information for complete details of the calculations). The xanthene backbone of Xantphos places the two P−C_{ipso} bonds in the same plane with a dihedral angle of 0°. In addition, the P−C_{ipso} bonds are essentially parallel with P−P−C_{ipso} and C_{ipso}−C_{ipso}−P angles close to 90°. We hypothesized that a 1,4-phenyl spacer could be inserted to conceptually extend this rectangular arrangement and maintain the relative orientation of the P−C_{ipso} bonds. DFT calculations on the resulting structure, XL-Xantphos, confirmed this design. The two P−C_{ipso} bonds of XL-Xantphos were calculated to be essentially in the same plane with a dihedral angle of 4°, and the P−P−C_{ipso} and C_{ipso}−C_{ipso}−P angles were very similar to those calculated for Xantphos. This spacer design is analogous to that used in the related family of diphosphine ligands based on 1,8-bis(*p*-(diphenylphosphino)phenyl)anthracene (**L1**),[11] which were designed to be selective for *trans* chelation. In this particular case, the phenyl spacer in **L1** excludes the possibility of C−H activation that results in formation of P−C−P pincer complexes with **L2**.[12] A related, electron-rich ligand with a 1,3-phenyl spacer, **L3**, has also been described and can support both *cis* and *trans* coordination modes.[13]



XL-Xantphos was synthesized as shown in Scheme 1 from the known diboronic acid, **1**.[14] Attempts to perform Suzuki couplings of **1** with 1,4-dibromobenzene were unsuccessful, however, use of 1-bromo-4-iodobenzene with 10 mol % $Pd(PPh_3)_4$ and K_2CO_3 in THF−H_2O gave dibromide **2** in modest yield. Lithium-halogen exchange of **2** followed by reaction with $ClPPh_2$ gave XL-Xantphos as a white crystalline solid. The $^{31}P\{^1H\}$ NMR spectrum of XL-Xantphos in $CDCl_3$ exhibited a singlet at δ −6.79. Like Xantphos,[15] XL-Xantphos exhibited virtual coupling of many of the aromatic signals in its $^{13}C\{^1H\}$ spectrum as a result of through-space coupling of the phosphorus atoms. Simulation of the *ipso* ^{13}C resonances as an

DOI: 10.1021/acs.organomet.9b00141
Organometallics XXXX, XXX, XXX−XXX

AA′XX′ system gave J_{P-C} = 12 Hz and J_{P-P}' = 17 Hz. This $^{31}P-^{31}P$ coupling constant of XL-Xantphos was significantly smaller than the $^{31}P-^{31}P$ coupling constant of 40−60 Hz reported by van Leeuwen[2] for Xantphos which indicated that XL-Xantphos has less through-space interaction of its two phosphorus nuclei. The structure of XL-Xantphos was confirmed by X-ray crystallography (Figure 2). The P···P

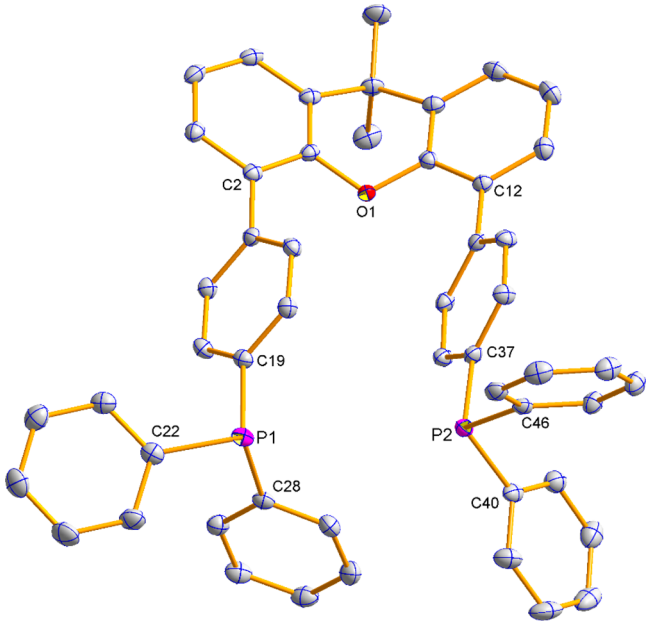
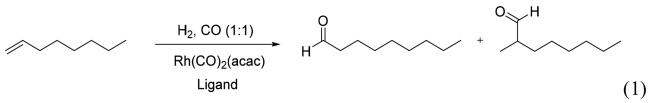


