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Synthesis of electron-withdrawing butane- and arene-sulfonylamino phosphines and use in rhodium-catalyzed hydroformylation †

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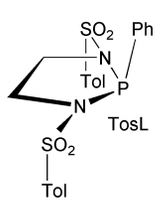
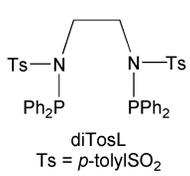
Reaction of $RSO_2N(H)CH_2CH_2N(H)SO_2R$ [R = Bu (**1**), 4-nitrobenzene (**7**), 1-naphthalene (**9a**), 2-naphthalene (**9b**)] with $PhPCl_2$ or $EtPCl_2$ gives monodentate phosphorus compounds **2** and **3** (R = Bu, PhP and EtP), and **8** (R = 4-nitrobenzene, PhP), and with Ph_2PCl gives the corresponding bidentate phosphine ligands $Ph_2PN(SO_2R)CH_2CH_2N(SO_2R)PPh_2$ [R = Bu (**10**), 4-nitrobenzene (**11**), 1- and 2-naphthalene (**12a**,**b**)]; similar reactions of *N*,*N*′-(1-butanesulfonyl)-2,2′-diaminobiphenyl (**4**) give monodentate **5** (PhP) and **6** (EtP) and *N*,*N*′-bis(diphenylphosphino)-*N*,*N*′-(1-butanesulfonyl)-2,2′-diaminobiphenyl (**16**). A monodentate analogue of **10** was also prepared, $Ph_2PN(Et)SO_2Bu$ (**14**). Diphosphorus compounds with two butanesulfonylamino groups on phosphorus were also prepared from **1** and $Cl_2P(CH_2)_nPCl_2$ (n = 2, 4) to give **19** and **20**. Details of the ^{13}C NMR false AA′X systems are reported for **19** and **20**. Rhodium-catalyzed hydroformylation reactions were run at 60 and 80 °C, at CO/H_2 pressures from 4–11 atm, and in THF, toluene, CH_2Cl_2, and dioxane. Results show that the highest ratios of linear (n) to branched (iso) aldehydes were obtained with arenesulfonamides (n:iso > 10) while the bidentate alkanesulfonamide **10** gave a lower n:iso ratio of 7.2 but the highest rate [k_1 = 1.98 h^{-1}, turnover frequency = 1130 mol aldehyde (mol Rh)$^{-1}$ h^{-1}] in THF at 80 °C. Both the rate and n:iso ratio for **10** were found to increase with decreasing CO/H_2 pressure in THF and in toluene, although the rate change was small for toluene. Both the rate and n:iso ratio for **10** also increased in CH_2Cl_2, but this was found *not* to be due to lower CO/H_2 concentrations in solution, on the basis of solubility measurements in THF and CH_2Cl_2.

Introduction

We recently reported a new series of trivalent phosphorus compounds that contain one or more phosphorus-*N*-sulfonyl linkages, including the monodentate 1,3,2-diazaphospholidine phenylphosphino compound TosL and the bidentate tosylamino-linked bis(diphenylphosphino) compound diTosL.[1] These phosphorus compounds were found to be remarkably electron-withdrawing. For instance, TosL is comparable to $(CF_3)_3P$, and diTosL to $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$, in donor and acceptor ability towards tungsten carbonyl complexes. Since the hydroformylation reaction is well known to be promoted more efficiently by electron-deficient phosphines than by electron-rich phosphines,[2–4] we examined rhodium-catalyzed hydroformylation in the presence of these and related phosphines.[5] The chelating diTosL ligand was found to be an effective promoter, while the non-chelating TosL was not. Attempts to synthesize analogues of diTosL with different bite-angles, in order to use Casey's and van Leeuwen's findings that increased bite-angle would give rise to better yields of linear aldehyde,[6,7] failed due to the unexpectedly high degree of steric hindrance of the arenesulfonylamino group. Attempts to synthesize chelating analogues of TosL, in order to determine whether two sulfonylamino moieties per phosphorus would be better than one, were successful, but the resulting compounds were so polar that they are insoluble in non-chlorinated hydroformylation solvents. While we were able to use CH_2Cl_2 successfully as a hydroformylation solvent, catalyst decomposition was accelerated under some conditions in this solvent, so discovery of a more soluble ligand remained a desirable goal. In order to try to solve both the steric bulk and solubility problems, we sought to use the butanesulfonyl group in place of the *p*-toluenesulfonyl group. We hoped that the twin four-carbon chains would render the bis-sulfonamides sufficiently lipophilic to be soluble in solvents such as THF and toluene, but without giving difficult-to-purify oils. We also hoped that the flexible chains would impart less steric hindrance than the toluene sulfonamides. In this paper we report the synthesis of a variety of butanesulfonylamino phosphine ligands, a short series of ethane-linked bis(diphenylphosphino) ligands, details of the NMR spectra of the new compounds, and the results of hydroformylation reactions with these new compounds including kinetics and solvent and pressure dependencies.





Results

Synthesis of monophosphorus compounds

Synthesis of the simplest compound desired, *N*,*N*′-dibutanesulfonyl-1,2-diaminoethane (**1**) was accomplished by reaction of $BuSO_2Cl$ and 1,2-diaminoethane in pyridine as shown in Scheme 1. This procedure allowed the product to be obtained as a white crystalline solid in low but adequate yield, and without chromatography. Initial attempts had been carried out by analogy to a literature procedure for reaction of $BuSO_2Cl$ with *trans*-1,2-diaminocyclohexane in methylene chloride,[8] but this procedure gave difficult-to-purify dark solids.

Reaction of **1** with $PhPCl_2$ or $EtPCl_2$ (Scheme 1) gave the required 1,3,2-diazaphospholidines **2** and **3** in good yield. These compounds were two of only three in this study that turned out

† Dedicated to the memory of Mohammad Salman Hamdani. Sal worked in our labs at Queens College as an undergraduate student from 1998–2001, and died as part of the rescue effort at the World Trade Center in New York City, September 11, 2001.

Electronic supplementary information (ESI) available: details of the syntheses, purification, and NMR and analytical data. See http://www.rsc.org/suppdata/dt/b2/b208089c/

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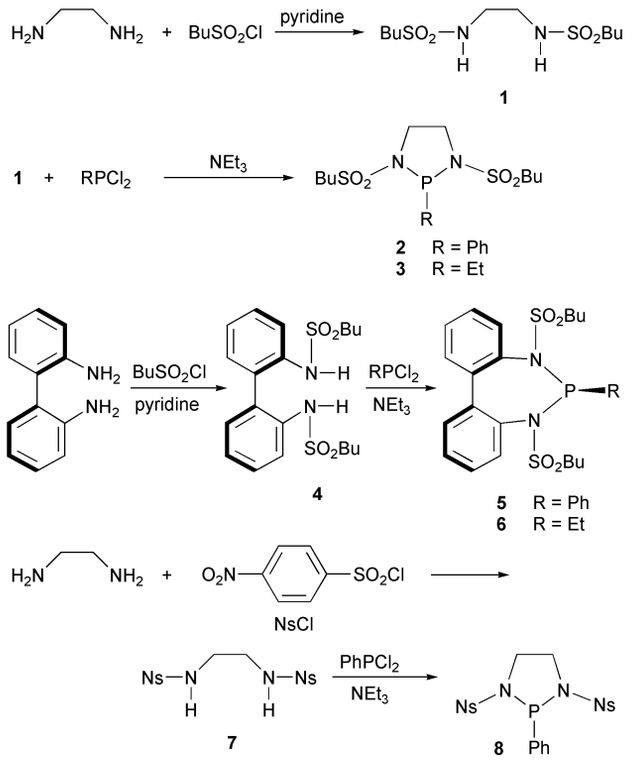


