# **Inorganic Chemistry**

### Steric and Electronic Influences of Buchwald-Type Alkyl-JohnPhos Ligands

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**S** Supporting Information

**ABSTRACT:** The electron-donating and steric properties of Buchwald-type ligands ([1,1'-biphenyl-2-yl]dialkylphosphine; R-JohnPhos, where R = Me, Et, <sup>i</sup>Pr, Cy, <sup>t</sup>Bu) were determined. The  $\pi$ -acidity and  $\sigma$ -donating properties of the R-JohnPhos ligands were quantified using a Cotton–Kraihanzel analysis of the Cr<sup>0</sup>(CO)<sub>5</sub>(R-JohnPhos) complexes. Somewhat surprisingly, the  $\sigma$ -donating abilities of the R-JohnPhos ligands follow the trend <sup>t</sup>Bu-JohnPhos < Et-JohnPhos < <sup>i</sup>Pr-JohnPhos < Cy-JohnPhos  $\ll$  Me-JohnPhos. This ordering is proposed to arise from competition between the intrinsic electron-donating ability of the R groups (Me < Et < <sup>i</sup>Pr  $\approx$  Cy < <sup>t</sup>Bu) and steric interactions (front and back strain) that



decrease the electron-donating ability of the phosphine. X-ray crystallographic data of 22 metal complexes (general forms: *trans*- $Cr^{0}(CO)_{4}(PR_{3})_{2}$ ,  $Pd^{0}(PR_{3})_{2}(\eta^{2}$ -dba), and *trans*- $Pd^{II}(CI)_{2}(PR_{3})_{2}$ ) were also analyzed to help explain the electronic trends measured for the R-JohnPhos ligands. The R-JohnPhos ligands are exceptionally sensitive to back strain in comparison to typical phosphines, and the strong  $\sigma$ -donating ability of the Methyl-JohnPhos ligand is attributed to its ability to avoid both front strain and back strain. Consequently, the  $-PMe_{2}$  moiety allows for very short phosphorus–metal bond distances. Because of the sterically dominating *o*-biphenyl and close phosphorus–metal bond distances, MeJPhos maintains a large overall steric profile that is actually larger than that of CyJPhos as measured by percent buried volume (% $V_{bur}$ ). Overall, the  $-PMe_{2}$  moiety is a powerful way to incorporate strong  $\sigma$ -donation into "designer" phosphines while retaining other advantageous structural and reactivity properties.

### INTRODUCTION

The advent of designer phosphines in the last two decades has led to a portfolio of homogeneous metal catalytic systems that impart distinctive reactivity using subtle structural variations in the phosphines.<sup>1</sup> Buchwald-type ligands have been particularly successful at forming highly active palladium catalysts for crosscoupling while exemplifying how subtle structural variations create critical reactivity differences at a palladium center (Figure 1).<sup>2-4</sup> Due to limitations in traditional phosphine synthetic methods, typical commercially available phosphine ligands are limited to bulky functional groups.<sup>5</sup> Consequently, the synthesis of dimethyl-functionalized designer phosphine ligands is rare.<sup>6</sup> In fact, the dimethylphosphine derivatives of most commercially available phosphine ligands have yet to be reported (e.g., dimethylphosphino-DIOP, -BINAP, -SPhos, etc.).<sup>7</sup> Such ligands would potentially provide better catalysts or, at the very least, conclusive information about electronic and structural trends for ligand design. The omission of the dimethylphosphine moiety in modern ligand design has been partially compensated for by predictive calculations;<sup>8-11</sup> however, many of these calculations have yet to be validated by experiment.

The recent preparation of [1,1'-biphenyl-2-yl]dimethylphosphine (Methyl-JohnPhos; MeJPhos for short) by our laboratory has given us the opportunity to study a representative series of alkyl-JohnPhos ligands.<sup>12</sup> Buchwald ligands have long been valued for two design features: namely, a strongly  $\sigma$  donating dialkylphosphine and a sterically demanding biphenyl moiety.<sup>13</sup> Though Buchwald-type ligands have been thoroughly studied for their properties by derivatization of the biphenyl moiety, very little effort has gone into determining effects of the alkyl groups at phosphorus.<sup>14–17</sup> Because only larger alkyl groups [*tert*-butyl, cyclohexyl (Cy), adamantyl, etc.] have been studied, it is not clear how small alkyl groups on the phosphine affect metal complex reactivity.

To investigate the effect of the alkyl groups, we synthesized and investigated a range of Buchwald-type ligands (Figure 2), with an emphasis on how the ligands contribute to the electronic and structural properties of metal complexes. We hypothesized that a shorter phosphorus—metal bond distance for the smaller R-JohnPhos ligands could provide superior  $\sigma$ donation (which is necessary for difficult oxidative additions at Pd metal centers; Figure 1b) while retaining enough steric hindrance at the biphenyl moiety (which is necessary for reductive eliminations in Pd cross-coupling reactions; Figure 1b). We report here the results of our study on Buchwald-type

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Figure 1. (a) Buchwald-type ligand structural features and their proposed effects on the palladium complex and catalytic properties for crosscoupling reactions.<sup>13</sup> (b) Mechanism of Buchwald–Hartwig cross-coupling.<sup>18</sup>



Figure 2. Structures, names, and abbreviated names of the R-JohnPhos ligands studied in this report.

ligands with smaller alkyl groups and the implications for structure-function relationships.

### RESULTS AND DISCUSSION

A complete series of alkyl-JohnPhos ligands (referred to as R-JohnPhos ligands from here forward) was synthesized (MeJPhos, EtJPhos, and <sup>i</sup>PrJPhos) or purchased (CyJPhos and <sup>t</sup>BuJPhos) (Figure 2). These served as a representative collection of alkyl groups at the phosphorus while maintaining the *o*-biphenyl moiety.

**Methyl-JohnPhos.** Given that MeJPhos has not been studied before, its properties are briefly discussed here. MeJPhos is a low-melting  $(55-56 \ ^{\circ}C)$  crystalline solid. The crystal structure exhibits a slightly distorted trigonal pyramid at phosphorus and a dihedral angle of 66.8° for the biphenyl (Figure 3). On the basis of the  $\angle C$ -P-C bond angles (100.3,



**Figure 3.** ORTEP crystal structure of MeJPhos (all H atoms refined). The biphenyl torsion angle is  $66.8^{\circ}$ , and the  $\angle C-P-C$  bond angles are 100.3, 102.7, and 98.7°. Thermal ellipsoids are drawn at 50% probability.

102.7, and 98.7°; Figure 3), there is relatively little steric strain in the solid state. It is notable that, both as a solid and in solution, MeJPhos resists oxidation by O<sub>2</sub>. Experimentally, after 85 h under 1 atm of O<sub>2</sub>, only 8% of a sample in C<sub>6</sub>D<sub>6</sub> solution was oxidized (see Figure S1 in the Supporting Information). In comparison to PPhMe<sub>2</sub> (a non-o-biphenyl structural analogue), this oxidation is approximately 10<sup>3</sup> slower. Other Buchwaldtype ligands displayed oxygen stability almost identical with that of MeJPhos. It is noted that the reasons for O<sub>2</sub> stability in Buchwald-type ligands have been studied.<sup>19</sup>

Electronic Analysis. In general, Buchwald-type ligands are known for their strong  $\sigma$ -donation, especially in comparison to triarylphosphine ligands (e.g., PPh<sub>3</sub>).<sup>3</sup> All phosphines with an aryl substituent are also capable of some  $\pi$ -accepting from the metal, although the  $\pi$ -accepting interaction is weaker than the  $\sigma$ -donation. Both the  $\sigma$ - and  $\pi$ -electronic influences at a metal center play crucial roles in determining the reactivity. Therefore, it is important to understand the degree to which both  $\sigma$ -basicity and  $\pi$ -acidity of the phosphine affect a metal. The traditional Tolman Ni<sup>0</sup>(CO)<sub>3</sub>PR<sub>3</sub> complexes used to measure the electronic parameters of ligands are straightforward to synthesize (in a room-temperature reaction) and can be compared against a large body of literature.<sup>20</sup> However, for our study Tolman's method is disadvantageous because of both the acute toxicity of  $Ni^0(CO)_4$  and the convolution of the  $\sigma$ ligand/metal and  $\pi$ -ligand/metal interactions. To quantify both the  $\pi$ -acidity and  $\sigma$ -basicity of the R-JohnPhos ligands in Figure 2, a series of pseudo-octahedral chromium carbonyl complexes  $(Cr^{0}(CO)_{5}PR_{3})$  was chosen to serve as spectroscopic proxies for the Ni complexes. The  $Cr^0(CO)_5PR_3$  complexes can be compared directly to the Ni<sup>0</sup>(CO)<sub>3</sub>PR<sub>3</sub> complexes by using a well-established linear relationship using <sup>13</sup>C NMR and IR data.<sup>21,22</sup> Solution measurements were chosen to avoid aberrations caused by crystal-packing forces of solid-state measurements.