Figure 2. Molecular structure of XL-Xantphos. Thermal ellipsoids are shown at 50% probability.

distance in XL-Xantphos (4.42 Å) was significantly longer than that observed in the structure of Xantphos (4.08 Å)[2] and was consistent with the observed smaller $^{31}P-^{31}P$ coupling constant of XL-Xantphos.

Catalytic Studies. The performance of XL-Xantphos and Xantphos in rhodium-catalyzed hydroformylation of 1-octene was compared at 70 °C and 100 psi H_2/CO using 0.5 mol % [$Rh(CO)_2(acac)$] as catalyst precursor (eq 1, Table 1). After 1



(1)

h under these conditions, Xantphos led to 89% conversion of 1-octene. Complete conversion was observed after 2 h. Gas chromatographic analysis of the reaction mixture after 2 h showed a 46.9:1 mixture of linear and branched nonanals

Table 1. Results from Rhodium-Catalyzed Hydroformylation of 1-Octene[a]

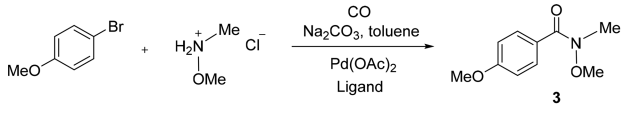
ligand	Rh (mol %)	solvent	time (h)	linear/ branched	% linear RCHO
Xantphos	0.5	THF	1	48.3	98.0
			2	46.9	97.9
XL-Xantphos	0.5	THF	1	34.3	97.2
			2	33.3	97.1
Biphephos	0.25	Heptane	1	24.8	96.1

[a]Conditions: 70 °C, 100 psi 1:1 H_2/CO, [diphosphine]/[$Rh(CO)_2(acac)$] = 2.

(97.9% linear aldehyde), in close agreement with the 58.2:1 isomer ratio (98.3% linear aldehyde) obtained by van Leeuven at 80 °C under 145 psi H_2/CO.[2] Hydroformylation of 1-octene using XL-Xantphos gave very similar results to Xantphos with quite high linear regioselectivity. Complete conversion was observed after only 1 h at 70 °C to give a 34.3:1 ratio of linear and branched aldehydes (97.2% linear). By comparison, the widely used bis-phosphite ligand, Biphephos,[16] led to 96.1% linear nonanal. Complete conversion was observed at 0.25 mol % Rh with the Biphephos ligand.

The similarly high linear regioselectivities for 1-octene hydroformylation with XL-Xantphos and Xantphos suggested that these two ligands can adopt similarly large P−Rh−P bite angles. The inability of the oxygen atom of XL-Xantphos to interact with the Rh center is strong evidence that a Rh···O interaction is not involved in the high regioselectivity of hydroformylation using Xantphos.

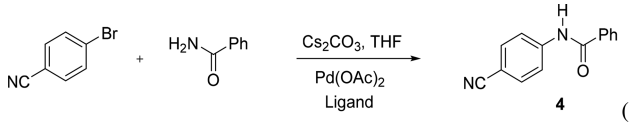
We were interested in evaluating XL-Xantphos in Pd-catalyzed reactions where Xantphos is particularly effective. Amidocarbonylation of aryl bromides to directly form Weinreb amides was reported by Buchwald.[6] Among all the ligands screened, Xantphos was found to be optimal and led to high conversion. The amidocarbonylation reaction of 4-bromoanisole with dimethylhydroxylamine hydrochloride under 1 atm CO in the presence of 2 mol % $Pd(OAc)_2$ and 4 mol % Xantphos was reported to give Weinreb amide **3** in 89% yield (eq 2). We found this reaction proceeds in a manner almost



(2)

identical to that with XL-Xantphos, leading to an 85% isolated yield under these conditions. The similar results observed with use of Xantphos and XL-Xantphos in eq 2 suggests that the xanthene oxygen plays no role in this chemistry.