Scheme 1

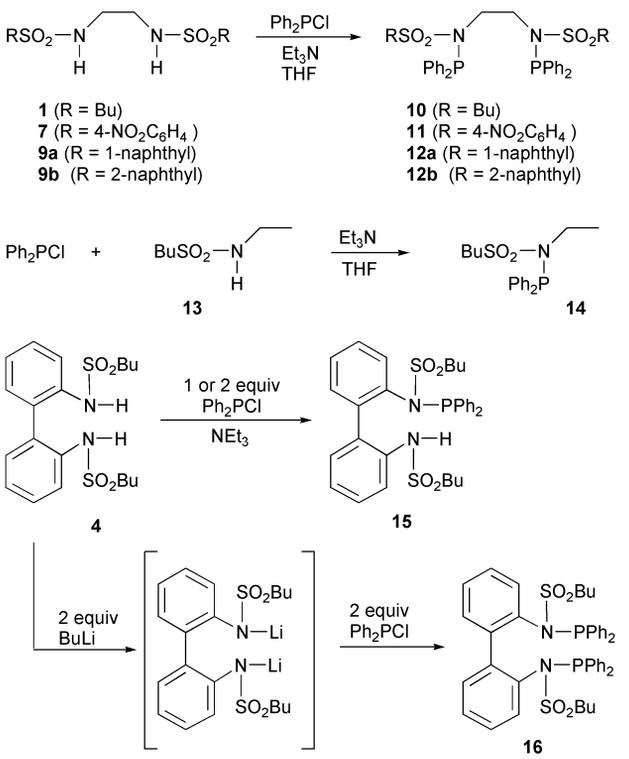
not to be crystalline solids, but the viscous oils were nevertheless easily isolated in analytically pure form. The structure of the ethyl-substituted heterocycle **3** was confirmed by 2D-COSY and HETCOR, which allowed all of the alkyl peaks to be identified unambiguously. Compound **3** was found not to be thermally stable over a period of weeks, decomposing at room temperature in the glovebox to a white solid that was found by ^{1}H and ^{31}P NMR to contain a number of uncharacterized products.

Reaction of 2,2′-diamino-1,1′-biphenyl with $BuSO_2Cl$ in pyridine gave the required bis-sulfonamide **4** in high yield (Scheme 1). Reaction of **4** with $PhPCl_2$ and $EtPCl_2$ as before gave the desired 7-membered ring 1,3,2-diazaphosphepine heterocycles **5** and **6**. The NMR spectra of **5** and **6** are much more complex than those of **4**, because while **4** has a C_2 symmetry axis, and so the phenyl rings and butyl groups are equivalent, the C_2 symmetry of **5** and **6** is broken by the phenyl or ethyl group on phosphorus, which lies on one side of the 7-membered ring. Each of the methylene carbon atoms of the two butyl groups exhibits distinct peaks in the ^{13}C NMR spectra as do the methyl groups of **6**. No peak broadening was observed in **5** and **6**, and since all of the biphenyl carbon atoms have different chemical shifts as do most of the two butanesulfonyl carbon atoms, there is no evidence of any rotation about the biphenyl carbon–carbon bond or for inversion at phosphorus. On the basis of the separation of the two closest peaks ($\Delta\nu = 4.7$ Hz for the butanesulfonyl $^{13}CH_3$ groups of **6** at 298 K) and simulation of the NMR spectrum, giving $k_{exch} < 5\ s^{-1}$, the barrier to rotation about the biphenyl carbon–carbon bond must be >16.5 kcal mol^{-1} at room temperature. In comparison, a 1,3,2-di*oxa*phosphepine, lacking the branching SO_2Bu moieties of **5** and **6**, exhibited a barrier to rotation of *ca.* 10 kcal mol^{-1}.[9]

One new bis(*N*-arenesulfonyl)-1,3,2-diazaphospholidine was prepared for this study, using the 4-nitrobenzene group as an electron-withdrawing analogue of the *p*-toluene group. Low but adequate yields of the bis-sulfonamide **7** and the desired heterocycle **8** were prepared using methods analogous to those used previously (Scheme 1), although the low solubility made the purifications difficult. For instance, **7** was isolated as the insoluble material filtered from hot ethanol; the soluble impurity was most likely *N*,*N*,*N*′-tris(4-nitrobenzenesulfonyl)-1,2-diaminoethane on the basis of ^{1}H NMR. Compound **8** is unusual in that it was recrystallized from THF/hexane, and is insoluble in chloroform.

Synthesis of bis(diphenylphosphino) compounds

The 1,2-diaminoethane derivatives were prepared as previously described for diTosL, by reaction of the bis-sulfonamides with 2 equivalents of Ph_2PCl in the presence of Et_3N in THF (Scheme 2). Compounds **11** and **12a**,**b** were somewhat insoluble in THF,



Scheme 2

CH_2Cl_2, and $CHCl_3$, and were isolated by filtration of the THF reaction mixtures and washing of the resultant solids with CH_2Cl_2 or $CHCl_3$ to remove the $Et_3NH^+Cl^-$ by-product. Crystallization of these compounds was difficult, yields were not optimized, and while they are spectroscopically pure, only **12b** was eventually obtained analytically pure.

One monodentate analogue of the bis(diphenylphosphino) compounds in Scheme 2 was also prepared in order to examine the effect of chelation. As shown, the monodentate analogue of **10** was prepared from Ph_2PCl and **13**, and while the synthesis and characterization were straightforward, the product **14**, like **2** and **3**, is an oil.

