Electron-Withdrawing Phosphine Compounds in Hydroformylation Reactions. 1. Syntheses and Reactions Using Mono- and Bis(*p*-toluenesulfonylamino) Phosphines

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The rhodium-catalyzed hydroformylation of 1-hexene has been examined in the presence of members of a new class of electron-withdrawing phosphorus ligands, the *N*-sulfonylphosphoramides. All of the phosphorus compounds in this initial study contain one or two *p*-toluenesulfonylamino (TsN) groups attached to the phosphorus atom, including three compounds that have been described previously, TosL (**1**), a monophosphorus compound with two TsN groups, diTosL (**2**), a diphosphorus compound with one TsN group on each phosphorus atom, and **3**, a chiral amino acid-derived ligand with one TsN and one *O*-acyl group on phosphorus. In addition, two new chelating analogues of **1** containing two- and four-carbon bridges between the phosphorus atoms (**5**, **7**), an analogue of **1** with an ethyl instead of a phenyl group on phosphorus (**8**), a nonchelating monophosphorus analogue of **2** (**10**), and a monophosphorus adduct of the ditosylate of *o*-phenylenediamine (**12**) have been synthesized and used in hydroformylations, and comparison reactions with PPh_3 in THF, toluene, and CH_2Cl_2 have been run. The ^{13}C NMR spectra of **5** and **7** and related diphosphorus compounds have been examined for evidence of false AA′X spectra in which the chemical shifts of the nominally equivalent phosphorus atoms are split by the presence of a single ^{13}C atom. The chelating compound **2** is by far the most effective hydroformylation ligand, giving high turnover frequencies (TOF) and linear to branched (n:i) ratios of the aldehyde product. Reactions of **2** run at a 1000:10:1 ratio of 1-hexene:**2**:Rh(acac)$(CO)_2$ at 84 psi CO/H_2 at 60 °C in THF gave TOF = 440 mol aldehyde/mol Rh/h and an n:i ratio of 10, and at 80 °C gave TOF = 760 and an n:i ratio of 15.8. Reactions with **2** were also run in toluene, giving similar results, and in CH_2Cl_2, giving rise to higher n:i ratios (up to 28.5) but also to faster catalyst deactivation. In the absence of chelation, **10** gave lower turnover frequencies (TOF) and linear-to-branched ratios (n:i), and **1** and **3** also gave lower TOF values and low n:i ratios similar to those of PPh_3 and **10**. The chelating analogues of **1**, **5** and **7**, were very poor ligands and gave n:i ratios characteristic of monophosphorus ligands. Compounds **8** and **12** inhibit all reaction.

Introduction

We recently reported the syntheses of members of a new class of phosphorus ligands, the *N*-sulfonylphosphoramides shown below.[1,2] These phosphorus compounds readily coordinate to tungsten carbonyl complexes, and the infrared and ^{31}P NMR spectra show them to be remarkably electron-withdrawing ligands. While fluorinated phosphines[3−7] are more electron-withdrawing, these *N*-sulfonylphosphoramides would appear to be more readily subject to electronic and steric tuning. One reaction that might be expected to benefit in terms of rate and regioselectivity from such phosphorus ligands is the rhodium-catalyzed hydroformylation reaction.[8] Intensive efforts in recent years have uncovered phosphorus promoters that give faster rates of reaction and higher ratios of linear (n) to branched (i) aldehydes for the hydroformylation of 1-alkenes than does PPh_3.[9,10] For instance, chelating bis(diphenylphosphino) ligands with large bite angles give high n:i ratios, but not at especially high rates,[11,12] and both higher rates and n:i ratios can be observed with trifluorom-

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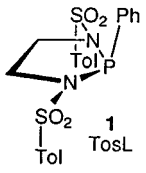
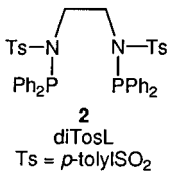
ethyl-substituted arene moieties on phosphorus.[13,14] Such a result was anticipated because strong donor ligands such as alkyl phosphines give relatively slow rates and low n:i ratios compared to ligands that are weaker donors and stronger π-acceptors such as phosphites.[9] Recent work has shown that bulky nonchelating phosphites can give extraordinary rates of reaction, albeit with low regioselectivity,[15] but bulky diphosphites can give both high rates and high n:i ratios.[16−18]

Considerations of electronic properties prompted Moloy's recent work on pyrrolyl phosphines,[19,20] and this class of electron-withdrawing phosphorus ligands in which P−N bonds are present holds promise in promoting the hydroformylation reaction.[21−23] van Leeuwen more recently described phosphorus diamide ligands, each possessing two P−N bonds, which are both electron-withdrawing and sterically bulky, and these ligands exhibit high reactivity but low n:i ratios.[24]

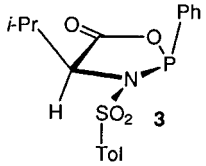
The sulfonylphosphoramides represent a third class of electron-withdrawing phosphorus ligands in which P−N bonds are present. In this paper, we describe initial hydroformylation results for this class, specifically those phosphines including TosL (**1**) and diTosL (**2**) that have one or two toluenesulfonylamino moieties on phosphorus, as well as **3**, which also has an *O*-acyl moiety on phosphorus. In addition, for this study we sought to prepare and test in catalytic reactions (1) potentially chelating analogues of TosL, in which the phenyl group on phosphorus would be replaced by a carbon bridge to another TosL moiety, (2) a nonchelating analogue of diTosL, in which the two-carbon bridge would be replaced by an electronically similar ethyl group, and (3) analogues of diTosL with different linking groups in place of the two-carbon bridge.



1 TosL



2 diTosL
Ts = *p*-tolylSO$_2$



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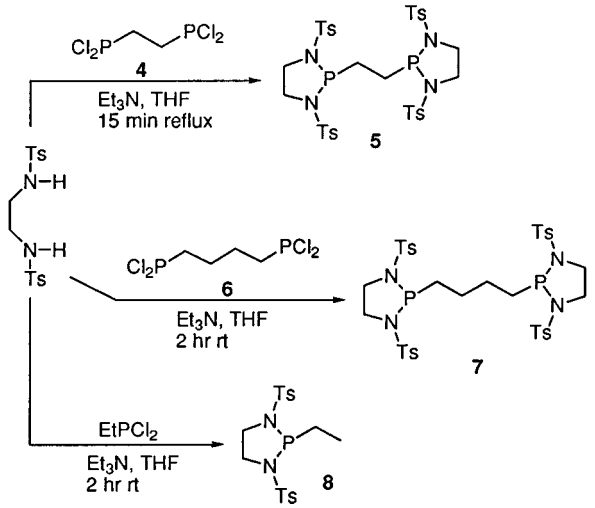
Scheme 1



Results

Synthesis of Analogues of TosL (1). To prepare potentially chelating analogues of TosL, the bis(dichlorophosphino) starting materials **4** and **6** shown in Scheme 1 were combined with *N*,*N*′-(ditoluenesulfonyl)-1,2-diaminoethane to give compound **5** with a two-carbon bridge between the phosphorus atoms and **7** with a four-carbon bridge. In addition, since both **5** and **7** have alkyl groups attached to phosphorus in the form of the C_2 and C_4 bridges rather than the phenyl group of TosL, the ethyl analogue of TosL (**8**) was also prepared as shown from $EtPCl_2$. The starting material **4** is commercially available, while **6** is available via a two-step procedure starting from $(Et_2N)_2PCl$ and the di-Grignard reagent from 1,4-dibromobutane to give $(Et_2N)_2P(CH_2)_4P(NEt_2)_2$ (**9**), which is then chlorinated with PCl_3 to give **6**.[25] While the crude yields of **5** and **7** were adequate, separation from the $Et_3NH^+Cl^-$ byproduct was challenging. For **5** this was accomplished by repeated treatment with methylene chloride, in which the ammonium salt dissolves more rapidly than does **5**, while for **7** one fraction was purified by selective removal of $Et_3NH^+Cl^-$ by methylene chloride as was done for **5**, while another fraction was purified by using chloroform instead to remove the salt. Both **5** and **7** are insoluble in most solvents, including benzene, ether, THF, acetone, ethanol, nitromethane, and acetonitrile, while they are slightly soluble in methylene chloride, DMF, and nitrobenzene and less soluble in chloroform.