A profound difference between Xantphos and XL-Xantphos, however, was observed in the Pd-catalyzed arylation of benzamides. Yin and Buchwald found that Xantphos was particularly useful for this transformation in comparison to other phosphine ligands.[5] The reaction of 4-bromobenzonitrile with benzamide in THF with Cs_2CO_3 using 1 mol % $Pd(OAc)_2$ and 1.5 mol % Xantphos at 45 °C was reported to give the coupled product, **4**, in 93% yield (eq 3). We



(3)

repeated this reaction and obtained **4** in 92% yield. Surprisingly, use of XL-Xantphos under identical conditions gave **4** in <4% yield by HPLC. In addition, as a catalyst precursor, isolated complex *trans*-[(XL-Xantphos)$PdCl_2$] led to similarly low yield. Given the similar results with XL-Xantphos and Xantphos for hydroformylation (eq 1) and amidocarbonylation of aryl bromides (eq 2), the lack of reactivity of XL-Xantphos in eq 3 is puzzling.

Model complexes were prepared to compare the XL-Xantphos ligand with Xantphos. The reaction of XL-Xantphos with [$(PhCN)_2PdCl_2$] in CH_2Cl_2 was monitored by $^{31}P\{^1H\}$

DOI: 10.1021/acs.organomet.9b00141
Organometallics XXXX, XXX, XXX−XXX

NMR. The resonance for XL-Xantphos disappeared, and two ^{31}P NMR singlets appeared at δ 21.29 and 30.85 in a 93:7 ratio. X-ray quality crystals were grown from a CH_2Cl_2−hexane solution of this mixture. The structure of product *trans*-[(XL-Xantphos)$PdCl_2$ displayed a distorted square planar structure with a *trans* orientation of the two phosphorus atoms and a P−Pd−P bite angle of 161.1° (Figure 3). The Cl−Pd−Cl bond

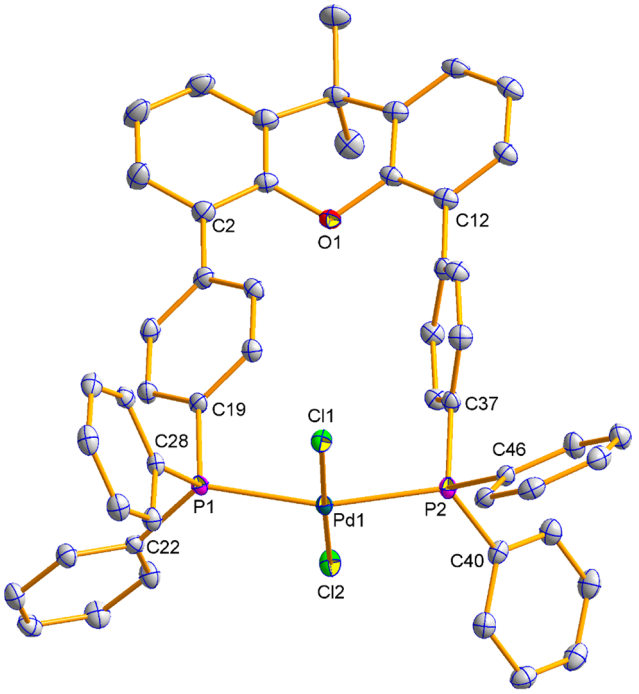


Figure 3. Molecular structure of *trans*-[(XL-Xantphos)$PdCl_2$]. Thermal ellipsoids are shown at 50% probability.

angle was 176.4°. Notably, the xanthene oxygen atom was far outside bonding distance with a Pd···O separation of 6.65 Å. The ability of XL-Xantphos to adopt a large bite angle in *trans*-[(XL-Xantphos)$PdCl_2$ is consistent with the observed high linear regioselectivity for 1-octene hydroformylation. The structure of *trans*-[(XL-Xantphos)$PdCl_2$ was similar to that of the *trans*-[(**L1**)$PdCl_2$] complex of the anthracene bridged ligand, **L1**, which also adopts a slightly distorted square planar geometry.[11a] However, the anthracene bridge of **L1** leads to an even larger P−Pd−P angle of 168.5° in comparison to that of XL-Xantphos.