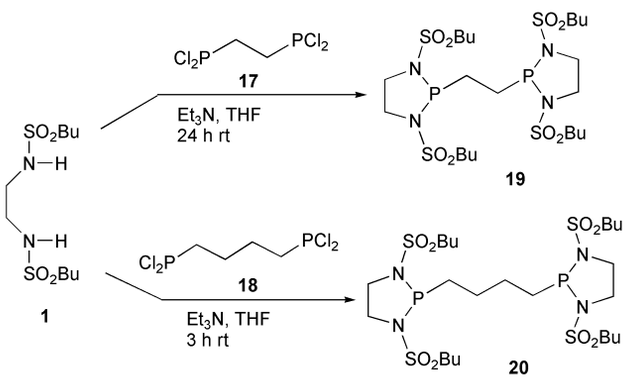
The reaction of **4** with Ph_2PCl in the presence of Et_3N, in a manner analogous to the previous syntheses, gave only the monophosphorus compound **15** (Scheme 2). Identification of this compound was not straightforward, due to the presence of atropisomers with respect to restricted rotation about the aryl–nitrogen bonds and/or stereocenters at nitrogen due to slow inversion at nitrogen, giving rise to a mixture of diastereomeric products.[10,11] Nevertheless, integration of the ^{1}H NMR spectrum and the fact that the same ^{1}H and ^{31}P NMR spectra were generated by adding either one or two equivalents of Ph_2PCl to **4** made it clear that only the monophosphorus compound formed. This result was not unexpected on the basis of previous results with the bis(toluenesulfonyl) analogue of **4**.[5]

Addition of 2 equiv. of BuLi to **4** gave what we presume to be the dianion, and reaction at −35 °C with Ph_2PCl gave a new

product that could be isolated as a white solid. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of this material were similar in complexity to those of **15**, again due to the presence of atropisomers/stereocenters at both nitrogen atoms. However, the integration of the ^{1}H NMR spectrum is consistent with it being the diphosphorus compound **16**, and the elemental analysis while not perfect is consistent with this formulation as well. However, **16** apparently is not very stable under many conditions and this may account for why it was not obtained analytically pure; for instance, 1 h of reaction between the dianion and Ph_2PCl appears optimal, since at longer reaction times increasing amounts of **15** were observed. In CD_3CN and $CDCl_3$, decomposition of **16** to both **15** and **4** occurred, although **16** appeared to be stable in C_6D_6 and toluene-d_8. The variable temperature NMR spectra of **15** and **16** will be described separately, since the results are interesting but of limited relevance to the hydroformylation results.

Synthesis of chelating TosL analogues

One of the principal goals of this study was the synthesis of chelating butanesulfonyl analogues of TosL. This was accomplished as shown in Scheme 3, by combining tetrachlorodiphos-



Scheme 3

phines **17** and **18** with bis-sulfonamide **1** in the presence of Et_3N. The resultant compounds (**19**, **20**) were quite soluble in THF and toluene, and were readily crystallized in analytically pure form. For both **19** and **20**, assignments of all alkyl peaks in the ^{1}H and ^{13}C NMR spectra were confirmed by 2D-COSY and HETCOR.

The ^{13}C NMR spectra exhibit interesting effects due to virtual coupling of the phosphorus atoms and the presence of false AA′X spin systems,[12] in which the presence of a single ^{13}C nucleus splits the symmetry of the molecule and gives rise to different ^{31}P chemical shifts, and hence to an ABX system (with the ^{13}C being the X nucleus). These effects have also been seen with the *p*-toluenesulfonyl analogues of **19** and **20**, **21** and **22** respectively,[5] and for completeness we note there are other examples[13,14] not previously cited.[12] Partial ^{13}C NMR spectra are shown for **19** and **20** in Fig. 1. Both **19** and its *p*-toluenesulfonyl analogue **21** exhibit six-line ABX multiplets for the carbon atom adjacent to phosphorus; for **19**, the spectra are best fit with $^{3}J_{PP'} = 17$ Hz and a shift difference of the phosphorus atoms for the $^{13}C_1$-isotopomer of 5.3 Hz (0.033 ppm) on a 400 MHz (^{1}H) NMR spectrometer [Fig. 1(b)]. The 'triplet' for the ring CH_2 arises due to virtual coupling to the distant phosphorus atom; that is, $^{5}J_{PC} = 0$ Hz but the previously fit $^{3}J_{PP'} = 17$ Hz gives rise to the central line in the multiplet [Fig. 1(a)]. The spectrum is sufficiently broad that little change is seen for values of $\Delta\nu_{PP'}$ between 0 and 2 Hz. In contrast, for **20** and **22** the much lower values of $^{5}J_{PP'}$ give rise to a doublet for the ring CH_2 of **22**, but in **20** a small pair of peaks in the middle of the doublet arises because in this case $\Delta\nu \neq 0$ Hz [Fig. 1(c)]. The doublet for C_1 of the 4-carbon bridge of **20** is best fit with $\Delta\nu =$

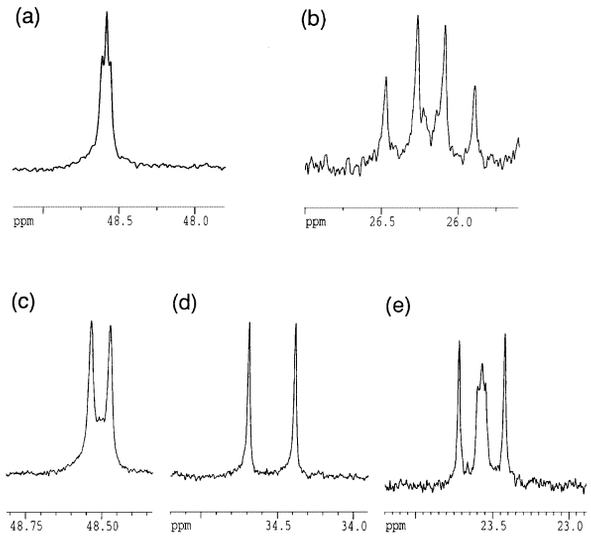
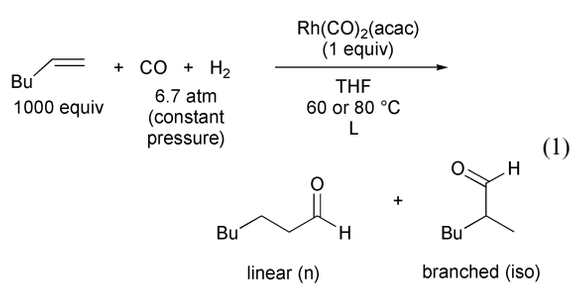


Fig. 1 Partial ^{13}C NMR spectra of **19** and **20**, exhibiting AA′X spectra for (a), (d), and (e), and ABX spectra for (b) and (c). **19**: (a) heterocycle ring CH_2, (b) bridging CH_2; **20**: (c) heterocycle ring CH_2, (d) C_1 of bridging carbon chain, (e) C_2 of bridging carbon chain. Spectrum (c) is plotted at twice the horizontal expansion as the others, and the vertical expansions are all different.

0 Hz, on the other hand [Fig. 1(d)], while the multiplet for C_2 (consisting of a doublet with a broad 'triplet' of slightly lesser height at the center) is best fit for a small non-zero value of $\Delta\nu$ [Fig. 1(e)].

Hydroformylation

Reactions were run according to the conditions in eqn. (1),



and data are collected in Table 1. For most of the reactions, time points were taken by removing a reaction sample with a gas-tight syringe, and the percentage yield of aldehyde *vs.* time was plotted. The turnover frequency (TOF) in units of mol aldehyde (mol Rh)$^{-1}$ h^{-1} was calculated for the initial portion of the reaction following any induction period, if present, as has been described previously.[5,15] Most of the reactions exhibited first-order kinetics in 1-hexene consumption and aldehyde formation, and for these the first-order rate constant was also calculated; several examples of zero-order kinetics were also seen and these are noted in Table 1. Representative zero-order and first-order plots are shown in Fig. 2.