The  $Cr^{0}(CO)_{5}PR_{3}$  complexes for MeJPhos, EtJPhos, <sup>i</sup>PrJ-Phos, CyJPhos, and <sup>t</sup>BuJPhos were generated in situ by irradiation ( $\lambda > 254$  nm) of  $Cr^{0}(CO)_{6}$  and the ligand in tetrahydrofuran (THF) with a high-pressure mercury arc lamp in a CaF<sub>2</sub> cell (Scheme 1). Substitution quickly occurred. This transformation was monitored over time by infrared spectros-

Scheme 1. In Situ Synthesis of  $Cr^{0}(CO)_{5}PR_{3}$  Species (Boxed for Clarity) Also Showing a Secondary Carbonyl Expulsion Leading to *trans*- $Cr^{0}(CO)_{4}(PR_{3})_{2}$ 

$$Cr^{0}(CO)_{6} \xrightarrow{PR_{3}} Cr^{0}(CO)_{5}PR_{3} \xrightarrow{PR_{3}} trans-Cr^{0}(CO)_{4}(PR_{3})_{2}$$



**Figure 4.** Time-resolved infrared spectroscopy of the carbonyl region for photolysis of  $Cr^{0}(CO)_{6}$  in THF solution with (a) <sup>t</sup>BuJPhos, (b) CyJPhos, (c) <sup>i</sup>PrJPhos, (d) EtJPhos, and (e) MeJPhos. Assigned stretches, complexes, and changes in absorbance intensities over time are noted.

copy to determine the stretching frequencies of the carbonyl ligands in the  $Cr^0(CO)_5PR_3$  product. From these spectra,  $Cr^0(CO)_5PR_3$  (the first species to form) was easily deconvoluted from the *trans*- $Cr^0(CO)_4(PR_3)_2$  complex that formed subsequently.

As shown in Figure 4, irradiation of  $Cr^{0}(CO)_{6}$  in the presence of ligand produced the  $Cr^{0}(CO)_{5}PR_{3}$  species (where  $PR_{3} = R$ -JohnPhos), with carbonyl absorption peaks assigned

according to known values of analogous solution-phase chromium complexes.<sup>23–26</sup> The vibrational force constants were calculated using the Cotton–Kraihanzel model (Figure S2 in the Supporting Information).<sup>24</sup> Note that the Cotton–Kraihanzel calculations do not provide absolute force constants but rather relative force constants for similar complexes. Therefore, the accuracy of the absolute force constants is not as relevant as the relative force constants. The comparison of

relative force constants is both quantitative and meaningful.<sup>27</sup> The results of the calculations are summarized in Table 1.

Table 1. Assigned CO Stretches and Force Constants for the Cr<sup>0</sup>(CO)<sub>s</sub>(R-JohnPhos) Complexes<sup>*a*</sup>

	MeJPhos	EtJPhos	<sup>i</sup> PrJPhos	CyJPhos	<sup>t</sup> BuJPhos
$A_1$	2059.6	2072.5	2072.8	2072.1	2072.1
$B_1$	2003.2	2058.5	2057.6	2056.7	2062.5
Е	1937.5	1935.3	1936.4	1937.1	1937.1
$k_1$	15.5	15.8	15.8	15.8	15.4
$k_2$	16.2	17.1	17.1	17.1	17.2
$k_{ m i}$	0.52	0.99	0.98	0.96	1.01

<sup>*a*</sup>A<sub>1</sub>, B<sub>1</sub>, and E are assigned CO stretches (in cm<sup>-1</sup>). Definitions:  $k_1$  = stretching force constant for CO groups trans to the phosphine (mdyn/Å);  $k_2$  = stretching force constant for CO groups cis to the phosphine (mdyn/Å);  $k_i$  = CO–CO interaction force constant (mdyn/Å).

The Graham treatment<sup>27</sup> (eqs 1 and 2) of these force constants was used to quantify the relative  $\sigma$ -basicity and  $\pi$ -acidity of the R-JohnPhos ligands. These data are summarized in Table 2.

 $\Delta k_1 = \Delta \sigma + 2\Delta \pi \tag{1}$ 

$$\Delta k_2 = \Delta \sigma + \Delta \pi \tag{2}$$

Table 2. Relative  $\sigma$ -Donating and  $\pi$ -Accepting Ability of the R-JohnPhos Ligands Using the Graham Treatment of the Force Constants for the Cr<sup>0</sup>(CO)<sub>5</sub>(R-JohnPhos) Complexes in Table 1 (Relative to <sup>t</sup>BuJPhos)<sup>*a*</sup>

	$\Delta k_1$	$\Delta k_2$	$\Delta \pi$	$\Delta \sigma$	$\Delta \pi$ (%)	$\Delta\sigma$ (%)
MeJPhos	0.321	0.974	-0.653	1.63	-3.80	9.47
EtJPhos	0.0414	0.0666	-0.0252	0.0918	-0.15	0.53
<sup>i</sup> PrJPhos	0.0346	0.0819	-0.0473	0.129	-0.28	0.75
CyJPhos	0.0326	0.0965	-0.0639	0.160	-0.37	0.93
<sup>t</sup> BuJPhos	0	0	0	0	0	0

<sup>*a*</sup>The  $\Delta k_1$ ,  $\Delta k_2$ ,  $\Delta \pi$ , and  $\Delta \sigma$  values are reported in mdyn/Å. The  $\Delta \pi$  and  $\Delta \sigma$  values were normalized over the value of the <sup>t</sup>BuJPhos  $k_2$  force constant (the strongest CO bond measured in this system).

Several interesting trends appear in the data shown in Table 2. First, as expected, the  $\sigma$ -donating and  $\pi$ -accepting abilities for each ligand have an inverse relationship with each other on the basis of the mathematical treatment. Second, a surprising finding is the "zigzag" shape of the  $\sigma$ -donating and  $\pi$ -accepting trends moving from MeJPhos to 'BuJPhos (Figure 5), which is seemingly counterintuitive. The zigzag results indicate there are at least two competing factors driving the trends.

The obvious electronic contributor to phosphine  $\sigma$ -donating ability is the electron-donating ability of the R groups, which follows the trend: Me < Et < <sup>i</sup>Pr  $\approx$  Cy < <sup>t</sup>Bu.<sup>20</sup> However, the observed ordering in Figure 5 (MeJPhos  $\gg$  CyJPhos > <sup>i</sup>PrJPhos > EtJPhos > <sup>t</sup>BuJPhos) is in contrast to the common assumption that groups at phosphorus with greater electron donation cause the phosphine to be a stronger  $\sigma$ -donor. Thus, the electron-donating abilities of the R groups appear to play only a minor role in determining the  $\sigma$ -donating ability of the R-JohnPhos ligands.

Because a higher electron density at phosphorus fails to explain the electronic trend of the R-JohnPhos ligands, it is



n-Acidity relative to 'BuJPhos (%)

-10

Me

**Figure 5.** Relative percent  $\sigma$ -donating and  $\pi$ -accepting data for  $Cr^{0}(CO)_{5}(R$ -JohnPhos) complexes from Table 2.

iÞr

Ċv

tBu

Ét

likely that steric factors account for the discrepancy. Steric influences that affect the electron-donating ability at phosphorus are manifested in two distinct ways for metal complexes: (1) steric hindrance between the metal complex and phosphine resulting in longer P–Cr bonds, a phenomenon known as "front strain", and (2) sterically induced geometric distortions at phosphorus changing the electronics of the lone pair and reducing the ability of the phosphine to  $\sigma$ -donate, known as "back strain".<sup>28,29</sup> The front strain of a phosphine with the  $Cr^{0}(CO)_{5}$  moiety in  $Cr^{0}(CO)_{5}PR_{3}$  is expected to be reasonably minimal (although it is not completely disregarded as playing a minor role in longer P–Pd bonds), suggesting that back strain at phosphorus is responsible for the R-JohnPhos trend in  $\sigma$ -donation. Specifically, it is suggested that the steric hindrance of the R groups on the R-JohnPhos ligands forces the geometry at P to change, leading to more p character in the HOMO and thus poorer overlap with the metal center (vide infra). The phenomenon of bulky alkyl groups causing back strain (and thus weaker basicity) for amines is well established.<sup>29</sup> Though phosphine basicity is typically less affected by back strain in comparison to amines,<sup>30</sup> it can clearly manifest itself in phosphines, as for example in the unpredictable  $pK_a$  shifts for ortho-substituted arylphosphines.<sup>31,32</sup>

Overall, it is suggested that the trend in  $\sigma$ -donation can be rationalized as two competing factors: (1) increasing electron density at phosphorus from MeJPhos to 'BuJPhos, which gives a slightly positive slope from EtJPhos to CyJPhos (Figure 5), and (2) stronger P–Cr bond overlap (increasing from 'BuJPhos to MeJPhos) due to steric factors (mostly due to decreasing back strain), which significantly affects the  $\sigma$ donation of MeJPhos and 'BuJPhos. To explore this hypothesis further, we turned to solid-state structural data for a closer analysis of R-JohnPhos–metal bonding.