Unlike the *trans* geometry of the XL-Xantphos ligand in [(XL-Xantphos)$PdCl_2$], [(Xantphos)$PdCl_2$] was reported to exhibit a *cis* orientation with a P−Pd−P bite angle of 101.2° in the solid state.[17] However, other examples of *cis* and *trans* coordination modes have been reported that illustrate the flexible coordinating ability of Xantphos. Both *cis* and *trans* structures of the iodo analog, [(Xantphos)PdI_2], which adopted P−Pd−P bite angles of 100.2 and 154.7°, respectively, were reported by Grushin.[18] The *trans* isomer exhibited a 2.55 Å separation between Pd and the xanthene oxygen; the corresponding distance in the *cis* isomer was 3.10 Å. Several additional complexes with Xantphos chelated in a *trans* orientation have been structurally characterized, including proposed catalytic intermediates resulting from oxidative addition of aryl halides. For example, [(Xantphos)Pd(CH_3)Cl] was found to adopt a *trans* geometry in the solid state (P−Pd−P = 152.6°, Pd···O = 2.66 Å).[19]

Since Xantphos and XL-Xantphos are both triarylphosphines, these ligands were expected to be very similar in their electron-donating properties. This was confirmed by comparison of the IR stretching frequencies of their $Mo(CO)_4$ complexes. XL-Xantphos was reacted with $Mo(CO)_6$ in toluene at reflux to form *cis*-[(XL-Xantphos)$Mo(CO)_4$]. Infrared spectra of *cis*-[(XL-Xantphos)$Mo(CO)_4$] and *cis*-[(Xantphos)$Mo(CO)_4$][20] exhibited carbonyl absorbances at 2018 and 2013 cm^{-1}, respectively. For comparison, the A_1 carbonyl band of *cis*-[$(PPh_3)_2Mo(CO)_4$] is at 2023 cm^{-1}.[21]

Computational Study. To better understand why Xantphos and XL-Xantphos differ in the geometries of their dichloropalladium(II) complexes, we performed a series of single point energy computations on Pd phosphine complexes at the DLPNO−CCSD(T)/def2-TZVPP level of theory using the ORCA program package.[22] Initially, geometries were optimized with the B3LYP-d method and LANL2TZ(F) basis set on palladium and 6-31G* on all other atoms. Further details on the methods, structures computed, coordinates, and energies are provided in the Supporting Information.

Calculations were first performed on *cis* and *trans* isomers of Pd(II) complexes of monodentate phosphine ligands to evaluate the thermodynamic preference in the absence of any geometric constraints imparted by a chelate backbone (Table 2). Results for these gas-phase calculations on [$(Ph_3P)_2PdCl_2$] showed the *trans* isomer was more stable than the *cis* complex by 4.0 kcal/mol, in excellent agreement with recent DFT calculations for this complex.[23] Likewise, [$(Me_3P)_2PdCl_2$] was

Table 2. Comparison of Calculated Energies in Gas Phase and Selected Structural Features of *cis* and *trans* Isomers of (Phosphine)PdX_2 Complexes[a]

complex		relative *E* (kcal/mol)	favored isomer	Pd···O distance (Å)	P−Pd−P angle (deg)	Cl−Pd−Cl angle (deg)
$(PPh_3)_2PdCl_2$	*cis*	4.0	*trans*	na	106.5	90.0
	trans	0.0		na	162.9	177.6
(XL-Xantphos)$PdCl_2$	*cis*	4.2	*trans*	6.83	104.2	87.6
	trans	0.0		6.73	159.3	178.3
(Xantphos)$PdCl_2$	*cis*	−4.2	*cis*	3.18	101.2	89.5
	trans	0.0		2.77	148.6	168.4
(Xantphos)PdI_2	*cis*	−4.2	*cis*	3.20	99.3	86.7
	trans	0.0		2.70	150.5	154.2
(Triptyphos)$PdCl_2$	*cis*	5.5	*trans*	Pd···H−C = 3.14	108.3	86.0
	trans	0.0		Pd···H−C = 2.39	146.2	171.8

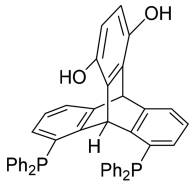
[a]Relative energies are the difference between pairs of *cis* and *trans* isomers.