An alternative bicyclic structure for **5**, shown in Figure 1, cannot be ruled out on the basis of the number of peaks observed in the NMR spectra. That is, the symmetries of the two structures are identical: for instance the four tolyl groups and the four carbon atoms bridging the nitrogen atoms are identical in each structure, and the hydrogen atoms on the carbon atoms linking the nitrogen atoms are an AA′BB′ set. However, the ^{13}C signal for the putative heterocycle carbon atom of **5** appears as a triplet with the outer two lines separated by 5.8 Hz, and compound **7** exhibits a doublet (but see below) for the analogous carbon with $^2J_{PC} = 5.8$ Hz. The ^{13}C triplet for **5** arises due to virtual

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Table 1. NMR Data for Phosphorus Compounds

compd[a]	$J_{PP'}$	C_1 ppm ($\Delta\nu$)[b]	$^1J_{PC}$	$^2J_{PC}$	C_2 ppm ($\Delta\nu$)[b]	$^2J_{PC}$	$^3J_{PC}$	$C_{1'}$ ppm[c]	$^2J_{PC}$
diphos[d]	35	23.81 (3)	15	−11					
diTosL (**2**)	0	49.20		0			0		
4	0	34.70	50	9					
5	18	28.15 (5.6)	34.5	−13				48.22	5.8
dppb	1.9	27.73	11.6		27.56 (0.8)	16	13		
6	0.8	41.86	45		23.49 (1)	13.5	10		
7	1.0	36.18	32		23.91	15.5	13.5	48.18	5.8
8		29.15	31		6.6	16		47.76	5.4
9	1.0	28.29	3.4		27.39 (1)	22.5	14.5	$C_{1'}$: 42.82	15.5
								$C_{2'}$: 15.24	$^3J_{PC}$: 2.8
Ph_2PNEt_2[e]								$C_{1'}$: 42.80	16.5
								$C_{2'}$: 14.61	$^3J_{PC}$: 2.8

[a] diphos: $Ph_2PCH_2CH_2PPh_2$; dppb: $Ph_2PCH_2CH_2CH_2CH_2PPh_2$. [b] $\Delta\nu$ is the shift difference in Hz (at 162 MHz ^{31}P) for the magnetically and chemical shift *in*equivalent phosphorus atoms in a nominally symmetrical P_2C_2 moiety where one phosphorus atom is near ^{13}C and one is near ^{12}C. [c] $\Delta\nu = 0$ Hz in all cases for C_1' (the carbon atom in the 1,3,2-diazaphospholidine ring). [d] Ref 26. [e] Ref 1.

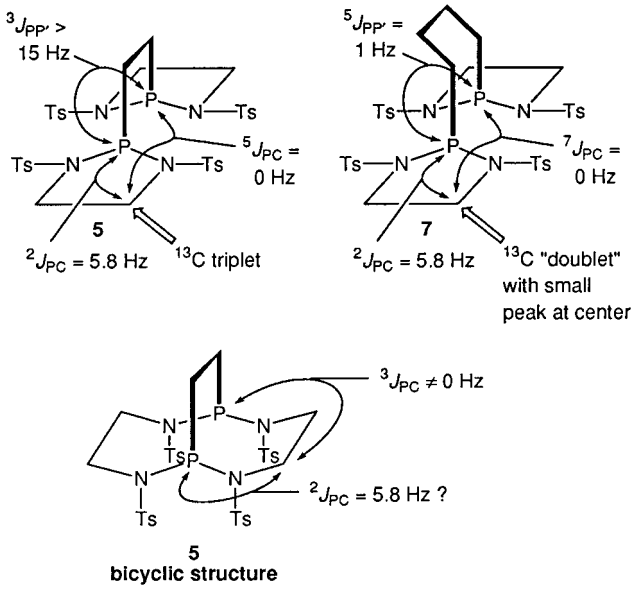

Figure 1. Comparison of structures and NMR coupling pathways for **5**, **7**, and a possible bicyclic stucture of **5**.

coupling to phosphorus since $^5J_{PC} = 0$ Hz and is consistent with $^3J_{PP'} > 15$ Hz and, exactly as in **7**, with $^2J_{PC} = 5.8$ Hz. The doublet for **7** in fact has a small inner peak that also arises due to virtual coupling (since $^7J_{PC} = 0$ Hz), due to $^5J_{PP'} = 1$ Hz. While the bicyclic structure of **5** seems improbable just from an entropic point of view, the similarity of the $^2J_{PC}$ values between the bicyclic version of **5** and bis(monocyclic) **7** would be surprising, given the differences in ring size and dihedral angle between carbon and the phosphorus lone pair. For the monophosphorus compounds TosL and its ethyl analogue **8** both the coupling constants ($^2J_{PC} = 5.7$ and 5.4 Hz, respectively, for TosL and **8**) and chemical shifts (47.98 and 47.76 ppm, respectively) are also similar to those in **5** and **7**, and so the simple 1,3,2-diazaphospholidine structure is the most plausible. A second possible problem for the bicyclic structure is that a triplet might not be expected because coupling to *both* phosphorus atoms (that is, $^3J_{PC}$ along with $^2J_{PC}$) would be present. That is, in the bicyclic structure there are two coupling pathways between the remote phosphorus atom and the carbon next to nitrogen, one of which is five bonds as in the nonbicyclic structure, but one which is only three bonds as shown. For four compounds with four-carbon bridges between the phosphorus atoms (**6**, **7**, **9**, and bis(diphenylphosphino)butane, dppb) that we have examined, $^3J_{PC}$ is only slightly lower than $^2J_{PC}$ (see Table 1). However, simulation of the NMR spectrum of bicyclic **5** shows that for reasonable values of $^3J_{PP'}$ and $^3J_{PC}$ the observed triplet is in fact still expected, so here too, there is no evidence to reject the bicyclic structure. Nonetheless, the coupling constant and chemical shift data are completely in accord with the expected nonbicyclic structure of **5**.

NMR Spectra of Diphosphines. The ^{13}C NMR spectra of **4** − **7** as well as a precursor to **6**, $(Et_2N)_2P(CH_2)_4P(NEt_2)_2$ (**9**), and several reference compounds were examined in order to look for additional examples of so-called false AA′X spin systems,[26] in which the presence of a single ^{13}C nucleus renders the two phosphorus atoms (the "AA′" pair) chemical-shift inequivalent and so the system exhibits an ABX spectrum. Data are collected in Table 1. The simplest spectrum is that due to **4**, a doublet of doublets with no indication of any splitting of the ^{31}P chemical shifts and also no indication of any phosphorus−phosphorus coupling. If $^3J_{PP'} \geq 0.5$ Hz, then a peak would be observed at the midpoint of the multiplet, but none is detected. The one-bond phosphorus−carbon coupling constant for **4** is high ($^1J_{PC} = 50$ Hz), but so is that for **6** ($^1J_{PC} = 45$ Hz), so there is no evidence that different parameters (that might include a nonzero $^3J_{PP'}$) should be sought to fit this spectrum. In contrast to **4**, the *N*-sulfonyl analogue **5** exhibits quite a large ^{31}P chemical shift split for the isotopomer with ^{13}C in the two-carbon bridge, $\Delta\nu_{PP'} = 5.6$ Hz (∼0.03 ppm at 162 MHz), on the basis of the observation of six peaks for this signal; in addition, unlike **4**, $^3J_{PP'} = 18$ Hz. We previously reported that for this isotopomer of diphos, $\Delta\nu_{PP'} = 3$ Hz (∼0.02 ppm at 162 MHz) and $^3J_{PP'} = 35$ Hz.[26]

The ^{13}C NMR spectra of the diphosphines with four-carbon bridges show little isotopic splitting of the phosphorus chemical shifts. The compounds all exhibit small values for $^5J_{PP'}$ of 0.8−1.9 Hz, and all exhibit a small chemical shift difference for the phosphorus atoms in the 2-^{13}C isotopomer with the exception of the new diphosphine **7**, for which $\Delta\nu_{PP'} = 0$ Hz. Values for diTosL are also included in Table 1 and might be comparable to these compounds since it has a four-atom bridge, but it exhibits a singlet for the bridging carbon atoms and so it is simplest to assume (albeit it is somewhat surprising) that all J_{PC} coupling constants are zero. The bis(diethylamino) phosphine **9** exhibits a surprisingly

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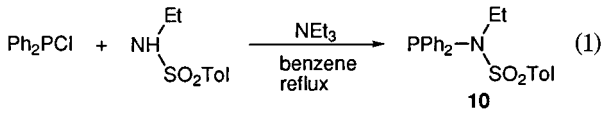
small value for $^1J_{CP}$ of 3.4 Hz, but the values for $^2J_{CP}$ and $^3J_{CP}$ are comparable to those of dppb, **6**, and **7**, and comparison to the chemical shifts and coupling constants of Ph_2PNEt_2 confirms the peak assignments. The NEt_2 group makes the phosphorus atom electron-rich in its binding to tungsten, in contrast to the groups attached to phosphorus in the other compounds, and so one could propose that, empirically, the value of $^1J_{CP}$ provides a suggestive correlation with electronic character of phosphorus. That is, chlorine renders phosphorus quite electron-deficient and gives the highest value of $^1J_{CP}$ (45 Hz in **6**), the *N*-sulfonyl moiety is somewhat less electron-withdrawing ($^1J_{CP}$ = 32 Hz in **7**), phenyl is even less so ($^1J_{CP}$ =11.6 Hz in dppb), and the electron-donor Et_2N moiety gives the lowest value of $^1J_{CP}$ = 3.4 Hz in **9**.