Solid-State Structural Analysis: Chromium(0) Complexes. We set out to structurally characterize the  $Cr^{0}(CO)_{5}(MeJPhos)$  complex because of the significant electronic difference we observed in a comparison between MeJPhos and the other R-JohnPhos ligands. Unfortunately, attempts to crystallize the  $Cr^{0}(CO)_{5}(MeJPhos)$  complex were unsuccessful; only the *trans*- $Cr^{0}(CO)_{4}(MeJPhos)_{2}$  complex

%

(Figure 6) was isolable. This crystal structure was compared to those of other chromium phosphine complexes and yielded



**Figure 6.** ORTEP crystal structure of trans- $Cr^{0}(CO)_{4}$ (MeJPhos)<sub>2</sub> (all H atoms refined). Thermal ellipsoids are drawn at 50% probability.



	d <sub>P-Cr</sub> (Å)	<b>d</b> <sub>C-Cr</sub> (Å)	d <sub>C-0</sub> (Å)
MeJPhos	2.319	1.882	1.148
PEt <sub>3</sub>	2.329	1.865	1.161
PPh <sub>3</sub>	2.356	1.884	1.149

Figure 7. Selected bond distances from crystal structure data of *trans*- $Cr^{0}(CO)_{4}(PEt_{3})_{2}$ , *trans*- $Cr^{0}(CO)_{4}(PEt_{3})_{2}$ , and *trans*- $Cr^{0}(CO)_{4}(MeJPhos)_{2}$ .

striking results (Figure 7). Surprisingly, the *trans*- $Cr^{0}(CO)_{4}$ (MeJPhos)<sub>2</sub> complex has a shorter P–Cr bond distance than the analogous *trans*- $Cr^{0}(CO)_{4}$ (PEt<sub>3</sub>)<sub>2</sub> complex. This result is surprising for two reasons: (1) PEt<sub>3</sub> is a stronger  $\sigma$ -donor than MeJPhos (vide infra), which should result in shorter P–Cr bonds, and (2) common metrics to quantify ligand sterics (e.g., the Tolman cone angle<sup>20</sup> and the percent buried volume<sup>33</sup>) show that the PEt<sub>3</sub> ligand is considerably smaller than the MeJPhos ligand (Table S1 in the Supporting Information).

The elongation of the carbonyl  $C\equiv O$  bonds in the *trans*- $Cr^{0}(CO)_{4}(PR_{3})_{2}$  complexes (due to back-bonding from the metal) can be used to determine the  $\sigma$ -donating ability of the phosphine ligands. The carbonyl bond distances show that MeJPhos (C–O bond distance 1.148 Å) is bracketed between PEt<sub>3</sub> (1.161 Å) and PPh<sub>3</sub> (1.149 Å) in its  $\sigma$ -donating ability, as expected for an aryl–alkyl mixed phosphine. From these data, it is concluded that the  $\sigma$ -donating ability of the ligands does not explain the shorter P–Cr bond distance for MeJPhos in comparison to PEt<sub>3</sub>.

The short P–Cr bond in *trans*-Cr<sup>0</sup>(CO)<sub>4</sub>(MeJPhos)<sub>2</sub> appears to be the result of steric interactions between the ligand and pseudo-octahedral metal complex. Even though the average steric profiles of PEt<sub>3</sub> and MeJPhos (as measured by the Tolman cone angle and the percent buried volume) show MeJPhos to be larger overall, the local steric influence of the -PMe<sub>2</sub> moiety must be smaller in comparison to the local steric influence of the PEt<sub>3</sub> ligand in order to form shorter P– Cr bonds. This observation suggests that MeJPhos is capable of retaining a large overall steric profile while sustaining strong and short bonds to metal complexes.

Solid-State Structural Analysis: Palladium(0) Complexes. To further explore the validity of the strong  $\sigma$ -donation and proposed steric explanation for the  $Cr^0(CO)_5(MeJPhos)$ and  $trans-Cr^0(CO)_4(MeJPhos)_2$  complexes, the  $Pd^0(MeJPhos)_2(\eta^2-dba)$  (dba = dibenzylideneacetone) complex was prepared and examined (Figure 8). Because



Figure 8. ORTEP crystal structure of  $Pd^0(MeJPhos)_2(\eta^2-dba)$  (all H atoms refined). Thermal ellipsoids are drawn at 50% probability.

 $Pd^{0}(PR_{3})_{2}(\eta^{2}-dba)$ -type complexes can serve as cross-coupling precatalysts, determining if steric and electronic trends for MeJPhos are general across different metal complexes has significant implications vis-à-vis catalysis. We expected that the significant electronic difference between MeJPhos and the other R-JohnPhos ligands would be manifested as measurable structural features. The structure of  $Pd^{0}(MeJPhos)_{2}(\eta^{2}-dba)$ displays a trigonal-planar palladium center. This structure was compared to two known structures,  $Pd^{0}(PCy_{3})_{2}(\eta^{2}-dba)$  and  $Pd^{0}(PPh_{3})_{2}(\eta^{2}-dba)$  (Figure 9).<sup>34</sup> Three structural features were notable: (1) the C-Pd bond distances in the MeJPhos complex are much shorter than those in the analogous PCy<sub>3</sub> and PPh<sub>3</sub> complexes, (2) the P-Pd bond distances in the MeJPhos complex are also considerably shorter than those in the analogous PCy<sub>3</sub> and PPh<sub>3</sub> complexes, and (3) the "bite angle" (the angle between the two phosphorus atoms and palladium; Figure 9,  $\theta_{P-Pd-P}$ ) is much smaller than those in the analogous PCy<sub>3</sub> and PPh<sub>3</sub> complexes.

Activation of the C=C bond by the palladium is another metric that is often used to determine the electron density at the palladium; however, it is dependent on in-plane conjugation of the adjacent phenyl ring. Unfortunately, it is difficult to deconvolute the effects of back-bonding (elongation of the C= C bond) from effects of phenyl ring conjugation (which is correlated to the dihedral angle,  $\varphi$ , between the C=C plane and the adjacent phenyl ring)<sup>35</sup> because both contribute significantly to the electronic nature of the C=C bond and because  $\varphi$  is inconsistent across the three crystal structures. Thus, the C=C bond distance is not a conclusive metric for these molecules. Likewise, hybridization at the ethylene carbons could not be used to determine activation because the hydrogen atoms were not refined for the Pd<sup>0</sup>(PCy<sub>3</sub>)<sub>2</sub>( $\eta^2$ -dba) and Pd<sup>0</sup>(PPh<sub>3</sub>)<sub>2</sub>( $\eta^2$ -dba) complexes.

Evidence of activation at the C=C bond may also be drawn from the  $\eta^2$ -Pd-(C=C) bond distance. Stronger back-bonding between the palladium and ethylene fragment will yield a shorter  $\eta^2$ -Pd-(C=C) bond distance. The Pd<sup>0</sup>(MeJPhos)<sub>2</sub>( $\eta^2$ -



Figure 9. Selected bond distances, bond angles, and torsion angles from crystal structure data of  $Pd^{0}(MeJPhos)_{2}(\eta^{2}-dba)$ ,  $Pd^{0}(PCy_{3})_{2}(\eta^{2}-dba)$ , and  $Pd^{0}(PPh_{3})_{2}(\eta^{2}-dba).$ 

dba) complex has a considerably shorter  $\eta^2$ -Pd-(C=C) bond distance (average C-Pd bond distance of 2.135 Å) in comparison to those in the analogous PCy<sub>3</sub> (2.175 Å) and  $PPh_3$  (2.163 Å) complexes. Overall, these findings support the hypothesis that MeJPhos is an especially strong  $\sigma$ -donor, even in comparison to PCy<sub>3</sub> or PPh<sub>3</sub>. This observation for the  $Pd^{0}(PR_{3})_{2}(\eta^{2}-dba)$  complexes may be due to front strain at the P-Pd<sup>0</sup> coordination site for the larger PCy<sub>3</sub> and PPh<sub>3</sub> ligands perturbing  $\sigma$ -orbital overlap between the phosphorus and palladium.