DOI: 10.1021/acs.organomet.9b00141
Organometallics XXXX, XXX, XXX−XXX

calculated to favor the *trans* isomer over the *cis* by 6.9 kcal/mol, again in agreement with previous calculations.[24]

Calculations on [(XL-Xantphos)$PdCl_2$] showed that like monodentate phosphine ligands the *trans* isomer is thermodynamically preferred over the *cis* isomer by 4.2 kcal/mol with a P−Pd−P angle of 161.1°. This result is consistent with our observation of the *trans* isomer of this complex in the solid state. As expected, the calculated Pd···O distance is extremely long at 6.73 Å and compares favorably with the 6.65 Å distance found in the crystal structure.

The Triptyphos ligand was designed, like Xantphos, to adopt large P−M−P bite angles.[25] Bidentate structures of Triptyphos, as well as tridentate, pincer complexes from C−H activation of the bicyclic bridge have been reported. The crystal structure of [(Triptyphos)$PdCl_2$] showed a *trans* orientation of the phosphorus atoms with P−Pd−P = 151.4°. In agreement with this reported structure, our calculations showed the *trans* isomer of [(Triptyphos)$PdCl_2$] to be 5.5 kcal/mol lower in energy than the *cis* isomer. The reported *trans* crystal structure exhibited a relatively short distance (2.29 Å) between Pd and the bicyclic C−*H* atom which was also observed in our computations (2.39 Å). The *cis* isomer was calculated to have a longer distance between Pd and this hydrogen atom (3.14 Å), as expected.

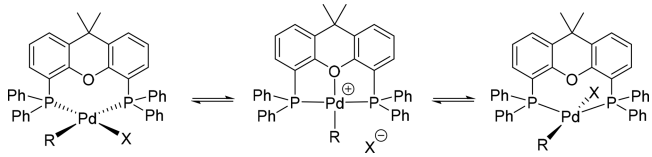


Triptyphos

Xantphos, unlike XL-Xantphos and Triptyphos, is unusual in that we calculated the *cis* dichloropalladium(II) isomer to be 4.2 kcal/mol lower in energy than the corresponding *trans* isomer. The lower calculated energy of the *cis* isomer was consistent with the three crystal structures that have been reported for *cis*-[(Xantphos)$PdCl_2$]. No crystal structures of the corresponding *trans* isomer have been reported. The Pd···O distance in the *cis* isomer of [(Xantphos)$PdCl_2$] was calculated to be 3.18 Å, in close agreement with reported crystal structures and significantly longer than the corresponding 2.77 Å Pd···O distance in the *trans* isomer. We also calculated the relative energy differences between *cis*- and *trans*-[(Xantphos)PdI_2], which were structurally characterized by Grushin.[19] Our calculations showed the difference in energy of the isomeric iodo complexes were identical to the energy difference calculated for *cis* and *trans* isomers of [(Xantphos)-$PdCl_2$] which was inconsistent with Grushin's observation of both isomers of the PdI_2 complex of Xantphos.

In the absence of geometric constraints imparted by a ligand backbone, multiple factors favor *cis* arrangements of two phosphines in square planar d^8 complexes.[24] Polar solvents preferentially stabilize the *cis* isomers of [$Pd(PR_3)_2Cl_2$] complexes which have larger dipoles than their *trans* isomers. This effect accounts for the common observation of both *cis* and *trans* isomers in solution for complexes of this type, even when only one isomer is found in the solid state.[26] van Leeuwen proposed a possible mechanism for interconversion of *cis* and *trans* Xantphos isomers which proceeded through a cationic intermediate where the xanthene oxygen atom occupied a vacant coordination site (Scheme 2).