Synthesis of Analogues of diTosL (2). Both chelating and nonchelating analogues of diTosL (**2**) were examined next. A monodentate analogue of diTosL that was expected to be electronically equivalent to it was prepared in a straightforward manner according to eq 1 to give **10**; the *N*-methyl analogue has been described



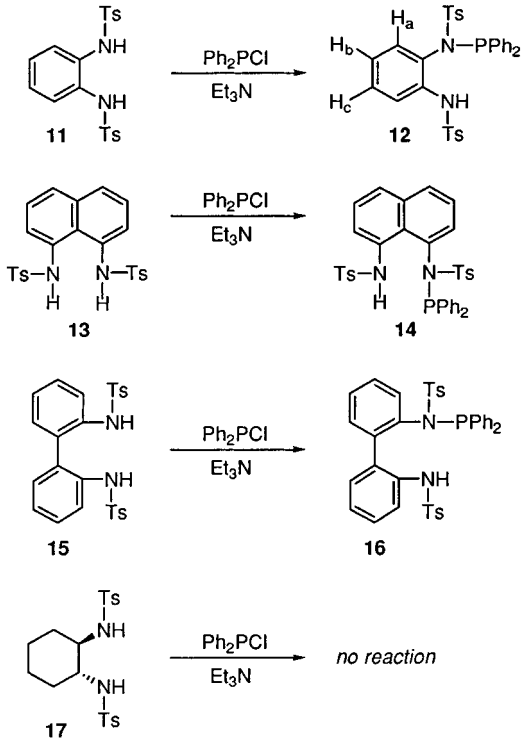
(1)

10

(in brief) previously.[27] In an attempt to prepare an acyclic analogue of TosL, TsN(H)Et was also combined with $PhPCl_2$, but interestingly only a single chloride could be displaced.[28] As will be described now, this was our first indication that the steric effect of the *N*-toluenesulfonyl group is significant.

Several attempts were made to prepare analogues of diTosL with different backbone groups linking the nitrogen atoms, but like the reaction above of TsN(H)Et and $PhPCl_2$, all failed due to what is apparently the unappreciated steric constraints imposed by the toluenesulfonyl moiety. As shown in Scheme 2, reaction of Ph_2PCl was carried out with four different bistoluenesulfonamides. Reaction of the bistoluenesulfonamide of *o*-phenylene diamine (**11**) with 2 equiv of Ph_2PCl and Et_3N immediately gave a material that exhibited in the ^{31}P NMR a peak at 82 ppm due to unreacted Ph_2PCl, one strong new peak at 72 ppm, and consistently also a new peak at 75 ppm that was as much as 15% of the total. Both new peaks are consistent with that expected for the desired product, since the chemical shifts of diTosL and **10** are 60.37 and 55.12 ppm, respectively. The relative ratio of these peaks changed little upon stirring for 48 h or refluxing for 1 h. The ^1H NMR spectrum exhibited two peaks of equal intensity due to toluene methyl groups, and the same ^1H and ^{31}P NMR spectra were obtained when only 1 equiv of Ph_2PCl and Et_3N were used. Isolation of the product and subsequent elemental analysis confirmed that the product is **12** (^{31}P NMR: 72.1 ppm), and only a single diphenylphosphine moiety is incorporated. In fact, this result has precedent in the work of Stetter, who found that **11** could not be *di*alkylated by any group larger than ethyl or allyl.[29]

Scheme 2



The ^1H NMR spectrum of **12** exhibits interesting aromatic proton chemical shifts. For comparison, the four phenyl protons of **11** exhibit an AA′BB′ pattern at 6.97−7.03 ppm. Upon incorporation of the Ph_2P moiety, the symmetry of the molecule is broken, and three of the four phenylene protons are well separated from the remaining tolyl and phenyl signals. While one signal appears as a triplet of doublets at 6.98 ppm ($^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.3 Hz) and so is assigned as H_c (Scheme 2), two signals are shifted well upfield, to 6.42 ppm (H_b, triplet of doublets, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.4 Hz) and 5.86 (H_a, doublet of doublets, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.4 Hz). We propose that the steric bulk of the Ph_2P moiety forces the geminal toluenesulfonyl group to lie in close proximity to H_a in particular, so that H_a lies above the face of the toluene group and so is shielded by over 1 ppm. While this shielding could also be due to an inductive effect from the Ph_2P moiety, the same reaction with the bis(*butane*sulfonyl) analogue of phenylene diamine gives comparable shifts for the phenylene triplets, but the ortho hydrogen doublet appears at 6.88 ppm.[30]

Several experiments were conducted using *n*-butyllithium to generate the dianion of **11** followed by reaction with Ph_2PCl. For instance when BuLi at −40 °C was used, complete reaction of **11** occurred, but only a ∼1:1 ratio of Ph_2PCl and **12** formed. While molecular models indicate that the bisdiphenylphosphino adduct of **11** is a feasible target, we have no evidence that it forms or is stable, and the identity of the material giving rise to the ^{31}P NMR peak at 75 ppm is unknown.

The reaction of **13** with Ph_2PCl indicated that even more steric hindrance is present. As with the reaction of **11** to give **12**, excess Ph_2PCl gave only the monophosphine adduct **14**; a single phosphorus peak is seen

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Table 2. Results of the Hydroformylation of 1-Hexene[a]

entry	L[b] (equiv), T[c] (°C)	solvent	time (h)	n/iso[d]	aldehyde yield (%)	2-hexene yield (%)	TOF[e]
1	none	THF	4	3.1	5	46	14
2	PPh_3 (10)	THF	4	3.1	99	1	250
3	PPh_3 (10)	toluene	4	3.1	100	0.3	390
4	PPh_3 (10)	CH_2Cl_2	4	3.3	95	0	430
5	**1** (10)	THF	4	2.8	37	41	120
6	**2** (2)	THF	5	9.8	76	8	300
7	**2** (10)	THF	5.5	10.1	85	9	440
8	**2** (20)[f]	THF	6	11.0	9	0	150
9a	**2** (10), 80	THF	3	15.8	83	18	760
9b[g]	**2** (10), 80	THF	2	15.1	86	10	760
10a	**2** (10), 80	toluene	3	13.3	79	13	710
10b[g]	**2** (10), 80	toluene	3	12.9	89	5	720
11	**2** (10)	CH_2Cl_2	4	17.3	82	11	280
12	**2** (2), 80	CH_2Cl_2	3	16.7	50	39	410
13a	**2** (10), 80	CH_2Cl_2	2	21.1	63	13	490
13b[g]	**2** (10), 80	CH_2Cl_2	2	17.5	53	15	340
14	**3** (10)	THF	6	3.5	19	3	120
15	**5** (2)	CH_2Cl_2	4	3.8	15	10	37
16	**7** (2)	CH_2Cl_2	4	2.8	15	14	50
17	**8** (10)	THF	4		0	0	0
18	**10** (5)	THF	4	2.6	58	15	170
19a	**10** (5)	THF	4	2.6	59	15	170
19b[g]	**10** (5)	THF	2	2.6	24	7	120
20	**10** (26)	THF	4	2.7	92	6	230
21	**12** (10)	THF	6	4.8	2	0.7	4

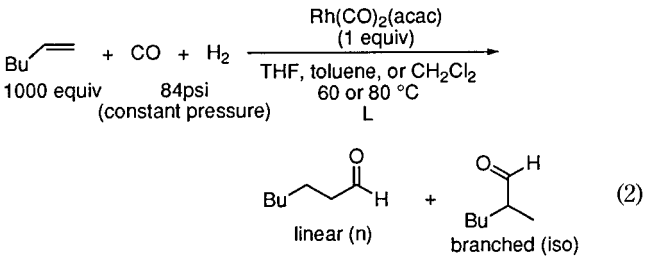
[a] For all reactions except as noted, catalyst precursor $[Rh(CO)_2(acac)] = 0.001$ M, [alkene] = 1.0 M, alkene:Rh = 1000:1, temperature = 60 °C, and CO/H_2 pressure = 84 psi (7 atm). [b] **1** is TosL, **2** is diTosL. [c] $T = 60$ °C if not indicated. [d] n/iso = ratio of linear aldehyde (heptanal) to 2-methylhexanal. [e] TOF = turnover frequency = mol aldehyde/mol Rh/h; value reported is for the linear region of the reaction (see text). [f] $[Rh(CO)_2(acac)] = 0.0001$ M, [alkene] = 1.0 M, alkene:Rh = 10000:1. [g] A second aliquot of 1000 equiv of 1-hexene was added to the reaction listed on the previous line in the table after the number of hours listed for that entry.

at 70.66 ppm, comparable to that seen for **12**, and two methyl signals for the two tolyl groups are seen in the ^{1}H NMR spectrum. Unlike **12**, however, longer reaction times or refluxing resulted in increased decomposition, so **14** itself may not be thermally stable. No further purification was attempted. While Stetter's results are consistent with ours for **11**, in the case of **13** he observed only monomethylation and did not report results for larger groups;[29] clearly at least reaction with the relatively large Ph_2P moiety is feasible.