PR<sub>3</sub>

PCy<sub>3</sub>

PPh<sub>3</sub>

The short  $P-Pd^0$  distances and narrow "bite angle" (Figure 9,  $\theta_{P-Pd-P}$ ) of MeJPhos (average P-Pd<sup>0</sup> bond distance of 2.301 Å,  $\theta_{P-Pd-P} = 105.7^{\circ}$ ) in comparison to those for the analogous PCy<sub>3</sub> (2.175 Å, 115.6°) and PPh<sub>3</sub> (2.163 Å, 114.9°) complexes suggest a very small steric profile (small front strain) at the phosphorus. In fact, to our knowledge Pd<sup>0</sup>(MeJPhos)<sub>2</sub>( $\eta^2$ -dba) makes the narrowest "bite angle" of any bis-monodentate complex of this type. This suggestion is also supported by comparison to bidentate phosphine palladium dba complexes  $(Pd^{0}(P_{2})(\eta^{2}-dba))$ , where  $P_{2}$  is a bidentate phosphine), which have much smaller bite angles because the phosphines are tethered. Rings formed by the bidentate phosphines and palladium in  $Pd^{0}(P_{2})(\eta^{2}-dba)$  complexes typically have the following bite angles: five-membered rings, ~88°; sixmembered rings,  $\sim 99^{\circ}$ ; eight-membered rings,  $\sim 112^{\circ}$ .<sup>36-41</sup> Bis-monodentate phosphine "bite angles" are wider still. The  $Pd^{0}(MeJPhos)_{2}(\eta^{2}-dba)$  complex has a "bite angle" (105.7°) approximately equivalent to that of a seven-membered ring with palladium. The -PMe2 moieties can make close contacts with the metal and position themselves relatively close to each other, despite MeJPhos being a sterically demanding ligand overall (see Table S1 in the Supporting Information). In summary, the ability of the MeJPhos ligand to form a closer P-Pd<sup>0</sup> bond in a sterically competitive environment likely leads to the superb  $\sigma$ -donation of MeJPhos in comparison to that of PCy<sub>3</sub> or PPh<sub>3</sub>. These findings also suggest that MeJPhos is particularly suited to form palladium complexes which would perform difficult oxidative additions if employed in crosscoupling catalysis (Figure 1).

Solid-State Structural Analysis: Palladium(II)-Phosphorus Bond Lengths (Front Strain). Sixteen trans- $Pd^{II}(Cl)_2(PR_3)_2$  complexes (PR<sub>3</sub> = various phosphines and R-JohnPhos ligands) were also analyzed to better understand structural differences induced by R-JohnPhos ligands. Most of

the 16 crystal structures were obtained through the Cambridge Crystallographic Data Centre (Table S1 in the Supporting Information). The solid-state structures of trans- $Pd^{II}(Cl)_{2}(MeJPhos)_{2}$  and trans- $Pd^{II}(Cl)_{2}({}^{i}PrJPhos)_{2}$  were obtained in this work (Figure 10).



Figure 10. ORTEP crystal structures of (a) trans-Pd<sup>II</sup>(Cl)<sub>2</sub>(MeJPhos)<sub>2</sub> (all H atoms refined) and (b) trans-Pd<sup>II</sup>(Cl)<sub>2</sub>(<sup>i</sup>PrJPhos)<sub>2</sub> (all H atoms refined). Thermal ellipsoids are drawn at 50% probability.

The analysis found the following. First, P–Pd<sup>II</sup> bond lengths varied from ~2.18 to 2.40 Å (Figure 11). On the basis of the other data discussed above, it is not surprising that MeJPhos makes the shortest bond (2.319 Å) to Pd<sup>II</sup> among the R-JohnPhos ligands. This bond distance is the fourth shortest bond of the 16 measured, behind PEt<sub>3</sub>, PMe<sub>3</sub>, and PPhEt<sub>2</sub>. The short P-Pd<sup>II</sup> bond distance for MeJPhos supports the notion that front strain for MeJPhos is very small, especially in comparison to that for the other R-JohnPhos ligands. Note that <sup>t</sup>BuJPhos is absent from Figure 1. This absence is due to the inability of 'BuJPhos to form the trans-Pd<sup>II</sup>(Cl)<sub>2</sub>('BuJPhos)<sub>2</sub> complex (even with considerable synthetic effort on our part). The inability of the complex to form is likely due to extreme steric crowding about the Pd<sup>II</sup> center. Qualitatively, this



*Trans*-Pd<sup>II</sup>(Cl)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> Complexes

**Figure 11.** Phosphorus-palladium bond distances from crystal structure data for 16 representative phosphines (including MeJPhos, EtJPhos, PhJPhos, <sup>i</sup>PrJPhos, and CyJPhos) on Pd<sup>II</sup>. The structural data error was measured at <0.1% at  $\pm 3\sigma$  for all complexes.

complex likely has a longer P–Pd<sup>II</sup> bond in comparison to the other R-JohnPhos ligands, consistent with the  $\sigma$ -donor trends discussed above.

PEt<sub>3</sub> forms a notably shorter  $P-Pd^{II}$  bond than does MeJPhos in the square-planar *trans*-Pd<sup>II</sup>(Cl)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> complexes, which is in contrast to the case (vide supra) of P–Cr bond lengths for the analogous *trans*-Cr<sup>0</sup>(CO)<sub>4</sub>(PR<sub>3</sub>)<sub>2</sub> complexes. This observation suggests that front strain between the ligand and metal complex is the reason that MeJPhos has a bond shorter than that of PEt<sub>3</sub> in the *trans*-Cr<sup>0</sup>(CO)<sub>4</sub>(PR<sub>3</sub>)<sub>2</sub> complexes discussed above. There is inherently less front strain between a ligand and a quare-planar metal complex in comparison to that with an analogous octahedral complex. In general, therefore, MeJPhos appears to form short phosphorus–metal bonds in coordination complexes, but especially so in comparison to other phosphine ligands in metal complexes with steric crowding (e.g., *trans*-Cr<sup>0</sup>(CO)<sub>4</sub>(PR<sub>3</sub>)<sub>2</sub> and Pd<sup>0</sup>(PR<sub>3</sub>)<sub>2</sub>( $\eta^2$ -dba)).

Solid-State Structural Analysis: Phosphine Back Strain on Palladium(II). The geometric distortion at the phosphorus was calculated from crystal structure data for the 16 trans-Pd<sup>II</sup>(Cl)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> complexes. The distortion is directly analogous to back strain experienced by sterically crowded amines.<sup>29</sup> For phosphines, this geometric distortion is measured using the symmetric deformation coordinate or S4' (Figure 12).<sup>28,42</sup> The S4' value is the angular difference between the three ligand  $\angle C-P-C$  angles and  $\angle C-P-Pd$  angles. The distortion from trigonal pyramidal at the phosphorus directly correlates to the hybridization of the lone pair. More distortion toward trigonal planar, caused by sterically bulky R groups at phosphorus, forces the lone pair (HOMO) into a p-like orbital that in turn



**Figure 12.** Structural and geometric parameters defining the symmetric deformation coordinate (S4'). S4' =  $(\alpha_1 + \alpha_2 + \alpha_3) - (\beta_1 + \beta_2 + \beta_3)$ .

has poorer overlap with the metal.<sup>43</sup> This distortion occurs when strong steric influence at phosphorus forces the geometry to be more planar, which results in near-zero or negative S4' values. Conversely, when the substituents directly bonded to phosphorus have low steric influence, there is little distortion and the lone pair is allowed to occupy an sp<sup>3</sup>-like orbital which has strong overlap and directionality to donate to a metal center, which results in larger S4' values. For the phosphines in Figure 13, the S4' values range from 8.6 to 35.3°.



Trans-Pd<sup>II</sup>(Cl)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> Complexes

**Figure 13.** Phosphorus S4' values from crystal structure data for 16 representative phosphines (including MeJPhos, EtJPhos, PhJPhos, <sup>i</sup>PrJPhos, and CyJPhos) on Pd<sup>II</sup>. The structural data error was measured at <1% at  $\pm 3\sigma$  for all complexes.

The calculations show that PhJPhos, EtJPhos, and MeJPhos all have relatively large S4' values (29.77, 29.26, and 27.96°, respectively). These compare very well with the values for low steric profile phosphines such as PPhMe<sub>2</sub> (32.81°) and PMe<sub>3</sub> (35.33°). This finding is in stark contrast to that for the larger CyJPhos, which has a considerable S4' value (16.91°). Again, although 'BuJPhos is not available for analysis here, it likely has a low S4' value on the basis of the two *tert*-butyl groups at phosphorus. The ligand most analogous to 'BuJPhos, PPh-('Bu)<sub>2</sub>, has an S4' value of 18.36°. 'BuJPhos very likely has an S4' value below 18.36°, which qualitatively gives it the smallest S4' value among the R-JohnPhos ligands. The S4' values show that back strain is likely a major contributor to the structural/ electronic relationship between the R-JohnPhos ligands and the metal center. The back strain is especially pronounced in R-JohnPhos ligands for the larger and more electron donating alkyl groups such as <sup>t</sup>Bu and Cy. It is proposed that the significant back strain of the larger R-JohnPhos ligands is a major influence in the poor  $\sigma$ -donating ability of <sup>t</sup>BuJPhos in comparison to the other R-JohnPhos ligands.