Scheme 2. Proposed Mechanism for Isomerization of *cis* and *trans* Chelated Complexes of Xantphos via a Four-Coordinate, Cationic Intermediate[20]



Our calculations do not reveal the reason why Xantphos has a preference for *cis*-coordination compared to XL-Xantphos or monodentate phosphines in [$Pd(PR_3)_2Cl_2$] complexes. Since our calculations were performed in the gas phase, our computational results likely overestimated the relative stability of *trans* over *cis* isomers. Single point calculations were also performed with a continuum solvation model (see the Supporting Information) and indicated stabilization of *cis*- over *trans*-[$Pd(PR_3)_2Cl_2$] isomers by typically 3−4 kcal/mol in benzene and 6−7 kcal/mol in methylene chloride. In addition to solvent stabilization of the *cis* isomers, the *trans* influence also favors structures with PR_3 *trans* to chloride ligands, therefore stabilizing the *cis*-[$Pd(PR_3)_2Cl_2$] isomer. However, solvent stabilization and the *trans* influence should impact all of the Pd complexes in our study to a similar extent.

CONCLUSIONS

XL-Xantphos was designed to bind to transition metals with a bite angle very similar to that of Xantphos but with no ability of the xanthene oxygen atom to coordinate. Two important conclusions can be made from our comparison of Xantphos with XL-Xantphos. First, coordination of the bridging oxygen atom of Xantphos is not involved in the Rh-catalyzed hydroformylation mechanism. The high linear regioselectivity for hydroformylation is largely a result of the large bite angles of Xantphos and XL-Xantphos. Our results with Pd-catalyzed amidocarbonylation also indicated that the oxygen of Xantphos does not bind to Pd, given the similar results observed with XL-Xantphos in this reaction. Second, compared to other diphosphines that were designed to adopt large P−M−P bite angles, Xantphos has a larger preference toward *cis* geometries. It is possible that differences in flexibility of these ligand backbones influence the relative energies of *cis* and *trans* coordinated structures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00141.

Experimental and computational details (PDF)

Crystallographic data for XL-Xantphos and *trans*-[(XL-Xantphos)$PdCl_2$] (XYZ)

Accession Codes

CCDC 1911572 and 1911573 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

DOI: 10.1021/acs.organomet.9b00141
Organometallics XXXX, XXX, XXX−XXX

AUTHOR INFORMATION

Corresponding Author

*E-mail: greg.whiteker@corteva.com.

ORCID

Gregory T. Whiteker: 0000-0002-9439-6696

Jerzy Klosin: 0000-0002-9045-7308

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Professors Seth Brown (Notre Dame) and Chris Uyeda (Purdue University) for helpful discussions. We thank Professor Graham Dobereiner (Temple University) for providing the infrared spectrum of *cis*-(Xantphos)Mo(CO)$_4$. Dow AgroSciences is acknowledged for financial support.

REFERENCES

(1) van Leeuwen, P. W. N. M.; Kamer, P. C. J. Featuring Xantphos. *Catal. Sci. Technol.* **2018**, *8*, 26.

(2) Kranenburg, M.; van der Burgt, Y. E. M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J. New Diphosphine Ligands Based on Heterocyclic Aromatics Inducing Very High Regioselectivity in Rhodium-Catalyzed Hydroformylation: Effect of the Bite Angle. *Organometallics* **1995**, *14*, 3081.

(3) Birkholz, M.; Freixa, Z.; van Leeuwen, P. W. N. M. Bite Angle Effects of Diphosphines in C-C and C-X Bond Forming Cross Coupling Reactions. *Chem. Soc. Rev.* **2009**, *38*, 1099.

(4) Fox, J. M.; Huang, X.; Chieffi, A.; Buchwald, S. L. Highly Active and Selective Catalysts for the Formation of α-Aryl Ketones. *J. Am. Chem. Soc.* **2000**, *122*, 1360.

(5) Yin, J.; Buchwald, S. L. Pd-Catalyzed Intermolecular Amidation of Aryl Halides: The Discovery that Xantphos Can Be *Trans*-Chelating in a Palladium Complex. *J. Am. Chem. Soc.* **2002**, *124*, 6043.