Solubility of CO

Because high n:iso ratios were seen at *low* CO/H_2 pressure when both THF and toluene were used as the reaction solvent, and in CH_2Cl_2 solvent at the *same* CO/H_2 pressure as for THF and toluene, gas solubility in different solvents was investigated as a possible cause of this observation. We focussed on CO since the rate dependence on $[H_2]$ is considered to be small.[4] Literature data for CO solubility are available for toluene, diethyl ether, and dioxane,[16,17] but not for THF and CH_2Cl_2. A method for prediction of gas solubility using a functional group contribu-

Table 1 Results of the hydroformylation of 1-hexene[a]

Entry	L (equiv.)	Solvent	Time/h	n:iso[b]	Aldehyde yield (%)	2-Hexene yield (%)	k_1/h^{-1}	TOF[c]
1	**2** (10)	THF	6	2.6	43	19	0.130 ± 0.001	87
2	**3** (10)	THF	4	1.7	89	10	~Zero-order	270
3	**5** (10)	THF	6	3.5	1	1		2
4	**6** (10)	THF	6	3.0	74	10	1.6 ± 0.2	630
5	**8** (10)	THF	6	2.8	19	27	0.110 ± 0.004	42
6	**10** (1)	THF	4	4.3	68	8	0.48 ± 0.03	345
7	**10** (2)	THF	6	4.4	92	7	0.47 ± 0.03	360
8	**10** (10)	THF	6	4.4	88	5	0.47 ± 0.01	330
9	**10** (10)	THF	4	5.1	91	6	Not determined	≥230[d]
9	**10** (10)	THF	4	5.0	86	7	Not determined	≥215[d]
10	**10** (50)	THF	5	4.3	79	5	0.39 ± 0.02	270
11	**10** (10), 3.9 atm	THF	6	6.6	85	15	0.93 ± 0.03	630
12	**10** (10), 11.9 atm	THF	6	3.3	82	3	0.30 ± 0.01	180
13	**10** (10), 80 °C	THF	2	7.2	84	11	1.98 ± 0.07	1130
14	**10** (10)	CH_2Cl_2	4	11.1	83	8	0.83 ± 0.05	530
15	**10** (10)	9:1 THF:CH_2Cl_2	5	5.0	89	6	0.52 ± 0.01	350
16	**10** (10), 3.7 atm	Toluene	6	8.2	95	5	0.481 ± 0.007	420
17	**10** (10)	Toluene	6	4.7	90	3	0.435 ± 0.006	300
18	**10** (10), 10.5 atm	Toluene	6	4.0	93	2	0.400 ± 0.007	290
19	**10** (10), 80 °C	Toluene	3.1	5.7	93	7	0.96 ± 0.07	850
20	**10** (10)	Dioxane	6.2	5.7	93	5	0.46 ± 0.03	450
21	**11** (2)	THF	4	10.8	50	8	~Zero-order	140
22	**12a** (10)	THF	6	4.4	75	4	~Zero-order (0.40 ± 0.03)[e]	180
23	**12b** (10)	THF	6	12.1	83	8	~Zero order (0.57 ± 0.05)[e]	290
24	dppb	THF	6	3.6	18	0	0.040 ± 0.001	34
25	**14** (10)	THF	3.2	2.6	89	8	Zero-order	310
26	**16** (2)	THF	5	3.4	39	9	~Zero-order	60
27	**19** (2)	THF	4	—	0.8	0		2
28	**20** (2)	THF	6	1.9	78	16	Not determined	180
29	**20** (2)	CH_2Cl_2	6	2.0	65	13	Not determined	200
30	**diTosL** (10)	THF	5.5	10.1	85	9	0.86 ± 0.05[f]	440
31	**diTosL** (10)	CH_2Cl_2	4	17.3	82	11	0.54 ± 0.05[f]	280

[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 = 6.7 atm. [b] n:iso = ratio of linear aldehyde (heptanal) to 2-methylhexanal. [c] TOF = turnover frequency = mol aldehyde (mol Rh)$^{-1}$ h^{-1}; value reported is for the initial portion of the reaction following any induction period if present (see text). [d] Successive aliquots of 1000 equiv. of 1-hexene were used and the reactions were only monitored at 4 h each. [e] A first-order rate constant can be approximated, but the kinetic order is closer to zero; see text. [f] Rate constant not previously reported for this reaction from ref. 5.

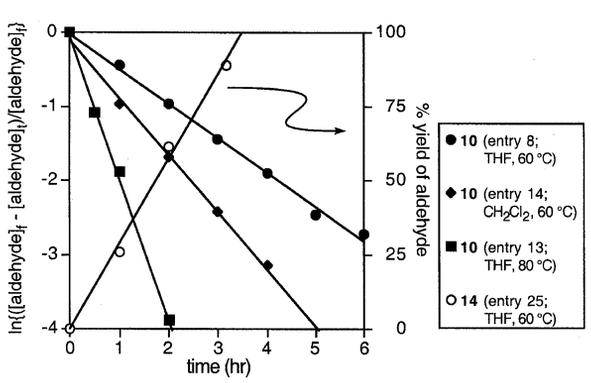


Fig. 2 First-order plots for representative reactions of **10** from Table 1 (left hand axis), and zero-order plot for reaction of **14** (right hand axis). All runs plotted are 10 equiv. of ligand.

tion method has been described,[18] but while it gives accurate solubilities for both CO and H_2 in diethyl ether, it fails for dioxane, which was presumably omitted from the diethyl ether and alcohol parameterization that was carried out. A prediction for THF using this method, therefore, was considered to be unreliable. In addition, the method was not parameterized for haloalkanes. We therefore measured CO solubilities in a manner based on that described in the literature,[19,20] using a simple vacuum line/manometer set-up.[21] For N_2 and CO in toluene, we reproducibly obtained values that were 7% higher than reported.[16] Because the vapor pressures of THF and CH_2Cl_2 are much higher than that of toluene and have the effect of increasing the error, we simply report our results without correcting for the likely systematic error. Results are collected in Table 2 for both literature data, calculations using the group contribution method, and our experimental data, and molar concentrations are tabulated to allow comparison with the other reactants. Data for H_2 are also included. The experimental and calculated values for solubility of CO in THF were found to be in reasonable agreement; that is, THF evidently bears more similarity to diethyl ether than to dioxane as a solvent for CO; however the calculated solubilities are poor for H_2 in both dioxane and THF. The CO solubilities for THF and CH_2Cl_2 are similar, and while the precise values are likely to be accurate only to within 10%, they nevertheless make clear that CO solubilities in these solvents are roughly twice that in toluene. The H_2 solubilities are all lower but in units of molarity do not differ very much.