Reaction of **15** with Ph_2PCl was expected to be much less subject to steric constraints; the 90° rotation of the two phenyl rings was expected to lower the hindrance at nitrogen. In addition of course, the desired diphosphine is analogous to the BISBI ligand (see Discussion section)[11,31] in which CH_2 groups are present in place of nitrogen. However, the reaction was once again comparable to that of **11** to give **12**; excess Ph_2PCl apparently gave only monophosphine adduct **16**. A variety of conditions (stirring at room temperature up to 6 days, refluxing for 17 h, using up to 6 equiv of Ph_2PCl) gave material that exhibited two peaks in the ^{31}P NMR at 74.1 and 72.2 ppm in a ~1:1.7 ratio and exhibited two sets of methyl singlets (due to the tolyl groups) in a similar ratio in the ^{1}H NMR spectrum, but integration of these signals suggested that only a single Ph_2P moiety was present. On the basis of work carried out with the butanesulfonyl analogue of **15**,[30] it is likely that the monophosphine compound exists as a mixture of interconverting diastereomers. Further work on this compound was dropped.

Last, reaction of the bis secondary amide **17** with Ph_2PCl failed to give any phosphorus-containing product. Whether the reaction was carried out at room temperature for 3 h or refluxed for 15−20 h in benzene or THF, no signals were observed in the ^{31}P NMR spectrum in the expected region around 70 ppm, and mostly unreacted Ph_2PCl (at room temperature) and **17** (even after reflux) were observed.

Hydroformylation Results. Reactions were carried out as shown in eq 2, and data are collected in Table 2. While the usual hydroformylation solvents are toluene



(2)

and benzene, TosL is insoluble in those solvents, and so we primarily used THF. Entry 1 is the "blank" reaction carried out in the absence of any phosphine and gave only a 5% yield of aldehyde in 4 h along with a 46% yield of the isomerized product 2-hexene. A more realistic point of comparison is entry 2, for PPh_3 in THF; in most cases a 10:1 ratio of ligand:Rh was used. Here a 99% yield of aldehyde with an n:i ratio of 3.1 was obtained after 4 h reaction with only 1% isomerization to 2-hexene. The same reaction in toluene and methylene chloride (see below) similarly gave essentially quantitative yields of aldehyde in 4 h, each with comparable n:i ratios (entries 3, 4). Turnover frequencies (TOF) were also determined for each reaction, in units of mol aldehyde/mol Rh/h as follows: Samples were withdrawn by gastight syringe at several time points

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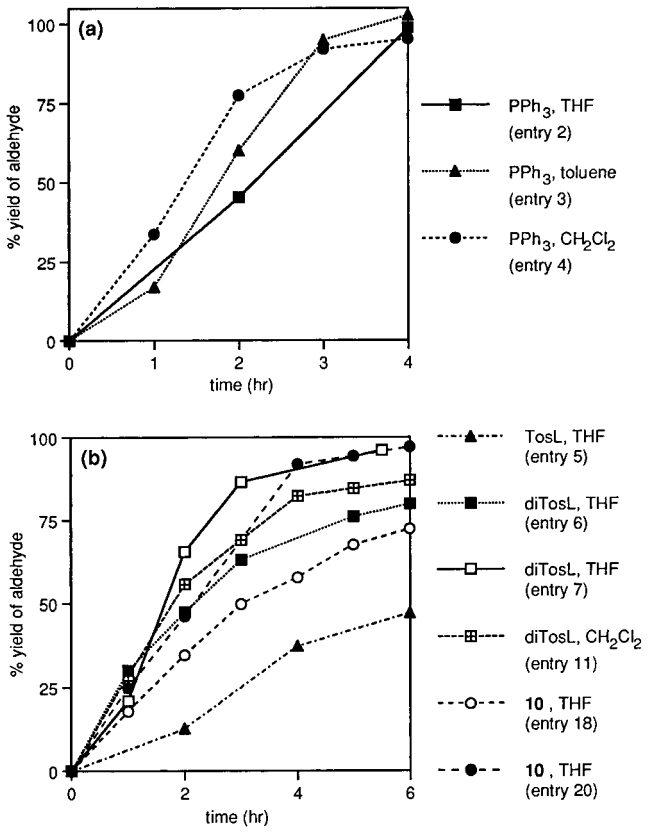


Figure 2. (a) Plot of % yield of aldehyde vs time for PPh_3-promoted hydroformylation reactions as a function of solvent. (b) Plot of % yield of aldehyde vs time for selected runs promoted by TosL, diTosL, and **10**.

from 1 to 6 h and analyzed by ^1H NMR (see Experimental Section for details). The yield of aldehyde was plotted against time, and the best fit straight line to the linear portion of the reaction was used to calculate the TOF. Data for the PPh_3 runs are plotted in Figure 2a and for several representative runs in Figure 2b. In many cases the TOF did not change significantly over the course of the reaction (i.e., entry 2) or increased after the first hour (i.e., a modest induction period was evident, as in entry 3, and to a lesser extent in entry 4) before declining as the hexene concentration dropped (entries 3, 4). Both from the raw data (Figure 2a) and from the derived TOF values, it can be seen that as a function of solvent, for PPh_3 the order of reactivity was CH_2Cl_2 > toluene > THF: for instance at the 2 h time points these three reactions range from 78 to 45% complete in that order, and the TOF values are 430, 390, and 250 mol aldehyde/mol Rh/h, respectively.

Use of the nonchelating ligand TosL (entry 5) showed it to be a poor ligand for hydroformylation, in terms of yield (37% in 4 h, TOF = 120), regioselectivity (n:i ratio = 2.8), and formation of 2-hexene (41% in 4 h). The chiral analogue of TosL, **3**, is also a poor ligand (entry 14), in that the reaction slowed significantly after 1 h (TOF = 120) and gave an aldehyde yield of only 19% in 6 h and a low n:i ratio of 3.5; unlike TosL, however, isomerization to 2-hexene was also slow, with a yield of only 3%.

Chelating ligand diTosL is a much more interesting ligand, giving a much higher n/i ratio of 10 for hydroformylation of 1-hexene in THF (entries 6−8). Three experiments were carried out at diTosL:Rh ratios of 2, 10, and 20, and each gave comparable n:i ratios. At the lowest diTosL:Rh ratio, the reaction rate was rapid during the first hour of reaction (TOF = 300) and then gradually decreased, while the best result (TOF = 440) was obtained at a diTosL:Rh ratio of 10:1. The experiment carried out at a 20:1 diTosL:Rh ratio was carried out at a 10,000:1 alkene:Rh ratio, rather than the usual 1000:1 ratio. After 6 h a 9% yield of aldehyde was obtained, giving a TOF of 150. This 2-fold drop in TOF for a 10-fold drop in rhodium concentration shows that the TOF is fairly insensitive to rhodium concentration and might be due to an induction period. Switching solvent from THF to methylene chloride (entry 11) gave a striking change in n:i ratio from 10 in THF to 17 in CH_2Cl_2, while giving a lower TOF value of 280 but a similar amount of isomerization to 2-hexene. Increasing the temperature to 80 °C in CH_2Cl_2 and using a 2:1 diTosL:Rh ratio gave after 1 h a 41% yield of aldehyde with a 28.5:1 n:i ratio (entry 12, TOF = 410), but unfortunately the amount of isomerization to 2-hexene dramatically increased, to an 18% yield. After 1 h, formation of aldehyde essentially stopped, but isomerization to 2-hexene continued.