Solid-State Structural Analysis: Overall Steric Profile of Phosphines on Palladium(II). Finally, crystal structure data for the 16 *trans*-Pd<sup>II</sup>(Cl)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> complexes was used to calculate the overall steric influence of each phosphine ligand. Though many steric metrics exist,<sup>44</sup> we chose to employ the percent buried volume calculation ( $(V_{bur})$ ).<sup>33,45</sup> This steric metric is related to front strain, but it is distinct in that it measures the influence of the entire ligand on the coordination sphere of the metal (even the distally located moieties that may not affect front strain). This steric analysis has been espthe ecially successful at determining steric profiles for structurally elaborate, large, and unsymmetrical ligands (e.g., N-heterocyclic carbenes and Buchwald-type ligands).  $(V_{bur})$  is defined as the percent of the total volume of a sphere around the metal that is occupied by a ligand (Figure 14). The sphere has a defined



**Figure 14.** Visual representation of the % $V_{\rm bur}$  steric calculation. For the 16 crystal structures analyzed, d = the crystallographic P–Pd bond distance (Å) (Figure 11), r = 3.5 Å, SambVca. mesh spacing was 0.05, all H atoms were included, and bond radii were scaled by 1.17 (as recommended by Cavallo).<sup>45</sup>

radius of 3.5 Å from the metal center, which represents the potential coordination sphere space around the metal. The %  $V_{\rm bur}$  calculation is well suited for crystal structure analysis because it uses a three-dimensional spatial model; thus, actual crystal structure data can be used to determine steric influence between the ligand and the metal. The % $V_{\rm bur}$  calculations were obtained using the SambVca. (Salerno molecular buried volume calculation) software developed by Cavallo and co-workers (available as an online tool).<sup>46</sup>

For the 16 complexes analyzed,  $\% V_{bur}$  varied from 23.6% to 35.0% (Figure 15). Two observations stand out for the  $\% V_{bur}$  values calculated: (1) the steric size of the R groups on PPh(R)<sub>2</sub> and PR<sub>3</sub> ligands trends reasonably well with the overall  $\% V_{bur}$  value, while the R-JohnPhos series does not, and (2) the R-JohnPhos ligands generally have a large  $\% V_{bur}$  (average of 33.6%) with a narrow range (32.7%–35.0%) in comparison with the PPh(R)<sub>2</sub> and PR<sub>3</sub> ligands. The discrepancy in the correlation between  $\% V_{bur}$  and the size of R for the R-JohnPhos ligands is partially due to P–Pd<sup>II</sup> bond distances (with shorter bond distances increasing the  $\% V_{bur}$ 



Figure 15. % $V_{\rm bur}$  calculations from crystal structure data for 16 representative phosphines (including MeJPhos, EtJPhos, PhJPhos, 'PrJPhos, and CyJPhos) on Pd<sup>II</sup>. The structural data error was measured at <1% at  $\pm 3\sigma$  for all complexes.

value). For example, even though cyclohexyl groups are much larger than methyl groups, CyJPhos ( ${}^{W}V_{bur}$  32.7% and P–Pd<sup>II</sup> distance 2.380 Å) is slightly smaller than MeJPhos ( ${}^{W}V_{bur}$  32.8% and P–Pd<sup>II</sup> distance 2.319 Å). Because bond distance alone does not explain the discrepancy across all the R-JohnPhos ligands, it is likely that the *o*-biphenyl moiety also has a dominating effect on the  ${}^{W}V_{bur}$  values for the R-JohnPhos ligands, as seen in the narrow range of values in comparison with the PPh(R)<sub>2</sub> and PR<sub>3</sub> ligands. That is to say, changing the R group on the R-JohnPhos ligands has a nominal effect on the overall steric profile because  ${}^{W}V_{bur}$  is mostly dependent on the *o*-biphenyl moiety's steric influence.

The overall steric profile of a ligand relates to its ability to perform reductive eliminations during cross-coupling (Figure 1). It is believed that a combination of both large steric profile  $({}^{\circ}V_{bur})$  and strong  $\sigma$ -donation are the primary factors responsible for a ligand's success in forming catalytically active Pd species.<sup>18</sup> In Buchwald–Hartwig cross-coupling, oxidative addition is typically the rate-limiting step in the catalytic cycle (especially so with aryl chlorides).<sup>47</sup> It is known that <sup>t</sup>BuJPhos, CyJPhos, and P(<sup>t</sup>Bu)<sub>3</sub> can perform Buchwald–Hartwig crosscoupling reactions with aryl chlorides.<sup>47,48</sup> MeJPhos appears to be an excellent candidate for Buchwald–Hartwig crosscoupling reactions with aryl chlorides because it has a  ${}^{\circ}V_{bur}$ value in the range of that for other ligands known to form catalytically active species (i.e., CyJPhos 32.7%, MeJPhos 32.8%, and P(<sup>t</sup>Bu)<sub>3</sub> 36.5%) and it is a very strong  $\sigma$ -donor.

### SUMMARY AND CONCLUSIONS

The  $\sigma$ -donating abilities of the R-JohnPhos ligands (where R = Me, Et, <sup>i</sup>Pr, Cy, <sup>t</sup>Bu) follow the trend <sup>t</sup>BuJPhos < EtJPhos < <sup>i</sup>PrJPhos < CyJPhos  $\ll$  MeJPhos. If this ordering were to follow a trend based solely on the electron-donating abilities of the R groups (Me < Et < <sup>i</sup>Pr  $\approx$  Cy < <sup>t</sup>Bu), then MeJPhos would be the weakest  $\sigma$ -donor rather than the strongest donor. The conclusion is that factors other than the  $\sigma$ -donating ability of the R group contribute to the net donor ability of these phosphine ligands. The  $\sigma$ -donor ordering is proposed to arise from competition between the intrinsic electron-donating ability of the R groups (increasing from MeJPhos to <sup>t</sup>BuJPhos) and steric interactions (increasing from MeJPhos to <sup>t</sup>BuJPhos) that decrease the electron-donating ability of the phosphine. The steric interactions that affect the electronic contributions of

the ligand to the metal can be divided into categories: (1) steric interactions between the metal moiety and the phosphine (front strain, as measured by the  $P-Pd^{II}$  bond distance) and (2) a distortion of the hybridization at phosphorus caused by interactions of the R groups (back strain, as measured by the S4' value). Both categories of steric interactions appear to play a significant role in determining phosphorus-metal bond distances and  $\sigma$ -donating ability for the R-JohnPhos ligands. Only MeJPhos appears to benefit from low back strain and low front strain. Consequently, MeJPhos can form close metal contacts and small "bite angles" (for bisphosphine complexes). Because the methyl groups are intrinsically poorer electron donating groups in comparison to the other R groups, it is concluded that MeJPhos is a much stronger  $\sigma$ -donor in comparison to the other R-JohnPhos ligands primarily for steric reasons

Another important conclusion of this study is that the  $\sigma$ donating abilities of the R-JohnPhos ligands are very sensitive to the back strain generated by alkyl groups at phosphorus. Back strain, of course, does affect the basicity of amines, but it is not a factor that is typically associated with phosphine donor ability. The R-JohnPhos ligands are unusual in this regard. As discussed in the text, other ortho-functionalized arylphosphines likely have a similar dependence of  $\sigma$ -donating ability on back strain.

Overall, the  $-PMe_2$  moiety of MeJPhos appears to be special in its ability to form short phosphorus—metal bonds while avoiding back strain. The *o*-biphenyl moiety serves to maintain an overall steric profile comparable to that of larger ligands (e.g., CyJPhos). Consequently, the  $-PMe_2$  moiety has a small S4' distortion, has excellent  $\sigma$ -donation to metals, and maintains a large  $%V_{bur}$ . This conclusion suggests that the  $-PMe_2$  moiety is a powerful way to incorporate strong  $\sigma$ donation into "designer" phosphines while retaining other advantageous structural and reactivity properties. For example, MeJPhos benefits from both the large steric profile of the *o*biphenyl and the oxygen resistance that is typical of Buchwaldtype ligands.

Finally, because of its strongly  $\sigma$  donating properties and overall size, it is hypothesized that MeJPhos will be an ideal ligand for Pd Buchwald–Hartwig cross-coupling catalysts. Catalytic cross-coupling studies using this ligand will be reported shortly.