Discussion

Four classes of ligand are evident, both in the results above and those that we have recently described,[5] namely: (1) inhibitors, (2) non-chelating ligands that give low n:iso ratios and which are poor promoters, (3) non-chelating ligands that give low n:iso ratios but which are good promoters, and (4) chelating ligands that give high n:iso ratios. The inhibitors are classified with respect to the 'blank' results obtained in the absence of any ligand, a 5% aldehyde yield and more importantly a 46% yield of isomerization.[5] The other classes of ligands can be

Table 2 Gas solubility data

	X_2 (CO)[a]	Calc. X_2 (CO)[a,b]	[CO]/M (3.35 atm)	X_2 (H_2)[a]	Calc. X_2 (H_2)[a,b]	[H_2]/M (3.35 atm)
Toluene	8.02[c]	8.02	0.025	3.15[d]	3.17	0.0099
THF	17.9	20.4	0.074	2.70[d]	4.89	0.011
CH_2Cl_2	15.4[e]	—	0.080	4.06[f]	—	0.013
Dioxane	4.9[c]	21.4	0.019	1.84[d]	4.15	0.0072
Diethyl ether	17.0[c]	16.6		6.24[g]	6.33	

[a] Mol fraction × 10^4, 298.15 K, 1 atm partial pressure. [b] Calculated according to ref. 18. [c] From ref. 17. [d] From ref. 31 [e] Measured at 5 °C to minimize errors due to vapor pressure; at 20 °C, $X_2 \times 10^4 = 35 \pm 11$. [f] For 1,1,2,2-tetrachloroethane, from ref. 32. [g] From ref. 32.

compared with PPh_3, which is used industrially, as a point of reference, and gave under our conditions modest n:iso and TOF values of 3.1 and 250, respectively, but a 99% aldehyde yield with only 1% isomerization to 2-hexene.[5]

Two compounds in this study are inhibitors, namely, the biphenyl heterocycle **5** and the 2-carbon bridged chelating analogue of TosL, **19**. Previously, we found that the EtP analogue of TosL, **23**, is also an inhibitor.[5] All of these compounds give virtually no aldehyde and no isomerization of 1-hexene. Therefore, they are not simply innocent non-binding ligands, but must bind to rhodium and prevent any further reaction. While each of these inhibitors has the bis(aminosulfonyl) functionality of TosL, several other bis(aminosulfonyl) compounds are *not* inhibitors. Of these, TosL, its close relative **8** (with arenesulfonyl and PhP moieties), the arenesulfonylamino chelating analogues **21** and **22**, and the butanesulfonylamino PhP compound **2** are poor hydroformylation promoters, giving TOF values from 37 to 120, and more importantly comparable amounts of hexene isomerization and aldehyde formation. However, the bis(butanesulfonylamino) alkylphosphines **3** and **20** are active hydroformylation promoters. Interestingly, **6** is the most active ligand we have found but the catalyst apparently reproducibly dies within 2 h of reaction, as evidenced by the absence of any further aldehyde formation or isomerization that accompanies the formation of a dark orange color of the reaction solution. Only **3**, **6**, and **20** have both an alkyl group on phosphorus and the alkanesulfonyl group on nitrogen, while all of the others except **19** have either an aromatic group on phosphorus and/or an arenesulfonyl group on nitrogen. At this stage, we have no single proposal that reasonably accounts for these facts. We can propose that **5** is so bulky that coordination of a single ligand to rhodium kills the catalytic activity, and that **23** binds and **19** chelates too tightly to allow catalysis, but then why is **3** a good catalyst rather than an inhibitor like **23**, and why are **21** and **22** just poor catalysts but **20** a good one and **19** an inhibitor? A correlation with *high* activity does seem to exist, even if we cannot suggest a reason *why* it exists: four compounds, namely, **3**, **6**, **19**, and **20**, are the only alkanesulfonylamino/alkyl phosphines, and these comprise the three good promoters and paradoxically one inhibitor (**19**). One might suppose that all four compounds bind tightly *via* one phosphorus atom; for instance **3** and **20** gave nearly identically low n:iso ratios (1.7 and 1.9, respectively), and we propose this means that both are non-chelating and so the 4-carbon bridging chain of **20** serves just to mimic the ethyl moiety of **3**. Compound **19**, then, might simply bind tightly *via* one phosphorus atom while the other serves as a bulky blocking group by virtue of the short 2-carbon bridge. The EtP compounds **3** and **6** are both more reactive than their PhP analogues **2** and **5**, so further testing of this simple correlation may be warranted; what is somewhat mysterious is why **2** is just a poor promoter but **5** is an inhibitor.

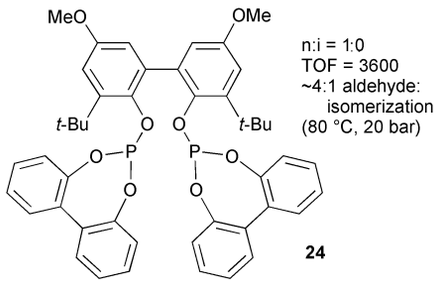
The bis(diphenylphosphino)sulfonylamino ligands generally give significantly higher n:iso ratios than the above ligands, and we have previously proposed that this is reasonably accounted for by chelation of these ligands.[5] That is, for instance, diTosL gave an n:iso ratio of 10, while its non-chelating analogue $Ph_2PN(Et)Ts$ gave a ratio of 2.7. Two of the other bis(diphenylphosphino)arenesulfonylamino ligands, **11** and **12b**, also gave high n:iso ratios, while the 1-naphthalenesulfonylamino ligand **12a** gave a lower n:iso value that may be due to increased steric hindrance. The bis(diphenylphosphino)*butane*sulfonylamino ligand **10** gave somewhat different results, however. At 60 °C in THF, n:iso ratios from 4.3 to 5.1 were observed, intermediate between the chelating values of *ca.* 10 for the arenesulfonylamino ligands and *ca.* 2 for the non-chelating ligands. The non-chelating analogue of **10**, $Ph_2PN(Et)SO_2Bu$ (**14**), gave a lower n:iso ratio of 2.6, and so once again it is reasonable to propose that the value seen for **10** is characteristic of chelation.

The exception to the above observations is biphenyl-linked **16**, which as noted is difficult to synthesize and is presumably quite sterically hindered; we propose that it does not chelate. All of the other bis(diphenylphosphino) compounds are relatively unhindered, and so are presumed to chelate. However, the high n:iso ratios evidently require not just a four-atom bridge between the phosphorus atoms, but also the *N*-sulfonyl group, since dppb (entry 24, Table 1) is clearly a poor hydroformylation promoter, as are previously described analogues with *N*-alkyl groups.[5,22]

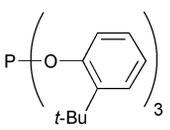
Ligand **10** gives a less active catalyst at 60 °C than diTosL – for instance at a 10:1 ligand:Rh ratio, TOF and k_1 values for **10** and diTosL were 330 and 440, and 0.47 and 0.86 h^{-1} (entries 8 and 30, Table 1), respectively.[5] The only other PPh_2 ligand to which these can be compared are their non-chelating analogues **14** and $Ph_2PN(Et)Ts$. While **10** and diTosL give reactions that are first-order in 1-hexene, **14** and $Ph_2PN(Et)Ts$ give zero-order reactions (Fig. 2), with TOF = 170–230 mol aldehyde (mol Rh)$^{-1}$ h^{-1} for $Ph_2PN(Et)Ts$ (for L:Rh = 5 and 26)[5] and TOF = 310 mol aldehyde (mol Rh)$^{-1}$ h^{-1} for **14** (L:Rh = 10). Hence, the butanesulfonyl analogue gives a higher rate when monodentate, and a lower rate when chelating, than the toluenesulfonyl analogue. One could propose that a second molecule of **10** competes with 1-hexene for coordination to rhodium, but since the same rates were seen at three different concentrations of **10**, the better explanation is that 1-hexene competes with CO for coordination to rhodium. The strong inverse dependence of rate on [CO] in THF is consistent with this, although the much weaker dependence in toluene is puzzling but could be related to the greater than 2-fold lower concentration of CO in toluene than in THF.