(6) Martinelli, J. R.; Watson, D. A.; Freckmann, D. M. M.; Barder, T. E.; Buchwald, S. L. Palladium-Catalyzed Carbonylation Reactions of Aryl Bromides at Atmospheric Pressure: A General System Based on Xantphos. *J. Org. Chem.* **2008**, *73*, 7102.

(7) Johns, A. M.; Utsunomiya, M.; Incarvito, C. D.; Hartwig, J. F. A Highly Active Palladium Catalyst for Intermolecular Hydroamination. Factors that Control Reactivity and Additions of Functionalized Anilines to Dienes and Vinylarenes. *J. Am. Chem. Soc.* **2006**, *128*, 1828.

(8) Adams, G. M.; Weller, A. S. POP-type Ligands: Variable Coordination and Helilabile Behaviour. *Coord. Chem. Rev.* **2018**, *355*, 150.

(9) Williams, G. L.; Parks, C. M.; Smith, C. R.; Adams, H.; Haynes, A.; Meijer, A. J. H. M.; Sunley, G. J.; Gaemers, S. Mechanistic Study of Rhodium/xantphos-Catalyzed Methanol Carbonylation. *Organometallics* **2011**, *30*, 6166.

(10) (a) Moxham, G. L.; Randell-Sly, H. E.; Brayshaw, S. K.; Woodward, R. L.; Weller, A. S.; Willis, M. C. A Second-Generation Catalyst for Intermolecular Hydroacylation of Alkenes and Alkynes Using β-S-Substituted Aldehydes: The Role of a Hemilabile P-O-P Ligand. *Angew. Chem., Int. Ed.* **2006**, *45*, 7618. (b) Ohshima, T.; Miyamoto, Y.; Ipposhi, J.; Nakahara, Y.; Utsunomiya, M.; Mashima, K. Platinum-Catalyzed Direct Amination of Allylic Alcohols under Mild Conditions: Ligand and Microwave Effects, Substrate Scope, and Mechanistic Study. *J. Am. Chem. Soc.* **2009**, *131*, 14317.

(11) (a) Kaganovsky, L.; Cho, K.-B.; Gelman, D. New Trans-Chelating Ligands and Their Complexes and Catalytic Properties in the Mizoroki-Heck Arylation of Cyclohexene. *Organometallics* **2008**, *27*, 5139. (b) Kaganovsky, L.; Gelman, D.; Rueck-Braun, K. Trans-Chelating Ligands in Palladium-Catalyzed Carbonylative Coupling and Methoxycarbonylation of Aryl Halides. *J. Organomet. Chem.* **2010**, *695*, 260.

(12) Haenel, M. W.; Jakubik, D.; Krueger, C.; Betz, P. 1,8-Bis(diphenylphosphino)anthracene and Metal Complexes. *Chem. Ber.* **1991**, *124*, 333.

(13) (a) Ding, K.; Miller, D. L.; Young, V. G.; Lu, C. C. Study of the Conformationally Flexible, Wide Bite-Angle Diphosphine 4,6-Bis(3-diisopropylphosphinophenyl)dibenzofuran in Rhodium(I) and Palladium(II) Coordination Complexes. *Inorg. Chem.* **2011**, *50*, 2545. (b) Marlier, E. E.; Tereniak, S. J.; Ding, K.; Mulliken, J. E.; Lu, C. C. First-Row Transition-Metal Chloride Complexes of the Wide Bite-Angle Diphosphine ^{iPr}DPDBFphos and Reactivity Studies of Monovalent Nickel. *Inorg. Chem.* **2011**, *50*, 9290.

(14) (a) Makino, T.; Yamasaki, R.; Saito, S. Concise Synthesis of Diborylxanthenes. *Synthesis* **2008**, *2008*, 859. (b) Hirotsu, M.; Ohno, N.; Nakajima, T.; Kushibe, C.; Ueno, K.; Kinoshita, I. Synthesis and Characterization of Xanthene-Bridged Schiff-Base Dimanganese(III) Complexes: Bimetallic Catalysts for Asymmetric Oxidation of Sulfides. *Dalton Trans.* **2010**, *39*, 139.