### EXPERIMENTAL SECTION

General Considerations. Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen using either standard Schlenk techniques or a drybox maintained at <1.0 ppm of O<sub>2</sub>. Diethyl ether and tetrahydrofuran (THF) were dried using a DriSolv system using CuO and molecular sieves under argon. All other reaction solvents were purified and dried according to the literature.<sup>49</sup> All commercially obtained reagents were used as received unless otherwise specified. Synthesized organomagnesium reagents were titrated before use using either diphenylacetic acid<sup>50</sup> or No-D NMR spectroscopy<sup>51</sup> to determine concentrations and were stored under Ar at room temperature. Thin-layer chromatography (TLC) was visualized using low-wavelength ultraviolet light (UV) for all aryl species or phosphomolybdic acid otherwise. <sup>1</sup>H NMR spectra were recorded on a 300 or 500 MHz Varian spectrometer (<sup>1</sup>H 300.09 or 500.02 MHz, respectively) and are reported relative to deuterated solvent signals or an internal reference. Data for <sup>1</sup>H NMR spectra are reported as follows: chemical shift ( $\delta$ , ppm), multiplicity, coupling constant (Hz), and relative integration. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a 300 or 500 MHz Varian spectrometer (<sup>31</sup>P 121.48 or 202.13 MHz, respectively) and are reported relative to the external

standard of 0.1% H<sub>3</sub>PO<sub>4</sub> in D<sub>2</sub>O at 0 ppm. Infrared spectra were recorded using a Nicolet Magna-550 Fourier transform infrared spectrophotometer using an air-free fluorite prism solution cell with a 0.1 mm cell thickness. All phosphines were either synthesized as previously reported (vide infra) or purchased. In the cases of [1,1'-biphenyl-2-yl]dicyclohexylphosphine (CyJPhos) and [1,1'-biphenyl-2-yl]di-*tert*-butylphosphine (<sup>t</sup>BuJPhos), the ligands were purchased from Strem Chemicals, Inc., and used without further purification.

X-ray Crystallography. Diffraction intensities were collected at 173 K (Pd<sup>0</sup>(MeJPhos)<sub>2</sub>( $\eta^2$ -dba), trans-Cr<sup>0</sup>(CO)<sub>4</sub>(MeJPhos)<sub>2</sub>, and trans-Pd<sup>II</sup>(Cl)<sub>2</sub>(<sup>i</sup>PrJPhos)<sub>2</sub>) and 200 K (Me-JohnPhos and trans-Pd<sup>II</sup>(Cl)<sub>2</sub>(MeJPhos)<sub>2</sub>) on a Bruker Apex2 CCD diffractometer using Mo K $\alpha$  (Me-JohnPhos, trans-Pd<sup>II</sup>(Cl)<sub>2</sub>(MeJPhos)<sub>2</sub>, and trans- $Pd^{II}(Cl)_2(PrJPhos)_2)$  and  $Cu K\alpha (Pd^0(MeJPhos)_2(\eta^2-dba))$  and trans-Cr<sup>0</sup>(CO)<sub>4</sub>(MeJPhos)<sub>2</sub>) radiation ( $\lambda = 0.71073$  and 1.54178 Å, respectively). Diffractions for  $Pd^{0}(MeJPhos)_{2}(\eta^{2}-dba)$  and trans- $Cr^{0}(CO)_{4}(MeJPhos)_{2}$  were weak; therefore, a strong Incoatec I $\mu S$ Cu source was used. Data for these two crystals were collected up to  $2\theta_{\text{max}} = 133.0^{\circ}$ , but only reflections with  $2\theta_{\text{max}} = 110.0^{\circ}$  have been used in the refinement for Pd<sup>0</sup>(MeJPhos)<sub>2</sub>( $\eta^2$ -dba), due to very weak reflections at the high angles. Even with such restrictions, the appropriate numbers of reflections per refined parameters were used. Space groups were determined on the basis of systematic absences (trans-Pd<sup>II</sup>(Cl)<sub>2</sub>(MeJPhos)<sub>2</sub>) and intensity statistics. Absorption corrections were applied by SADABS.<sup>54</sup> Structures were solved by direct methods and Fourier techniques and then refined on  $F^2$  using full-matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. H atoms in all structures were found from the residual density maps and refined with isotropic thermal parameters without any restrictions, except those in  $Pd^{0}(MeJPhos)_{2}(\eta^{2}-dba)$ , which were refined in calculated positions in a rigid group model. All calculations were performed with the Bruker SHELXL-2013 package.5

**Synthesis of Ligands.** [1,1'-Biphenyl-2-yl]dimethylphosphine (MeJPhos). The synthesis of MeJPhos has been described by our laboratory previously.<sup>12</sup> The general scheme is given below.



MeJPhos was isolated as a white crystalline solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.37 (ddd, *J* = 7.0, 4.1, 1.9 Hz, 1H), 7.29–7.25 (m, 4H), 7.25–7.19 (m, 3H), 7.11 (ddd, *J* = 6.2, 3.9, 2.1 Hz, 1H), 0.97 (d, *J* = 3.8 Hz, 6H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>):  $\delta$  –51.86. The compound was further characterized by single-crystal XRD (Table 3).

[1,1'-Biphenyl-2-yl]diethylphosphine (EJPhos). The synthesis of EtJPhos has been previously described.<sup>16</sup> The general scheme is given below.



In a 25 mL Schlenk flask was placed 2-bromobiphenyl (0.9474 g, 4.0 mmol), and it was then charged with 6 mL of  $Et_2O$ . The solution was then freeze–pump–thawed three times and the flask back-filled with N<sub>2</sub>. The solution was cooled to -10 °C, and freshly titrated *n*-BuLi (4.40 mL, 0.93 M in hexanes, 4.04 mmol) was added dropwise

#### Table 3. Crystallographic Data for Me-JohnPhos<sup>a</sup>

formula: C <sub>14</sub> H <sub>15</sub> P	Z = 4, Z' = 2
formula weight: 214.23	cryst syst: triclinic
a = 7.9111(5) Å	space group: $P\overline{1}$
b = 11.4369(8) Å	T = 200(2)  K
c = 13.9141(9) Å	$\lambda=0.71073~\text{\AA}$
$\alpha = 78.752(3)^{\circ}$	$D_c = 1.183 \text{ Mg/m}^3$
$\beta = 80.116(3)^{\circ}$	$\mu$ (Mo) = 0.193 mm <sup>-1</sup>
$\gamma = 79.644(3)^{\circ}$	$R(F_{\rm o}) = 3.90\%$
$V = 1202.40(14) \text{ Å}^3$	$R_{\rm w}(F_{\rm o}) = 9.22\%$

<sup>*a*</sup>Additional parameters: crystal dimensions  $0.25 \times 0.21 \times 0.14$  mm, F(000) = 456,  $2\theta_{max} = 56.0^{\circ}$ , 26879 reflections, 5817 independent reflections ( $R_{int} = 0.0452$ ), R1 = 0.0390, wR2 = 0.0922, and GOF = 1.012 for 5817 reflections (392 parameters) with  $I > 2\sigma(I)$ , R1 = 0.0563, wR2 = 0.1045, and GOF = 1.012 for all reflections, maximum/ minimum residual electron density +0.277/-0.258 e Å<sup>-3</sup>.

over 15 min. The solution turned yellow upon *n*-BuLi addition, and a white precipitate formed after ~1.5 mL was added. The mixture was stirred at -10 °C for 3 h. A solution of PCl(Et)<sub>2</sub> (504.0 mg, 4.01 mmol, in ~1.0 mL of Et<sub>2</sub>O) was added dropwise over 20 min. The mixture turned orange-red, and a considerable precipitate formed. The mixture was stirred and warmed to room temperature overnight. The mixture was quenched on silica and directly loaded onto a flash-chromatography column for purification (60 mesh silica; either Et<sub>2</sub>O ( $R_f = 0.9$ ) or hexanes ( $R_f = 0.4$ ) can be used) to give a colorless oil (678.1 mg, 70.0% yield). <sup>1</sup>H NMR (300 MHz, benzene- $d_6$ ):  $\delta$  7.45 (dddd, J = 8.1, 5.0, 2.3, 1.2 Hz, 3H), 7.40–7.31 (m, 1H), 7.28–7.06 (m, 5H), 1.52–1.27 (m, 4H), 0.84 (dt, J = 14.3, 7.6 Hz, 6H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene- $d_6$ ):  $\delta$  –26.76.

[1,1'-Biphenyl-2-yl]diisopropylphosphine (<sup>P</sup>PJPhos). The synthesis of <sup>i</sup>PrJPhos has been previously described.<sup>52</sup> The general scheme is given below.