The difference in reaction order as well as the difference in n:iso ratio suggests that the active catalyst from **14** or $Ph_2PN(Et)Ts$ would contain the $LRh(CO)_3$ unit [L = **14**, $Ph_2PN(Et)Ts$], which readily dissociates CO giving zero-order kinetics; L_2Rh might not form for steric reasons or is simply not catalytic. Typically, electron donor ligands like PPh_3 give first-order kinetics,[23] and electron-poor phosphite ligands give zero-order kinetics,[23,24] so **14** and $Ph_2PN(Et)Ts$ behave like monodentate phosphites. On the other hand, the bulky chelating diphosphite **24** has not only been reported to give first-order kinetics, but also gives a rate that is relatively insensitive to [H_2] and is inversely proportional to [CO].[25] Evidently, chelating **10** and diTosL behave like **24** and the active catalyst presumably contains the $LRh(CO)_2$ unit (L = **10**, diTosL).

Like diTosL, **10** exhibits the same unusual CH_2Cl_2 and thermal effects on the n:iso ratio. For instance, diTosL in

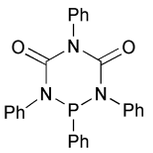


24



25

n:i = 1.6
TOF = 5300
(60 °C, 20 bar)



26

n:i = 2.6
TOF = 24500
(80 °C, 20 bar)

CH_2Cl_2 resulted in an increase of the n:iso ratio to 17.3 from 10.1 in THF at 60 °C (entry 31, Table 1), although the TOF declined.[5] For **10**, the n:iso ratio increased from *ca.* 5 to 11, and the TOF increased from 330 to 530. Since it would be reasonable to suppose that the effect was due to a reaction of the catalyst with CH_2Cl_2, a run was carried out in which the THF solvent contained 10% CH_2Cl_2 by volume. However, both the n:iso and TOF values were the same as those observed in pure THF. Finally, a run was carried out using the chelating TosL analogue **20** in CH_2Cl_2 (entry 29, Table 1), but it gave n:iso and TOF values that were virtually the same as in THF.

A somewhat smaller thermal effect on the n:iso ratio was previously observed as well. At 80 °C diTosL was found to give both higher n:iso and TOF values, increasing to n:iso = 15.8 and TOF = 760.[5] For ligand **10**, a similar effect was seen for n:iso, increasing from *ca.* 5 to 7.2, but the TOF value increased by more than a factor of 3, to 1130, and the rate by a factor of 4, to 1.98 h^{-1}. In toluene, both effects are muted, with n:iso increasing from 4.7 at 60 °C to 5.7 at 80 °C, and the TOF and rate constants increasing from 300 and 0.44 h^{-1} at 60 °C to 850 and 0.96 h^{-1} at 80 °C. In comparison to other ligands, which we have described in some detail,[5] we note that there are no previous reports of the CH_2Cl_2 effect, and other ligands give rise to a *decrease* in n:iso ratio as the temperature is increased.[7,26] The TOF value for **10** at 80 °C is still lower than that for phosphite **25**[24] and bis-amide **26**[27] but the n:iso ratio for **10** is much higher; bulky chelating phosphite **24** gave higher TOF and n:iso ratios, but also more isomerization.[25,28]

A further curious fact is that for *both* **10** and **24**, which exhibit similar kinetics, the n:iso ratio is inversely proportional to CO pressure. We therefore wondered whether any of the CH_2Cl_2 and thermal effects could be explained by CO *solubility* in particular (little effect is seen for [H_2] with **24**). Under the low pressure and temperature conditions used, gas solubility is proportional to gas pressure (Henry's Law), but obviously the propotionality constant will change with temperature and solvent. Gas solubility is expected to *increase* at higher temperature,[16–18] however, so this would lead to a *decrease* in n:iso ratio at high temperature (with constant pressure), in contrast to what is observed. Since CO is more soluble in THF than in toluene, one might again expect lower n:iso ratios in THF, but again that did not occur. Since literature data were available for dioxane, that was tested; diethyl ether could not be used due to the insolubility of **10**. Clearly here, gas solubility does not play a role: CO is less soluble in dioxane than in toluene and in THF, yet the rate constant is the same as in THF and toluene, while the n:iso ratio is only somewhat higher. Since the largest rate and n:iso ratio changes were seen for CH_2Cl_2, this provided the best test case, but it was also the solvent in which it was most difficult to measure gas solubility due to its high vapor pressure. Nonetheless, even though the CO solubility was measured at lower temperature (20 and 5 °C), the actual solubility was comparable to that in THF at 25 °C. We also checked whether or not the vapor pressure of CH_2Cl_2 could be contributing to the total measured pressure, and so bring down the actual partial pressure of the CO/H_2, but under our reaction conditions (where the solvent is heated but not the total apparatus), the vapor pressure of the CH_2Cl_2 is negligible at 60 °C. Hence, the higher rate and n:iso ratio must depend on some curious solvent effect of the CH_2Cl_2 on the reaction; it is *not* due to lowered gas solubility.

Conclusion

This study completes an initial phase of screening of *N*-sulfonylamino phosphine ligands for the hydroformylation reaction. We have shown that these ligands can be active promoters, as well as, paradoxically, active inhibitors of the reaction. Seemingly minute changes in the structure of the ligands give rise to a switch from active promoter to active inhibitor. The bis(sulfonylamino) phosphine ligands have not exhibited any favorable qualities for rate or selectivity with the striking exception of the biphenyl 7-membered ring compound **6**. Since this ligand gives an exceptionally active catalyst before apparent decomposition occurs, it is possible that the problem with this class is rapid catalyst decomposition; future work will address this issue. The sulfonylamino diphenylphosphine ligands exhibit good rates for non-chelating ligands, and good rates and selectivity for chelating ligands. Compound **10** is the most active promoter we have discovered, giving at 80 °C a turnover frequency of 1130 mol aldehyde (mol Rh)$^{-1}$ h^{-1}, with a linear:branched ratio of 7.2. A curious solvent effect has been discovered for CH_2Cl_2 which was found not to be due to solubility effects or direct reaction of the catalyst with the solvent, so examination of a broader range of solvents for hydroformylation may be fruitful. Future work on these compounds will combine a mechanistic approach involving the synthesis of rhodium complexes of these ligands and examination of the hydroformylation reactions by NMR, with the empirical approach of this study which will continue with a search for new linkers between the nitrogen atoms and a combinatorial approach to varying the groups on nitrogen and phosphorus, to elucidate features that contribute to both inhibition and promotion of hydroformylation.