(15) Freixa, Z.; van Leeuwen, P. W. N. M. Trans-Chelating Diphosphines, the Elusive Ligands. *Coord. Chem. Rev.* **2008**, *252*, 1755.

(16) (a) Billig, E.; Abatjoglou, A. G.; Bryant, D. R. Transition metal complex catalyzed processes. U.S. Patent 4769498A, 1988. (b) Cuny, G. D.; Buchwald, S. L. Practical, High-Yield, Regioselective, Rhodium-Catalyzed Hydroformylation of Functionalized Alpha-Olefins. *J. Am. Chem. Soc.* **1993**, *115*, 2066.

(17) (a) Saikia, K.; Deb, B.; Borah, B. J.; Sarmah, P. P.; Dutta, D. K. Palladium Complexes of P,P and P,S Type Bidentate Ligands: Implication in Suzuki-Miyaura Cross-Coupling Reaction. *J. Organomet. Chem.* **2012**, *696*, 4293.

(18) Miloserdov, F. M.; McMullin, C. L.; Belmonte, M. M.; Benet-Buchholz, J.; Bakhmutov, V. I.; Macgregor, S. A.; Grushin, V. V. The Challenge of Palladium-Catalyzed Aromatic Azidocarbonylation: From Mechanistic and Catalyst Deactivation Studies to a Highly Efficient Process. *Organometallics* **2014**, *33*, 736.

(19) Zuideveld, M. A.; Swennenhuis, B. H. G.; Boele, M. D. K.; Guari, Y.; Van Strijdonck, G. P. F; Reek, J. N. H; Kamer, P. C. J.; Goubitz, K.; Fraanje, J.; Lutz, M.; Spek, A. L.; van Leeuwen, P. W. N. M. The Coordination Behaviour of Large Natural Bite Angle Diphosphine Ligands Towards Methyl and 4-Cyanophenylpalladium-(II) Complexes. *Dalton Trans.* **2002**, 2308.

(20) (a) Becica, J.; Glaze, O. D.; Wozniak, D. I.; Dobereiner, G. E. Selective Isomerization of Terminal Alkenes to (*Z*)-2-Alkenes Catalyzed by an Air-Stable Molybdenum(0) Complex. *Organometallics* **2018**, *37*, 482. (b) Graham, D., personal communication, Temple University, 2018.

(21) Darensbourg, D. J.; Kump, R. L. A Convenient Synthesis of *cis*-Mo(CO)$_4$L$_2$ Derivatives (L = Group 5a Ligand) and a Qualitative Study of their Thermal Reactivity Toward Ligand Dissociation. *Inorg. Chem.* **1978**, *17*, 2680.

(22) Neese, F. The ORCA Program System. *Comput. Mol. Sci.* **2012**, *2*, 73−78.

(23) Kokan, Z.; Perić, B.; Kovačević, G.; Brozovic, A.; Metzler-Nolte, N.; Kirin, S. I. Cis-Versus Trans-Square-Planar Palladium(II) and Platinum(II) Complexes with Triphenylphosphine Amino Acid Bioconjugates. *Eur. J. Inorg. Chem.* **2017**, *2017*, 3928.

(24) Harvey, J. N.; Heslop, K. M.; Orpen, A. G.; Pringle, P. G. Factors Controlling the Relative Stabilities of *cis*-and *trans*-[PtX$_2$L$_2$] Isomers: Chatt and Wilkins-50 Years On. *Chem. Commun.* **2003**, 278.

(25) Tauchert, M. E.; Warth, D. C. M.; Braun, S. M.; Gruber, I.; Ziesak, A.; Rominger, F.; Hofmann, P. *Organometallics* **2011**, *30*, 2790−2809.

(26) Redfield, D. A.; Nelson, J. H. Equilibrium Energetics of Cis-Trans Isomerization for two Square-Planar Palladium(II)-Phosphine Complexes. *Inorg. Chem.* **1973**, *12*, 15.

DOI: 10.1021/acs.organomet.9b00141
Organometallics XXXX, XXX, XXX−XXX