#### 68%

In a 25 mL Schlenk flask was placed 2-bromobiphenyl (0.9380 g, 4.0 mmol), and it was then charged with 6 mL of Et<sub>2</sub>O. The solution was then freeze-pump-thawed three times and the flask back-filled with N<sub>2</sub>. The solution was cooled to -10 °C, and freshly titrated *n*-BuLi (2.0 mL, 2.06 M in hexanes, 4.04 mmol) was added dropwise over 15 min. The solution turned yellow upon n-BuLi addition, and a white precipitate formed after ~1.5 mL was added. The mixture was stirred at -10 °C for 3 h. A solution of PCl(<sup>i</sup>Pr)<sub>2</sub> (625.0 mg, 4.01 mmol, in ~1.0 mL of Et<sub>2</sub>O) was added dropwise over 20 min. The mixture turned pink-red and a considerable precipitate formed. The mixture was stirred and warmed to room temperature overnight. The mixture was quenched on silica and directly loaded onto a flashchromatography column for purification (60 mesh silica; either Et<sub>2</sub>O  $(R_{\rm f} = 0.8)$  or hexanes  $(R_{\rm f} = 0.3)$  can be used) to yield a colorless crystalline solid (734.0 mg, 68.1% yield). <sup>1</sup>H NMR (500 MHz, benzene- $d_6$ ):  $\delta$  7.50–7.38 (m, 3H), 7.26 (dddd, J = 21.0, 7.7, 5.0, 2.3Hz, 2H), 7.18–7.10 (m, 4H), 1.85 (heptd, J = 7.0, 1.4 Hz, 2H), 0.98– 0.86 (m, 12H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, benzene- $d_6$ ):  $\delta$  -5.29.

(iii). Synthesis of Metal Complexes. trans- $Cr^{0}(CO)_{4}$ (MeJPhos)<sub>2</sub>. Under an inert atmosphere of N<sub>2</sub>,  $Cr^{0}(CO)_{6}$  (25.0 mg, 114  $\mu$ mol) with MeJPhos (31.2 mg, 137  $\mu$ mol) and THF- $d_{8}$  (0.5 mL) were placed in a J. Young adapted NMR tube. The sample was frozen, and the headspace was replaced with Ar. The sample was heated to 60 °C for 8 h, observed by NMR, and then freeze–pump–thawed, back-filled with Ar, and heated for another 8 h at 60 °C. After the complete conversion by <sup>31</sup>P NMR, the now yellow solution was vacuumed to dryness and triturated with hexanes, leaving a residue of yellow solids. These solids were taken up into THF and allowed to crystallize by slow evaporation under N<sub>2</sub>, yielding 40.4 mg (60%) of yellow crystalline *trans*- $Cr^{0}(CO)_{4}(MeJPhos)_{2}$ . The compound was further characterized by single-crystal XRD (Table 4). <sup>1</sup>H NMR (500 MHz, chloroform-*d*):  $\delta$ 

### Table 4. Crystallographic Data for *trans*- $Cr^{0}(CO)_{4}(MeJPhos)_{2}^{a}$

formula: C <sub>32</sub> H <sub>30</sub> CrO <sub>4</sub> P <sub>2</sub>	Z = 1, Z' = 0.5
formula wt: 592.50	cryst syst: triclinic
a = 7.3216(3) Å	space group: P1
b = 9.6435(4) Å	T = 173(2)  K
c = 11.8158(4) Å	$\lambda = 1.54178 \text{ Å}$
$\alpha = 67.621(2)^{\circ}$	$D_{\rm c} = 1.350 \ {\rm Mg/m^3}$
$\beta = 72.584(2)^{\circ}$	$\mu$ (Cu) = 4.553 mm <sup>-1</sup>
$\gamma = 76.173(2)^{\circ}$	$R(F_{\rm o}) = 3.54\%$
$V = 728.64(5) \text{ Å}^3$	$R_{\rm w}(F_{\rm o}) = 9.08\%$

<sup>*a*</sup>Additional parameters: crystal dimensions 0.10 × 0.07 × 0.02 mm, F(000) = 308,  $2\theta_{max} = 133.0^{\circ}$ , 8026 reflections, 2550 independent reflections ( $R_{int} = 0.0429$ ), R1 = 0.0354, wR2 = 0.0908, and GOF = 1.057 for 2550 reflections (238 parameters) with  $I > 2\sigma(I)$ , R1 = 0.0395, wR2 = 0.0934, and GOF = 1.057 for all reflections, maximum/ minimum residual electron density +0.290/-0.262 e Å<sup>-3</sup>.

7.66 (dt, J = 12.0, 5.6 Hz, 2H), 7.54–7.49 (m, 4H), 7.25 (t, J = 7.6 Hz, 4H), 7.10 (dt, J = 14.4, 7.6 Hz, 4H), 7.04 (d, J = 7.6 Hz, 2H), 6.98 (t, J = 7.4 Hz, 2H), 1.35–1.18 (m, 12H). <sup>31</sup>P{<sup>1</sup>H} MMR (202 MHz, chloroform-d):  $\delta$  39.66. <sup>13</sup>C NMR (126 MHz, chloroform-d):  $\delta$  223.66 (*carbonyl resonance*, t, J = 12.3 Hz), 144.09–143.93 (m), 143.72, 142.32 (d, J = 11.7 Hz), 142.20 (d, J = 11.8 Hz), 132.00, 131.25, 130.35, 129.14, 128.29–128.15 (m), 22.29 (dd, J = 14.2, 11.1 Hz).

trans-Pd<sup>II</sup>(CI)<sub>2</sub>(MeJPhos)<sub>2</sub>. Pd<sup>II</sup>Cl<sub>2</sub> (58.0 mg, 0.30 mmol) was added to dry THF (2.0 mL) and the mixture stirred vigorously. A solution of MeJPhos (140 mg, 0.60 mmol, 2 mL of THF, ca. 300 mM) was added dropwise to the stirred slurry, and this mixture was stirred overnight at room temperature. The solution went from a purple slurry to a yellow slurry. The mixture was filtered through diatomaceous earth and reduced via vacuum to a yellow-white solid. This mixture was taken up into a minimal amount of THF (ca. 0.5 mL) and dropped into hexanes to precipitate a flocculent yellow solid. This solid was collected and recrystallized by layering a saturated THF solution with hexanes, yielding a yellow crystalline solid (161.6 mg, 68.8%). <sup>1</sup>H NMR (500 MHz, benzene- $d_6$ ):  $\delta$  7.85–7.76 (m, 1H), 7.70–7.61 (m, 1H), 7.27 (t, J = 7.7 Hz, 1H), 7.17–7.00 (m, 2H), 1.26 (t, J = 3.4 Hz, 3H). <sup>13</sup>C NMR (126 MHz, benzene- $d_6$ ):  $\delta$  145.77–144.89 (m), 141.63 (t, J = 1.5 Hz), 133.14–132.49 (m), 132.16 (d, J = 22.5 Hz), 131.04–130.49 (m), 129.86, 129.43, 128.46, 127.96, 127.76, 126.49 (t, J = 4.4 Hz), 112.49, 12.76 (t, J = 15.5 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, benzene- $d_6$ ):  $\delta$  -3.10. The compound was further characterized by single-crystal XRD (Table 5).

trans-Pd<sup>II</sup>(CI)<sub>2</sub>(EtJPhos)<sub>2</sub>. Pd<sup>II</sup>Cl<sub>2</sub> (71.2 mg, 0.4 mmol) was added to dry THF (5 mL) and the mixture stirred vigorously. A solution of EtJPhos (193.9 mg, 0.8 mmol, 5 mL of THF, ca. 160 mM) was added dropwise to the stirred slurry, and this mixture was stirred overnight at room temperature. The solution went from a purple slurry to a redorange slurry. The mixture was filtered through diatomaceous earth and reduced via vacuum to a red-orange oil. This mixture was taken up into a minimal amount of THF (ca. 1 mL) and dropped into hexanes to precipitate a flocculent orange solid. This solid was collected and recrystallized by layering a saturated THF solution with hexanes, yielding a yellow-orange crystalline solid (123.0 mg, 46.3%). <sup>1</sup>H NMR (500 MHz, chloroform-d):  $\delta$  7.95 (d, J = 7.4 Hz, 4H), 7.66 (t, J = 7.5 Hz, 4H), 7.58 (q, J = 10.5, 9.0 Hz, 6H), 7.47–7.33 (m, 4H), 1.95 (ddt, J = 327.6, 14.2, 7.6 Hz, 8H), 1.16 (dt, J = 18.5, 7.7 Hz, 12H). <sup>31</sup>P NMR (202 MHz, chloroform-d):  $\delta$  32.87.

trans- $Pd''(CI)_2(^{\dagger}PrJPhos)_2$ .  $Pd''Cl_2$  (32.8 mg, 0.18 mmol) was added to dry THF (2 mL) and the mixture stirred vigorously. A solution of  $^{\dagger}PrJPhos$  (99.7 mg, 0.40 mmol, 2 mL of THF, ca. 200 mM) was added

## Table 5. Crystallographic Data for *trans*- $Pd^{II}(Cl)_2(MeJPhos)_2^{a}$

formula: C <sub>28</sub> H <sub>30</sub> Cl <sub>2</sub> P <sub>2</sub> Pd	Z = 2, Z' = 0.5
formula wt: 605.76	cryst syst: triclinic
a = 11.6418(13) Å	space group: $P2_1/n$
b = 7.1671(8) Å	T = 200(2)  K
c = 16.4230(17) Å	$\lambda = 0.71073$ Å
$\alpha = 90^{\circ}$	$D_{\rm c} = 1.470 \ {\rm Mg/m^3}$
$\beta = 92.638(5)^{\circ}$	$\mu$ (Mo) = 1.005 mm <sup>-1</sup>
$\gamma = 90^{\circ}$	$R(F_{\rm o}) = 3.76\%$
$V = 1368.8(3) \text{ Å}^3$	$R_{\rm w}(F_{\rm o}) = 8.18\%$