Three other experiments were carried out at 80 °C, and since the above reaction in CH_2Cl_2 suggested that catalyst decomposition occurred, catalyst lifetime was checked by addition of a second aliquot of 1-hexene. Increasing the diTosL:Rh ratio to 10 in CH_2Cl_2 gave a higher yield and TOF (490) in the first hour of reaction (entry 13a), and the reaction slowed but did not stop in the second hour of reaction. Addition of a second aliquot of 1-hexene (entry 13b) to the catalyst solution resulted in continued hydroformylation at a high but somewhat slower rate (TOF = 340) with a high but again somwhat lower n:i selectivity (17.5 vs 21.1 for the first aliquot of 1-hexene). Use of THF as the solvent at high temperature (entries 9a,b) gave complete consumption of 1-hexene within 2 h, with a higher n:i selectivity (15.8 vs 10.1 at 60 °C) and higher rate (TOF = 760 vs 440 at 60 °C). More isomerization to 2-hexene was also observed. After waiting an additional hour, the second aliquot of 1-hexene was added, and the reaction resumed at the same rate, with essentially the same n:i ratio, but with less isomerization to 2-hexene. Since diTosL is soluble in toluene, unlike TosL, this solvent was also checked, albeit only at 80 °C, and the results (entries 10a,b) were found to be comparable to THF: both slightly lower n:i ratios of 13:1 and TOF values of 710−720 were seen, and the results for the second aliquot of 1-hexene were little changed from the first.

Phosphine **10** was prepared because it is an exact nonchelating analogue of diTosL, having an ethyl moiety on nitrogen instead of the two-carbon link to another sulfonamide. For two reaction runs (entries 18, 20), yields and TOF increased with the ratio of **10**:Rh, from 58% aldehyde with a TOF of 170 at **10**:Rh = 5, to 92% aldehyde with a TOF of 230 at **10**:Rh = 26, both at 4 h. In both cases, n:i ≈ 2.6, and in both cases, the rate of reaction was quite linear, especially for the 26:1 **10**:Rh run, where the amount of isomerization to 2-hexene was significantly lower. A third experiment (entry 19a,b) was run at a **10**:Rh ratio of 5, in which a second aliquot of 1-hexene was added after 4 h (and 80% conversion of the initial 1-hexene). While the n:i ratio remained

unchanged, the reaction was slower (TOF = 120) during the next 2 h.

Since **12**, another nonchelating ligand, was isolated and fully characterized in order to ascertain its structure, it too was tested (entry 21) and was found to give an n:i ratio of 4.8 but in extremely poor yield (2%). In fact, the yield was lower than in the absence of any ligand (entry 1), but unlike entry 1 less than 1% isomerization of 1-hexene was observed, so this result suggests that **12** does in fact coordinate to rhodium.

The final goal for this initial study was the preparation of diphosphorus analogues of TosL, since clearly the diphosphorus compound diTosL is far superior to its monophosphorus analogue **10**. While the desired compounds **5** and **7** were prepared, they are very insoluble in most nonchlorinated organic solvents. However, they are soluble in methylene chloride, and this solvent has been used for hydroformylation reactions.[32−35] It was for this reason that PPh_3 and diTosL were tested in methylene chloride. Unlike these ligands, however, **5** and **7** turned out to be poor hydroformylation ligands. Using a ligand:Rh ratio of 2:1 (entries 15, 16), both gave low yields of aldehyde after 4 h (15%), fairly high yields of isomerization to 2-hexene (10−14%), poor n:i ratios (3.8 for **5** and 2.8 for **7**), and TOF values near 40−50. While the TOF for **5** was fairly constant over 5 h, a 1 h induction period was observed for **7** during which time almost no reaction occurred.

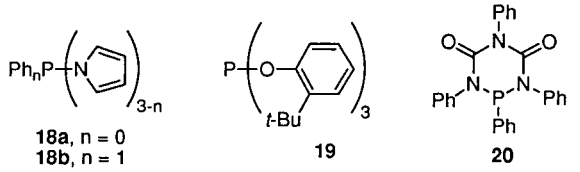
While **5** and **7** are clearly diphosphorus analogues of TosL, they are imperfect analogues since TosL has a phenyl group on phosphorus, while **5** and **7** have alkyl bridges. Testing of the *ethyl* analogue of TosL, **8** (entry 17), gave the surprising result that *no* reaction occurred, that is, no hydroformylation and no isomerization, unlike even the blank reaction (entry 1). Because this result was so unexpected, the reaction was repeated at both 10:1 and 2:1 ratios of **8**:Rh, with nearly identical results; in these reactions traces of aldehyde were observed at 4 h reaction.

Discussion

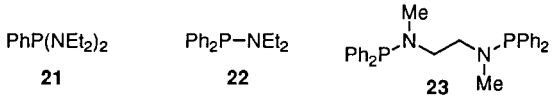
While the monophosphorus ligand TosL is an electron-withdrawing phosphine ligand, it is a poor promoter of the hydroformylation reaction. Rather surprisingly, the ethyl analogue of TosL, **8**, is an *inhibitor* of both hydroformylation and isomerization; it is not simply a poor promoter that is an innocent bystander, because in the *absence* of any phosphine, a reaction occurs as seen in entry 1. Compound **8** is a crystalline analytically pure solid, so we do not believe that it is contaminated by any impurity that poisons the catalyst, and during the course of the reaction essentially no color change occurred (the solution remained pale green throughout) in contrast to the reaction of TosL, which gave a dark orange color that we associate with catalyst decomposition. We have no explanation for these observations at present, but it is instructive that such a small structural change can have such a large effect on reactivity. In the same vein, **12** also appears to be an inhibitor, but here the structural change is large; one can propose that the phosphorus coordination in this case sterically blocks 1-hexene coordination or that the free sulfonamide hydrogen serves to poison the catalyst, but in either case no further work on this compound is planned.

Chart 1

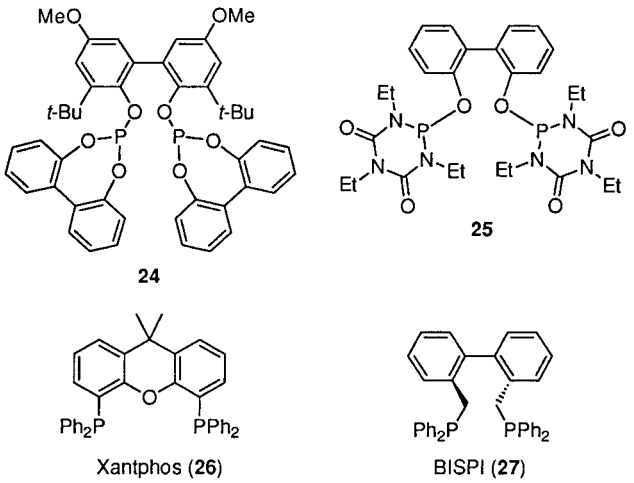
Monodentate electron-withdrawing phosphorus compounds



Alkylamino phosphorus compounds



Bidentate phosphorus compounds



While we have characterized TosL as a poor hydroformylation promoter by comparison to PPh_3, it is appropriate to compare it to other nonchelating electron-withdrawing phosphines (Chart 1, Table 3). For instance, the pyrrolyl phosphines **18a**,**b** gave in the best cases excellent n:i ratios of 15−31 under mild conditions comparable to those described here, with a 1-hexene:Rh ratio of 630, a ligand:Rh ratio of 4−8, temperatures of 40−60 °C, and 10 atm of CO/H_2, giving ∼10% isomerization to 2-hexene and TOF values of 340−380 mol aldehyde/mol Rh/h.[22] Hence the reactivity of this class of ligand is not dramatically different from TosL (TOF = 120), but the selectivity is far superior. On the other hand, van Leeuwen has reported nonchelating ligands such as **19** and **20** that are tremendously reactive, but give low n:i ratios. For instance, the bulky phosphite **19** when used at a 1-octene:ligand:Rh ratio of 8600:50:1 at 20 bar CO/H_2 at 60 °C gave a TOF of 5300 mol aldehyde/mol Rh/h (and at 80 °C TOF = 40 000!), but while little isomerization occurred at 60 °C (4%), the n:i selectivity of less than 2 was low.[15] Another bulky phosphine described by van Leeuwen, **20**, is more similar to TosL, in that it has two electron-withdrawing amide functional groups attached to phosphorus in a heterocycle, with phenyl groups attached

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Table 3. Selected Hydroformylation Results for Rhodium-Catalyzed Reactions Promoted by Ligands in Chart 1