Experimental

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), CD_2Cl_2 (δ 5.32), or DMSO-d_6 (δ 2.49) for ^1H NMR, to C_6D_6 at 128.0 ppm, $CDCl_3$ at 77.0 ppm, CD_2Cl_2 at 53.8 ppm, or DMSO-d_6 at 39.5 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, and 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. Triethyl-

amine and 1,2-diaminoethane were 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 passed through a column of basic alumina, 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 and $PhPCl_2$ (Aldrich), and butanesulfonyl chloride, 1-naphthalenesulfonyl chloride, 2-naphthalenesulfonyl chloride, 4-nitrobenzenesulfonyl chloride, and $EtPCl_2$ (ACROS). The following compounds were prepared as previously described: **18**[5,29] and $Rh(CO)_2(acac)$.[30]

Hydroformylation reactions were carried out as previously described in a 90 mL Fisher–Porter vessel (Andrews Glass Co.) attached to an Andrews Glass Co. multi-ported stirring assembly.[5]

Syntheses

Sulfonamides. The butanesulfonyl compounds **1**, **4**, and **13**, were prepared by addition of *n*-butanesulfonyl chloride to a pyridine solution of the amine. The 4-nitrobenzenesulfonyl compound **7** was prepared by addition of 4-nitrobenzenesulfonyl chloride to the amine in aqueous NaOH solution, and the naphthalenesulfonyl compounds **9a**,**b** were prepared in THF with Et_3N as the base. Details of the syntheses, purification, and NMR and analytical data may be found as ESI †. A representative procedure follows.

N,N′-*bis(1-butanesulfonyl)-1,2-diaminoethane* (**1**): to a solution of 1,2-diaminoethane (3.3 mL, 50 mmol) in 25 mL of pyridine cooled to 0 °C, *n*-butanesulfonyl chloride (13.0 mL, 100 mmol) was added dropwise *via* syringe and then the reaction mixture was allowed to stir at room temperature overnight. The resultant dark brown mixture was poured into a flask containing 30 mL of concentrated HCl and 55 g of ice. The precipitate was filtered and washed with water to give 10 g of a brown solid. This material was dissolved in 60 mL of ethanol and boiled with 2.5 g Norit for 5 min and then filtered. Water was added to the yellow solution until it became cloudy (*ca.* 60 mL), and then it was warmed to redissolve the product and allowed to cool slowly to −20 °C. After filtration and washing with water, 4.7 g of a light yellow solid was obtained. A second treatment failed to remove the color. Heating 4 g of this material with 1 g of Norit in 30 mL of boiling CH_2Cl_2 was followed by the addition of hexane until the solution turned cloudy. Cooling to −20 °C gave 3.5 g of white crystals (25% yield). ^{1}H NMR ($CDCl_3$): δ 4.90 (s, br, 2H, NH), 3.30 [*ca.* 1:0.5:1 $A_2A'_2X$ multiplet, $^3J_{(CH)(NH)}$ = 6 Hz, $^4J_{(CH')(NH)}$ = 0 Hz, $^3J_{HH'}$ ≈ 6 Hz, 4H, NCH_2CH_2N], 3.05 (AA′BB′, J_{HH} ≈ 8.0 Hz, 4H, SO_2CH_2), 1.80 (~quintet, J_{HH} ≈ 7.8 Hz, 4H, $SO_2CH_2CH_2$), 1.46 (sextet, J_{HH} = 7.7 Hz, 4H, $SO_2CH_2CH_2CH_2$), 0.96 (t, J_{HH} = 7.4 Hz, 6H, $SO_2CH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$; assignments from HETCOR): δ 52.72 (SO_2CH_2), 43.76 (NCH_2), 25.59 ($SO_2CH_2CH_2$), 21.52 ($SO_2CH_2CH_2CH_2$), 13.56 ($SO_2CH_2CH_2CH_2CH_3$). Anal. calc. for $C_{10}H_{24}N_2O_4S_2$: C, 39.98; H, 8.05; N, 9.32. Found: C, 40.13; H, 8.34; N, 9.14%.

1,3,2-Diazaphospholidines and 1,3,2-diazaphosphepines. The phosphorus heterocycles **2**, **3**, **5**, **6**, **8**, **19**, and **20** were prepared by combining either $PhPCl_2$, $EtPCl_2$, $Cl_2PCH_2CH_2PCl_2$, or $Cl_2PCH_2CH_2CH_2CH_2PCl_2$ with the appropriate sulfonamide and Et_3N in THF. Details of the syntheses, purification, and NMR and analytical data may be found as ESI †. A representative procedure follows.

2-Phenyl-1,3-bis(1-butanesulfonyl)-1,3,2-diazaphospholidine (**2**): in the glovebox a solution of Et_3N (632 mg, 6.25 mmol) in 3 mL THF was added to a solution of **1** (752 mg, 2.50 mmol) in 10 mL THF, and the resultant solution was cooled for 10 min in a −35 °C freezer. A solution of $PhPCl_2$ (447 mg, 2.50 mmol) in 3 mL of THF was then added dropwise with stirring, with immediate formation of a cloudy white mixture. The mixture was then stirred at room temperature for 1.5 h and then filtered to remove Et_3NHCl. Solvent removal *in vacuo* gave a viscous yellow oil which was dissolved in 6 mL of CH_2Cl_2 and passed through a *ca.* 7 mL pad of silica gel packed in CH_2Cl_2 on a 15 mL sintered glass frit. The product was eluted with a further 40 mL CH_2Cl_2, and the solvent removed under vacuum to give 0.6 g (60% yield) of product as a clear oil. ^{1}H NMR (CD_2Cl_2): δ 7.61 (m, 2H, PPh), 7.46 (m, 3H, PPh), 3.79 [m, 2H, $C(H_a)H_b$-$C(H_a)H_b$], 3.59 [m, 2H, $C(H_a)H_bC(H_a)H_b$], 3.17 (AA′BB′, J_{HH} ≈ 8.0 Hz, 4H, SO_2CH_2), 1.82 (~quintet, J_{HH} ≈ 7.8 Hz, 4H, $SO_2CH_2CH_2$), 1.46 (sextet, J_{HH} = 7.4 Hz, 4H, SO_2CH_2-CH_2CH_2), 0.94 (t, J_{HH} = 7.3 Hz, 6H, $SO_2CH_2CH_2CH_2CH_3$). ^{31}P NMR (CD_2Cl_2): δ 91.27 ppm. ^{13}C NMR (CD_2Cl_2): δ 138.82 (d, $^1J_{PC}$ = 30.6 Hz), 131.03 (s), 129.60 (d, $^2J_{PC}$ = 21.1 Hz), 129.24 (d, $^3J_{PC}$ = 5.6 Hz), 52.96 (SO_2CH_2), 49.09 (d, $^2J_{PC}$ = 5.9 Hz, ring CH_2), 25.75 ($SO_2CH_2CH_2$), 21.90 ($SO_2CH_2CH_2CH_2$), 13.68 ($SO_2CH_2CH_2CH_2CH_3$). Anal. calc. for $C_{16}H_{27}N_2O_4S_2P$: C, 47.28; H, 6.70; N, 6.89. Found: C, 47.36; H, 6.65; N, 6.81%.