<sup>*a*</sup>Additional parameters: crystal dimensions 0.27 × 0.16 × 0.08 mm, F(000) = 616,  $2\theta_{max} = 56.0^{\circ}$ , 19508 reflections, 4177 independent reflections ( $R_{int} = 0.0425$ ), R1 = 0.0376, wR2 = 0.0818, and GOF = 1.024 for 4177 reflections (211 parameters) with  $I > 2\sigma(I)$ , R1 = 0.0583, wR2 = 0.0930, and GOF = 1.024 for all reflections, maximum/ minimum residual electron density +0.799/-0.703 e Å<sup>-3</sup>.

dropwise to the stirred slurry, and this mixture was stirred overnight at room temperature. The solution went from a purple slurry to a yellow slurry. The mixture was filtered through diatomaceous earth and reduced via vacuum to a yellow-white solid. This mixture was taken up into a minimal amount of THF (ca. 0.5 mL) and dropped into hexanes to precipitate a flocculent light yellow solid. This solid was collected and recrystallized by layering a saturated THF solution with hexanes, yielding a yellow crystalline solid (88.2 mg, 61.4%). <sup>1</sup>H NMR (500 MHz, benzene-*d*<sub>6</sub>):  $\delta$  8.09 (q, *J* = 6.1 Hz, 2H), 7.75 (d, *J* = 7.3 Hz, 4H), 7.24–7.08 (m, 8H), 7.08–7.00 (m, 4H), 2.77–2.57 (m, 4H), 1.24 (dq, *J* = 146.2, 7.4 Hz, 24H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, benzene-*d*<sub>6</sub>):  $\delta$  42.42 (broad). The compound was further characterized by singl-crystal XRD (Table 6).

# Table 6. Crystallographic Data for *trans*- $Pd^{II}(Cl)_2({}^{i}PrJPhos)_2{}^{a}$

formula: C <sub>36</sub> H <sub>46</sub> Cl <sub>2</sub> P <sub>2</sub> Pd	Z = 2, Z' = 0
formula wt: 717.97	cryst syst: triclinic
a = 11.0565(18) Å	space group: $P\overline{1}$
b = 12.827(2) Å	T = 173(2)  K
c = 13.891(2) Å	$\lambda=0.71073~{\rm \AA}$
$\alpha = 71.824(3)^{\circ}$	$D_{\rm c} = 1.378 \ {\rm Mg/m^3}$
$\beta = 73.300(3)^{\circ}$	$\mu$ (Mo) = 0.807 mm <sup>-1</sup>
$\gamma = 70.806(3)^{\circ}$	$R(F_{\rm o}) = 4.66\%$
$V = 1729.8(5) \text{ Å}^3$	$R_{\rm w}(F_{\rm o}) = 8.20\%$

<sup>*a*</sup>Additional parameters: crystal dimensions 0.14 × 0.13 × 0.07 mm, F(000) = 744,  $2\theta_{max} = 56.0^{\circ}$ , 35568 reflections, 8457 independent reflections ( $R_{int} = 0.0964$ ), R1 = 0.0466, wR2 = 0.0820, and GOF = 1.017 for 8457 reflections (370 parameters) with  $I > 2\sigma(I)$ , R1 = 0.0955, wR2 = 0.0984, and GOF = 1.017 for all reflections, maximum/ minimum residual electron density +0.559/-0.989 e Å<sup>-3</sup>.

 $Pd^0(MeJPhos)_2(\eta^2-dba)$ . To a solution of freshly recrystallized<sup>53</sup>  $Pd^0_2(dba)_3 \cdot CHCl_3$  (87.0 mg, 80  $\mu$ mol, 2 mL of THF, ca. 40 mM) was added dropwise a solution of MeJPhos (70.0 mg, 320  $\mu$ mol, 2 mL of THF, ca. 160 mM). Note that if the stoichiometry is less than 2:1 phosphine to Pd, a green insoluble polymeric solid results. The mixture was stirred overnight at room temperature. The brown-red solution was filtered through diatomaceous earth and reduced via vacuum to a brown-red sludge. This mixture was taken up into a minimum amount of Et<sub>2</sub>O (ca. 0.5 mL) and diluted with hexanes to 20 mL, resulting in a brown-red solution. Note that the target complex is insoluble in hexanes but will oil under almost all crystallization conditions (any trace solvent except pure hexanes). The Et<sub>2</sub>O/hexanes mixture was then left to evaporate slowly (the Et<sub>2</sub>O evaporates first), yielding deep red crystals (Pd<sup>0</sup>(MeJPhos)\_2(\eta^2-dba)) in a yellow solution (displaced dba) which can be decanted to purity. Crystals

should be washed several times with hexanes to ensure that any residual dba has been rinsed away. This procedure reliably produced the product in excellent yields (116.9 mg, 95.0%). The complex can also be isolated using gradient column chromatography (60 mesh silica, CH<sub>3</sub>CN,  $R_f$  = 0.9). <sup>1</sup>H NMR (300 MHz, benzene- $d_6$ ):  $\delta$  8.00 (d, J = 15.7 Hz, 1H), 7.86–7.65 (m, 8H), 7.37–6.69 (m, 21H), 5.21–4.71 (m, 2H), 0.92 (dd, J = 93.2, 5.3 Hz, 6H), 0.71–0.59 (m, 6H). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, benzene- $d_6$ ):  $\delta$  –12.47 (d, J = 5.8 Hz), -14.61 (d, J = 5.8 Hz). The compound was further characterized by single-crystal XRD (Table 7).

### Table 7. Crystallographic Data for $Pd^{0}(MeJPhos)_{2}(\eta^{2}-dba)^{a}$

formula: C <sub>45</sub> H <sub>44</sub> OP <sub>2</sub> Pd	Z = 2, Z' = 0
formula wt: 769.14	cryst syst: triclinic
a = 11.1180(6) Å	space group: $P\overline{1}$
b = 11.4477(6) Å	T = 173  K
c = 15.4317(9) Å	$\lambda = 1.54178 \text{ \AA}$
$\alpha = 81.426(2)^{\circ}$	$D_{\rm c} = 1.357 \ {\rm Mg/m^3}$
$\beta = 78.935(2)^{\circ}$	$\mu(Cu) = 5.030 \text{ mm}^{-1}$
$\gamma = 79.538(2)^{\circ}$	$R(F_{\rm o}) = 7.00\%$
$V = 1882.20(18) \text{ Å}^3$	$R_w(F_o) = 16.49\%$

<sup>*a*</sup>Additional parameters: crystal dimensions 0.07 × 0.04 × 0.02 mm, F(000) = 796,  $2\theta_{max} = 110.0^{\circ}$ , 11800 reflections, 4684 independent reflections ( $R_{int} = 0.0824$ ), R1 = 0.0700, wR2 = 0.1649, and GOF = 1.023 for 4684 reflections (442 parameters) with  $I > 2\sigma(I)$ , R1 = 0.0889, wR2 = 0.1755, and GOF = 1.023 for all reflections, maximum/ minimum residual electron density +0.450/-1.114 e Å<sup>-3</sup>.

Time-Resolved Infrared Spectroscopy and Photolysis of Chromium Complexes: General Procedure. Under an inert atmosphere of  $N_2$ ,  $Cr^0(CO)_6$  (2.2 mg, 10  $\mu$ mol) and the R-JohnPhos ligand (10  $\mu$ mol) were placed in a 1.00 mL volumetric flask. The flask was filled to the 1.00 mL mark with THF and mixed until all solids were dissolved. The colorless solution was injected into a fluorite prism liquid IR cell and sealed with air-free Teflon stoppers. Photolysis was performed by sequential exposure of the window of the cell (6 in. from refocusing lens) for varying times (4–144 s) to broad-band UV from a high-pressure Hg arc lamp followed by immediate collection of IR spectra. All solutions turned yellow upon exposure to UV radiation. Displayed spectra are THF subtracted from a blank using the same fluorite prism liquid cell and baseline corrected.

### ASSOCIATED CONTENT

### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02996.

Detailed mathematical treatment of carbonyl absorbance data, calculations of carbonyl force constants, crystallographic data, Tolman cone angle calculations, percent buried volume calculations, <sup>1</sup>H and <sup>31</sup>P NMR spectra of new complexes, and data for selected additional experiments (PDF)

X-ray crystallographic data in CIF format (CIF)

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#### Notes

The authors declare no competing financial interest.

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