L (equiv)	alkene:Rh (alkene)[a]	CO/H_2 pressure	*T* (°C)	solvent	time (h)	n/iso[b]	aldehyde yield (%)	2-alkene yield (%)	TOF
18a (4)	630 (C_6)	10 atm	40	benzene	1.5	31.0	80	10	340
19 (50)	8600 (C_8)	20 bar	60	toluene	~0.35	1.6	22	1	5300
20 (50)	3200 (C_8)	20 bar	80	toluene	~0.03	2.6	25	5	24 500
21 (2)	1060 (C_6)	25 atm	80	benzene	15	2.0	42		30
22 (2)	1060 (C_6)	25 atm	80	benzene	15	1.5	78		55
23 (2)	1060 (C_6)	25 atm	80	benzene	15	2.3	80		56
24 (16)	2500 (C_8)	20 bar	80	toluene	~0.2	*n* only	25	6	3600
25 (100)	3200 (C_8)	20 bar	80	toluene	~1.1	6.8	28	1	780
26 (2.2)	674 (C_8)	10 bar	80	toluene	16[c]	53.5	99.5	0.5	800
27 (2.2)	674 (C_8)	10 bar	80	toluene	16[c]	80.5	90.7	9.3	850

[a] C_6 and C_8 are 1-hexene and 1-octene, respectively. [b] Ratio of linear to isoaldehyde. [c] While these reactions were run for 16 h, on the basis of the reported TOF values, they should have been complete in ~1 h.

to the flanking nitrogen atoms rather than the tosyl groups of TosL. Under fairly mild conditions (3200:50:1 1-octene:ligand:Rh, 80 °C, 20 bar CO/H_2), selectivity was low (n:i = 2.6, 17% isomerization to 2-octene), but reactivity was high (TOF = 24 500).[24]

While the chiral ligand **3** was not a focus of this study, we are aware of one report of a group of related diphosphorus compounds that contain both an *O*-acyl phosphite and a phosphite;[36] the structures are related to **24** (Chart 1, see discussion below). The reported ligands gave active catalysts at 130 °C using a 10:1 ligand:Rh ratio, so the catalyst decomposition seen in **3** (entry 14) may not be due to the *O*-acyl moiety; further work on this type of heterocycle is planned.

In contrast to TosL and **3**, the diphosphorus ligand diTosL exhibits good reactivity and high regioselectivity. While it is potentially chelating and does in fact readily give a seven-membered-ring chelate tungsten complex,[1] we have not carried out any stoichiometric reactions with rhodium. Of the nonchelating ligands described above in Chart 1, diTosL is most similar to **18**, giving TOF values near 400 in THF, n:i ratios of 10, and isomerization to 2-hexene of less than 10% at 60 °C. Upon increasing the temperature to 80 °C, excellent TOF values of greater than 700 were obtained in THF and toluene without loss in catalyst activity upon the addition of a second aliquot of 1-hexene. Surprisingly, the n:i ratio was higher at the higher temperature in THF (increasing from 10 to 15), and the same temperature dependence was seen in methylene chloride. While the increase in TOF is expected, the increase in n:i ratio is not; for instance in the reaction promoted by **18a** the n:i ratio dropped from 31 to 10 to 4 at 40, 60, and 80 °C, respectively.[22] A number of bis(diphenylphosphino) ligands (including Xantphos (**26**), Chart 1; see discussion below) gave *lower* n:i ratios upon raising the temperature; only BISPI (**27**) gave a higher n:i ratio, going from 58 at 40 °C to 81 at 80 °C.[12]

The hydroformylation results in methylene chloride were both exciting and disappointing. The n:i ratios were much higher, nearly double that of THF at 80 °C, giving a best 1 h n:i ratio of 28.5. However, TOF values were lower than in THF, possibly due to rapid loss of catalyst activity. Use of higher diTosL:Rh ratios clearly increased the catalyst lifetime, but we have not yet tested whether this effect is a consequence of ligand decomposition or catalyst stabilization.

Strong evidence that diTosL is a chelating ligand in the catalyst is provided by comparison to nonchelating analogue **10**. This ligand is much more effective than TosL and at the high **10**:Rh ratio of 26 gave a TOF value (230) and isomerization yield (6%) that compares favorably to diTosL; in particular the reaction was perfectly linear in aldehyde yield vs time. Nonetheless, the n:i ratio of 2.7 is clearly a "nonchelating" value, comparable to PPh_3. While addition of excess ligand can give a catalyst that has multiple phosphines coordinated to rhodium, chelation seems necessary for this class of ligand to give high n:i ratios, and we suggest this value is diagnostic of chelation for diTosL in the catalytic species.

The runs using the low ratio of **10**:Rh = 5 were only linear for the first 2−3 h, after which the reactions slowed. This was confirmed by the run in which a second aliquot of 1-hexene was added, where the TOF dropped from 170 to 120. Either ligand decomposition is occurring and this is only visible at relatively low ligand concentration, or the low ligand concentration fails to "protect" the catalyst itself from decomposition.

The toluenesulfonyl moiety has a dramatic effect on promotion of hydroformylation, as illustrated by results with compounds **21**−**23**,[37] which are alkylamine analogues of TosL, diTosL, and **10** (Chart 1, Table 3). These phosphines are expected to be electron-donating, rather than withdrawing, as we have shown previously.[1] In fact, the hydroformylation results bear out the prediction that these should be poor promoters. The donor amines all gave n/i ratios in the nonchelating range (suggesting that diphosphine **23** is nonchelating) and low TOF values, despite execution of the reactions at higher temperature (80 °C) and pressure (25 atm).

Chelating diphosphorus compounds (Chart 1, Table 3) typically give much higher n:i ratios for hydroformylation of 1-alkenes, as seen here for diTosL compared to TosL and **10**. The best ligands are analogues of **19** such as **24**.[16−18] This ligand, for instance, gave no detectable branched aldehyde from 1-octene at 80 °C and 20 bar CO/H_2 and a very high TOF value of 3600; it also gave 18% isomerization of 1-octene.[18] Chelating analogues of **20** do not have the high reactivity of **20**; for instance **25** gave an n:i ratio of 6.8 for 1-octene at 80 °C and 20 bar CO/H_2 but a TOF value of only 780.[24] Some diphosphines with a variety of linking groups have also been examined, and under similar conditions (1-

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octene, 80 °C, 10 bar CO/H_2), n:i ratios greater than 50 have been observed, although Xantphos (**26**) gave only 0.5% isomerization while BISPI (**27**) gave 9% isomerization. While these selectivities are better than that of diTosL, the TOF values of 800−850 are comparable. These results demonstrate that the sulfonylaminophosphine is a viable functional group for a new class of highly effective hydroformylation promoter.

Finally, this study also reveals an unanticipated problem with the tosyl group. While we chose this group for its electronic properties, it is evident that its steric properties are also significant. No controls have been carried out for its steric bulk yet. This size, we presume, also accounts for the difficulties in synthesis of other diphosphorus compounds with which to compare reactivity to diTosL. Once a rigid linker is used, the nucleophilic attack of nitrogen on Ph_2PCl is impeded, whereas in diTosL the freely rotating ethylidene bridge allows the bulky groups to adopt an anti conformation. Molecular modeling suggests that the desired compounds are feasible targets and would coordinate to a metal, even though we have been unable to prepare them. A second potential problem, that of the polarity of these phosphines, which prevents us from testing the hydroformylation reactivity of chelating analogues of TosL in THF or toluene, has been solved by conducting the reactions in methylene chloride. Interestingly, this solution also results in a significant improvement in regioselectivity for diTosL. However, the results with the chelating analogues of TosL, **5** and **7**, show that while chelating diTosL is much more effective than nonchelating **10**, **5** and **7** are not more effective than TosL. Whether the lower reactivity is due to difficulties with coordination to rhodium, since steric hindrance will be larger for the chelating analogues, or simply due to the alkyl group on phosphorus, given that the ethyl analogue of TosL, **8**, inhibits all reaction, is unknown. Since the sulfonyl groups of chelating analogues of TosL are not likely to be sterically innocent, any electronic effect of binding two *N*-tosyl moieties to phosphorus may be masked.

Conclusion

The diphosphorus compound diTosL provides evidence that the *N*-sulfonylphosphoramide functionality, specifically a bis(*p*-toluenesulfonylamino) phosphine, holds promise as a promoting ligand for hydroformylation. In CH_2Cl_2 as solvent, an n:i ratio of 17−28.5 was observed, comparable to that seen with the pyrrolyl phosphines, and in THF at 80 °C, an n:i ratio of greater than 15 was observed. Turnover frequencies for diTosL of 440 mol aldehyde/mol Rh/h at 60 °C and 760 mol aldehyde/mol Rh/h at 80 °C are comparable to both the pyrrolyl phosphines as well as Xantphos and BISPI, although these latter two give higher n:i ratios. While many modifications to the diTosL structure are readily imagined, we have also shown that the *N*-sulfonyl group is so sterically bulky as to inhibit facile syntheses of diphosphorus analogues. Future work will need to take account of these steric issues in the design of better promoters.