Diphenylphosphino compounds. The diphosphine compounds **10**, **11**, and **12a**,**b**, and the monophosphine compounds **14** and **15** were prepared by reaction of Ph_2PCl with the appropriate sulfonamide and Et_3N in THF. Details of the syntheses, purification, and NMR and analytical data may be found as ESI †. A representative procedure follows.

N,N′-*Bis(diphenylphosphino)*-N,N′-*(1-butanesulfonyl)-1,2-diaminoethane* (**10**): in the glovebox, a solution of Et_3N (632 mg, 6.25 mmol) in 2 mL THF was added to a solution of **1** (751 mg, 2.50 mmol) in 20 mL THF, and then a solution of Ph_2PCl (1.10 g, 5.00 mmol) in 3 mL THF was added dropwise with magnetic stirring, immediately giving a white precipitate. The mixture was allowed to stir overnight at room temperature. After filtering off the Et_3NHCl, solvent removal *in vacuo* gave 1.64 g of product as a light yellow solid. This was taken up in 5 mL of CH_2Cl_2 and 10 mL of diethyl ether was layered on. Cooling to −35 °C overnight gave 1.32 g of white crystals, and a second crystallization using 4.5 mL CH_2Cl_2 and 9 mL of diethyl ether in the same way gave 1.16 g (70% yield) of product as analytically pure white crystals. ^{1}H NMR (CD_2Cl_2): δ 7.40 (m, 20H, Ph), 3.19 (br ~t, $A_2A'_2X_2$ m, $^3J_{PH}$ ≈ 3.2 Hz, 4H, CH_2CH_2), 2.86 (AA′BB′, J_{HH} ≈ 7.9 Hz, 4H, SO_2CH_2), 1.57 (m, 4H, $SO_2CH_2CH_2$), 1.33 (sextet, J_{HH} = 7.4 Hz, 4H, SO_2CH_2-CH_2CH_2), 0.88 (t, J_{HH} = 7.3 Hz, 6H, $SO_2CH_2CH_2CH_2CH_3$). ^{31}P NMR (CD_2Cl_2): δ 59.21 ppm. ^{13}C NMR (CD_2Cl_2): δ 135.11 (d, $^1J_{PC}$ = 16.7 Hz), 132.95 (d, $^2J_{PC}$ = 21.6 Hz), 130.26 (s, C_4), 128.96 (d, $^3J_{PC}$ = 6.2 Hz), 53.74 (d, $^2J_{PC}$ = 3.1 Hz, CH_2), 49.24 (SO_2CH_2), 25.58 ($SO_2CH_2CH_2$), 21.81 ($SO_2CH_2CH_2CH_2$), 13.67 ($SO_2CH_2CH_2CH_2CH_3$). Anal. calc. for $C_{34}H_{42}N_2O_4S_2P_2$: C, 61.06; H, 6.33; N, 4.19. Found: C, 60.69; H, 6.39; N, 4.11%.

N,N′-*bis(diphenylphosphino)*-N,N′-*(1-butanesulfonyl)-2,2′-diaminobiphenyl* (**16**): in the glovebox 2.75 mL of *n*-BuLi (1.6 M in hexane, 4.4 mmol) was added dropwise to a solution of **4** (850 mg, 2.0 mmol) in 20 mL of THF that had been pre-cooled at −35 °C. The mixture was stored in the glovebox freezer at −35 °C for 0.5 h, and then a solution of Ph_2PCl (883 mg, 4.0 mmol) in 4 mL of THF was added dropwise. The mixture was allowed to warm to rt with stirring for 1 h, and then the THF was removed *in vacuo*. Methylene chloride (30 mL) was added to precipitate out LiCl, and the mixture was filtered through Celite and the solvent removed to give a sticky yellow solid. This material was resuspended in 8 mL of benzene, filtered through Celite, and the solvent was removed to give a yellow powder. Recrystallization from CH_2Cl_2–hexane (1:3) at −35 °C gave 600 mg (38% yield) of fine white crystals. ^{1}H NMR (C_6D_6): δ 8.92 (d, 7.6 Hz, 1H), 8.08 (~t, 6.7 Hz, 5H), 7.76 (d, 8.0 Hz, 1H), 7.70 (br s, 2H), 7.45 (~t, 6.7 Hz, 1H), 7.04–7.25 (m, 17 H), 6.90 (t, 7.3 Hz, 1H), 2.80 (m, 1H), 2.41 (m, 1H), 1.90 (br m, 2H),

1.52 (m, 2H), 1.37 (m, 1H), 1.17 (m, 1H), 0.93–1.04 (m, 4H), 0.54–0.91 (m, 6H). ^{31}P NMR (C_6D_6, *ca.* 21 °C): δ 70.08, 69.83, 67.99 (*ca.* 4:54:42). ^{13}C NMR (C_6D_6): δ 140.01, 136.78, 136.24, 134.89, 131.27, 131.09, 130.51, 129.25, 129.16, additional peaks likely overlapping C_6D_6 at 128–129, 56.12, 53.87, 32.12, 25.37, 23.21, 21.89, 21.68, 14.52, 13.57. Anal. calc. for $C_{44}H_{46}N_2O_4S_2P_2$: C, 66.65; H, 5.85; N, 3.53. Found: C, 65.16; H, 5.64; N, 3.36%.

Measurement of gas solubility

Dry distilled solvent was placed in a 1 L flask attached to a vacuum stopcock, which was connected to a known volume attached to a vacuum line and mercury manometer. The solvent was degassed by opening it to the evacuated known volume and manometer, and (with rapid stirring) allowing it to degas; equilibration was rapid, and since the process was repeated many times as described below, stirring speed is not important. The solvent stopcock was closed and the system re-evacuated. Since the vapor volume in the solvent flask and the known volume were comparable, this had the effect of reducing the gas concentration by around half with each cycle. By 8–11 cycles, the vapor pressure was constant, and this value was used in the final determination of gas solubility. An aliquot of gas was then admitted to the known volume (with manometric pressure determination), and then the stopcock was opened to the rapidly stirred solvent. After equilibration, the pressure minus the known vapor pressure allowed the amount of gas in solution to be calculated by difference. The volume of solvent was then determined by weight (since some is lost during the degassing procedure). The final solubility was then extrapolated to 1 atm partial pressure assuming Henry's law ($P_{gas} = K_{Henry}X_2$) where X_2 is the mole fraction of gas in solution (and by convention X_1 is the mole fraction of solvent).[16,19,20] Duplicate determinations were made for each solvent (toluene with N_2 and CO, THF with CO, and CH_2Cl_2 with CO at 20 and 5 °C), using different initial gas pressures to reduce a possible source of systematic error. Minor effects that were quantified were the volume of the stir bar, and the variable known volume due to the changes in the height of the mercury column. More major effects that were not well controlled were the difference in gas and solvent temperature, although successful use of such a set-up has been reported;[21] the solvent was stirred in a thermostatted water bath, while the gas temperature was approximated as that of the lab, rather than holding the entire apparatus in a thermostatted compartment.[19]

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