Experimental Section

General Procedures. All manipulations of air-sensitive compounds were carried out either in a Vacuum Atmospheres inert atmosphere glovebox under recirculating nitrogen or by using standard Schlenk techniques. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker DPX-400 spectrometer; chemical shifts are reported relative to TMS or residual hydrogens in $CDCl_3$ (δ 7.24), C_6D_6 (δ 7.15), or CD_2Cl_2 (δ 5.32) for ^1H NMR, to C_6D_6 at 128.0 ppm, $CDCl_3$ at 77.0 ppm, or CD_2Cl_2 at 53.8 ppm for ^{13}C NMR, and to external 85% H_3PO_4 at 0 ppm (positive values downfield) for ^{31}P NMR. Elemental analyses were performed by Desert Analytics, Tucson, AZ. NMR line-shape analyses were carried out using gNMR (Cherwell Scientific Publishing, Inc.) on a Macintosh computer.

All solvents were treated under nitrogen. Benzene, diethyl ether, and tetrahydrofuran were distilled from sodium benzophenone ketyl. Hexane was purified by washing successively with 5% nitric acid in sulfuric acid, water, sodium bicarbonate solution, and water, then dried over calcium chloride, and distilled from *n*-butyllithium in hexane. Methylene chloride was distilled from phosphorus pentoxide. Pyridine was dried over potassium hydroxide pellets and distilled from BaO. Triethylamine was distilled under N_2 from CaH_2. NMR solvents were treated as follows: $CDCl_3$ and CD_2Cl_2 were vacuum-transferred from phosphorus pentoxide, and C_6D_6 was vacuum-transferred from sodium benzophenone ketyl. The 1-hexene used for hydroformylation was stirred over sodium, vacuum-transferred, and stored under N_2 in the glovebox.

The following chemicals were used as received: $Cl_2PCH_2CH_2PCl_2$ (Strem Chemicals), Ph_2PCl, $PhPCl_2$, *p*-toluenesulfonyl chloride (Aldrich), and $EtPCl_2$ (ACROS). The following compounds were prepared as previously described: $(Et_2N)_2PCl$,[38] **6**,[25] **9**,[25] **11**,[29] **13**,[29] **15**,[39,40] and $Rh(CO)_2(acac)$.[41]

***P,P′*-1,2-Ethanediylbis(1,3-di-*p*-toluenesulfonyl-1,3,2-diazaphospholidine) (5).** In the glovebox, a solution of 0.536 g (2.31 mmol) of 1,2-bis(dichlorophosphino)ethane in 6 mL of THF was added dropwise to a suspension of of $TsNHCH_2CH_2NHTs$ (1.71 g, 4.64 mmol) in 30 mL of THF in the presence of 1.61 mL (11.6 mmol) of triethylamine. After stirring for 30 min, the mixture was refluxed for 15 min outside the box under nitrogen and then filtered in air through a frit. The solid was washed two times with a small amount of THF and then dried in vacuo for 1 h to give 2.42 g of white solid. This material was washed with 50 mL of methylene chloride in portions to give 1.08 g (57% yield) of **5** as a white, air-stable solid that was nearly spectroscopically pure. Two recrystallizations from boiling CH_2Cl_2 in the air followed by cooling at −20 °C gave analytically pure material (34% overall recovery) as a white powder: ^1H NMR (CD_2Cl_2) δ 7.55 (d, 8.2 Hz, 8H), 7.18 (d, 8.2 Hz, 8H), 3.70 (m, 4H, cis or trans ring CH), 3.08 (m, 4H, trans or cis ring CH), 2.43 (s, 12H, CH_3), 2.01 (t, $J_{PH} = 7.5$ Hz, 4H, chain CH_2); ^{31}P NMR (CD_2Cl_2) δ 107.68; ^{13}C NMR (CD_2Cl_2) δ 144.45 (ipso), 135.82 (ipso), 130.12 (CH), 127.45 (CH), 48.22 (t, ring CH_2), 28.15 (ABX, chain CH_2), 21.74 (CH_3). Anal. Calcd for $C_{34}H_{40}N_4O_8P_2S_4$: C, 49.63; H, 4.90; N, 6.81. Found: C, 49.32; H, 4.91; N, 6.59.

***P,P′*-1,4-Butanediylbis(1,3-di-*p*-toluenesulfonyl-1,3,2-diazaphospholidine) (7).** In the glovebox, a solution of 0.645 g (2.48 mmol) of 1,4-bis(dichlorophosphino)butane in 6 mL of THF was added dropwise to a suspension of $TsNHCH_2CH_2NHTs$ (1.83 g, 4.96 mmol) and 1.51 g (14.9 mmol) of Et_3N in 35 mL of THF. The mixture was stirred for 2 h and then removed from the box and filtered to give 2.03 g of white powder that was 39% **7** by weight (38% yield) as judged by NMR in CD_2Cl_2. The solid was suspended in 40 mL of CH_2Cl_2 and filtered, the resultant solid was washed with 5 mL more of CH_2Cl_2 to give 0.18 g solid, and this was then crystallized from 50 mL of $CHCl_3$ (heating only to 50 °C in the air) at −20

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°C to give 0.12 g (6% yield) of analytically pure **7** as a white, air-stable solid. Additional **7** was obtained from the initial CH_2Cl_2-soluble fraction. Solvent removal under vacuum gave 1.6 g of powder, which was washed with 9 mL of $CHCl_3$ to give 0.44 g of powder. Crystallization from 90 mL of $CHCl_3$ as described above gave 0.32 g (15% yield) more of spectroscopically pure **7**: ^{1}H NMR (CD_2Cl_2) δ 7.54 (d, 8.2 Hz, 8H), 7.16 (d, 8.2 Hz, 8H), 3.65 (m, 4H, cis or trans ring CH), 3.05 (m, 4H, trans or cis ring CH), 2.43 (s, 12H, CH_3), 1.88 (m, 4H, chain CH_2), 1.75 (m, 4H, chain CH_2); ^{31}P NMR (CD_2Cl_2) δ 111.09; ^{13}C NMR (CD_2Cl_2) δ 144.28 (ipso), 135.94 (ipso), 130.05 and 127.44 (d, J_{PC} = 1.9 Hz) (aryl), 48.18 (d, 5.8 Hz, ring CH_2), 36.18 (d, chain CH_2), 23.91 (ABX, chain CH_2), 21.73 (CH_3). Anal. Calcd for $C_{36}H_{44}N_4O_8P_2S_4$: C, 50.81; H, 5.21; N, 6.58. Found: C, 51.07; H, 4.83; N, 6.50.

2-Ethyl-1,3-di-*p*-toluenesulfonyl-1,3,2-diazaphospholidine (8). In the glovebox, a solution of 212 mg of $EtPCl_2$ (1.62 mmol, 1.02 equiv) in 2 mL of THF was added dropwise to a stirred suspension of $TsNHCH_2CH_2NHTs$ (586 mg, 1.59 mmol, 1 equiv) and Et_3N (406 mg, 4.01 mmol, 2.5 equiv). After 3 h of stirring the cloudy white suspension was filtered through Celite and the solvent removed under vacuum. The resultant white solid was taken up in the minimum amount of toluene, 22 mL, and filtered, and the solution was cooled to −30 °C to give after filtration 443 mg (65% yield) of product as analytically pure, small white crystals: ^{1}H NMR ($CDCl_3$) δ 7.56 (d, 8 Hz, 4H), 7.13 (d, 8 Hz, 4H), 3.63 (m, 2H), 3.05 (m, 2H), 2.42 (s, 6H), 1.86 (dq, 2H, $^2J_{PH}$ = 5.8 Hz, J_{HH} = 7.7 Hz), 1.19 (dt, 3H, $^3J_{PH}$ = 18.1 Hz, J_{HH} = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 143.66 (ipso), 135.56 (ipso), 129.62, 127.21 (d, J_{PC} = 3 Hz), 47.76 (d, $^2J_{PC}$ = 5.4 Hz), 29.15 (d, $^1J_{PC}$ = 31 Hz), 21.61, 6.64 (d, $^2J_{PC}$ = 15.8 Hz); ^{31}P NMR ($CDCl_3$) δ 114.75 ppm. Anal. Calcd for $C_{18}H_{23}N_2O_4PS_2$: C, 50.69; H, 5.44; N, 6.57. Found: C, 50.86; H, 5.34; N, 6.49.

***N*-Diphenylphosphino-*N*-ethyl-*p*-toluenesulfonamide (10).** In the glovebox, 1.9 mL (2.3 g, 10.5 mmol) of Ph_2PCl was added in three portions to a stirred solution of 2.00 g (10 mmol) of $TsNHEt$[42,43] and 1.7 mL (1.2 g, 12 mmol) of Et_3N in 50 mL of benzene. The mixture was refluxed under nitrogen outside the box for 2 h. The solvent was then removed on the vacuum line, and the solid was brought into the box. Benzene (20 mL) was added to extract the product from the $Et_3NH^+Cl^-$, the suspension was filtered through Celite and washed with two 7 mL portions of benzene, and the solvent in the filtrate was removed in vacuo again. The resultant 3.4 g of solid slowly dissolved in 170 mL of anhydrous diethyl ether in air at ambient temperature and was concentrated to 60 mL before cooling at −20 °C in a freezer for 2 days to give 1.3 g of $Ph_2PN(Et)Ts$ contaminated by a small amount of TsN(H)Et. This material was recrystallized from 50 mL of ether to give 0.47 g (12% yield) of analytically pure **10**, which was used for hydroformylation reactions: mp 119−120 °C; ^{1}H NMR ($CDCl_3$) δ 7.80 (d, 8.2 Hz, 2H), 7.28 (d, 8.2 Hz, 2H), 7.33−7.18 (m, 10H), 3.42 (qd, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 2.2 Hz, 2H), 2.44 (s, 3H), 0.63 (t, $^3J_{HH}$ = 7.0 Hz, 3H); ^{31}P NMR ($CDCl_3$) δ 55.12; ^{13}C NMR ($CDCl_3$) (assignments based on diTosL data[1]) δ 143.25 (tolyl C_1), 138.88 (tolyl C_4), 135.21 (d, $^1J_{PC}$ = 17.2 Hz, phenyl C_1), 132.33 (d, $^2J_{PC}$ = 21.3 Hz, phenyl C_2), 129.62 and 129.44 (tolyl $C_{2,3}$), 128.55 (d, $^3J_{PC}$ = 6.0 Hz, phenyl C_3), 127.42 (d, $^4J_{PC}$ = 3.0 Hz, phenyl C_4), 44.14 (d, $^2J_{PC}$ = 2.4 Hz, CH_2), 21.56 (tolyl CH_3), 15.36 (ethyl CH_3). Anal. Calcd for $C_{21}H_{22}NO_2PS$: C, 65.78; H, 5.78; N, 3.65. Found: C, 65.80; H, 5.84; N, 3.53.

***N*-(Diphenylphosphino)-*N*,*N*′-1,2-phenylenebis-*p*-toluenesulfonamide (12).** In the glovebox, 0.54 g (2.4 mmol) of Ph_2PCl was added to a solution of 1.0 g (2.4 mmol) of **11** and 0.49 g (4.8 mmol) of triethylamine in 17 mL of THF. After stirring for 2 h, the mixture was filtered through Celite to remove Et_3NHCl and washed twice with a small amount of THF, and the solvent was removed in vacuo. The resultant solid was recrystallized from about 10 mL of $CHCl_3$/ether (1:1 v/v) at −40 °C overnight to give 1.1 g (76% yield) of **12** as analytically pure white crystals: ^{1}H NMR ($CDCl_3$) δ 7.14−7.61 (m, 20H), 6.98 (td, 7.8 Hz, 1.3 Hz, H_c, Scheme 2), 6.42 (td, 7.7 Hz, 1.4 Hz, H_b), 5.86 (dd, 8.0 Hz, 1.4 Hz, H_a), 2.41 (s, 3H), 2.32 (s, 3H); ^{31}P NMR ($CDCl_3$) δ 72.10 ppm; ^{13}C NMR ($CDCl_3$) δ 144.41, 143.66, 136.92, 136.40, 135.72, 134.75 (d, 17.3 Hz), 134.20 (d, 25.2 Hz), 133.06 (d, 21.5 Hz), 132.10, 130.27, 129.43, 129.04 (d, 1.6 Hz), 128.97, 128.34 (t, 2.7 Hz), 128.24, 127.53, 122.53, 117.49, 21.66, 21.53. Anal. Calcd for $C_{32}H_{29}N_2O_4PS_2$: C, 63.99; H, 4.87; N, 4.66. Found: C, 64.03; H, 4.86; N, 4.72.

NMR Spectra. Full NMR spectra of known compounds not previously reported are as follows.

$(Et_2N)_2PCl$: ^{1}H NMR ($CDCl_3$) δ 3.13 (br, 4H), 1.10 (t, 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 41.10 (d, 18 Hz, CH_2), 13.79 (d, 4.7 Hz, CH_3); ^{31}P NMR ($CDCl_3$) δ 160.73.

$Cl_2P(CH_2)_4PCl_2$ (6): ^{1}H NMR (C_6D_6) δ 1.44 (m, 4H), 1.08 (m, 4H); ^{13}C NMR (C_6D_6) δ 41.86 (d, 45.0 Hz), 23.49 (ABX pattern, see Table 1); ^{31}P NMR (C_6D_6) δ 194.45 (neat, 192−194 ppm[25]).

$(Et_2N)_2P(CH_2)_4P(NEt_2)_2$ (9). This compound is unstable in chloroform: ^{1}H NMR (C_6D_6) δ 2.96 (m, 16H, ethyl CH_2), 1.67 (b, 8H, chain CH_2), 0.98 (t, 7 Hz, 24 H); ^{13}C NMR (C_6D_6) δ 42.82 (d, 15.5 Hz, ethyl CH_2), 28.29 (d, $^1J_{PC}$ = 3.4 Hz, chain CH_2), 27.39 (ABX pattern, see Table 1), 15.24 (d, 2.8 Hz, CH_3); ^{31}P NMR (C_6D_6) δ 89.26.

***N*-Ethyl-*p*-toluenesulfonamide:** ^{1}H NMR ($CDCl_3$) δ 7.76 (d, 2H, 8.2 Hz), 7.31 (d, 2H, 8.2 Hz), 4.43 (br, 1H), 3.00 (m, 2H), 2.43 (s, 3H), 1.10 (t, 3H, 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 143.39, 136.95, 129.71, 127.13, 38.24, 21.53, 15.08.

Hydroformylation Reactions. In a typical reaction, $Rh(CO)_2(acac)$ (3.1 mg, 0.0120 mmol) and diTosL (**2**, 88.5 mg, 0.120 mmol) were placed in a 90 mL Fisher-Porter vessel (Andrews Glass Co.) in the glovebox, followed by 10 mL of THF, 1-hexene (1.006 g, 11.95 mmol), and toluene as an internal standard (0.505 g, 5.481 mmol). A sample was taken for NMR analysis, by adding a few drops of the reaction solution to $CDCl_3$ in an NMR tube in the glovebox. The vessel was sealed with a rubber stopper, brought out of the box, and then quickly attached to an Andrews Glass Co. multiported stirring assembly. The stirring paddles on the stirrer were tied up with a stainless steel wire to prevent scratching the glass vessel, and the device was equipped with a pressure gauge, gas inlet, gas outlet, and a valve with a standard 1/4 in. Swagelok attachment containing a GC septum. The vessel was flushed with 1:1 CO/H_2 synthesis gas at 84 psi three times and pressurized to 84 psi. The solution was then heated, with mechanical stirring, to 60 °C in a temperature-controlled (±0.2 °C) oil bath. Every 1−2 h, a sample was withdrawn for NMR analysis by opening the valve to the GC septum, inserting a 24 in. needle connected to a 1 mL gastight syringe, and withdrawing about 0.5 mL of solution. The procedure could be done with no visible drop in pressure, with the gas inlet turned off (for safety). A few drops of this sample were immediately added to an NMR tube containing $CDCl_3$ for analysis. For reactions in which a second aliquot of 1-hexene was added to the reaction mixture, the addition was carried out by taking 1-hexene from the glovebox in the gastight syringe (sealed by a rubber stopper) followed by injection as above. After cooling the reaction mixture, the pressure of the system was released, and a final time point sample was collected. Peaks used in the NMR analysis are as follows: δ 9.76, CHO for heptanal; 9.61, CHO for 2-methylhexanal; 7.26−7.12, tolyl (5H); 5.80, 1-hexene CH; 5.40, 2-hexene (2H); 5.00−4.90, CH_2, 2H, 1-hexene; 2.34, tolyl Me (3H). For reactions run in toluene, naphthalene was used as the internal NMR standard, and both naphthalene peaks were used. To obtain

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accurate integrals, it was found to be necessary to use very short pulse widths (<8°); use of a normal 30° pulse necessitated the use of extremely long relaxation delays (≥64 s), perhaps due to the large amount of protio-THF present in the sample. To provide a wide margin of error, spectra were collected using a 2.8° pulse and a relaxation delay of 4 s.

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